Synthese von Organischen und Anorganischen Derivativen der Meldrumsäure

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Synthesis of Organic and Inorganic Derivatives of Meldrum's Acid

DISSERTATION

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Dekan: Prof. Dr. S. Laufer

1. Berichterstatter: Prof. Dr. N. Kuhn

2. Berichterstatter: Prof. Dr. H. A. Mayer

To my

parents, wife, sisters, brothers,

children Nour and Mohammed,

and to my developing country

Die vorliegende Arbeit wurde am
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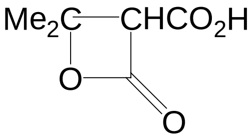
1 Introduction

1.1 Meldrum’s acid preparation and structure

In 1908, A.N. Meldrum reported that the condensation of malonic acid with acetone, in acetic anhydride containing a small amount of sulphuric acid, gave a white crystalline solid, $C_6H_8O_4$, which titrated as a monobasic acid and lost carbon dioxide on heating [1]. He assumed to be the ß-lactone of ß -hydroxy isopropyl malonic acid **1**.



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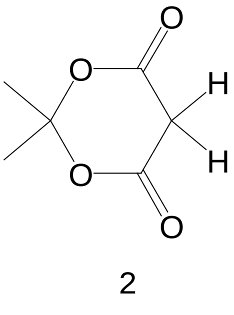
After fourty years, Davidson and Bernhard [2] correctly assigned the structure of Meldrum’s acid as 2,2-dimethyl-4,6-dioxo -1,3-dioxan **2**.



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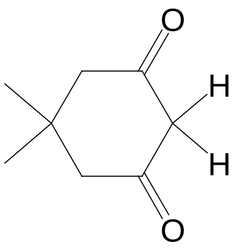
The properties of Meldrum's acid relate to those of other cyclic 1,3-diones such as dimedone **3** and barbituric acid **4**.



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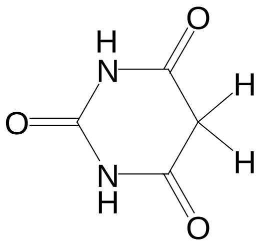

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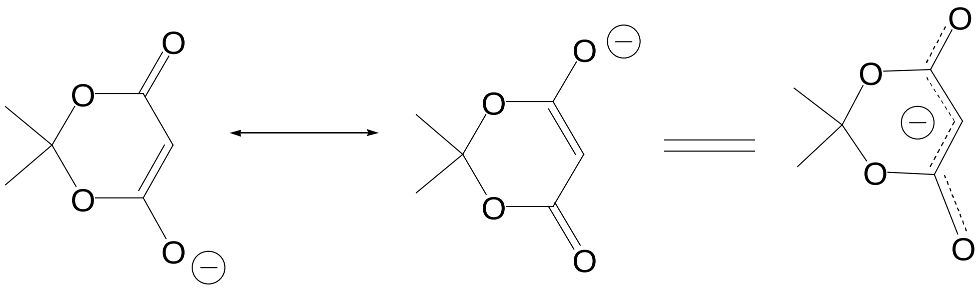
1.2 Physical properties of Meldrum's acid

The acidity of Meldrum's acid (pKa 4.83) [3] is comparable in strength to acetic acid (pKa 4.76) and is some ten pKa units more acidic than acyclic malonate esters such as dimethyl malonate (pKa15.9).

The high acidity of Meldrum's acid can be attributed to the presence of hydrogen atoms attached to a carbon atom which is between two carbonyl groups and that give stability of the resultant anion **5**.



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Despite this acidic character, IR spectroscopy [4], and ^{13}C NMR [5] studies have shown that Meldrum's acid does not enolize to any appreciable extent in either the solid state or in solution., and the predominant form is the diketo tautomer.

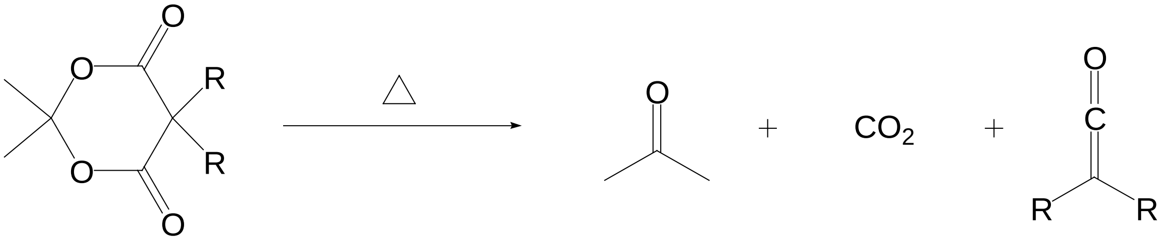
The X-ray structure investigation of Meldrum's acid [6], considering the question of the molecular conformation was shown that the molecular conformation in solid-state is boat.

1.3 Chemistry of Meldrum's acid

The chemistry of Meldrum's acid is dominated by its susceptiplity to nucleophlilic attack at the carbonyl carbon atoms followed by ring fragmentation.

Simple hydrolysis to the malonic acid is a common example of nucleophilic attack, and may be accomplished under acidic or basic conditions.

Fragmentation of the ring may also be accomplished directly by pyrolysis. The pyrolysis of Meldrum's acid derivatives **6** gives ketenes. The mechanism presumably involves homolysis of a C—O bond, followed by cleavage of acetone and carbon dioxide, both of which are found in the pyrolysate along with the ketene [7].



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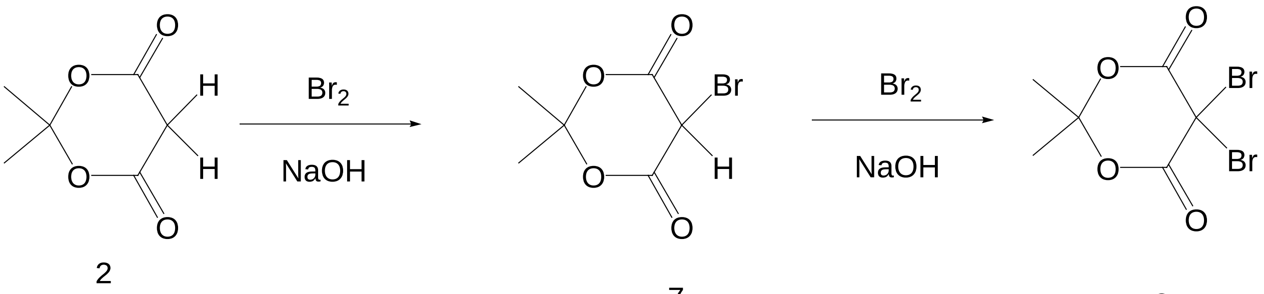
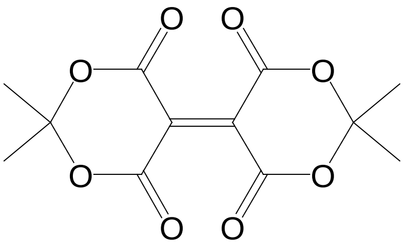
The 5-bromo **7** and the 5,5-dibromo **8** derivations are formed by direct bromination of Meldrum's acid in the presence of base.



2 7 8

The famous reaction of these two compounds is the formation of Meldrum's olefin **9** which form by simple dissolution of **7** and **8** in dimethyl formamide [8].



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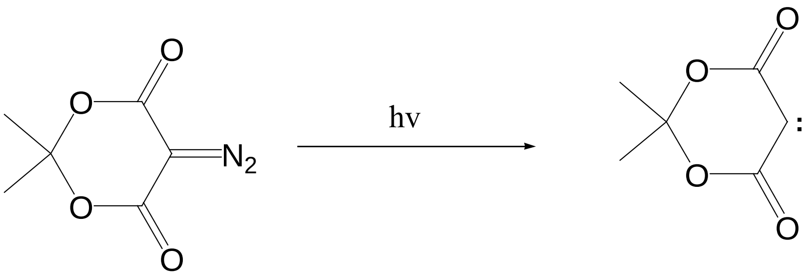
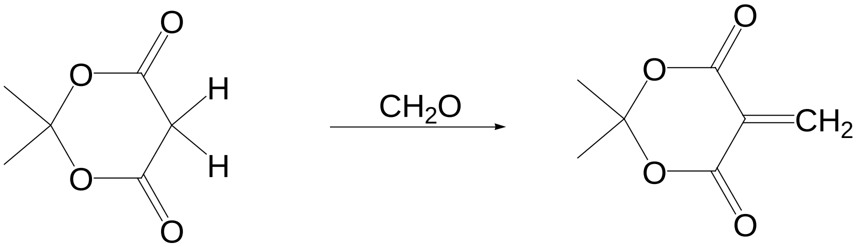
The most important nitrogen- containing derivative of Meldrum's acid is the diazo-compound **10**, formed by diazotization of the amine [4], or by direct reaction with p-toluenesulphonyl azide [9]. Photolysis or thermolysis of **10** generates unstable Meldrum's carbene**11** as intermediate[10] .



10 11

The methylene Meldrum's acid **12** is apparently highly reactive, and can not be prepared by standard methods. However, **12** can only be generated in situ by adding 37% aqueous formaldehyde to a solution containing Meldrum's acid.



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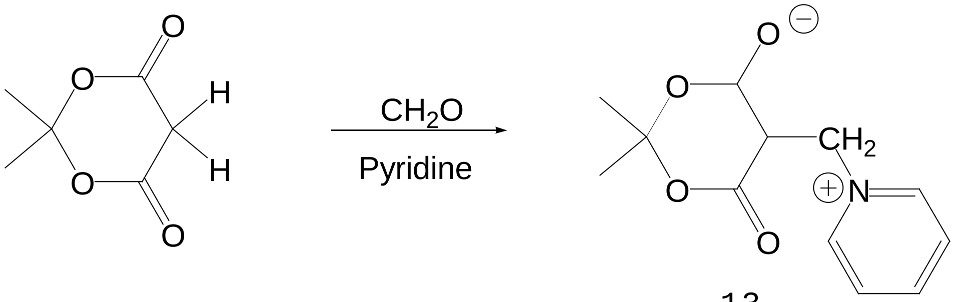
1-[(6-hydroxy -2,2-dimethyl-4-oxo-4H-1,3 dioxin-5-yl) methyl] pyridinium hydroxide **13** is a stable precursor for methylene Meldrum's acid [11].



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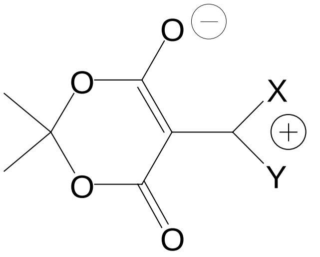
13

The tendency of Meldrum’s acid fragments to form betaine structures has been proved in numerous organic derivatives **14** [12-19] and in ylidic adducts **15** (E: S, Se, I) [20-24].



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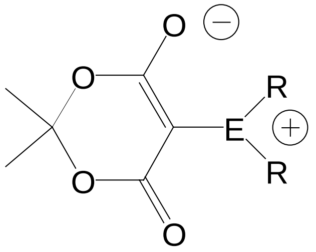

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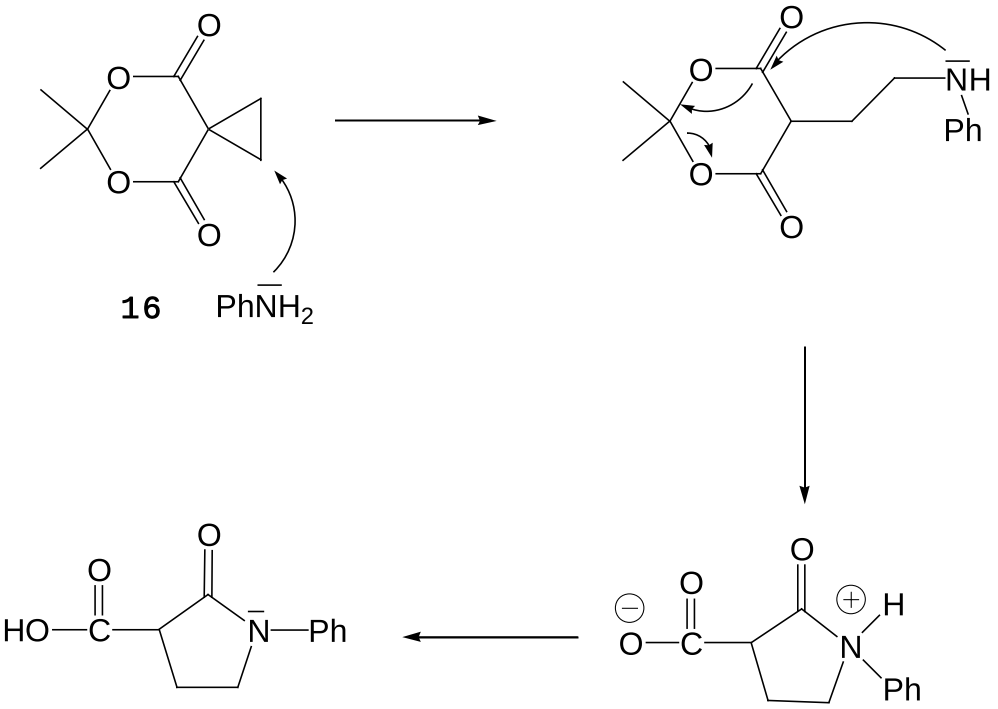
The intermolecular cleavage of Meldrum’s acid by other nucleophiles gives useful products. A particularly beautiful example is the intramolecular decompostion of the spiro caclopropyl derivativies **16**, where the ring-opened product lead to lactames[25,26].

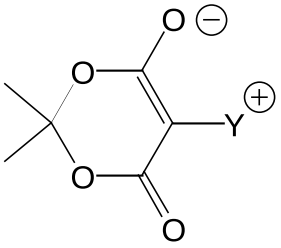

16
PhNH2
NH
Ph
O
N
H
Ph
HO
C
N
Ph

Aim of Study

The aim of this study is preparation of some useful organic and inorganic derivatives of Meldrum's acid using new and simple methods and their characterisation by X-ray structure analysis.

The derivatives can be classifed to:

1. Zwitterionic derivatives of Meldrum's acid.



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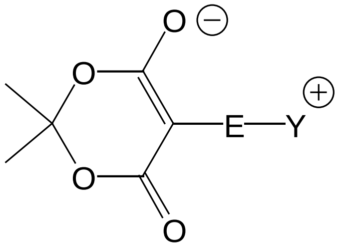

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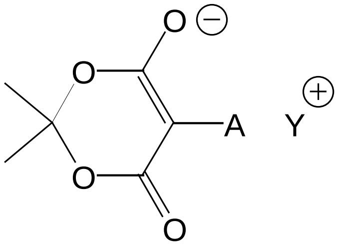
2. Salt derivatives of Meldrum's acid.



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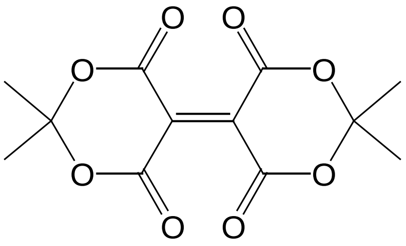
3. Neutral derivatives of Meldrum's acid



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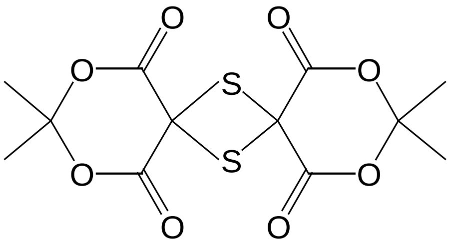

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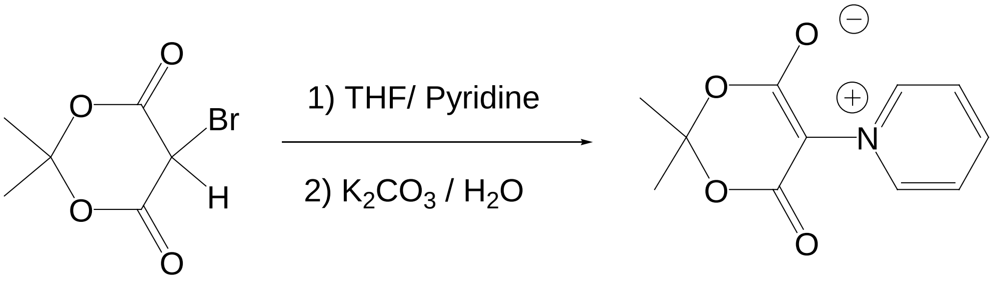
3 Results and Discussion

3.1 Meldrum's acid derivatives consisting of nucleophilic attack at 5-bromo-2,2-dimethyl-4,6- dioxo-1,3-dioxan in the presence of bases

3.1.1 Synthesis 2,2-dimethyl-4,6-dioxo-5-(1-pyridinio)-1,3- dioxan-5-yl- pyridinium ylide

By reacting 5-bromo-2,2-dimethyl-4,6- dioxo-1,3-dioxan **7** with stoichiometric amounts of pyridine followed by aqueous carbonate work up the pyridinium adduct **21** is formed in good yield.



7

21

A comparison of spectroscopic data reveals the π-electron shift into the six-membered ring going from **7** to its derivative **21**. The formal negative charge of the exocyclic oxygen atoms in the betaine **21** and the lowering of the corresponding CO bond order cause a significant shift of the CO stretching frequences (ν_{CO}: **7** 1788, 1750; **21** 1624 cm^{-1}) to lower wave numbers as mentioned for other betaine Meldrum's acid derivatives. Surprisingly, the chemical shift values in the ^{13}C-NMR spectra for the carboxylate carbon atoms (δ: **7** 160.9, **21** 160.3) are not influenced markedly by the charge distribution. The stability of the central C-N bond is revealed by the fragmentation pattern of **21** in the mass spectrum which does not contain the mass of the Meldrum's carbene fragment.

The crystal structure of **21**(Table 1-3, Fig. 1) [27] was determined to compare with other Meldrum's acid derivatives. The crystal structure of **21** reveals bond lengths and angles in the Meldrum's acid ring very similar to other betaine type structures.

Interestingly, the pyridine and malonate fragments are not coplanar [C(1)-N(1)-C(6)-C(7) -54.3(2)°], and only weak and distored intramolecular C-H-O hydrogen bonds between them are detected [C(1)-H(1) 0.94(2), H(1)-O(1) 2.65(2), C(5)-H(5) 0.96(2), H(5)-O(3) 2.82(2) Å, C(1)-H(1)-O(1) 100.7(1), C(5)-H(5)-O(3) 95.4(1)°].

The central C-N bond [N(1)-C(6) 1.440(1) Å] is in the range of an elongated single bond. On comparison with the structure of Meldrum's acid **2** itself [6], the enolate structure of the dioxan ring is reflected by elongated exocyclic C-O bonds [C(7)-O(1) 1.225(1), C(8)-O(3) 1.227(1) Å] and by short endocyclic C-C and C-O bonds [C(6)-C(7) 1.411(1), C(6)-C(8) 1.411(1), C(7)-O(2) 1.380(1), C(8)-O(4) 1.375(1) Å].

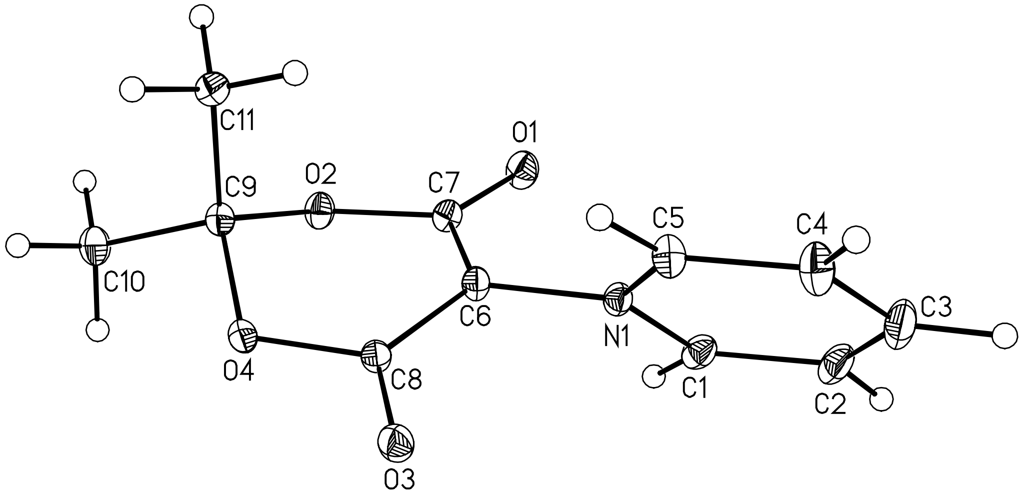
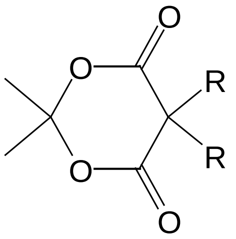


Fig. 1: The Structure of $C_{11}H_{11}NO_4$ **(21)** in the crystal

There have been severals structures reported for Meldrum's acid derivatives which belong to the types **6**, **22** and **23**, most of them containing organic substituents in 2-position [6, 13-19, 28-32]. Apparently, **21** clearly represents the type **23**, no resonance formula avoiding charge separation being possible. The strongest betaine character, on comparison with the known structures of **23** [14-18, 31-32], is indicated by it's elongated exocyclic C-O and short endocyclic C-C bonds in the Meldrum's fragment as well as by the central C-N single bond and the nonplanar arrangement of the heterocyclic rings. Apparently, the steric demand of the pyridine fragment forces the deviation from planarity which is documented for systems like **24** [19].

The other reported example in which the substituents in 2-position are connected through a nitrogen atom, is the phenylhydrazone derivative **25** [33]. The length of the central C-N bond (*ca.* 1.31 Å) clearly reflects the character of a double bond, and therefore these compounds clearly belong to the type **22** series.



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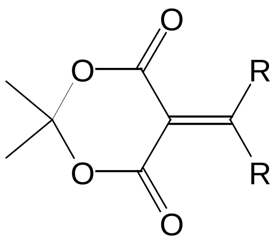

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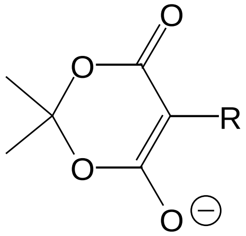

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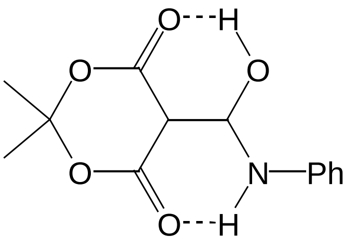

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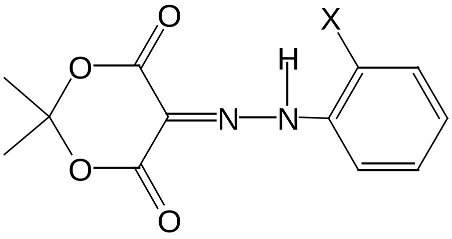

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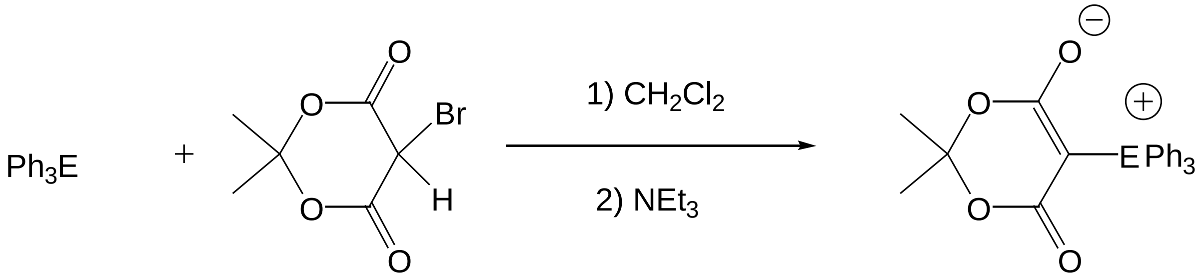
3.1.2 Synthesis of arsonium, stibonium and bismuthonium 2,2-dimethyl-4,6-dioxo-1,3-dioxanides

The reactions of **7** with Ph_3E (E = As, Sb, Bi) followed by addition of triethylamine give the compounds **26** as stable crystalline solids in good yields.



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26

The x-ray structures of **26** were determined (Tables 4-8, Figs. 2-4) [34]. Surprisingly, the ylides do not form isotypic crystals as a consequence both from different orientations of the Ph_3E fragments with respect to the heterocyclic ring [**26a** 179.2(3); **26b** 176.4(3); **26c** 166.1(2)°] and from the relative orientation of the phenyl rings. The ylidic E-C bond lengths are in the range of short single bonds [**26a** 1.859(2), **26b** 2.044(2), **26c** 2.139(7) Å] on comparison with the corresponding E-Ph distances. There are only minor differences in the geometry of the dioxin fragments (Table 5) including the folding angle along the axis of the endocyclic oxygen atoms [**26a** 42.6(2), **26b** 43.4(3), **26c** 41.9(4)°]. The enolate nature of the heterocyclic ring apparently causes a marked oxygen basicity which is revealed by short contacts between the hetero atoms and one of the exocyclic oxygen atoms [**26a** 2.926, **26b** 3.010, **26c** 3.162 Å].

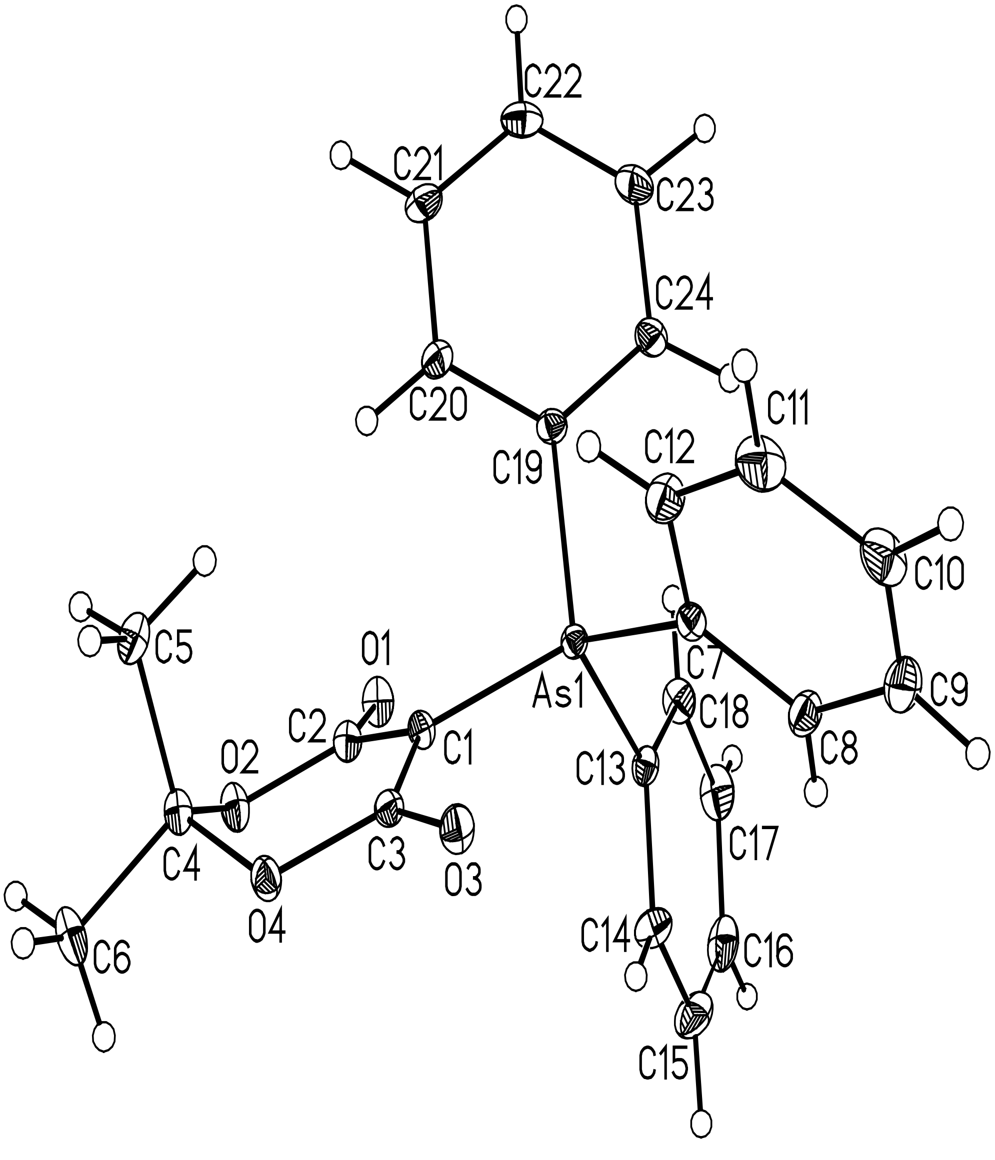


Fig. 2: The structure of $Ph_3As\text{-}C_6H_6O_4$ **(26a)** in the crystal.

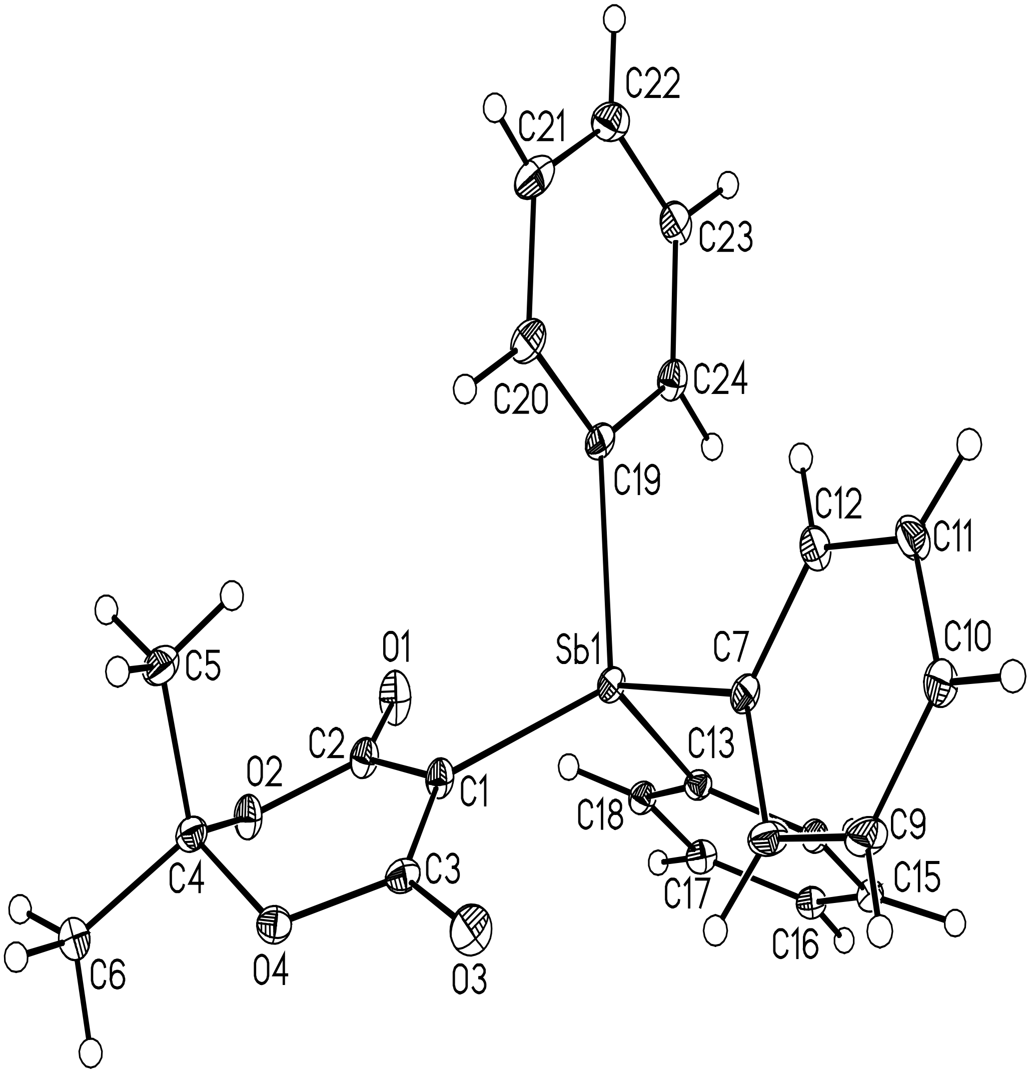


Fig. 3: The structure of $Ph_3Sb\text{-}C_6H_6O_4$ **(26b)** in the crystal.

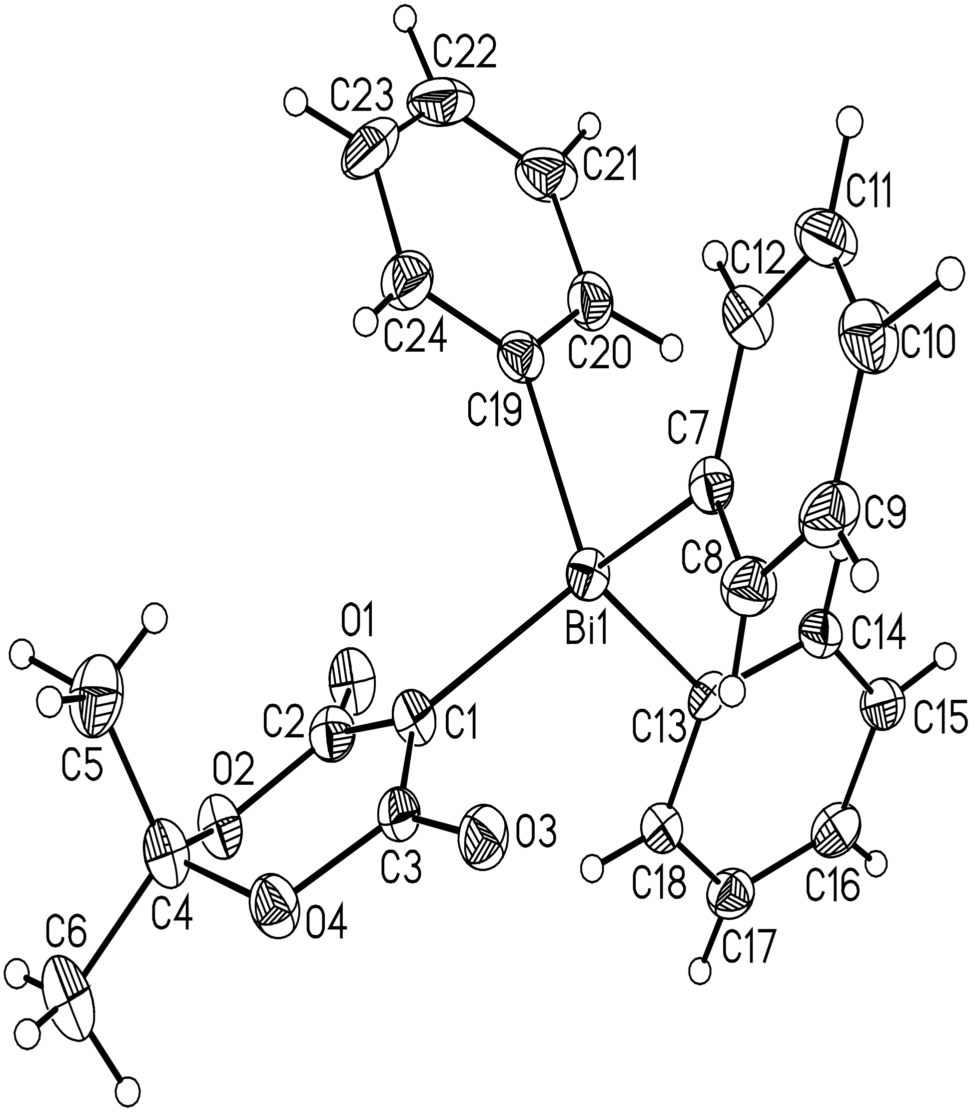
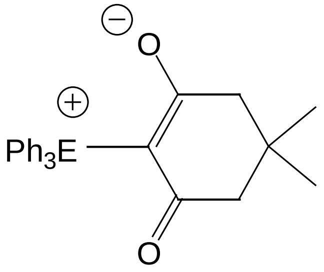


Fig. 4: The structure of $Ph_3Bi\text{-}C_6H_6O_4$ **(26c)** in the crystal.

As expected, the crystal structures demonstrate **26** to be stabilised ylides, and no marked differences are observed going from arsenic to it’s heavier neighbours. Small deviations may be influenced by packing effects. The structure of their dioxin fragments are very close to that of it’s pyridine adduct **21** which underlines the betaine nature of **26**.

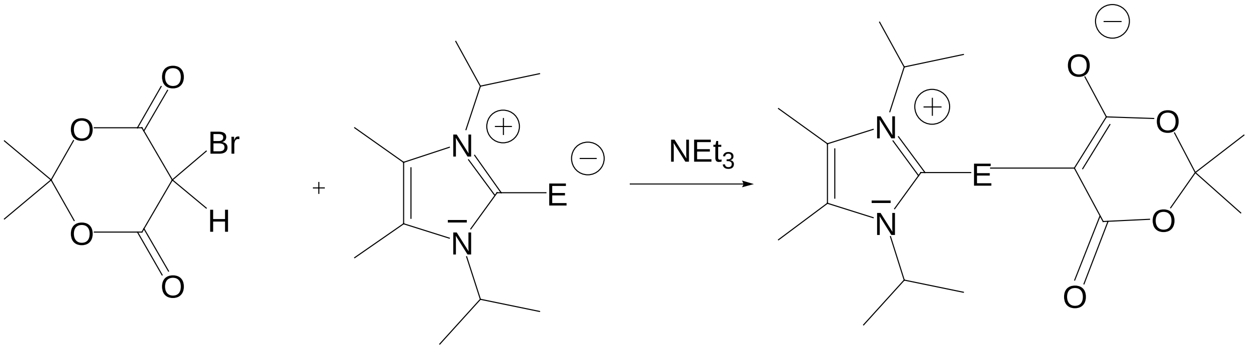
A comparison of **26** with the structures of the dimedone derivatives **27** [35-36] reveals only minor differences in the ability of the heterocyclic fragments to stabilise charge separation. In fact, the central E-C bond lengths are a little bit shorter for **26**.



27

3.1.3 Synthesis of zwitterionic sulfides, selenides and tellurides

The reactions of **7** with mesoionic ureas **28** (E = S (a), Se (b), Te (c)) [37-39] followed by addition of triethylamine give **29** as stable crystalline solids in good yields.



7 **28** **29**

E = S (a), Se (b), Te (c)

The NMR and IR data confirm the presence of partial charges in both fragments (experimental section). In ^{77}Se and ^{125}Te NMR [δ = 181.7 **(29b)**, 301.7 **(29c)**], the resonances are shifted towards high field and of the diarylselenide and diaryltelluride ranges [40] and obey the prediction of *Mc Farlaine's* straight line [41].

To get a better insight into their bonding, the crystal structures of **29** (Tables 9-13, Figs. 5-7) [42] were investigated. While **29a** and **29b** form isotypic crystals in the space group *C*mc2$_1$, the tellurium compound **29c** crystallizes in the monoclinic space group *P*2$_1$/c. In the sulfur and selenium derivatives, as well as in **26**, we observe only short intermolecular distances between the exocyclic oxygen and chalcogen atoms [**29a**: S(1)-O(2) 3.082(2) Å, S(1)-O(2)-C(8)62.4(1)^o; **29b**: Se(1)-O(2) 3.151 Å, Se(1)-O(2)-C(8)64.7(1)^o].

The tellurium compound **29c** adopts a dimeric structure by additional intermolecular tellurium to oxygen contacts [**29c**: Te(1)-O(2) 3.225(8), Te(1)-O(2) 3.28(1) Å , Te(1)-O(2)-Te(1A) 112.5(1), O(2)-Te(1)-O(2A) 67.5 (1)^o]. Despite these differences, there are only minor deviations in the structures of the Meldrum's fragments in **29a-c** (Table 5). Comparing the structure of their dioxan rings with Meldrum's acid, it could be seen that the enolate nature of **29** was confirmed. Consequently, their imidazolium part resembles closely to the structures of imidazolium salts [43-44].

Though both being formally of bond order one in the zwitterionic resonance structure, the E-C bond lengths in each compounds **29** differ markedly, especially in the case of the tellurium compound **29c**, though being in the range of S-C, Se-C and Te-C bonds in their diaryl derivatives [45-47]. In every case, the bond lengths between E and the coordinating imidazolium carbon atom are the shorter ones [S(1)-C(1) 1.7630(18), S(1)-C(7) 1.7449(19); Se(1)-C(1) 1.911(2), Se(1)-C(7) 1.876(3), Te(1) C(1) 2.163(3), Te(1)-C(7) 2.070(3) Å]. As expected, these E-C bond lengths are elongated on coordination of **28** [**28a**: S-C 1.690(2) Å; **28b**: Se-C 1.853(49; **28c**: Te-C 2.087] [38, 48-48] to give **29** as it has been observed for halogen adducts [49-53] and metal complexes [39] of **28**. The C-E-C\` bond angles in **29** are in the range expected for diaryl chalcogenides [45-47] and decrease in the series S>Se>Te according to the predictions of the *VSEPR* model [54].

In **29a** and **29b**, the planes of the C3 (dioxanide) and CN2 (imidazolium) fragments both are in perpendicular orientation, with respect to the central EC2 plane, from reasons of crystallographic symmetry. In **29c**, the corresponding interplanar angles are also far away from coplanarity [C(1)Te(1)C(7)/N(1)C(1)N(11)72.0(9)^o, C(1)Te(1)C(7)/C(8)C(7)C(81)102.6(9)^o].

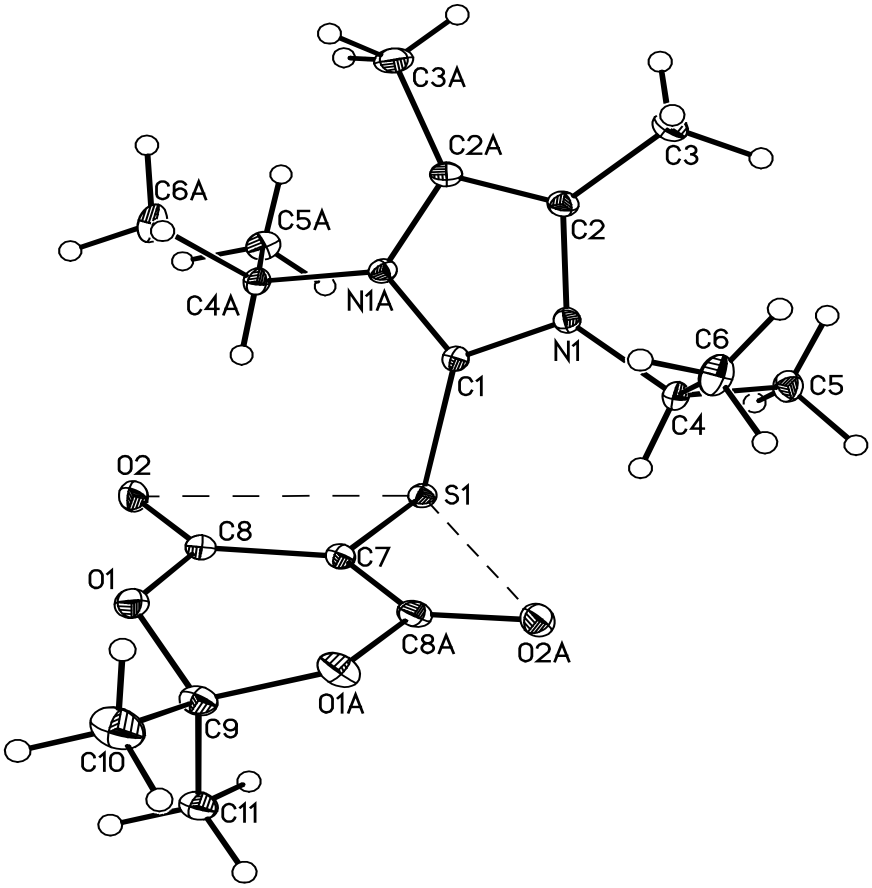


Fig. 5: The structure of $C_{17}H_{26}N_2O_4S$ **(29a)** in the crystal.

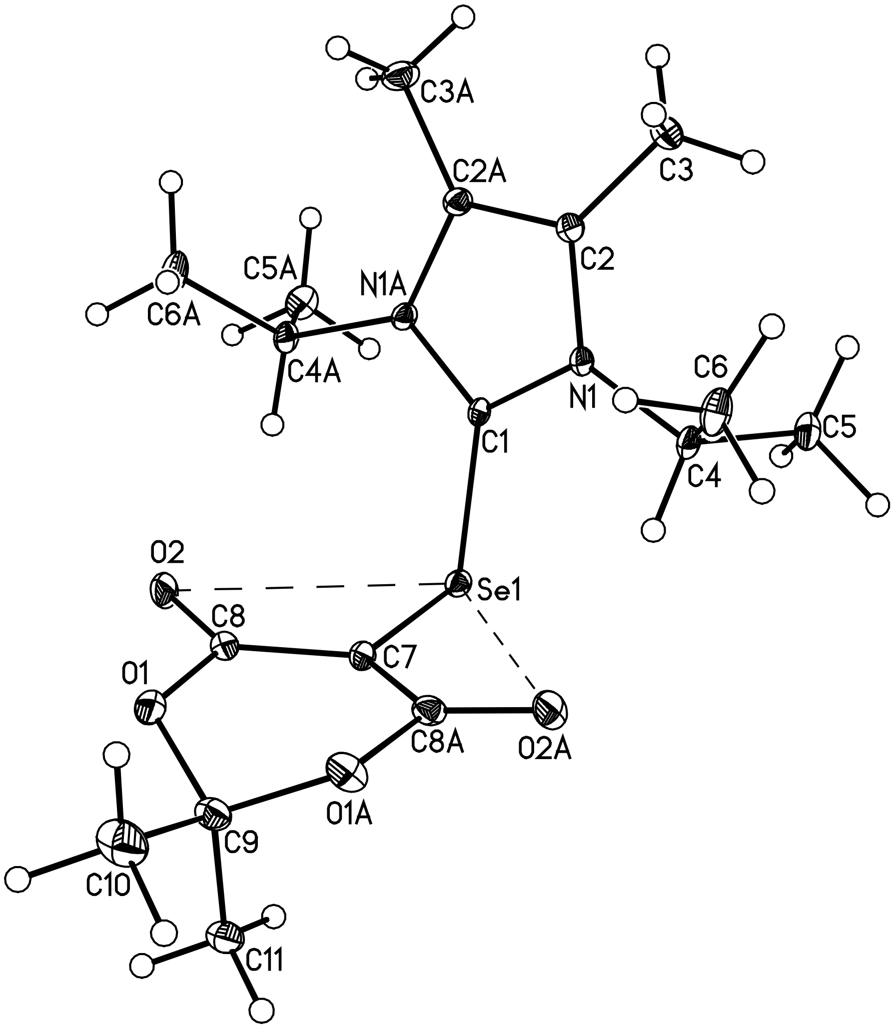


Fig. 6: The structure of $C_{17}H_{26}N_2O_4Se$ **(29b)** in the crystal.

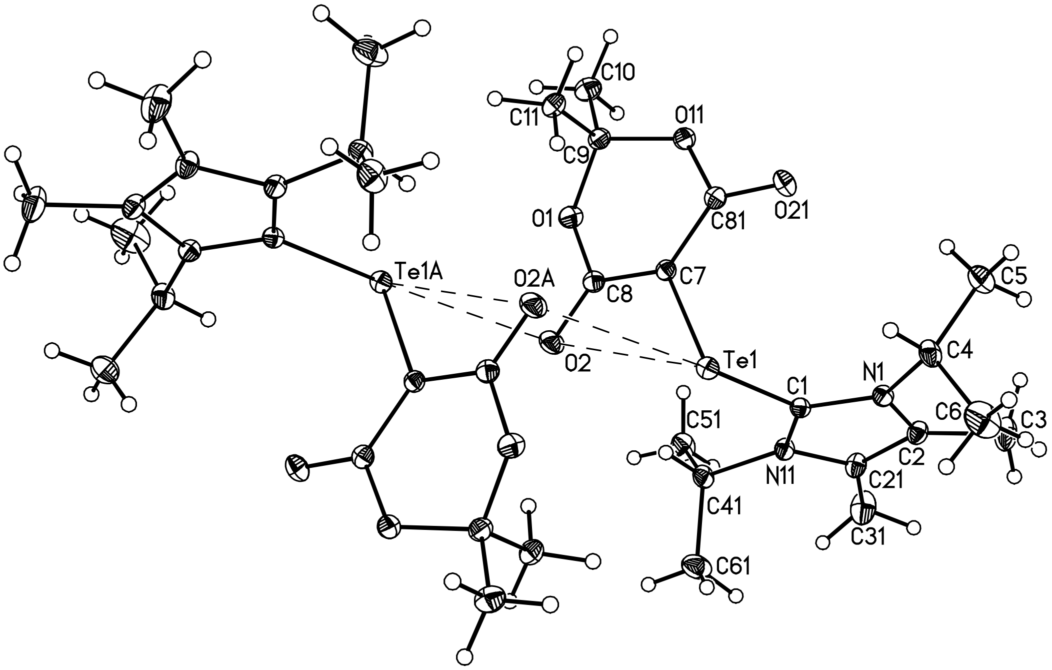
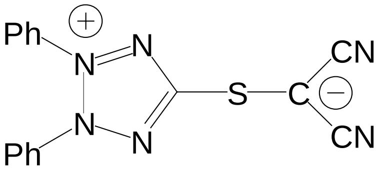


Fig. 7: The structure of $C_{17}H_{26}N_2O_4Te$ **(29c)** in the crystal.

As expected, the imidazolium and dioxanide fragments present in **29** cause a most effective stabilization of their zwitterionic structures. In fact, comparison of the structures of **30** and **29** indicates a stronger charge separation for the **29**, and the high thermal stability of the compounds **29** is worth to be underlined. Even the tellurium derivative **29c** melts above 160 °C without decomposition. Therefore, the title compounds resemble more closely to diaryl derivatives than to ylides.

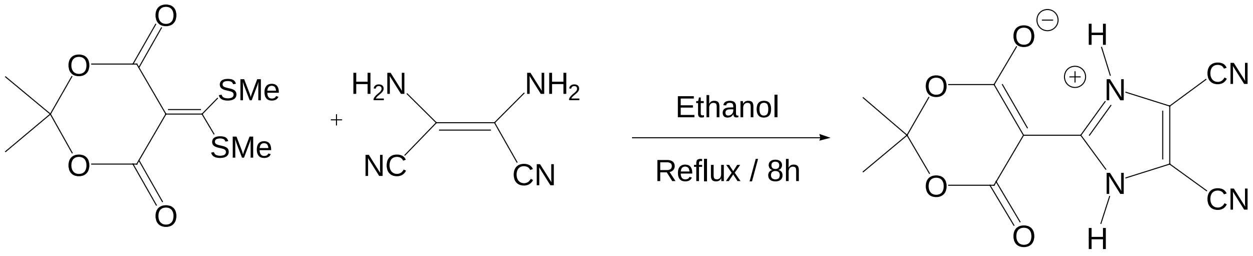


30

3.2 Synthesis of a zwitterionic imidazolium 1,3-dioxanide by Huang's method[14]

3.2.1 Synthesis of 2,2-dimethyl-4,6-dioxo-5-[2-(4,5-dicyano)]imidazolio-1,3-dioxan-5-yl-imidazolium ylide

The reactions of **31** [55] with cis-1,2-diamino-1,2-dicyanoethylene give **32** as stable crystalline solids in good yields.



31 **32**

The crystal structure of (**32**x C_2H_6OS) (Tables 14-18, Fig . 8) [56] reveals the presence of dimeric betaine solvate units connected via hydrogen bonds. In **32**, the heterocyclic ring fragments are nearly coplanar the twist angle between the planes N(1)C(1)N(2) and C(6)C(8)C(7) being 5.9°. The length of the central olefinic bond [C(1)-C(8) 1.4178(18)Å] is intermediate between the range of typical single and double bonds. The structures of the imidazolium and dioxanide rings (Table2) agree well with that of isolated imidazolium ions [43] and 1,3-dioxanide ions **5** thus confirming the zwitterionic nature of the compound. The N-H-O distances and angles [N(1)-H(1) 0.801(2), O(1)-H(1) 2.240(2) Å, N(1)-H(1)-O(1) 119.7(1)°; N(2)-H(2) 0.911(1), O(2)-H(2) 2.236(2) Å, N(2)-H(2)-O(2) 114.0(1) °] are at the upper and lower end expected for intramolecular hydrogen bonds, respectively. Interestingly, the hydrogen bonds to the solvent molecule [O(5)-H(2) 1.853 Å, N(2)-H(2)-O(5) 152.7(1) Å] and the intermolecular hydrogen bonds of the central four-membered ring unit [H(1)-O(1A) 2.069(1) Å, O(1)-H(1)-O(1A) 83.8(1), H(1)-O(1)-H(1A) 96.2(1) Å] are significantly shorter than the intramolecular ones.

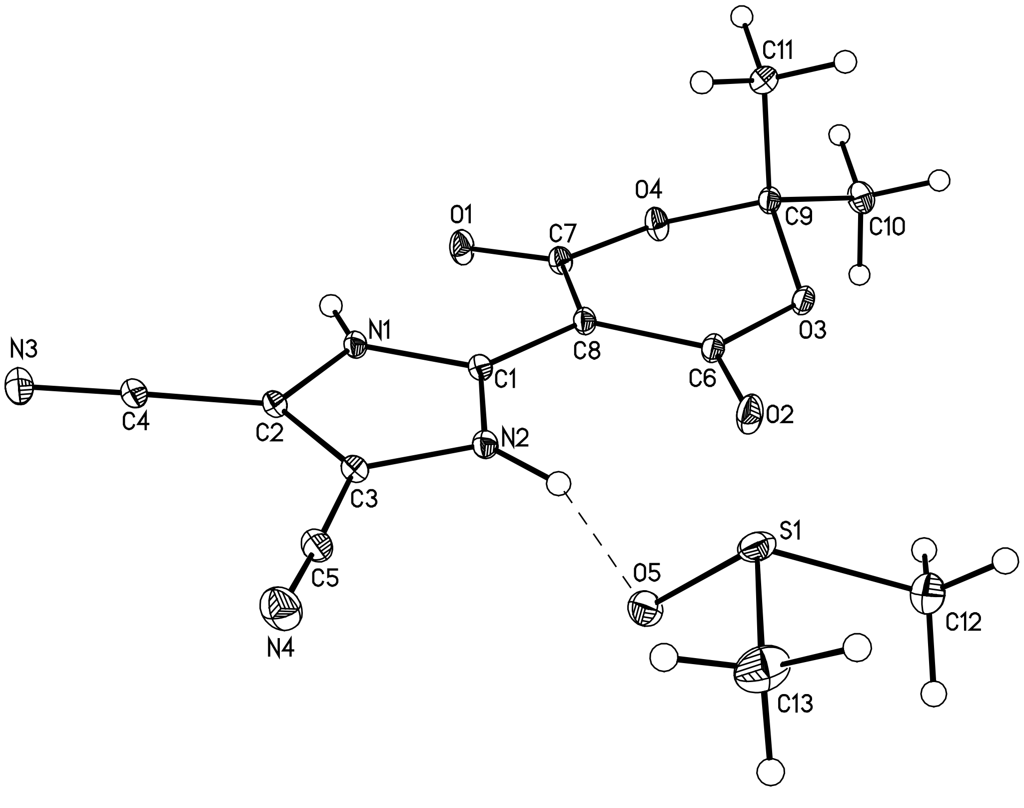
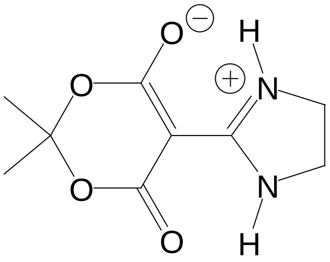


Fig. 8: The structure of $C_{11}H_8 N_4O_4$ **(32)** in the crystal.

Over all, structural data of **32** clearly confirm its zwitterionic nature. The marked charge separation of the central olefinic bond is also indicated by the extreme shift difference of its carbon atoms in the ^{13}C NMR spectrum [δ = 71.6 ($C5_M$,148.5 ($C2_I$)].

With the presentation of structural and spectroscopic properties the imidazolium dioxanide **32** confirms the results of Westrup on push-pull ethylenes [57]. Though there is only a minor difference in the length of the central olefinic bonds and their adjacent atoms in **32** and **33**, the ^{13}C NMR shifts of $C5_M$ (δ **32** 71.6, **33** 65.4) indicate a less effective charge separation in **32** presumably as a consequence of the lower donor capacity of the intrinsic 4,5-dicyano-imidazol- 2-ylidene.

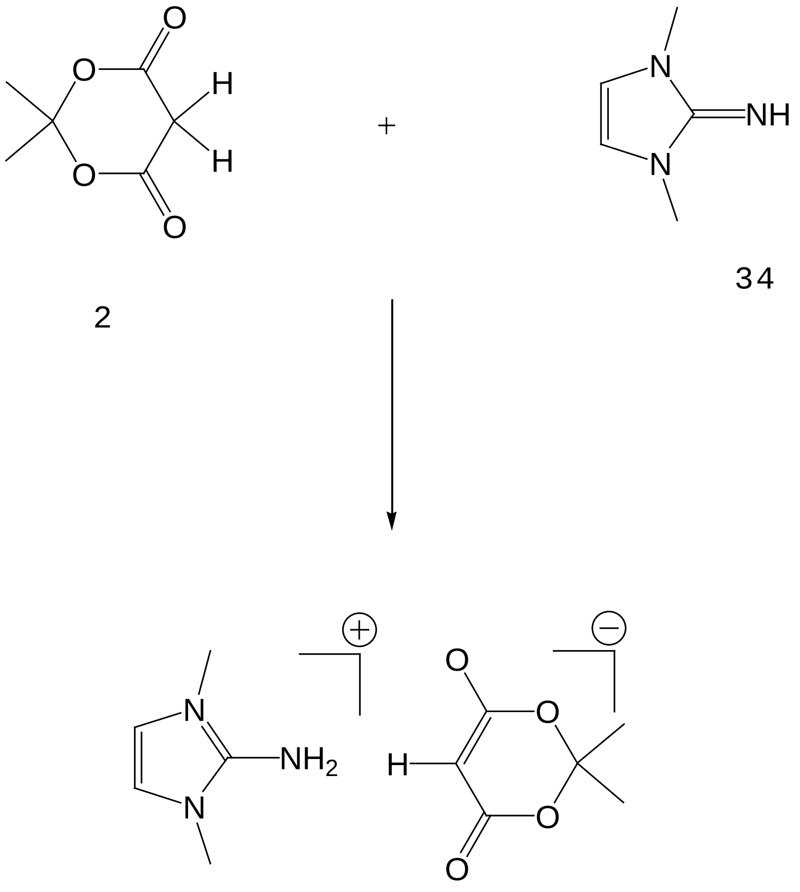


33

3.3 Meldrum's acid salts

3.3.1 Synthesis of 2-Amino-1,3-dimethylimidazolium-2,2-dimethyl-4,6-dioxo-1,3-dioxanide

Reaction of **2** with the strong ylide type base **34** [58] gives 2-amino-1,3-dimethylimidazolium 2,2-dimethyl-4,6-dioxo-1,3-dioxanide **35** as colourless stable crystals in excellent yield.



2

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35

35 crystallises in the orthorhombic space group *Pnma*. [59] (Tables 19-20, Fig 9). The unit cell contains two crystallographically independent anions lying on crystallographic mirror planes.

There are only small differences in the geometry of the anions A and B (Table 20, the values for A are used in the following discussion). On comparison with the structure of **2** [6], significant shortening of the endocyclic C-C bonds and elongation of the exocyclic and endocyclic C-O carboxylate bonds is detected for the anion [C(6)-C(7) 1.4006(13), C(7)-O(1)

1.2347(13), C(7)-O(2) 1.3850(12) Å], while the other C-O bond lengths of the dioxan ring remain nearly unchanged [O(2)-C(8) 1.4303(10) Å]. The folding angles along the endocyclic dioxygen axis are in the expected range [O(2)C(8)O(2A)/O(2)C(7)C(7A)O(2A) 43.8, O(4)C(13)O(4A)/O(4)C(12)C(12A)O(4A) 45.0 °].

The structure of the cation (Table 20) is close to that observed for its chloride salt [58], in which isolated ions have been found. Therefore, the isolated cation may be regarded as an immonium ion more than an ammonium species (MO calculations [60]). In contrast to its chloride salt, the cation in **35** contains a pyramidal NH_2 substituent apparently as a consequence of the hydrogen bonding mentioned below [C(1)-N(3)-H(1a) 119.5, C(1)-N(3)-H(1b) 117.7, H(1a)-N(3)-H(1b) 118.2 °]. These bonds also may cause the nonplanar arrangement of the five-membered ring and the CNH_2 fragment [H(1a)N(3)H(1b)/N(1)C(1)N(2) 23.0 °].

The anions are connected to the cations via N-H-O hydrogen bonds incorporating the exocyclic nitrogen and oxygen atoms [N(3aa)-H(1ac) 0.844, N(3aa)-H(1bc) 0.893, O(1a)-H(1bc) 1.917, O(3b)-H(1ac) 2.002 Å; N(3aa)-H(1bc)-O(1a) 172.1, N(3aa)-H(1ac)-O(3b) 163.6, H(1bc)-O(1a)-C(7a) 152.8, H(1ac)-O(3b)-C(12b) 137.9 °] thus forming a wave-like polymeric structure.

The bond lengths and angles indicate a strong interaction compared with the hydrogen bonding in **2**. Apparently, neither the endocyclic oxygen atoms nor C(6)-H and C(11)-H are part of hydrogen bonds.

As expected, the enolate nature of the anion of **35** causes on comparison with the structure of **2** a shortening of the endocyclic C-C distances accompanied by elongated exocyclic C-O bonds. The presence of the hydrogen bonds seems to be of minor influence on the enolate structure as revealed by comparison with the pyridinium compound **21**(d C=C 1.411(1), 1.354(1), C-O 1.225(1), 1.227(1) Å).

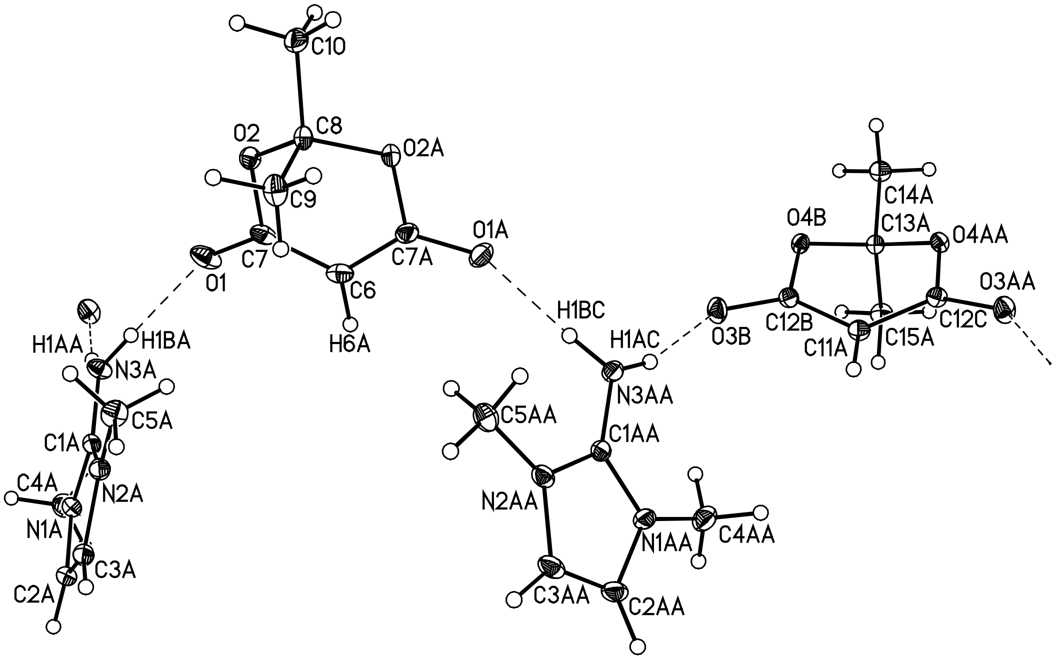
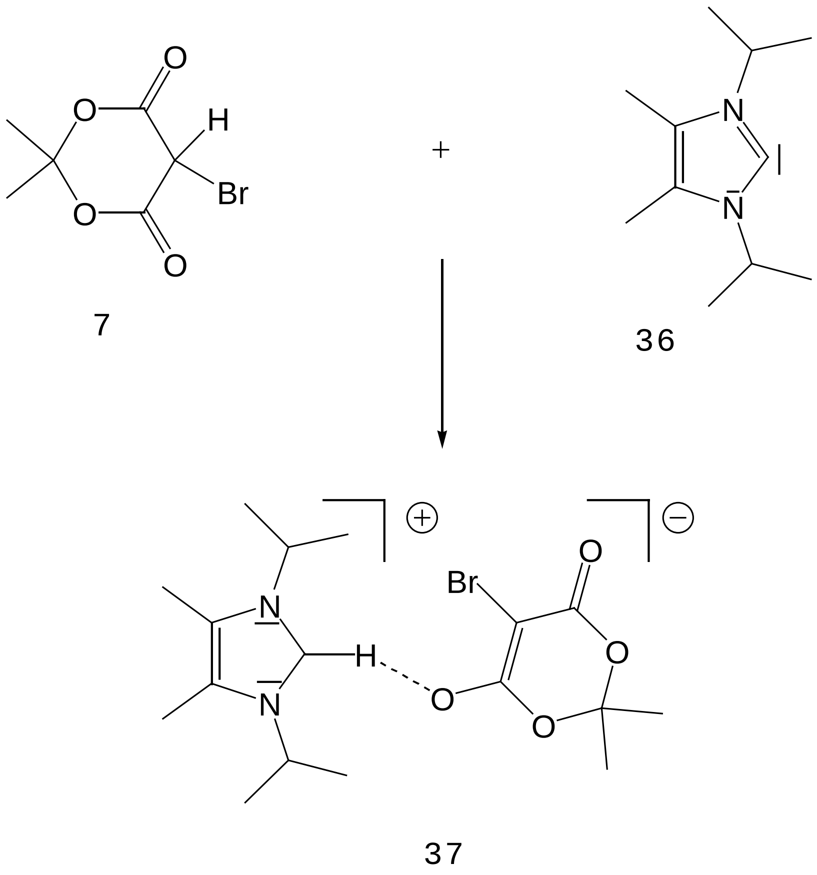


Fig. 9: The structure of $C_{11}H_{17}N_3O_4$ **(35)** in the crystal.

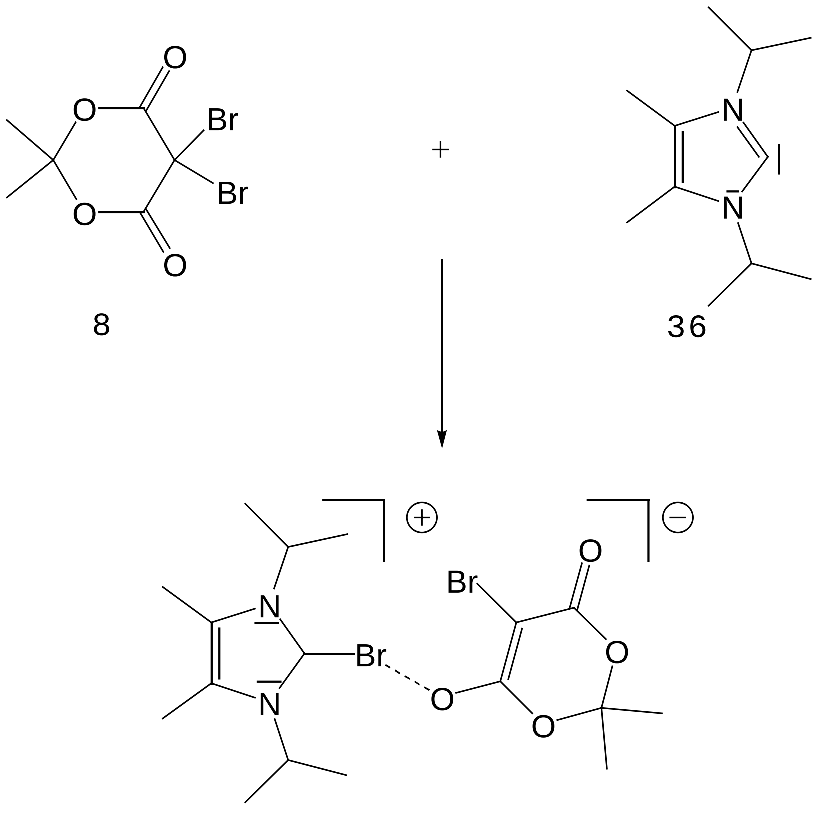
3.3.2 Reaction of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylides with 5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxan **(7)** and 5,5-dibromo-2,2-dimethyl-4,6-dioxo-1,3-dioxan **(8).**

The reaction of **7** with carbene **36** [61] gives a stable solid salt [ImH][MelBr] **37** in good yield.



The spectroscopic data of the cation ImH (experimantal part) are close to that observed in others salts of this cation [62].

Carben **36** was also reacted with dibrom-derivative **8** and gave a stable solid salt [ImBr] [MelBr] **38** in good yield. The spectroscopic data (experimental part) are close to those of the anion of **37** [MelBr] and the cation [ImBr] is close to those of the other salts. [63].



8

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38

The NMR spectra of **37** and **38** show signals of the isolated anions. ^{13}C-NMR- spectra of C5$_{M}$ in the anion of **37** ($\delta = 63$) close to the spectra of the anion of **35** ($\delta = 64.7$) .

The IR spectra clearly show a small shift of the wave number of the C=O stretching frequencies (ν_{CO} **7**: 1773, 1753; **8**: 1754; **37**: 1618; 1624 cm^{-1}).

The X-ray structure for **37** and **38** were determined [64] (Tables 21-24, Fig. 10,11). In both compounds, the anions are connected with the cations by exocyclic oxygen atoms.

The hydrogen bond trained in **37** [C(1)-H(1A) 0.910(2), H(1A)...O(1) 2.163(1), O(1)-C(13) 1.219(5) Å, C(1)-H(1A)...O(1) 175.3 (2), H(1A)...O(1)-C(13) 117.3(2) °] lies within the standard range of linear C...H...O bridge. Into **38,** the unexpected Br...O contact lies within the van-der Waals distance [O(1)...Br(1) 2.872(1), O(1)-C(13) 1.230(4), Br(1)-C(1) 1.846(4) Å, Br(1)...O(1)-C(13) 116.7(1),C(1)-Br(1)...O(1) 153.6(2) °], while the shortest interionic Br...Br contact with 4.056 Å lies outside of the interaction binding range.

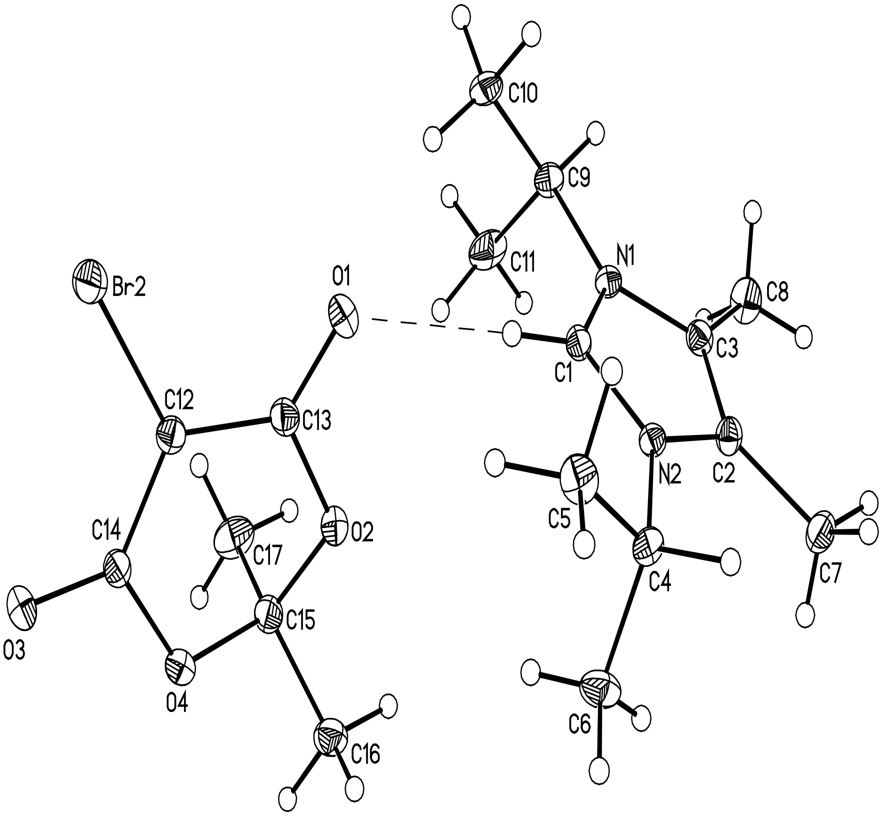


Fig. 10: The structure of $C_{17}H_{27}BrN_2O_4$ **(37)** in the crystal.

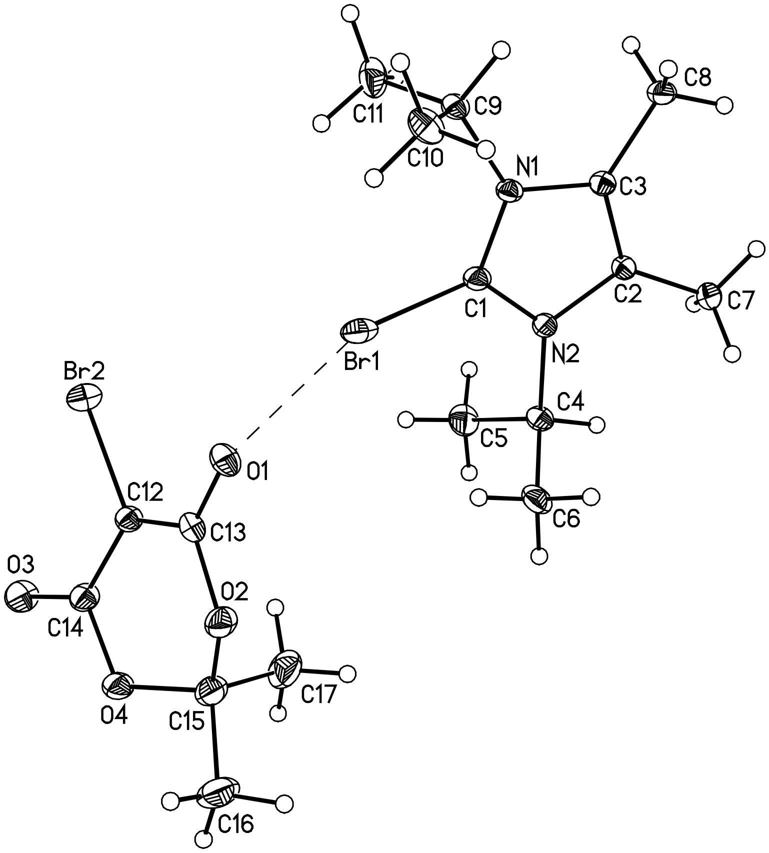
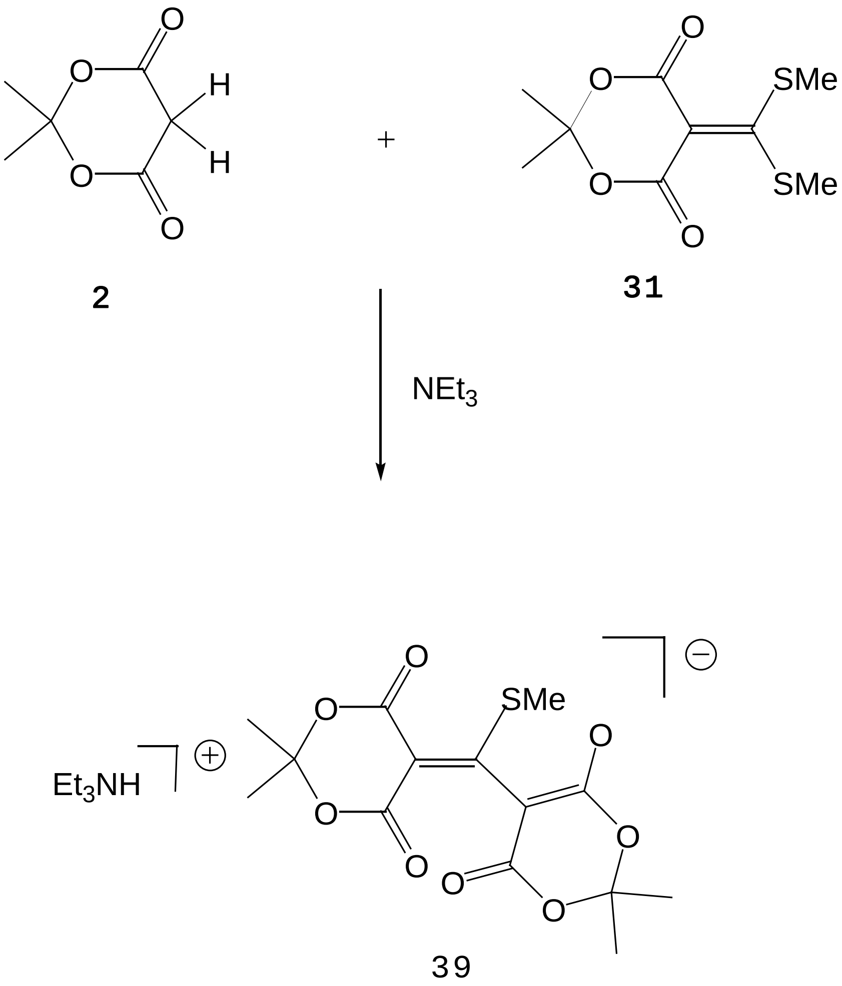


Fig. 11: The structure of $C_{17}H_{26}Br_2N_2O_4$ **(38)** in the crystal.

3.3.3 Synthesis of 2,2-dimethyl-4,6-dioxo-5-[((methylsulfanyl)methy-lene)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl]-1,3-dioxanide triethyl ammonium salt

Reaction of **2** with **31** in the presence of triethylamine gives **39** as stable crystalline solid in good yield.



The crystal analysis (Tables 25-27, Fig. 12) [65] shows for the anion of **39** concerning the central C$_3$-Fragments an 'unsymmetrical' structure [C(1)-C(11) 1.455(5), C(1)-C(21) 1.379(5) Å; C(11)-C(1)-C(21) 122.1(3) °] with significant deviations of the associated ring fragments from the coplanarity [interplanar angle C(1)C(11)C(12)/C(1)C(21)C(22) 59.12 °].

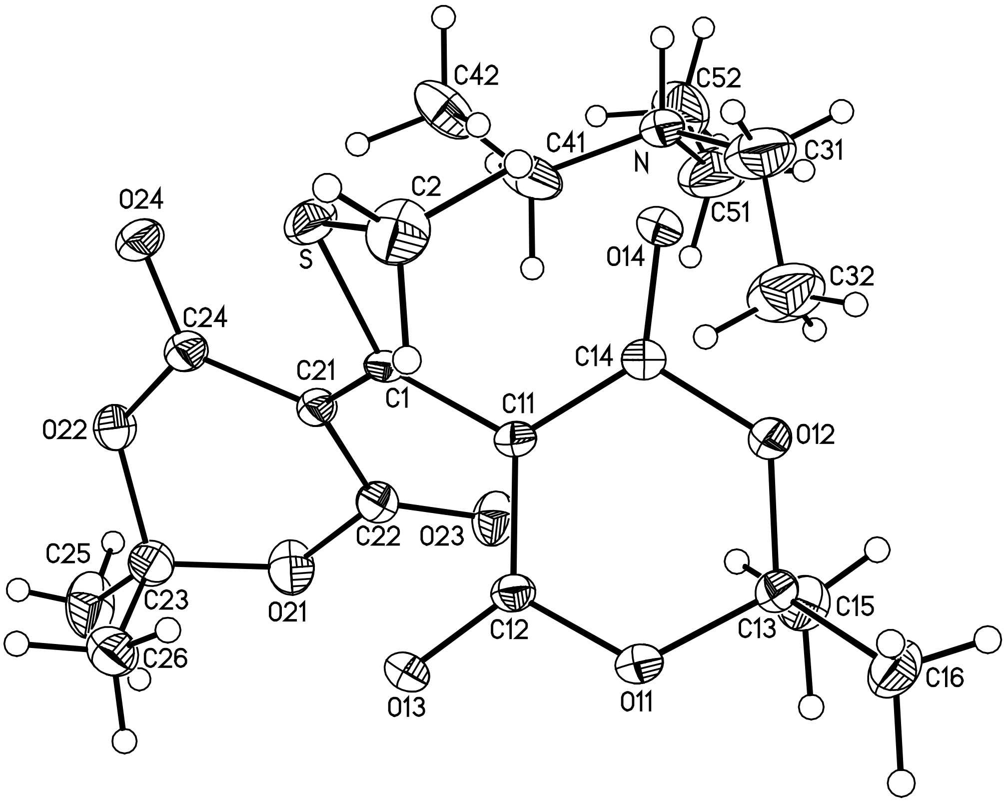
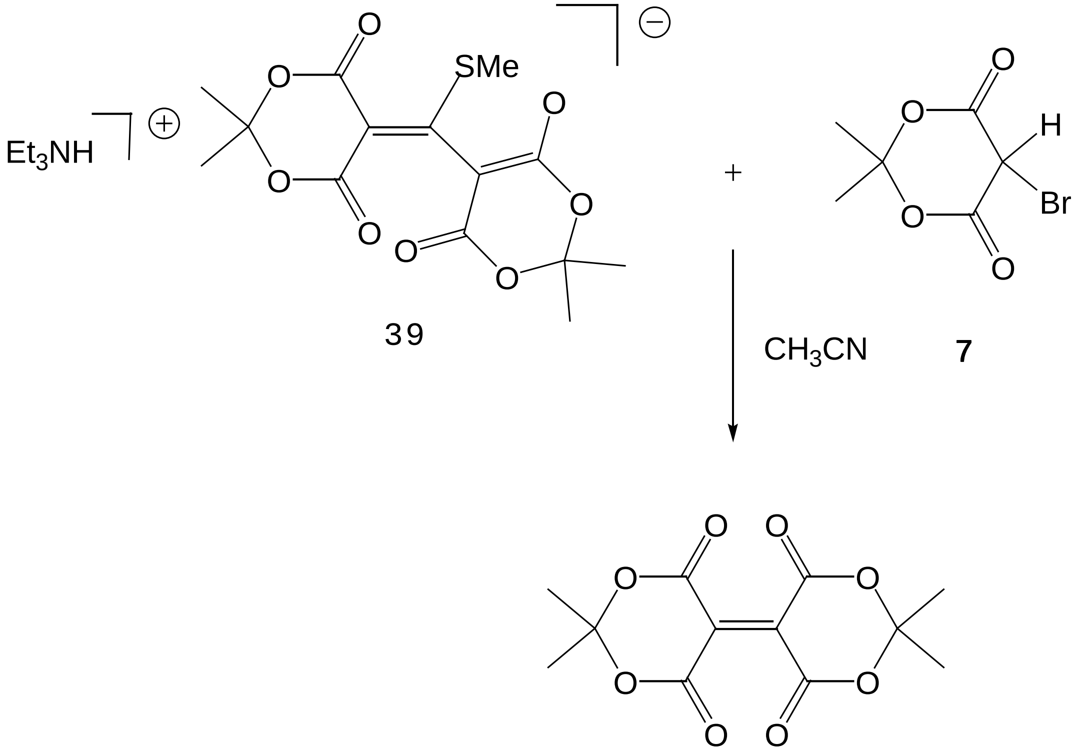


Fig. 12: The structure of [HN(C_2H_5)$_3$][$C_{14}H_{15}O_8S$] **(39)** in the crystal.

3.4 Synthesis of Meldrum's olefin

Reaction of **39** with **7** in CH_3CN gives **9** as stable solid in low yield.



9

9 is not soluble in all usual solvents over the temperature range from r.t. to the boiling point. It was soluble only in boiling nitromethan, and after slow cooling of this solution a single crystal suitable to the crystal analysis was formed.

9 crystallises in the triclinic space group P-1 (Tables 28-30, Fig. 13) [66]. The center of the olefinic double bond lies on the crystallographic inversion center. The two dioxin rings are not coplanar [interplanar angle C(2)C(1)C(3)/C(2)C(3)O(1) 34,9°], and the intramolecular distance between each opposite exocyclic oxygen atoms [O(3).... O(4A) 2,88 Å] lies within the *van der Waals* contact range. The central C=C double bond [C(1)-C(1A) 1.3501 (19) Å] lies in the expectation range of non-polarized olefins.

The invers symmetrical structure of the molecule of **9** in the crystal is illustrated also by the chemical unequivalence of the carbonyl groups [δ = 157,3, 160,1] and methyl groups [δ = 27,4, 28,0] in the ^{13}C-NMR-Spectrum (MAS).

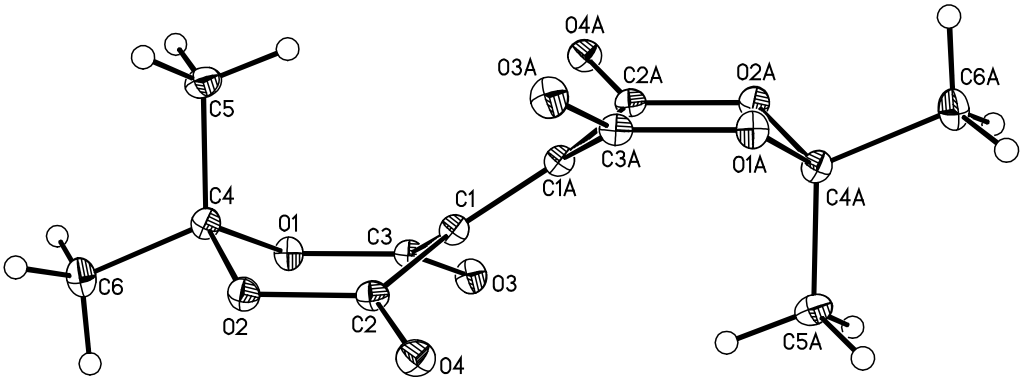


Fig. 13: The structure of $C_{12}H_{12}O_8$ **(9)** in the crystal.

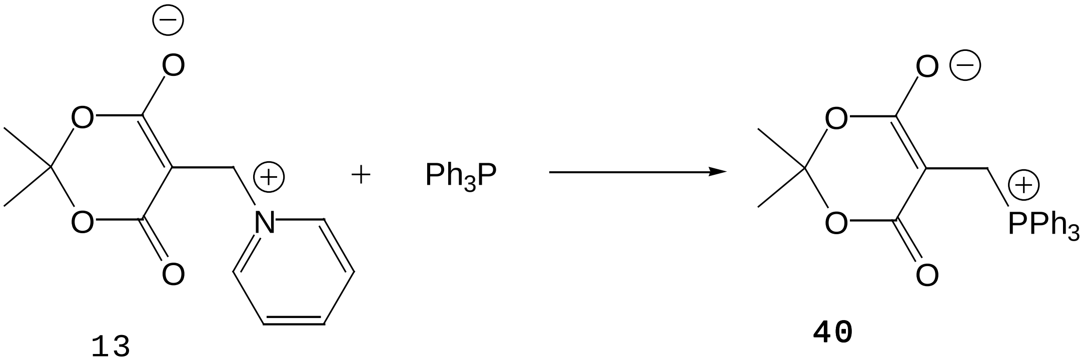
The thermal or solvent supported splitting of the double bond into carbene fragments, which was observed in olefins of the Wanzlick type [67], was not observed in Meldrum's olefin.

Also in the mass spectrum (EI) it was observed neither the molecular ion nor the associated fragment monomers of the carbene.

3.5 Derivatieves of methylene Meldrum’s acid

3.5.1 Synthesis 2,2-dimethyl-4,6-dioxo-5-[(triphenylphosphonio)methyl]-1,3-dioxan-5-yl-phosphonium ylide.

The reaction of **13** with triphenyl phosphine gives **40** as stable crystalline solid in good yield.



The structure of **40** was initially assigned in solution by ^{1}H and ^{13}C NMR. The ^{13}C NMR spectrum shows a large chemical shift of C5$_M$ (62.8 ppm) relative to its position in Meldrum’s acid (35.20 ppm).

The molecular structure of **40** was confirmed by X-ray crystallography [68] (Tables 31-35, Fig 14). **40** crystallizes in the monoclinic space group P2(1).

The C(3)-C(1)-P(1) angle is 115.75(11)°. The C=O bond lengths of [O(1)-C(2) 1.233(2)Å, (O(3)-C(4) 1.234(2) Å] are slightly longer than those of carbonyl group in Meldrum’s acid (1.19 Å), and the C-C bond lengths of [(C(2)-C(3) 1.412(2)Å, (C(3)-C(4) 1.421(2)Å] are intermediate between those of carbon-carbon single and double bonds.

From the chemical shifts of the *sp*^{2} hybridized center and from the X-ray analysis data, it was concluded that **40** adopts the enolate nature.

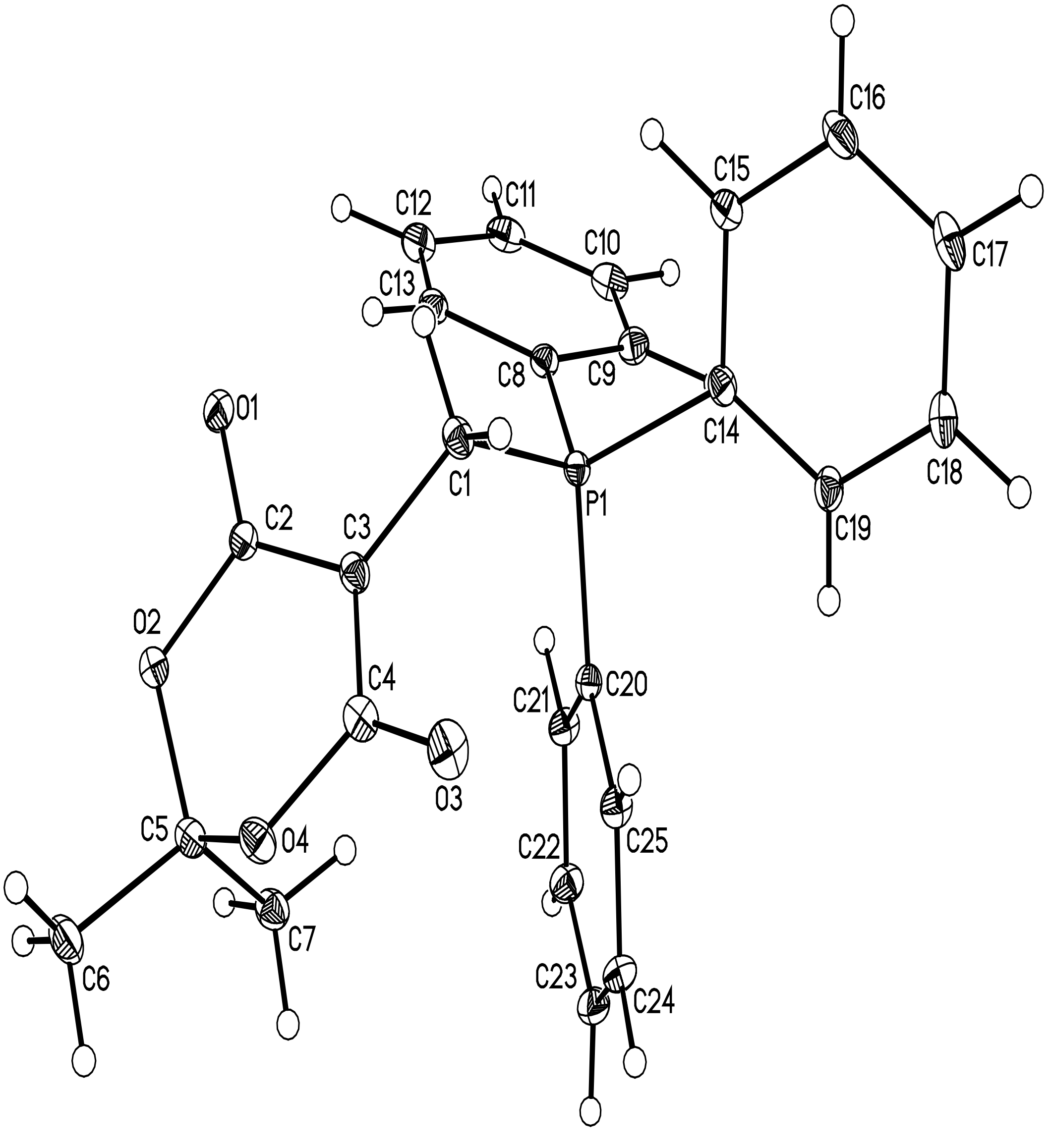
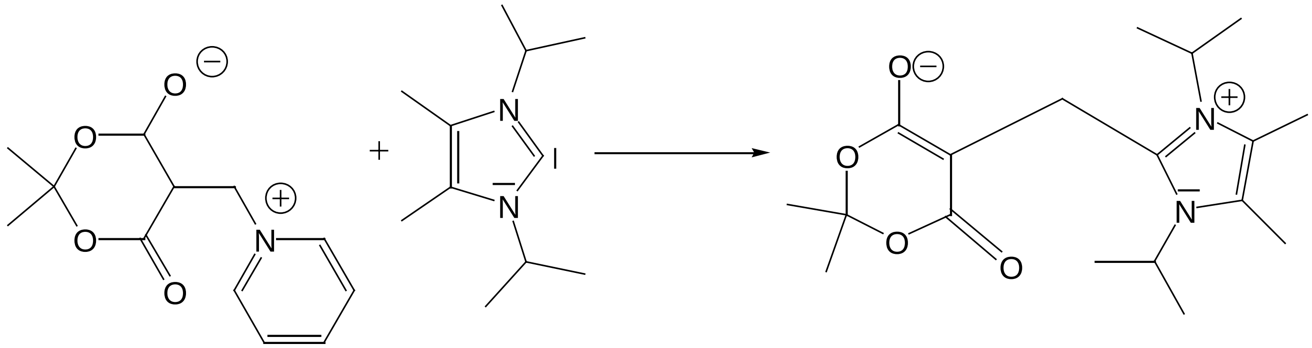


Fig. 14: The structure of $C_{26}H_{23}O_4P$**(40)** in the crystal.

3.5.2 Synthesis of 2,2-dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)methyl]-1,3-dioxan-5-yl-imidazolium ylide.

The reaction of **13** with carbene **36** gives **41** as stable crystalline solid in good yield.



13 **36** **41**

The molecular structure of **41** was confirmed by X-ray crystallography (Tables 36-40, Fig 15) [69]. **41** crystallises in the monoclinic space group C2/c

By comparing the structure of its dioxin ring with Meldrum's acid, the enolate nature of **41** is reflected by elongated exocyclic C=O bonds [(O(3)-C(1) 1.227(2)Å, (O(4)-C(8) 1.226(2) Å] and by shortage endocyclic C-C bonds [C(3)-C(1) 1.398(2)Å, (C(3)-C(8) 1.408(2)Å]. Consequently, their imidazolium part resembles closely to the structures of imidazolium salts [43-44].

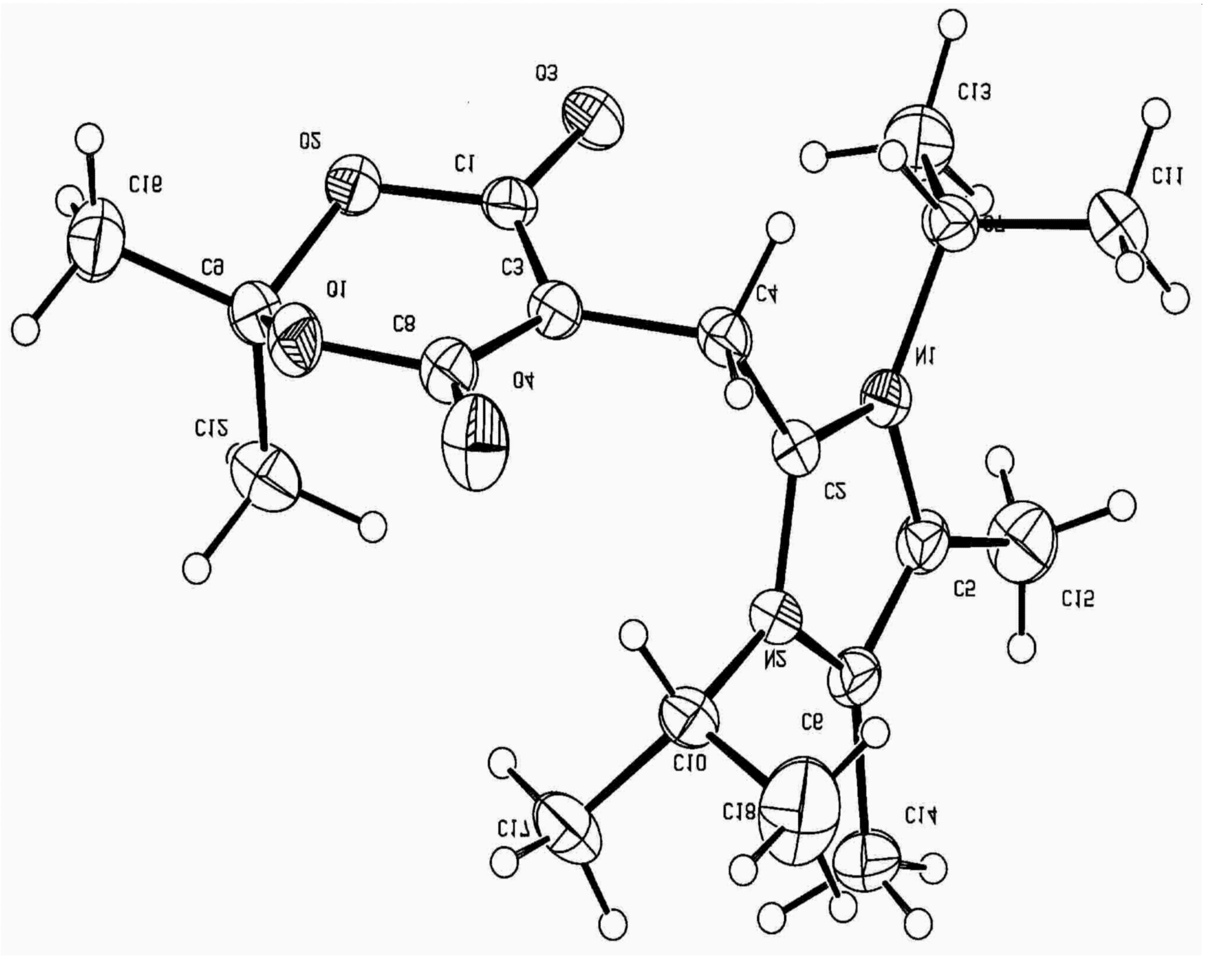
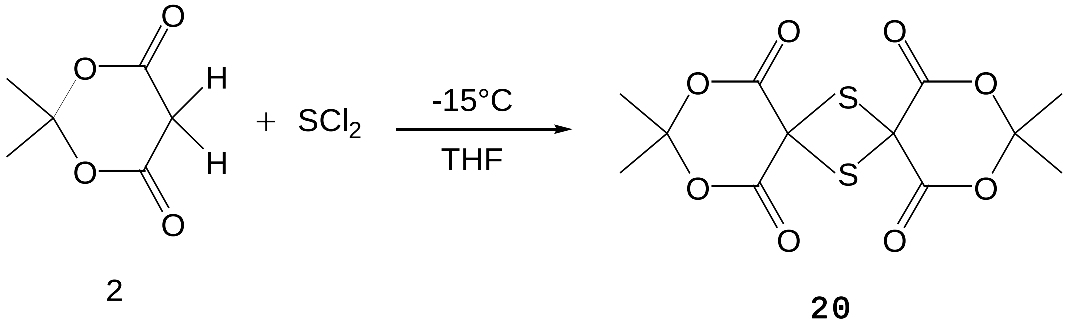


Fig. 15: The structure of $C_{18}H_{28}N_2O_4$ **(41)** in the crystal.

3.6 The dimer of thioxo Meldrum's acid and its derivatives

3.6.1 Dimer of thioxo Meldrum's acid

The reaction of **2** with SCl_2 gives **20** as stable crystalline solid in good yield.



The molecular structure of **20** was confirmed by X-ray crystallography (Tables 41-44, Fig. 16) [70]. **20** crystallises in the triclinic space group *P*-1.

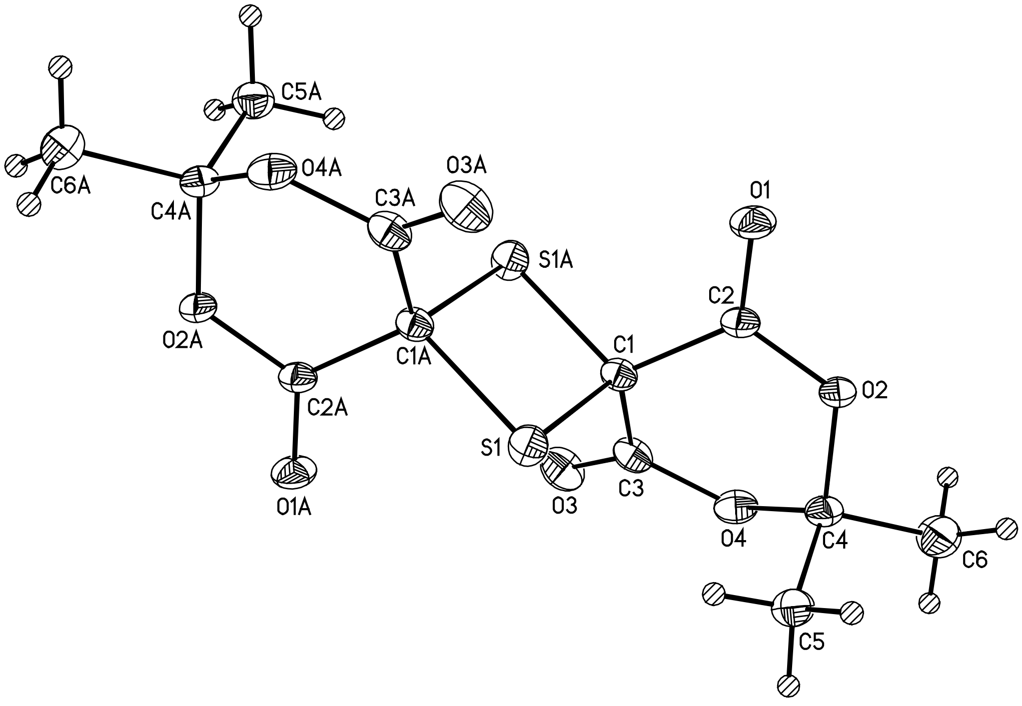


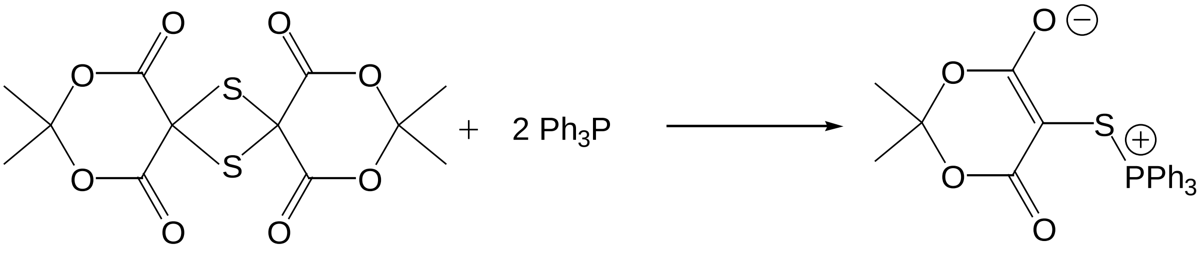
Fig. 16: The structure of $C_{16}H_{16}O_5S_2$ **(20)** in the crystal.

20 sits across a crystallographic inversion center and as a consequence, the 1,3-dithietane ring is planar (Fig. 16). The literature reports only 6 other structures that have a 1,3-dithietane ring with unsubstituted S and *sp*^{3} C atoms [71].

The C-S bond lengths [S(1)-C(3) 1.848 (2) Å and S(1)-C(3a) 1.809 (3) Å] lie in the normal range of the C-S single bond. The C-S-C bond angles are significantly less than 90° [C(3)-S(1)-C(3a) 86.55°] , while the S-C-S angles are correspondingly larger than 90° [S(1)-C(3)-S(1a) 93.45°], It is interesting to note that the S...S and C...C distances of the four-membered ring, 2.6626 and 2.507 Å, respectively, lie in the *van der Waals* range.

3.6.2 Synthesis of 2,2-dimethyl-4,6-dioxo-5-[(triphenylphosphonio)sulfanyl]-1,3-dioxan-5-yl-phosphonium ylide.

The reaction of **20** and triphenylphosphine gives the zwitterionic compound **42** as stable crystalline solid in good yield.



The ^{13}C NMR spectrum shows the shift of the C5$_M$ signal to 56.2 ppm. In the in ^{31}P NMR spectrum, the signal (46.2 ppm) is in the range of phosphonium-salts as expected.

The molecular structure of **42** was confirmed by X-ray crystallography (Tables 45-49, Fig 17). **42** crystallizes in the monoclinic space group P2(1) [72].

The central C(3)-S(1)-P(1) angle is 105.65(7)°. The C-S and S-P bond lengths are in range of normal bond length with very small shortage [C(1)-S(1) 1.7399(19), S(1)-P(1) 2.0893(7) Å].

Consequently, the enolate nature of Meldrum's acid ring was confirmed. By elongation of the C=O bonds [(O(1)-C(2) 1.223(3)Å, (O(3)-C(3) 1.221(3) Å], and shortange of the endocyclic C-C bonds [(C(1-C(2) 1.436(3)Å, (C(1)-C(3) 1.423(3)Å] .

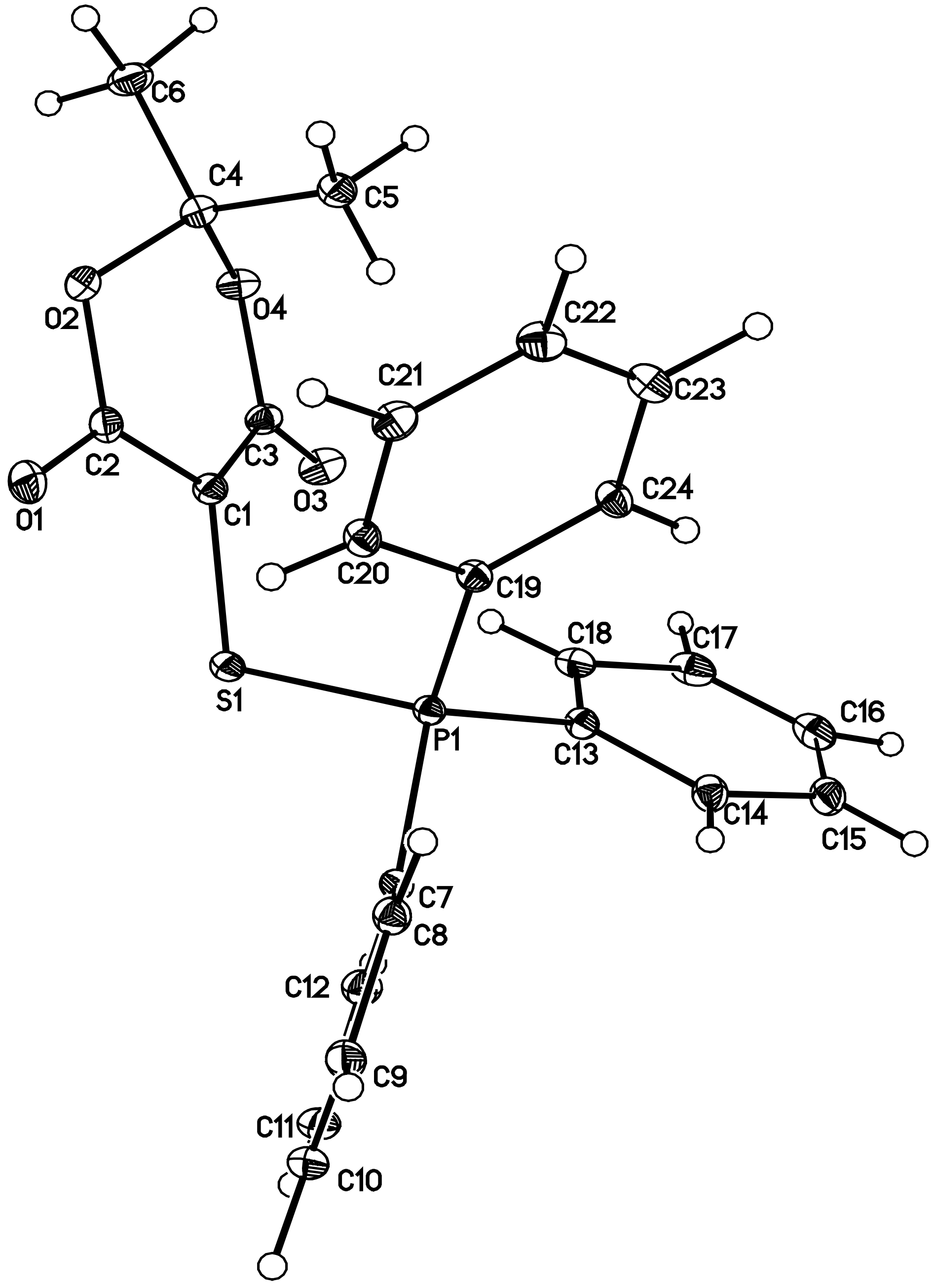
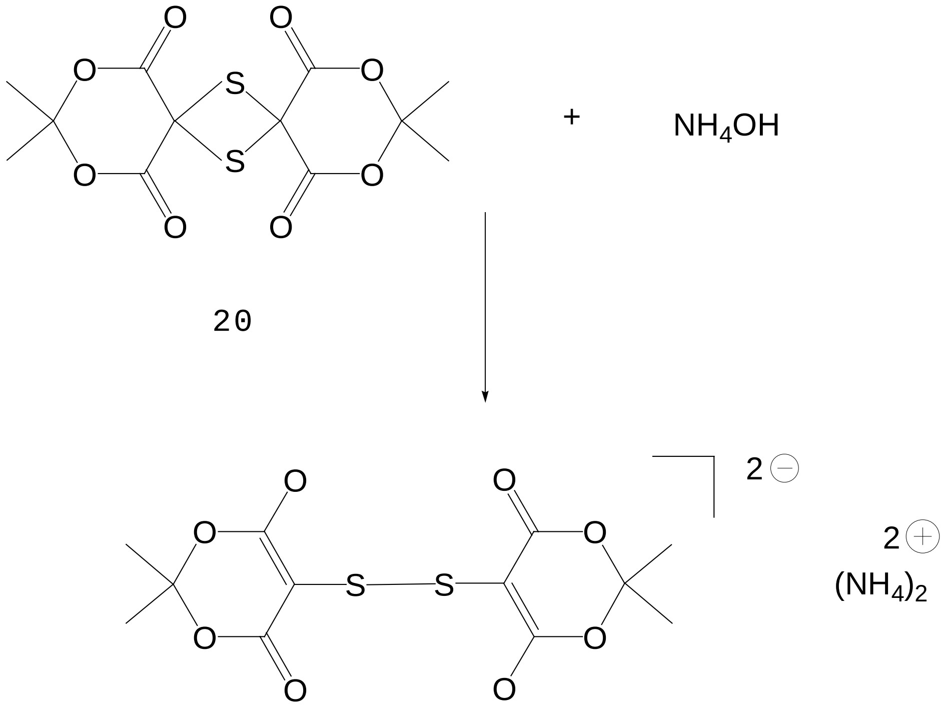


Fig. 17: The structure of $C_{24}H_{21}O_4SP$ **(42)** in the crystal.

3.6.3 The hydrolysis of the thioxo dimer of Meldrum's acid

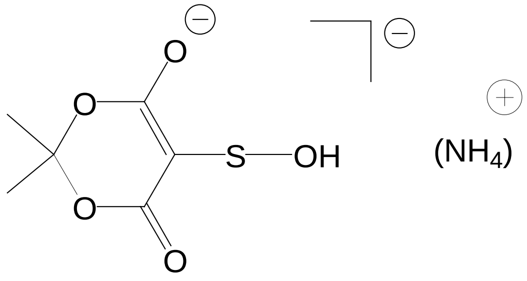
By reaction of **20** with aqueous ammonia, the resulting product was the disulfan **43** as its ammonium salt.



20

43

and not the expected sulphonic acid **44**.



44

The crystal structure analysis (Tables ,Fig.) [73] shows that the center of the S-S bond is a crystal inversion center and shows a standard S-S bond and small shortage C-S bond [S(1)-S(1A) 2.1466(15), S(1)-C(1) 1.740(2)A, C(1)-S(1)-S(1A) 100.60(9)°].

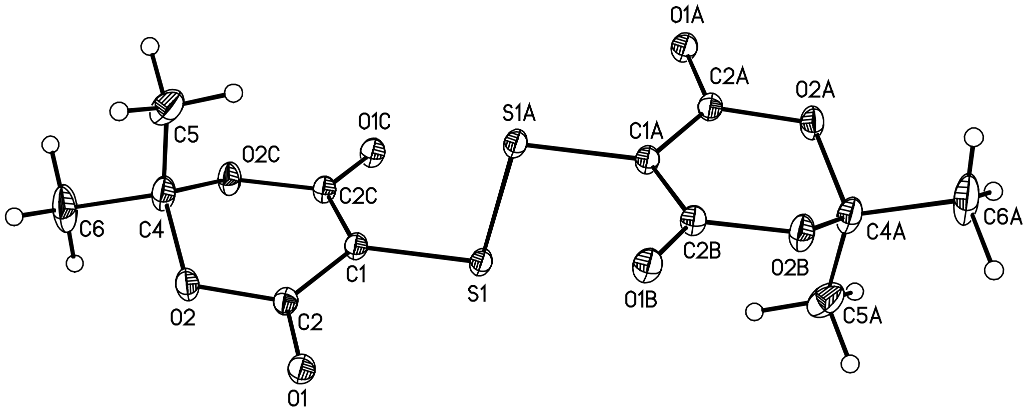


Fig. 18: The structure of the anion of $C_{28}H_{50}N_4O_{17}S_4$ **(43)** in the crystal.

The hydrogen bonds to the ammonium ion [N(3)-H(3A) 0.908, H(3A)-O(1C) 1.932A, N(3)-H(3A)-O(1C) 158.5 °].confirm a sechs membered ring unit (Fig. 19).

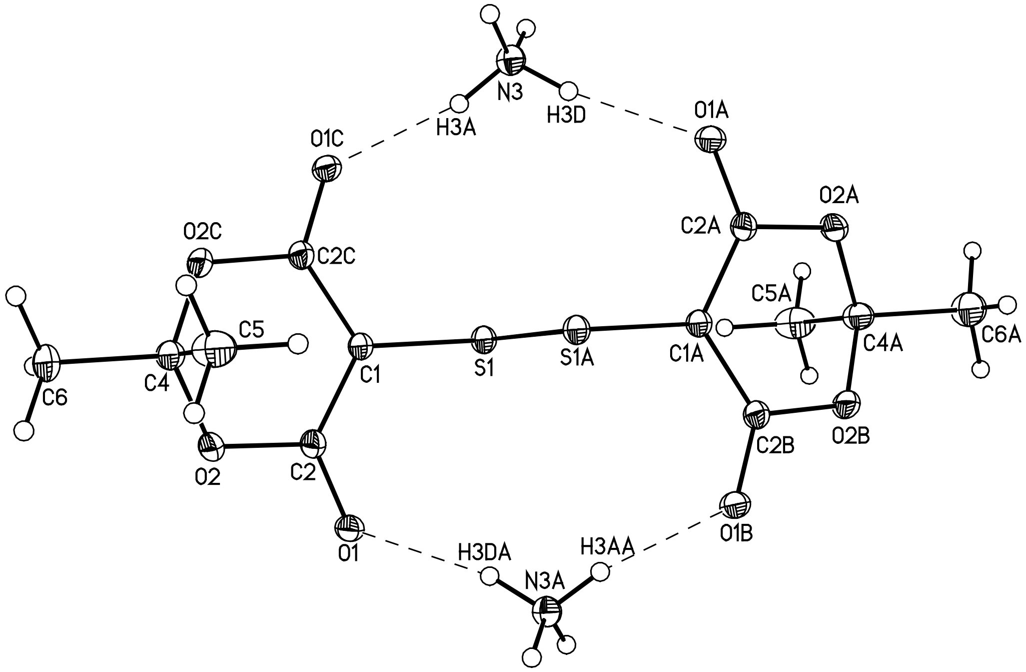


Fig. 19: The structure of $C_{28}H_{50}N_4O_{17}S_4$ **(43)** in the crystal.

4 Experimental Section

4.1 Methods of analysis

4.1.1 Elemental analysis

The elemental analysis was measured by an elemental analyzer from Carlo Erba Company, Modell 1106.

The accuracy was attached

Carbon: ± 0,3%

Hydrogen: ± 0,3%

Nitrogen: ± 0,3%

Chlor: ± 0,3%

4.1.2 Melting point determination

The melting point device is from Büchi Company, type Büchi 510. All melting points are not corrected.

4.1.3 Mass spectra

The EI-Mass spectra were acquired on a Finnigan TQS 70, by 70 eV at (200 °C). The FAB-Mass spectra were acquired on a Finnigan TQS 70, by 70 eV in Nitrobenzylalcohol-Matrix at 30°C, instrument modified by AMD and reported as mass/charge (*m/z*).

4.1.4 NMR spectra

The high resolution NMR spectra were acquired by Bruker DRX 250 NMR spectrometer operating at (^{1}H: 250,13MHz; ^{13}C: 62,90MHz; ^{31}P: 101,20MHz; ^{19}F: 235,34MHz). The spectra were measured relative to TMS (^{1}H, ^{13}C); C_6F_6 (^{19}F) as internal standard and Me_2Se (^{77}Se); Me_2Te(^{125}Te); 85% H_3PO_4 (^{31}P) as external standerd .

The following abbreviations were used in the discription of the spectra:

s	Singlet
d	Doublet
t	Triplet
q	Quartet
m	Multiplet

4.1.5 IR spectra

The FTIR spectra were acquired by a Bruker IFS 25 IR spectrometers. The measuring range was from 4000 to 225 cm-^{1}. The sample preparation were taken place in the form of KBr pressing or films.

4.1.6 Crystal structure analyses

The crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer (**21, 26a, 26b, 29a, 29b, 32, 35, 37, 38, 40, 42, 43**), a Nonius Kappa CCD diffractometer (**26c, 39, 41, 20**), and a Stoe IPDS diffractometer (**29c, 9**) using graphite-monochromated Mo–K_α radiation. The lattice constants were determined by 25 precisely centered high-angle reflections and refined by least-squares methods. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-93 or SHELXTL-97.

4.2 General comments

All experiments were carried out under an atmosphere of argon.

4.3 Solvents

The solvents needed for the reactions were dried by conventional procedures and were stored over molecular sieves.

4.4 Starting materials

2,2-Dimethyl- 4,6- dioxo- 1,3- dioxane (Meldrum’s acid)	[2]
5- Bromo- 2,2-dimethyl- 4,6- dioxo- 1,3- dioxine	[8]
5,5- Dibromo- 2,2-dimethyl- 4,6- dioxo- 1,3- dioxine	[8]

4.5 Preparation of the Compounds

4.5.1 Preparation of 2,2-Dimethyl-4,6-dioxo-5-(1-pyridinio)-1,3- dioxan-5-yl-pyridinium ylide (**21**)

A solution of 1.115 g (5 mmol) of **7** and 0.41 ml (5 mmol) of pyridine in 30 ml of tetrahydrofuran was stirred for 12 h at r.t. The solvent was removed *in vacuo* and the residue dissolved in 30 ml of water. After addition of 10 ml of a saturated aqueous solution of K_2CO_3, the yellow solution was extracted three times with 10 ml of dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was recrystallised from dichloromethane/diethylether to give 0.57 g (52 %), pale yellow crystals; m.p. 204 - 206 °C.

^{1}H-NMR (CD_2Cl_2):

δ= 1.65	[s, 6 H, Me]
δ= 7.73- 8.81	[m, 5 H, Pyr]

^{13}C-NMR (CD_2Cl_2):

δ= 25.2	[Me]
δ=101.7	[C2]
δ=125.3, 140.1, 145.5	[py]
δ=160.3	[C4,6]
δ= not observed	[C5]

MS (EI, 70 eV): *m/z* (%) = 221 (70) [M^+], 163 (70) [M^+ - C_3H_6O], 119 (80) [M^+ - C_3H_6O, CO_2], 91 (100) [M^+ - C_3H_6O, CO_2, CO], 79 (20) [$C_5H_5N^+$] and further fragments.

IR (KBr): ν_{CO} = 1624 cm^{-1}.

Elemental analysis for $C_{11}H_{11}NO_4$ (221.07g/mol):

Found (calc.) C 59.73 (58.92), H 5.01 (4.27), N 6.33 (6.14)%.

4.5.2 Preparation of arsonium 2,2-dimethyl-4,6-dioxo-1,3-dioxanides (**26a**)

1.53 g (5 mmol) of Ph_3As were added to a solution of 1.115 g (5 mmol) of **7** in 30 ml of dichloromethane, and the mixture was stirred at r.t. for 1 h. After addition of 0.90 ml (6.5 mmol) of triethylamine and stirring for further 1 h, the solution was extracted with 10 ml of water. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/diethylether to give 1.45 g (95 %), colourless crystals; m.p. 215-216 °C.

^{1}H-NMR ($CDCl_3$):

δ= 1.78	[s, 6 H, Me]
δ= 7.45-7.65	[m, 15 H, Ph]

^{13}C-NMR ($CDCl_3$):

δ= 26.0	[Me]
δ=103.2	[C2]
δ=126.4, 129.5, 132.3, 132.7	[Ph]
δ=165.3	[C4,6]
δ= 57.4	[C5]

MS (FAB): *m/z* (%) = 449 [6, M^+ + H], 391 [100, M^+ - Me_2CO], 347 [30, M^+ - Me_2CO, CO_2] and further fragments.

IR (KBr): ν_{CO} = 1648 cm^{-1}.

Elemental analysis for $C_{24}H_{21}AsO_4$ (448.35 g/mol):

Found (calc.) C 64.16 (64.29), H 4.58 (4.72) %.

4.5.3 Preparation of stibonium 2,2-dimethyl-4,6- dioxo-1,3-dioxanides (**26b**)

1.77 g (5 mmol) of Ph_3Sb were added to a solution of 1.115 g (5 mmol) of **7** in 30 ml of dichloromethane, and the mixture was stirred at r.t. for 1 h. After addition of 0.90 ml (6.5 mmol) of triethylamine and stirring for further 1 h, the solution was extracted with 10 ml of water. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/diethylether to give 1.59g (90 %), colourless crystals; m.p. 110-113 °C.

^{1}H-NMR ($CDCl_3$):

δ= 1.80	[s, 6 H, Me]
δ= 7.38-7.75	[m, 15 H, Ph]

^{13}C-NMR ($CDCl_3$):

δ= 26.4	[Me]
δ=103.7	[C2]
δ=128.9, 130.0, 132.8, 135.7	[Ph]
δ=165.8	[C4,6]
δ= 58.5	[C5]

MS (FAB): *m/z* (%) = 504 [100, M^+ + Na, - Me], 437 [28, M^+ - Me_2CO], 393 [8, M^+ - Me_2CO, CO_2] and further fragments.

IR (KBr): ν_{CO} = 1658 cm^{-1}.

Elemental analysis for $C_{24}H_{21}O_4Sb$ (495.18 g/mol):

Found (calc.) C 58.13 (58.21), H 3.93 (4.27) %.

4.5.4 Preparation of bismuthonium 2,2-dimethyl-4,6-dioxo-1,3-dioxanides (**26c**)

2.20 g (5 mmol) of Ph_3Bi were added to a solution of 1.115 g (5 mmol) of **7** in 30 ml of dichloromethane, and the mixture was stirred at r.t. for 1 h. After addition of 0.90 ml (6.5 mmol) of triethylamine and stirring for further 1 h, the solution was extracted with 10 ml of water. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/ditehylether to give 1.60 g (55 %), colourless crystals; m.p. 90-91 °C.

^{1}H-NMR ($CDCl_3$):

δ= 1.78	[s, 6 H, Me]
δ= 7.48-7.67	[m, 15 H, Ph]

^{13}C-NMR ($CDCl_3$):

δ= 26.5	[Me]
δ=103.7	[C2]
δ=126.4, 130.1, 132.8, 133.2	[Ph]
δ=165.8	[C4,6]
δ= 57.8	[C5]

MS (FAB): m/z (%) = 552 [3, M^+ - 2 Me], 525 [8, M^+ - Me_2CO], 363 [36, Ph_2Bi^+], 286 [66, $PhBi^+$], 209 [100, Bi^+] and further fragments.

IR (KBr): ν_{CO} = 1581 cm^{-1}.

Elemental analysis for $C_{24}H_{21}BiO_4$ (582.41 g/mol):

Found (calc.) C 48.90 (49.50), H 3.25 (3.63) %.

4.5.5 Preparation of 2,2-dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)sulfanyl]-1,3-dioxan-5-yl-imidazolium ylide.(**29a**)

1.06 g (5 mmol) of **28a** were added to a solution of 1.115 g (5 mmol) of **7** in 30 ml of dichloromethane, and the mixture was stirred at r.t. for 1 h. After addition of 0.90 ml (6.5 mmol) of triethylamine and stirring for further 1 h, the solution was extracted with 10 ml of water. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/diethylether to give 1.68 g (95 %), colourless crystals; m.p. 213 °C.

^{1}H-NMR ($CDCl_3$):

δ= 1.50	[d, 12 H, CH*Me₂*,]
δ= 1.54	[s, 6 H,2- Me_M]
δ= 2.27	[s,6H,4,5-Me_I]
δ= 6.11	[sept, 2H, C*H*Me_2]

^{13}C-NMR ($CDCl_3$):

δ= 9.5	[4,5-Me_I]
δ=20.4	[CH*Me₂*]

δ=25.1	[2-Me$_M$]
δ=51.9	[*C*HMe$_2$]
δ= 61.5	[C5$_M$]
δ= 100.5	[C2$_M$]
δ= 126.4	[C4,5$_I$]
δ= 165.3	[C4,6$_M$]
δ= not observed	[C2$_I$]

MS (FAB): *m/z* (%) = 354[16, M$^+$], 297 [8, M$^+$ - 2Me,CO], 212 [100, M$^+$ - $C_6H_6O_4$], 128 [96, M$^+$ - $C_{11}H_{19}O_4$] and further fragments.

IR (KBr): ν_{CO} = 1649 cm^{-1}.

Elemental analysis for $C_{17}H_{26}N_2O_4S$ (354.46 g/mol):

Found (calc.) C 57.5 (57.60), H 7.87 (7.39), N 7.95(7.90), S 8.86 (9.05) %.

4.5.6 Preparation of 2,2-dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)selanyl]-1,3-dioxan-5-yl-imidazolium ylide. (**29b**)

1.30 g (5 mmol) of **28b** were added to a solution of 1.115 g (5 mmol) of **7** in 30 ml of dichloromethane, and the mixture was stirred at r.t. for 1 h. After addition of 0.90 ml (6.5 mmol) of triethylamine and stirring for further 1 h, the solution was extracted with 10 ml of water. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/diethylether to give 1.91 g (95 %), colourless crystals; m.p. 201 °C.

^{1}H-NMR ($CDCl_3$):

δ= 1.51	[d, 12 H, CH*Me*$_2$,]
δ= 1.56	[s, 6 H,2- Me$_M$]
δ= 2.28	[s,6H,4,5-Me$_I$]
δ= 6.0	[sept, 2H, C*H*Me$_2$]

^{13}C-NMR (CDCl$_3$):

δ= 9.5	[4,5-Me$_I$]
δ=20.4	[CH*Me*$_2$]
δ=25.0	[2-Me$_M$]
δ=53.7	[*C*HMe$_2$]
δ= 62.2	[C5$_M$]
δ= 100.7	[C2$_M$]
δ= 127.0	[C4,5$_I$]
δ= 165.2	[C4,6$_M$]
δ= not observed	[C2$_I$]

MS (FAB): *m/z* (%) = 403 [24, M$^+$], 345 [100, M$^+$ - 2Me,CO], 259 [68, M$^+$ - $C_6H_6O_4$], 181 [32, M$^+$- $C_6H_6O_4Se$] and further fragments.

IR (KBr): ν_{CO} = 1643 cm^{-1}.

Elemental analysis for $C_{17}H_{26}N_2O_4Se$ (401.36 g/mol):

Found (calc.) C 50.05 (50.87), H 5.89 (6.53), N 6.76(6.98) %.

4.5.7 Preparation of 2,2-dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)tellanyl]-1,3-dioxan-5-yl-imidazolium ylide **(29c)**

1.54 g (5 mmol) of **28c** were added to a solution of 1.115 g (5 mmol) of **7** in 30 ml of dichloromethane, and the mixture was stirred at r.t. for 1 h. After addition of 0.90 ml (6.5 mmol) of triethylamine and stirring for further 1 h, the solution was extracted with 10 ml of water. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/diethylether to give 2:21 g (98 %), colourless crystals; m.p. 165 °C.

^{1}H-NMR ($CDCl_3$):

δ= 1.51	[d, 12 H, CHMe_2,]
δ= 1.55	[s, 6 H,2- Me$_M$]
δ= 2.28	[s,6H,4,5-Me$_I$]
δ= 5:8	[sept, 2H, C*H*Me$_2$]

^{13}C-NMR ($CDCl_3$):

δ= 9.6	[4,5-Me$_I$]
δ=20.4	[CHMe_2]
δ=24.9	[2-Me$_M$]
δ=51.2	[*C*HMe$_2$]
δ= 57:0	[C5$_M$]
δ= 100.1	[C2$_M$]
δ= 127.8	[C4,5$_I$]
δ= 166.5	[C4,6$_M$]

δ= not observed	[C2_I]

MS (FAB): *m/z* (%) = 452 [8, M^+], 393 [68, M^+ - 2Me,CO], 307 [56, M^+ - $C_6H_6O_4$], 181 [100, M^+- $C_6H_6O_4$Te] and further fragments.

IR (KBr): ν_{CO} = 1637 cm^{-1}.

Elemental analysis for $C_{17}H_{26}N_2O_4$Te (450 g/mol):

Found (calc.) C 45.09 (45.37), H 5.53 (5.82), N 6.20 (6.23) %.

4.5.8 2,2-dimethyl-4,6-dioxo-5-[2-(4,5-dicyano)] imidazolio–1,3-dioxane-5-yl-imidazolium ylide (**32**).

A mixture of 1.24 g (5 mmol) of **31** and 0.54 g (5 mmol) of cis-1,2-diamino-1,2-dicyano ethylene in 30 ml of absolute ethanol was refluxed for 8 h. After cooling, the product was recrystallised from dimethyl sulfoxide / dichloromethane to give 0.90 g(69%) colorless crystals, m.p. 209 °C.

^{1}H NMR (DMSO):

δ= 1.51	[s, 6 H,2- Me_M]
δ= 12.2	[s, 2 H, NH]

^{13}C-NMR (DMSO):

δ=26.4	[2-Me_M]
δ=51.2	[*C*HMe_2]
δ= 71.6	[C5_M]
δ= 103.2	[C2_M]

δ= 109.2	[CN]
δ= 111.2	[C4,5$_{I}$]
δ= 148.5	[C2$_{I}$]
δ= 166.5	[C=O]

MS (FAB (-)): *m/z* (%) = 304.7 [30, M^+ + 2Na], 258.8 [45, M^+ - H], 153 [100, M^+ - Me_2CO, CO_2] and forther fragments.

IR (KBr): ν_{CO} = 1635 cm^{-1}.

ν_{CN} = 2244 cm^{-1}

Elemental analysis for $C_{11}H_8N_4O_4$ (260 g/mol):

Found (calc.) C 50.68 (50.77), H 3.18 (3.10), N 21.73 (21.23) %.

4.5.9 Preparation of 2-Amino-1,3-dimethylimidazolium-2,2-dimethyl-4,6-dioxo-1,3-dioxanide (**35**)

0.56 g (5 mmol) of **35** were added to a solution of 0.72 g (5 mmol) of **2 i**n 20 ml of acetonitril was stirred for 3h. The solvent was removed *in vacuo.* The residue was recrystallised from dichloromethane /diethylether to give 1.25 g (98 %), colourless crystals, m.p. 141 °C.

^{1}H-NMR ($CDCl_3$):

δ= 1.54	[s, 6 H,2- Me$_{M}$]
δ= 3.51	[s, 6 H, N-Me]
δ= 3.85	[s, 1 H, 5-H]
δ= 6.50	[s, 2 H, 2,5-H]
δ= 8.49	[s, 2 H, NH_2

^{13}C-NMR ($CDCl_3$):

δ= 26.1	[2-Me_M]
δ=33.6	[N-Me]
δ=64.7	[$C5_M$]
δ=102.6	[$C2_M$]
δ= 116.5	[C4,5]
δ= 147.5	[C2]
δ= 166.5	[C4,6_M]

Elemental analysis for $C_{11}H_{17}N_3O_4$ (255.27 g/mol):

Found (calc.) C 51.76 (51.54), H 6.71 (6.50), N 16.46 (16.49) %.

4.5.10 Preparation of 1,3-Diisopropyl-4,5-dimethylimidazolium-5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxanide (**37**).

A solution of 1.56 g of **7** (7 mmol) in 20 ml of tetrahydrofuran was added to 1.27 g (7 mmol) **36** in 20 ml of tetrahydrofuran at -78 °C. After the reaction mixture was warmed to r.t the precipitate was filtered off and dried *in vacuo*. Yield after recrystallisation from dichloromethane/diethylether 2.4g (85 %), pale yallew crystals

^{1}H-NMR ($CDCl_3$):

δ= 1.51	[s, 6 H,2- Me_M]
δ= 1.53	[d, 12H, CHMe_2]
δ= 2.2	[s,6H,4,5-Me_I]
δ= 4.38	[sept, 2H, C*H*Me_2]

δ= 9.6	[s, 1 H, 2H$_I$]

^{13}C-NMR ($CDCl_3$):

δ= 9.1	[4,5-Me$_I$]
δ=23.0	[CHMe_2]
δ=26.1	[2-Me$_M$]
δ=51.3	[CHMe$_2$]
δ= 62.0	[C5$_M$]
δ=101.0	[C2$_M$]
δ= 126.5	[C4,5]
δ= 132.0	[C2]
δ= 166.5	[C4,6$_M$]

IR (KBr): ν_{CO} = 1618 (sst,br) cm^{-1}

Elemental analysis for $C_{17}H_{27}BrN_2O_4$ (403.32 g/mol):

Found (calc.) C 50.49 (50.63), H 6.65 (6.75), N 6.88 (6.95) %.

4.5.11 Preparation of 1,3-Diisopropyl-4,5-dimethyl-2-bromoimidazolium-5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxanide (**38**)

A solution of 2.12 g of **8** (7 mmol) in 20 ml of diehylether was added to 1.27 g (7 mmol) **36** in 20 ml of diehylether at -10 °C. After the reaction mixture was warmed to r.t the precipitate was filtered off and dried *in vacuo*. Yield after recrystallisation from dichloromethane /diethylether 2.8g (83 %), pale yallew crystals

^{1}H-NMR (CDCl$_3$):

δ= 1.48	[s, 6 H,2- Me$_M$]
δ= 1.55	[d, 12H, CH*Me*$_2$]
δ= 2.3	[s,6H,4,5-Me$_I$]
δ= 4.88	[sept, 2H, C*H*Me$_2$]

^{13}C-NMR (CDCl$_3$):

δ= 10.8	[4,5-Me$_I$]
δ=20.9	[CH*Me*$_2$]
δ=26.0	[2-Me$_M$]
δ=54.4	[*C*HMe$_2$]
δ= 63.0	[C5$_M$]
δ=101.0	[C2$_M$]
δ= 126.4	[C4,5]
δ= 143.0	[C2]
δ= 163.0	[C4,6$_M$]

IR (KBr): ν_{CO} = 1624 (sst,br) cm^{-1}

Elemental analysis for $C_{17}H_{26}Br_2N_2O_4$ (482.21 g/mol):

Found (calc.) C 42.55 (42.34), H 5.22 (5.43), N 5.70 (5.81) %.

4.5.12 Preparation of 2,2-dimethyl-4,6-dioxo-5-[((methylsulfanyl)methy-lene)-2,2-dimethyl-4,6-dioxo1,3-dioxan-5-yl]-1,3-dioxanide triethyl ammonium salt (**39**)

To a solution of 0.72 g (5 mmol) of **21** and 1.24 g (5 mmol) of **31** in 30 ml of absolute THF was added triethylamine (2 ml, 15 mmol). The mixture was then refluxed for 8 h. After cooling, the precipitate was filtered to give (1.45g, 65%) as stable yellow crystals.

^{1}H NMR (CDCl$_3$):

δ= 1.23	[t, 9 H,$\mathrm{CH_2C}H_3$]
δ= 1.71	[s, 12 H, 2-Me]
δ= 2.39	[s, 3 H, SMe]
δ= 3.03	[q, 6 H,$\mathrm{C}H_2\mathrm{CH_3}$]
δ= 9.72	[s, 1 H,NH]

^{13}C-NMR (CDCl$_3$):

δ= 8.5	[$\mathrm{CH_2}C\mathrm{H_3}$]
δ= 17.4	[SMe]
δ=26.6	[2-Me]
δ=46.1	[$C\mathrm{H_2CH_3}$]
δ= 67.0	[C5]
δ= 102.7	[C2]
δ= 163.0	[C=O]
δ= 180.1	[*C*SMe]

IR (KBr): ν_{CO} = 1745,1700 (sst,br) cm^{-1}.

$\nu_{C=C}$ = 1597 (sst) cm^{-1}

Elemental analysis for $[HN(C_2H_5)_3][(C_6H_6O_4)_2CSCH_3]$ (445.53 g/mol):

Found (calc.) C 54.07 (53.92), H 6.74 (7.01) %.

4.5.13 Preparation of Meldrum's olefin (**9**)

To a solution of 0.44 g (1 mmol) of **39** in 30 ml of absolute CH_3CN was added 0.22g (1 mmol) of **7**. The mixture was then stirred for 15 min. at r.t. and the dimer **9** is precipitate immediatly. The precipitate was filtered to give (0.57g, 20%) as stable colorless crystals.

^{13}C-NMR (MAS):

δ= 27.4, 28.0	[C5, C6]
δ= 110.9	[C4]
δ= 133.4	[C1]
δ= 157.0, 160.0	[C2, C3]

MS (70 eV, EI): m/z = 182 (8 %), 154 (33), 128 (2), 125 (2), 101 (20), 80 (38), 58 (44), 43 (100) and forther fragments.

IR (KBr): ν (CO) = 1752 (sst, br) cm^{-1}.

Elemental analysis for $C_{12}H_{12}O_8$ (284.22 g/mol):

Found (calc.) C50.71 (50.33), H 4.26(4.30).

.

4.5.14 2,2-dimethyl-4,6-dioxo-5-[(triphenylphosphonio)methyl]-1,3-dioxan-5-yl-phosphonium ylide.(**40**)

A solution of 0.50 g of **13** (2.13 mmol) in 10 ml dichloromethane was added to 0.56 g (2.13 mmol) of PPh_3 in 10 ml of dichloromethane at r.t. After the reaction mixture was stirred over neight the solution was evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/diethylether to give 0.82 g (92 %), colourless crystals.

^{1}H-NMR ($CDCl_3$):

δ= 1.30	[d,12H,$CH\mathit{Me}_2$]
δ= 3.92	[d, 2H, $C\mathit{H}_2$]
δ= 5.25	[d, 2H, $C\mathit{H}_2$]
δ= 7.26-7.73	[m, 15 H, Ph]

^{13}C-NMR ($CDCl_3$):

δ=26.01	[2-Me_M]
δ= 62.83	[$C5_M$]
δ=101.38	[$C2_M$]
δ=120.21, 130.1, 134.49	[Ph]
δ= 166.98	[$C4,6_M$]

^{31}P-NMR ($CDCl_3$):

δ= 25.54	[$CH_2\mathit{P}Ph_3$]

MS (FAB): *m/z* (%) = 419 [18, M^+], 361 [100, M^+ - 2Me,CO], 262 [50, ph_3P^+], 183 [30, M^+-$C_7H_8O_4$ph] and further fragments.

IR (KBr): v_{CO} = 1609 (sst,br) cm^{-1}

Elemental analysis for $C_{25}H_{23}O_4P$ (418 g/mol):

Found (calc.) C 71.5 (71.8), H 4.8 (5.5) %.

. 4.5.15 Preparation of 2,2-dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)methyl]-1,3-dioxan-5-yl-imidazolium ylide.(**41**)

A solution of 0.50 g of **13** (2.13 mmol) in 10 ml THF was added to 0.38 g (2.13 mmol) of carben in 10 ml of THF at r.t. After the reaction mixture was stirred over neight the precipitate was filtered off and dried *in vacuo*. Yield after recrystallisation from dichloromethane/ diethylether 0.64g (90 %), wheite crystals.

^{1}H-NMR ($CDCl_3$):

δ= 1.51	[d,12H, CHMe_2]
δ= 1.57	[s, 6 H,2- $\mathrm{Me_M}$]
δ= 2.25	[s,6H,4,5-$\mathrm{Me_I}$]
δ= 3.69	[s, 2H, CH_2]
δ= 5.35	[sept, 2H, C*H*Me_2]

^{13}C-NMR ($CDCl_3$):

δ= 10.85	[4,5-$\mathrm{Me_I}$]
δ=21.72	[CHMe_2]
δ=26.39	[2-$\mathrm{Me_M}$]
δ=50.87	[*C*HMe_2]
δ= 66.75	[$\mathrm{C5_M}$]

δ=99.61 [C2$_M$]

δ= 125.4 [C4,5]

δ= 146.51 [C2]

δ= 166.0 [C4,6$_M$]

MS (FAB): *m/z* (%) = 337 [45, M$^+$], 279 [100, M$^+$ - 2Me,CO], 235 [20, M$^+$ - $C_4H_6O_3$], 205 [20, M$^+$- $C_6H_6O_3$] and further fragments.

IR (KBr): ν_{CO} = 1606 (sst,br) cm^{-1}

Elemental analysis for $C_{18}H_{28}N_2O_4$ (336 g/mol):

Found (calc.) C 64.1 (64.3), H 7.7 (7.7), N8.5 (8.3) %.

. 4.5.16 Preparation of Dimer of thioxo Meldrum's acid (**20**)

1ml (15mmol) of SCl2 was added to a solution of 2.2g (15mmol) of **2** in 10ml THF at (-15°C). After the reaction mixture was stirred 15 min. the dimer **20** is precipitate immediatly. The precipitate was filtreted to give (4g, 74 %) as stable colorless crystals.

^{13}C-NMR (MAS):

δ=27.5 , 29.7 [2-Me$_M$]

δ= 36.0 [C5$_M$]

δ=109.1 [C2$_M$]

δ= 163.1, 166.0 [C4,6$_M$]

IR (KBr): ν_{CO} = 1780 (sst), 1742 (sst) cm^{-1}

MS (FAB): m/z (%) = 256 [20,S_8^+], 224[28, S_7^+], 192[51, S_6^+], 160 [65, S_5^+], 128[32, S_4^+], 96 [32, S_3^+], 76 [35, C S_2^+], 64 [71, S_2^+], 44 [100, CO_2^+].

Elemental analysis for $C_{12}H_{12}O_8S_2$ (348 g/mol):

Found (calc.) C 41.12 (41.38), H 3.36 (3.47), S 18.37 (18.41) %.

. 4.5.17 Preparation of 2,2-dimethyl-4,6-dioxo-5-[(triphenylphosphonio)sulfanyl]-1,3-dioxan-5-yl-phosphonium ylide. (**42**).

A solution of 0.75 g (2.87 mmol) PPh_3 in 10 ml of dichloromethane was added to a suspention solution of 0.50 g of **20** (2.87 mmol) in 10 ml dichloromethane at r.t. After the reaction mixture was stirred 1h the solution was evaporated *in vacuo* to dryness. The residue was recrystallised from dichloromethane/diethylether to give 1.00 g (80 %), colourless crystals.

^{1}H-NMR ($CDCl_3$):

δ= 1.31	[s,6H, CHMe_2]
δ= 7.52-7.84	[m, 15 H, Ph]

^{13}C-NMR ($CDCl_3$):

δ=26.18	[2-Me$_M$]
δ= 52.6	[C5$_M$]
δ=101.87	[C2$_M$]
δ=120.84	[d, C1$_{Ph}$, ^1J = 75.5 Hz]
δ=130.0	[C3,5$_{Ph}$,, ^1J = 12.6 Hz]

δ=134.8	[C2,6$_{Ph,}$, ^1J = 6.3 Hz]
δ= 166.98	[C4,6$_{M}$]
δ=not observed	[C4$_{Ph,}$]

^{31}P-NMR ($CDCl_3$):

δ= 46.2	[S*P*Ph$_3$]

IR (KBr): v_{CO} = 1641 (sst,br) cm^{-1}

MS (FAB): m/z (%) = 436 [4,M$^+$], 379 [100, M$^+$-2 Me,CO], 262[59, ph$_3$P$^+$] and forther fragments.

Elemental analysis for $C_{24}H_{21}O_4PS$ (436 g/mol):

Found (calc.) C 65.62 (65.29), H 4.62 (4.85), S 7.19 (7.35) %.

. 4.5.18 2,2-dimethyl-4,6-dioxo-5-[(2,2-Dimethyl-4,6-dioxo-1,3-dioxan)disulfonyl]-1,3-dioxan-5-yl-ammonium salt (**43**).

4 ml (2.87 mmol) NH_4OH was added to a suspention solution of 0.50 g of dimer thioxo meldrum's acid (1.44 mmol) in 10 ml water at 0 °C. After the reaction mixture was stirred 1h the solution was evaporated *in vacuo* to dryness. The residue was recrystallised from methanol/diethylether to give 0.50 g (90 %), pale yelow crystals.

^{13}C-NMR (D_2O):

δ=25.3	[2-Me$_{M}$]
δ= 74.4	[C5$_{M}$]
δ=103.5	[C2$_{M}$]

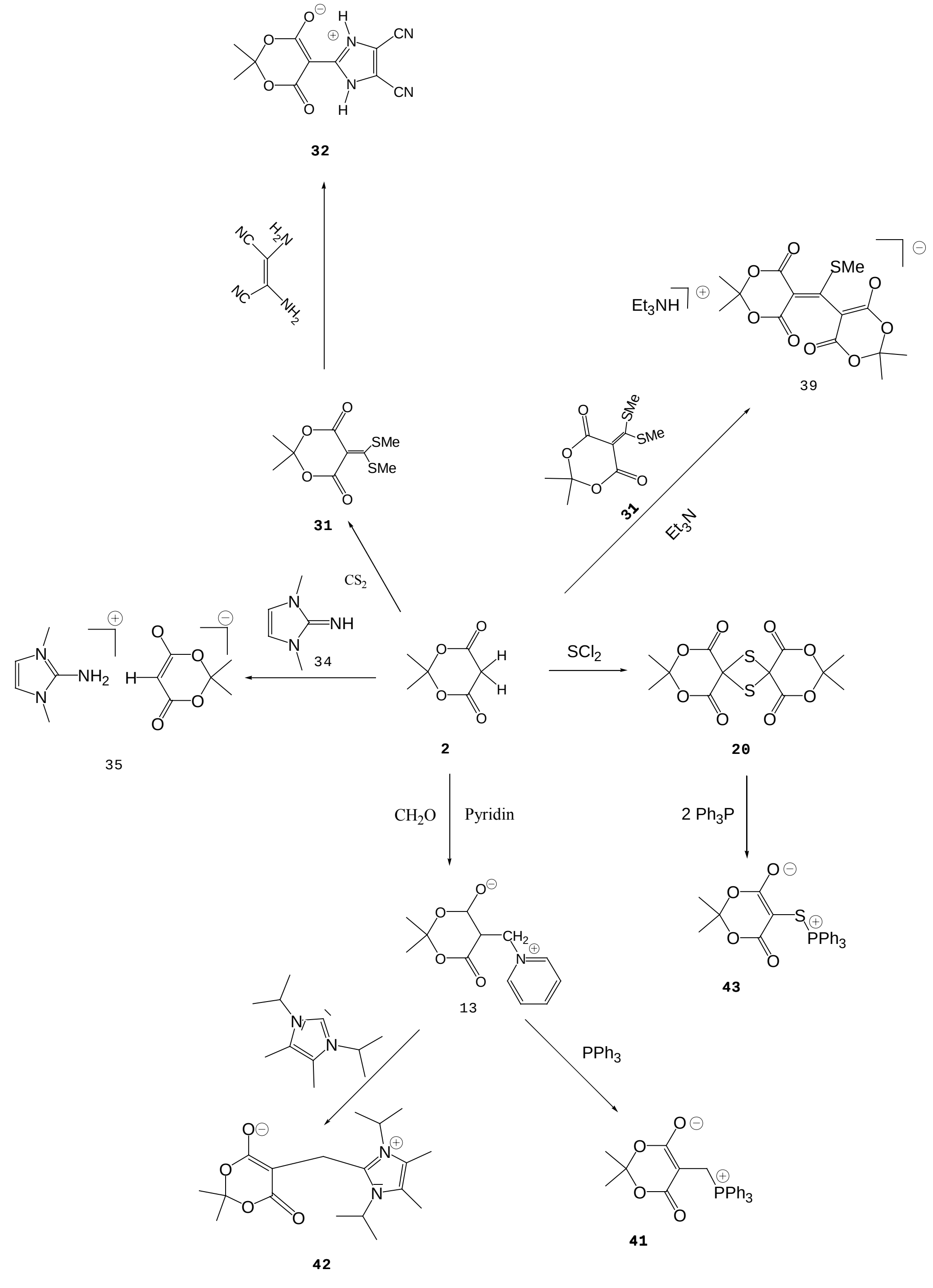
δ= 169.8 [C4,6 $_{M}$]

Elemental analysis for $C_{12}H_{20}O_8N_4S_2$ (384.42 g/mol):

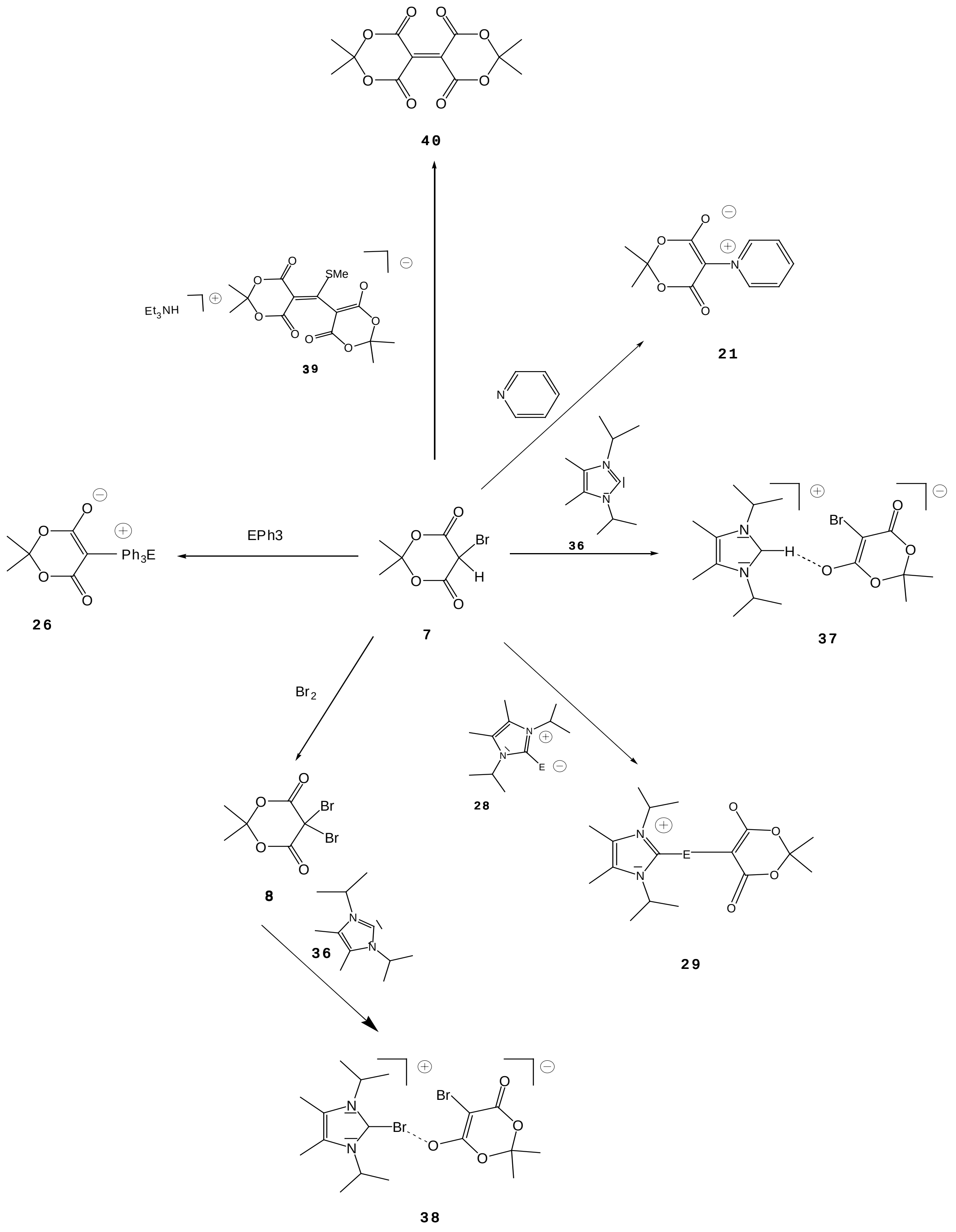
Found (calc.) C 37.28 (37.49), H 5.78 (5.24), N 7.16(7.29) %.

5 Summary

Objective of the present work is the synthesis of different types of Meldrum’s acid derivatives. There were two methods to achieve this purpose. The first by starting with Meldrum’s acid it self (scheme1)



The second by using monobromo Meldrum’s acid **7** as starting material (scheme 2).



The resulting derivatives from the previous two methods are classified into ylides, salts and neutral compounds. The ylide compounds (**21**, **26**, **29**) were obtained from nucleophilic attack at monobromo Meldrum's acid in the presence of base or by nucleophilic attack at the methylene and thioxo of Meldrum's acid (**41**, **42**, **43**).

The salt type compounds (**35**, **37**, **38**) were obtained from reaction of Meldrum's acid or it's bromo dirivatives **7** with very strong ylide types bases (**34**, **36**).

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7 Appendix

7.1 Abbreviations andDefinitions

Å	Angstrom (10^{-10})
δ	Chemical shift
DMSO	Dimethyl sulfoxide
EI	Electron ionization (mass spectroscopy)
Et2O	Diethylether
eV	Electron Volt
FAB	Fast atom bombordment (mass spectroscopy)
FT	Fourier transformation
g	Grams
h	Hour
Hz	Hertz
I	Imidazole
Im	Imidazole
i-Pr	Isopropyl
IR	Infrared spectroscopy
M	Meldrum's acid
Mel	Meldrum's acid
Me	Methyl
MeCN	Acetonitrile
m.p.	Melting point
ml	Milliliter
mmol	Millimol

MS	Mass spectroscopy
NMR	Nuclear magnetic resonance spectroscopy
Ph	Phenyl
ppm	Parts per million
Py	Pyridine
r.t	Room tempreture
Tab.	Table
THF	Tetrahydrofuran
TMS	Tetramethylsilane
ν	Frequency

7.2 Numbering of Compounds

1	β-Lactone-β-Hydroxy isopropyl malonic acid
2	2,2-Dimethyl-4,6-dioxo-1,3-dioxan
3	5,5-Dimethyl-1,3-cyclohexanedione
4	2,4,6-(1H, 3H, 5H)-Pyrimidinetrione.
5	2,2-Dimethyl-4,6-dioxo-1,3-dioxan anion
6	5,5-Dialkyl-2,2-dimethyl-4,6-dioxo-1,3-dioxan
7	5-Bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxan
8	5,5-Dibromo-2,2-dimethyl-4,6-dioxo-1,3-dioxan
9	Diisopropylidene ethylenetetracarboxylate
10	5-Diazo-2,2-dimethyl-4,6-dioxo-1,3-dioxan
11	2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-yliden
12	5- Methylene-2,2-dimethyl-4,6-dioxo-1,3-dioxan

13	2,2-Dimethyl-4,6-dioxo-5-[(pyridinio)methyl]-1,3-dioxan-5-yl-pyridinium ylide.
14	Meldrum’s betaine
15	Meldrum’s ylidic adducts.
16	2,2-Propanediol-cyclic-1,1-cyclopropanedicarboxylate
17	Meldrum’s zwitterionic
18	Meldrum’s zwitterionic
19	Meldrum’s salts
20	Dimer of Meldrum’s thione
21	2,2-Dimethyl-4,6-dioxo-5-(1-pyridinio)-1,3- dioxan-5-yl- pyridinium ylide
22	2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-(1-alkylethylidene)
23	2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-alkyl anion
24	2,2-Dimethyl-4,6-dioxo-1,3- dioxan-5-[hydroxy(phenylamino)methylene]
25	2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-[(2-halophenyl)hydrazone]
26a	Arsonium 2,2-Dimethyl-4,6-dioxo-1,3-dioxanides
26b	Stibonium 2,2-Dimethyl-4,6-dioxo-1,3-dioxanides
26c	Bismuthonium 2,2-Dimethyl-4,6-dioxo-1,3-dioxanides
27a	Arsonium 4,4-dimethyl-2,6-dioxocyclohexylide
27b	Stibonium 4,4-dimethyl-2,6-dioxocyclohexylide
27c	Bismuthonium 4,4-dimethyl-2,6-dioxocyclohexylide
28a	1,3-diisopropyl-4,5-dimethylimidazolin-2-thion
28b	1,3-diisopropyl-4,5-dimethylimidazolin-2-selone
28c	1,3-diisopropyl-4,5-dimethylimidazolin-2-tellone
29a	2,2-Dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)sulfanyl]-1,3-dioxan-5-yl-imidazolium ylide.

29b	2,2-Dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)selanyl]-1,3-dioxan-5-yl-imidazolium ylide.
29c	2,2-Dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)tellanyl]-1,3-dioxan-5-yl-imidazolium ylide.
30	2-(2,3-Diphenyl-2H-tetrazol-5-yl-sulfanyl)-malononitrile.
31	2,2-Dimethyl-4,6-dioxo-5-bis(methylthio) methylene-1,3-dioxan
32	2,2-Dimethyl-4,6-dioxo-5-[2-(4,5-dicyano)] imidazolio-1,3-dioxane-5-yl-imidazolium ylide
33	5-(2-Imidazolidinyl)-2,2-dimethyl-1,3-dioxane-4,6-dione
34	2-Imino-1,3-dimethylimidazoline
35	2-Amino-1,3-dimethylimidazolium-2,2-dimethyl-4,6-dioxo-1,3-dioxanide
36	1,3-Diisopropyl-4,5-dimethylimidazol-2-yliden
37	1,3-Diisopropyl-4,5-dimethylimidazolium-5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxanide
38	1,3-Diisopropyl-4,5-dimethyl-2-bromoimidazolium-5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxanide
39	2,2-Dimethyl-4,6-dioxo-5-[((methylsulfanyl)methy-lene)-2,2-dimethyl-4,6-dioxo1,3-dioxan-5-yl]-1,3-dioxanide triethyl ammonium salt
40	2,2-Dimethyl-4,6-dioxo-5-[(triphenylphosphonio)methyl]-1,3-dioxan-5-yl-phosphonium ylide.
41	2,2-Dimethyl-4,6-dioxo-5-[(1,3-diisopropyl-4,5,-dimethyl-2,3-dihydro-1H-imidazol-2-yl)methyl]-1,3-dioxan-5-yl-imidazolium ylide.
42	2,2-Dimethyl-4,6-dioxo-5-[(triphenylphosphonio)sulfanyl]-1,3-dioxan-5-yl-phosphonium ylide.

43 2,2-Dimethyl-4,6-dioxo-5-[(2,2-Dimethyl-4,6-dioxo-1,3-dioxan)disulfonyl]-1,3-dioxan-5-yl-ammonium salt

7.3 Crystal Structure's data

7.3.1 Crystal data for $C_{11}H_{11}NO_4$ **(21)**

Tab.1: $C_{11}H_{11}NO_4$ **(21)**: Crystal data and structure refinement

Empirical formula	$C_{11}H_{11}NO_4$	
Formula weight	221.21	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.963(2) Å	
	b = 8.404(3) Å	β= 100.60(2)°
	c = 11.238(4) Å	
Volume	1017.8(5) $Å^3$	
Z	4	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	464	
Crystal size	0.50 x 0.15 x 0.15 mm^3	
Theta range for data collection	2.39 to 30.51°.	
Index ranges	-15<=h<=14, -12<=k<=12, -15<=l<=16	
Reflections collected	10907	
Independent reflections	3104 [R(int) = 0.0339]	
Completeness to theta = 30.51°	100.0 %	
Absorption correction	None	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3104 / 0 / 190
Goodness-of-fit on F^2	0.971
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.1079
R indices (all data)	R1 = 0.0470, wR2 = 0.1153
Extinction coefficient	0.036(4)
Largest diff. peak and hole	0.340 and -0.184 e.Å^{-3}

Tab.2: $C_{11}H_{11}NO_4$ **(21)**: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	7726(1)	-47(1)	1257(1)	24(1)
O(1)	9188(1)	1750(1)	-103(1)	34(1)
O(2)	7902(1)	1199(1)	-1835(1)	29(1)
O(3)	5778(1)	-1693(1)	-252(1)	31(1)
O(4)	6138(1)	-451(1)	-1901(1)	27(1)
C(1)	8853(1)	-630(1)	1763(1)	30(1)
C(2)	9169(1)	-795(2)	3005(1)	39(1)
C(3)	8321(1)	-392(2)	3718(1)	46(1)
C(4)	7158(1)	171(2)	3183(1)	44(1)
C(5)	6881(1)	345(1)	1942(1)	32(1)
C(6)	7417(1)	170(1)	-35(1)	24(1)
C(7)	8228(1)	1093(1)	-592(1)	26(1)
C(8)	6408(1)	-708(1)	-672(1)	24(1)
C(9)	6612(1)	985(1)	-2355(1)	26(1)

C(10)	6557(1)	731(2)	-3696(1)	36(1)
C(11)	5854(1)	2407(1)	-2093(1)	32(1)

Tab.3: $C_{11}H_{11}NO_4$ **(21)**: Selected bond lengths [Å] and angles [°].

N(1)-C(5)	1.350(1)	O(4)-C(8)	1.375(1)
N(1)-C(1)	1.354(1)	O(4)-C(9)	1.444(1)
N(1)-C(6)	1.440(1)	C(1)-C(2)	1.382(2)
O(1)-C(7)	1.225(1)	C(2)-C(3)	1.377(2)
O(2)-C(7)	1.379(1)	C(3)-C(4)	1.388(2)
O(2)-C(9)	1.439(1)	C(4)-C(5)	1.379(2)
O(3)-C(8)	1.227(1)	C(6)-C(8)	1.411(1)
		C(6)-C(7)	1.411(1)

C(5)-N(1)-C(1)	121.19(9)	C(7)-C(6)-N(1)	117.82(8)
C(5)-N(1)-C(6)	119.01(8)	O(1)-C(7)-O(2)	117.78(9)
C(1)-N(1)-C(6)	119.80(9)	O(1)-C(7)-C(6)	127.44(9)
C(7)-O(2)-C(9)	117.06(7)	O(2)-C(7)-C(6)	114.73(8)
C(8)-O(4)-C(9)	117.43(7)	O(3)-C(8)-O(4)	117.40(8)
C(8)-C(6)-C(7)	124.14(8)	O(3)-C(8)-C(6)	126.97(9)
C(8)-C(6)-N(1)	117.58(8)	O(4)-C(8)-C(6)	115.60(8)
		O(2)-C(9)-O(4)	110.63(8)

7.3.2 Crystal data of the compounds $Ph_3E\text{-}C_6H_6O_4$ (**26**)

Tab. 4: $Ph_3E\text{-}C_6H_6O_4$ (**26**) Crystal data and structure refinement

	26a (E=As)	**26b** (E=Sb)	**26c** (E=Bi)
Unit cell dimension:			
a[Å]	9.728(3)	9.586(5)	12.013(2)
b[Å]	10.334(3)	9.743(6)	12.943(3)
c[Å]	11.654(4)	12.287(6)	14.555(3)
α[°]	64.69(2)	73.63(4)	
β[°]	80.70(2)	69.37(2)	105.62(3)
γ[°]	78.02(2)	84.13(4)	
Cell volume / $Å^3$	1032.5(6)	1030(1)	2179.6(8)
Z	2	2	4
density [calc. g/cm^{-3}]	1.442	1.596	1.775
crystal system	triclinic	Triclinic	monoclinic
Space group	P -1	P-1	$P2_1/n$
measurement device	Siemens P4		CAD-4
wave length	0.71073	0.71073	1.54184
temperature [°C]	-100	-100	-60
theta range [θ	2.15 – 29.50	2.18 – 27.50	2.36 – 24.69
reflections:			
collected	7930	9430	4677
observed $[F_0>4\sigma(F_0)]$	5538	4723	3692
refinement	full matrix least-squares method on F^2		
parameter	347	347	347
solution and refinement	ShelXTL V5.1 (NT)		
R_1-Value $[I>2\sigma(I)]$	0.0294	0.0295	0.0342
wR2-Value $[I>2\sigma(I)]$	0.0733	0.0776	0.0818
$_1$R-Value [all data]	0.0300	0.0300	0.0495
wR2-Value [all data]	0.0762	0.0782	0.0876
largest difference peak and hole [e· $Å^3$]	+0.88, -1.11	+1.40, -1.68	+1.15, -1.02

Tab. 5: $Ph_3As-C_6H_6O_4$ (**26a**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
As(1)	3821(1)	1879(1)	1751(1)	20(1)
O(1)	874(1)	1725(1)	2757(1)	33(1)
O(2)	855(1)	-648(1)	3661(1)	31(1)
O(3)	4874(1)	-1563(1)	2373(1)	32(1)
O(4)	2868(1)	-2284(1)	3442(1)	30(1)
C(1)	3018(1)	203(2)	2660(1)	22(1)
C(2)	1553(1)	514(2)	3011(1)	25(1)
C(3)	3697(2)	-1204(2)	2791(1)	23(1)
C(4)	1708(2)	-2032(2)	4290(2)	27(1)
C(5)	2233(2)	-2102(2)	5475(2)	34(1)
C(6)	765(2)	-3144(2)	4574(2)	43(1)
C(7)	5782(1)	1513(2)	1238(1)	23(1)
C(8)	6274(2)	1948(2)	-36(2)	33(1)
C(9)	7730(2)	1761(3)	-357(2)	45(1)
C(10)	8662(2)	1146(3)	592(3)	47(1)
C(11)	8154(2)	693(3)	1863(3)	47(1)
C(12)	6710(2)	880(2)	2193(2)	37(1)
C(13)	2828(1)	3095(2)	271(1)	25(1)
C(14)	2624(2)	2455(2)	-517(2)	35(1)

C(15)	1821(2)	3270(3)	-1554(2)	46(1)
C(16)	1232(2)	4698(3)	-1794(2)	45(1)
C(17)	1460(2)	5332(2)	-1028(2)	44(1)
C(18)	2260(2)	4534(2)	18(2)	34(1)
C(19)	3796(2)	2847(2)	2840(1)	25(1)
C(20)	3277(2)	2218(2)	4111(2)	32(1)
C(21)	3364(2)	2859(2)	4929(2)	38(1)
C(22)	3926(2)	4134(2)	4466(2)	38(1)
C(23)	4451(2)	4759(2)	3202(2)	37(1)
C(24)	4402(2)	4111(2)	2382(2)	31(1)

Tab. 6: Ph_3Sb-$C_6H_6O_4$ (**26b**):Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb(1)	6650(1)	7575(1)	6696(1)	21(1)
O(1)	8512(2)	4957(2)	6317(2)	37(1)
O(2)	8975(2)	4011(2)	8037(2)	28(1)
O(3)	7064(2)	7263(2)	9425(2)	39(1)
O(4)	8121(2)	5126(2)	9629(2)	28(1)
C(1)	7521(2)	6127(2)	7855(2)	24(1)
C(3)	7503(2)	6264(3)	8984(2)	25(1)
C(2)	8325(3)	5040(2)	7338(2)	25(1)
C(4)	8285(2)	3796(3)	9318(2)	25(1)

C(5)	6786(3)	3077(3)	9745(3)	36(1)
C(6)	9366(3)	2906(3)	9887(3)	35(1)
C(7)	5311(2)	9174(2)	7438(2)	22(1)
C(8)	5722(3)	9912(3)	8101(3)	33(1)
C(9)	4748(3)	10909(3)	8594(3)	36(1)
C(10)	3383(3)	11179(3)	8432(2)	29(1)
C(11)	2978(3)	10457(3)	7773(3)	32(1)
C(12)	3941(3)	9455(3)	7272(2)	29(1)
C(13)	8230(2)	8676(2)	5058(2)	21(1)
C(14)	8143(2)	10164(2)	4733(2)	23(1)
C(15)	9136(3)	10948(3)	3658(2)	26(1)
C(16)	10223(3)	10246(3)	2906(2)	27(1)
C(17)	10322(3)	8764(3)	3249(2)	27(1)
C(18)	9332(3)	7959(3)	4319(2)	24(1)
C(19)	5091(2)	6595(2)	6296(2)	23(1)
C(20)	4054(3)	5643(3)	7218(2)	31(1)
C(21)	2897(3)	5150(3)	6991(3)	39(1)
C(22)	2781(3)	5597(3)	5845(3)	38(1)
C(23)	3822(3)	6520(3)	4928(3)	35(1)
C(24)	4981(3)	7037(3)	5147(2)	28(1)

Tab. 7: $Ph_3Bi\text{-}C_6H_6O_4$ (**26c**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3).U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Bi(1)	8710(1)	4208(1)	2333(1)	45(1)
O(1)	7727(5)	6448(5)	1738(4)	61(2)
O(2)	9102(5)	7240(4)	1253(4)	57(1)
O(3)	11339(5)	4938(4)	2096(4)	59(1)
O(4)	10902(5)	6451(4)	1400(4)	61(2)
C(1)	9415(7)	5511(6)	1781(6)	49(2)
C(2)	8674(7)	6374(6)	1599(6)	51(2)
C(3)	10579(7)	5553(6)	1778(5)	46(2)
C(4)	10015(8)	7076(7)	812(7)	60(2)
C(5)	9543(13)	6581(12)	-158(8)	81(3)
C(6)	10550(15)	8121(10)	764(13)	89(4)
C(7)	9637(7)	2734(6)	2309(5)	45(2)
C(8)	10817(8)	2656(8)	2573(7)	62(2)
C(9)	11325(10)	1725(8)	2486(8)	67(3)
C(10)	10667(9)	882(7)	2132(8)	70(3)
C(11)	9478(9)	951(7)	1862(8)	72(3)
C(12)	8959(8)	1890(7)	1953(7)	57(2)
C(13)	8504(6)	4573(6)	3757(5)	42(2)
C(14)	8129(8)	3828(7)	4277(6)	51(2)
C(15)	7961(9)	4085(8)	5147(6)	63(2)

C(16)	8177(8)	5071(8)	5486(7)	60(2)
C(17)	8584(8)	5801(7)	4986(6)	60(2)
C(18)	8733(7)	5566(6)	4103(6)	50(2)
C(19)	6977(7)	3899(6)	1389(6)	52(2)
C(20)	6108(8)	3585(7)	1777(7)	65(2)
C(21)	5015(10)	3409(9)	1163(10)	87(3)
C(22)	4808(12)	3523(9)	211(11)	95(4)
C(23)	5663(14)	3807(10)	-171(8)	90(4)
C(24)	6777(11)	4009(8)	410(7)	69(3)

Tab. 8: $Ph_3E-C_6H_6O_4$ (**26**): Selected bond lengths [Å] and angles [°].

	26a (E=As)	**26b** (E=Sb)	**26c** (E=Bi)
E – C(1)	1.859(2)	2.044(2)	2.139(7)
E – C(7)	1.915(2)	2.116(2)	2.214(7)
E – C(13)	1.915(2)	2.113(2)	2.205(7)
E – C(19)	1.917(2)	2.113(2)	2.200(8)
C(2) – O(1)	1.222(2)	1.228(3)	1.212(9)
C(2) – O(2)	1.368(2)	1.377(3)	1.384(2)
C(3) – O(3)	1.219(2)	1.213(3)	1.205(9)
C(3) – O(4)	1.386(2)	1.381(3)	1.385(9)
C(4) – O(4)	1.434(2)	1.429(3)	1.425(10)
C(4) – O(2)	1.442(2)	1.438(3)	1.428(10)
C(1) – C(2)	1.426(2)	1.410(3)	1.408(11)

C(1) – C(3)	1.421(2)	1.424(3)	1.401(11)
C(4) – C(5)	1.512(2)	1.516(3)	1.507(15)
C(4) – C(6)	1.516(2)	1.516(3)	1.515(15)
C(1) – E – C(7)	113.51(6)	114.13(9)	115.0(3)
C(1) – E – C(13)	109.83(6)	115.3(1)	109.9(3)
C(1) – E – C(19)	109.21(7)	111.0(1)	108.2(3)
C(7) – E – C(13)	109.00(7)	105.83(9)	112.6(3)
C(7) – E – C(19)	103.42(6)	100.94(9)	103.2(3)
C(13) – E – C(19)	111.76(7)	108.53(9)	107.4(3)
C(2) – O(2) – C(4)	116.66(11)	115.55(18)	116.6(6)
C(3) – O(4) – C(4)	108.00(12)	117.94(18)	118.1(6)
C(2) – C(1) – C(3)	122.75(13)	122.6(2)	123.4(7)
C(2) – C(1) – E	124.2010)	111.55(16)	113.7(6)
C(3) – C(1) – E	112.08(10)	125.41(17)	121.9(6)
O(1) – C(2) – O(2)	117.82(13)	118.0(2)	117.1(7)
O(1) – C(2) – C(1)	125.45(14)	125.4(2)	127.3(8)
O(2) – C(2) – C(1)	116.71(13)	116.5(2)	115.6(7)
O(3) – C(3) – O(4)	117.02(13)	116.5(2)	116.3(7)
O(3) – C(3) – C(1)	128.56(14)	128.4(2)	128.8(7)
O(4) – C(3) – C(1)	114.37(12)	115.0(2)	114.8(7)
O(2) – C(4) – O(4)	110.66(12)	110.67(19)	110.8(7)
O(2) – C(4) – C(5)	110.18(14)	109.8(2)	106.0(8)
O(4) – C(4) – C(5)	110.64(13)	110.7(2)	106.1(10)

O(2) – C(4) C(6)	105.25(13)	106.5(2)	110.0(9)
O(4) – C(4) – C(6)	106.81(15)	106.25(19)	110.6(8)
C(5) – C(4) – C(6)	113.15(15)	112.8(2)	113.2(11)

7.3.3 Crystal data of the compounds $C_{11}H_{20}N_2$-E-$C_6H_6O_4$ (**29**)

Tab. 9: $C_{11}H_{20}N_2$-E-$C_6H_6O_4$ (**29**): Crystal data and structure refinment

	29a (E=S)	**29a** (E=Se)	**29a** (E=Te)
Unit cell dimension:			
a[Å]	14.455(6)	14.445(8)	8.685(1)
b[Å]	13.360(7)	13.342(2)	22.031(4)
c[Å]	9.635(6)	9.756(2)	10.843(2)
α[°]	90	90	90
β[°]	90	90	111.48(3)
γ[°]	90	90	90
Cell volume / $Å^3$	1860(2)	1880(1)	1930.6(7)
Z	4	4	4
density [calc. g/cm^{-3}]	1.265	1.418	1.548
crystal system	orthorhombic	orthorhombic	monoclinic
Space group	Cmc2(1)	Cmc2(1)	$P2_1/c$
measurement device	Siemens P4		Stoe IPDS-1
wave length	0.71073	0.71073	0.71073
temperature [°C]	-100	-100	-60
theta range [θ	2.15 – 27.49	2.18 – 27.53	2.52 – 25.75
reflections:			
collected	5458	9503	16372
observed [$F_0>4\sigma(F_0)$]	2228	2254	3676
refinement	full matrix least-squares method on F^2		
parameter	173	173	322
solution and refinement	ShelXTL V5.1 (NT)		
R_1-Value [I>2σ(I)]	0.0266	0.0221	0.0286
wR2-Value [I>2σ(I)]	0.0685	0.0574	0.0672
$_1$R-Value [all data]	0.0282	0.0223	0.0382
wR2-Value [all data]	0.0704	0.0574	0.0692
largest difference peak and hole [e· $Å^3$]	+0.23, -0.18	+0.39, -0.54	+1.19, -0.37

Tab.10: $C_{11}H_{20}N_2$-S-$C_6H_6O_4$ (**29a**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5000	9503(1)	7596(1)	21(1)
N(1)	4243(1)	11122(1)	6177(1)	22(1)
O(1)	5816(1)	7336(1)	5006(1)	35(1)
O(2)	6639(1)	8443(1)	6173(2)	39(1)
C(1)	5000	10600(1)	6578(2)	20(1)
C(2)	4526(1)	11990(1)	5517(1)	24(1)
C(3)	3888(1)	12743(1)	4884(2)	36(1)
C(4)	3275(1)	10770(1)	6416(1)	24(1)
C(5)	2786(1)	11412(1)	7491(2)	30(1)
C(6)	2746(1)	10688(1)	5050(2)	35(1)
C(7)	5000	8516(1)	6410(2)	23(1)
C(8)	5863(1)	8136(1)	5919(2)	27(1)
C(9)	5000	6733(1)	5018(2)	30(1)
C(10)	5000	6141(2)	3679(3)	52(1)
C(11)	5000	6056(1)	6286(3)	33(1)

Tab.11: $C_{11}H_{20}N_2$-Se-$C_6H_6O_4$ (**29b**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Se(1)	5000	507(1)	5876(1)	21(1)
N(1)	5754(1)	-1171(1)	4322(2)	20(1)
O(1)	4188(1)	2680(1)	3130(2)	34(1)
O(2)	3372(1)	1573(1)	4298(2)	38(1)
C(1)	5000	-657(2)	4732(2)	18(1)
C(2)	5472(1)	-2035(1)	3651(2)	23(1)
C(3)	6109(2)	-2780(2)	3017(3)	35(1)
C(4)	6715(1)	-806(1)	4553(2)	22(1)
C(5)	7199(1)	-1429(2)	5643(2)	30(1)
C(6)	7251(1)	-739(2)	3209(2)	34(1)
C(7)	5000	1550(2)	4587(3)	22(1)
C(8)	4139(1)	1896(1)	4057(2)	26(1)
C(9)	5000	3287(2)	3136(3)	29(1)
C(10)	5000	3866(3)	1807(4)	50(1)
C(11)	5000	3972(2)	4379(4)	33(1)

Tab.12: $C_{11}H_{20}N_2$-Te-$C_6H_6O_4$ (**29c**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Te(1)	743(1)	6181(1)	10624(1)	28(1)
N(1)	2245(3)	7425(1)	10150(3)	28(1)
N(11)	3906(3)	6682(1)	10172(3)	29(1)
O(1)	-338(3)	5100(1)	7099(2)	35(1)
O(11)	-1948(3)	5993(1)	6433(2)	34(1)
O(2)	1449(3)	4967(1)	9157(2)	42(1)
O(21)	-1818(3)	6747(1)	7828(2)	41(1)
C(1)	2435(4)	6818(1)	10272(3)	25(1)
C(2)	3640(4)	7681(1)	9996(3)	32(1)
C(21)	4681(4)	7215(1)	10019(3)	33(1)
C(3)	3909(6)	8342(2)	9849(6)	57(1)
C(31)	6340(6)	7265(2)	9896(7)	58(1)
C(4)	817(4)	7759(2)	10275(4)	37(1)
C(41)	4612(4)	6054(1)	10321(4)	34(1)
C(5)	-91(6)	8141(2)	9075(5)	55(1)
C(51)	5027(6)	5862(2)	9131(4)	47(1)
C(6)	1377(8)	8099(3)	11577(5)	72(2)
C(61)	6058(6)	5993(2)	11633(4)	53(1)
C(7)	-207(4)	5862(1)	8696(3)	26(1)

C(8)	371(4)	5297(1)	8407(3)	30(1)
C(81)	-1353(4)	6232(1)	7715(3)	29(1)
C(9)	-1927(4)	5346(1)	6324(3)	33(1)
C(10)	-2175(6)	5216(2)	4889(4)	45(1)
C(11)	-3266(5)	5075(2)	6754(4)	38(1)

Table 13: $C_{11}H_{20}N_2$-E-$C_6H_6O_4$ (**29**): Selected bond lengths [Å] and angles [°].

	29a (E=S)	**29b** (E=Se)	**29c** (E=Te)
E – C(1)	1.763(2)	1.911(2)	2.165(3)
E – C(7)	1.745(2)	1.876(3)	2.069(3)
C(1) – N(1)	1.354(1)	1.348(2)	1.347(4)
C(1) – N(11)			1.355(4)
N(1) – C(2)	1.384(2)	1.387(2)	1.401(4)
N(11) – C(21)			1.393(4)
C(2) – C(2a)	1.371(3)	1.365(4)	
C(2) – C(21)			1.362(4)
C(7) – C(8)	1.428(2)	1.424(2)	1.419(4)
C(7) – C(81)			1.419(4)
C(8) – O(1)	1.386(2)	1.385(2)	1.393(4)
C(81) – O(11)			1.397(4)
C(8) – O(2)			1.229(4)
C(81) – O(21)			1.226(4)

O(1) – C(9)	1.429(2)	1.425(2)	1.434(4)
O(11) – C(9)			1.429(4)

C(1) – E – C(7)	105.3(1)	102.2(1)	95.0(1)
E – C(1) – N(1)	126.0(1)	125.9(1)	126.4(2)
E – C(1) – N(11)			126.3(2)
C(1) – N(1) – C(2)	108.9(1)	109.1(2)	109.3(2)
C(1) – N(11) – C(21)			109.5(2)
N(1) – C(2) – C(2a)	107.2(1)	107.1(1)	
N(1) – C(2) – C(21)			107.0(3)
N(11) – C(21) – C(2)			106.9(3)
N(1) – C(1) – N(1a)	107.8(2)	107.8(2)	
N(1) – C(1) – N(11)			107.3(2)
E – C(7) – C(8)	119.1(1)	119.0(1)	118.6(2)
E – C(7) – C(81)			118.2(2)
C(7) – C(8) – O(1)	116.2(1)	116.0(2)	116.0(3
C(7) – C(81) – O(11)			115.5(3)
C(7) – C(8) – O(2)			128.2(3)
C(7) – C(81) – O(21)			128.6(3)
C(8) – O(1) – C(9)	118.1(1)	117.9(2)	116.8(2)
C(81) – O(11) – C(9)			116.6(2)
O(1) – C(9) – O(1a)	111.3(2)	110.7(2)	
O(1) – C(9) – O(11)			111.6(3)
C(10) – C(9) – C(11)	112.0(2)	112.2(3)	113.7(3)

7.3.4 Crystal data for $C_{13}H_{14}N_4O_5S$ (**32**)

Tab.14: $C_{13}H_{14}N_4O_5S$ (**32**): Crystal data and structure refinement

Empirical formula	$C_{13}H_{14}N_4O_5S$	
Formula weight	338.34	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/c	
Unit cell dimensions	a = 12.7858(18) Å	α= 90°.
	b = 5.2218(10) Å	β= 103.000(11)°.
	c = 23.628(3) Å	β = 90°.
Volume	1537.1(4) $Å^3$	
Z	4	
Density (calculated)	1.462 Mg/m^3	
Absorption coefficient	0.242 mm^{-1}	
F(000)	704	
Crystal size	0.35 x 0.45 x 0.45 mm^3	
Theta range for data collection	2.12 to 27.50°.	
Index ranges	-16<=h<=0, -6<=k<=6, -29<=l<=30	
Reflections collected	6642	
Independent reflections	3537 [R(int) = 0.0662]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3537 / 0 / 259	
Goodness-of-fit on F^2	1.920	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1139	
R indices (all data)	R1 = 0.0544, wR2 = 0.1240	
Extinction coefficient	0.005(3)	
Largest diff. peak and hole	0.419 and -0.586 $e.Å^{-3}$	

Tab.15: $C_{13}H_{14}N_4O_5S$ (**32**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	9719(1)	10100(1)	6033(1)	28(1)
N(1)	6240(1)	7559(2)	5688(1)	19(1)
N(2)	7373(1)	4384(3)	5869(1)	20(1)
N(3)	6088(2)	10530(3)	7021(1)	34(1)
N(4)	8472(2)	4055(4)	7381(1)	37(1)
O(1)	5159(1)	8209(3)	4564(1)	29(1)
O(2)	7847(1)	1886(3)	4940(1)	33(1)
O(3)	7065(1)	3054(2)	4045(1)	23(1)
O(4)	5703(1)	6201(3)	3857(1)	25(1)
O(5)	8624(1)	10228(3)	6171(1)	31(1)
C(1)	6726(1)	5715(3)	5436(1)	19(1)
C(2)	6593(1)	7410(3)	6283(1)	19(1)
C(3)	7301(1)	5429(3)	6396(1)	20(1)
C(4)	6295(1)	9151(3)	6682(1)	23(1)
C(5)	7949(1)	4624(3)	6940(1)	24(1)
C(6)	7216(1)	3341(3)	4634(1)	21(1)
C(7)	5796(1)	6704(3)	4431(1)	20(1)
C(8)	6599(1)	5302(3)	4832(1)	19(1)
C(9)	6627(1)	5177(3)	3682(1)	20(1)
C(10)	6227(1)	4112(4)	3078(1)	27(1)

C(11)	7468(2)	7234(3)	3708(1)	28(1)
C(12)	9672(2)	7568(4)	5518(1)	39(1)
C(13)	10564(2)	8590(5)	6647(1)	45(1)

Tab.16: $C_{13}H_{14}N_4O_5S$ (**32**): Bond lengths [Å] and angles [°].

S(1)-O(5)	1.5093(14)		
S(1)-C(13)	1.785(2)	O(3)-C(6)	1.3687(17)
S(1)-C(12)	1.790(2)	O(3)-C(9)	1.4371(17)
N(1)-C(1)	1.3541(18)	O(4)-C(7)	1.3598(17)
N(1)-C(2)	1.3772(18)	O(4)-C(9)	1.4383(18)
N(2)-C(1)	1.3534(19)	C(1)-C(8)	1.4178(18)
N(2)-C(3)	1.3804(17)	C(2)-C(3)	1.361(2)
N(3)-C(4)	1.151(2)	C(2)-C(4)	1.423(2)
N(4)-C(5)	1.143(3)	C(3)-C(5)	1.428(2)
O(1)-C(7)	1.223(2)	C(6)-C(8)	1.4333(19)
O(2)-C(6)	1.219(2)	C(7)-C(8)	1.432(2)
		C(9)-C(10)	1.508(2)
		C(9)-C(11)	1.512(2)
O(5)-S(1)-C(13)	105.40(10)	N(3)-C(4)-C(2)	177.34(19)
O(5)-S(1)-C(12)	106.79(10)	N(4)-C(5)-C(3)	178.0(2)
C(13)-S(1)-C(12)	98.50(12)	O(2)-C(6)-O(3)	117.20(13)
C(1)-N(1)-C(2)	109.31(12)	O(2)-C(6)-C(8)	126.28(14)

C(1)-N(2)-C(3)	108.95(12)	C(10)-C(9)-C(11)	112.76(13)
C(6)-O(3)-C(9)	118.06(11)	O(5)-S(1)-C(13)	105.40(10)
C(7)-O(4)-C(9)	117.73(12)	O(5)-S(1)-C(12)	106.79(10)
N(2)-C(1)-N(1)	107.21(12)	C(13)-S(1)-C(12)	98.50(12)
N(2)-C(1)-C(8)	126.52(13)	C(1)-N(1)-C(2)	109.31(12)
N(1)-C(1)-C(8)	126.26(14)	C(1)-N(2)-C(3)	108.95(12)
C(3)-C(2)-N(1)	107.09(12)	C(6)-O(3)-C(9)	118.06(11)
C(3)-C(2)-C(4)	128.41(14)	C(7)-O(4)-C(9)	117.73(12)
N(1)-C(2)-C(4)	124.40(14)	N(2)-C(1)-N(1)	107.21(12)
C(2)-C(3)-N(2)	107.43(13)	N(2)-C(1)-C(8)	126.52(13)
C(2)-C(3)-C(5)	128.75(14)	N(1)-C(1)-C(8)	126.26(14)
N(2)-C(3)-C(5)	123.60(14)	C(3)-C(2)-N(1)	107.09(12)
O(3)-C(6)-C(8)	116.51(13)	C(3)-C(2)-C(4)	128.41(14)
O(1)-C(7)-O(4)	117.83(14)	N(1)-C(2)-C(4)	124.40(14)
O(1)-C(7)-C(8)	125.35(14)	C(2)-C(3)-N(2)	107.43(13)
O(4)-C(7)-C(8)	116.72(13)	C(2)-C(3)-C(5)	128.75(14)
C(1)-C(8)-C(7)	119.43(13)	N(2)-C(3)-C(5)	123.60(14)
C(1)-C(8)-C(6)	119.35(13)	N(3)-C(4)-C(2)	177.34(19)
C(7)-C(8)-C(6)	121.02(13)	N(4)-C(5)-C(3)	178.0(2)
O(3)-C(9)-O(4)	110.49(12)	O(2)-C(6)-O(3)	117.20(13)
O(3)-C(9)-C(10)	106.52(12)	O(2)-C(6)-C(8)	126.28(14)
O(4)-C(9)-C(10)	106.45(13)	O(3)-C(6)-C(8)	116.51(13)
O(3)-C(9)-C(11)	110.20(13)	O(1)-C(7)-O(4)	117.83(14)
O(4)-C(9)-C(11)	110.31(13)	O(1)-C(7)-C(8)	125.35(14)

O(4)-C(7)-C(8)	116.72(13)	O(3)-C(9)-C(10)	106.52(12)
C(1)-C(8)-C(7)	119.43(13)	O(4)-C(9)-C(10)	106.45(13)
C(1)-C(8)-C(6)	119.35(13)	O(3)-C(9)-C(11)	110.20(13)
C(7)-C(8)-C(6)	121.02(13)	O(4)-C(9)-C(11)	110.31(13)
O(3)-C(9)-O(4)	110.49(12)	C(10)-C(9)-C(11)	112.76(13)

Symmetry transformations used to generate equivalent atoms:

Tab.17: $C_{13}H_{14}N_4O_5S$ (**32**): Anisotropic displacement parameters ($Å^2 x 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	25(1)	19(1)	41(1)	7(1)	11(1)	3(1)
N(1)	22(1)	18(1)	19(1)	0(1)	9(1)	5(1)
N(2)	22(1)	19(1)	20(1)	1(1)	8(1)	4(1)
N(3)	47(1)	30(1)	28(1)	-4(1)	15(1)	4(1)
N(4)	40(1)	45(1)	26(1)	3(1)	5(1)	4(1)
O(1)	30(1)	32(1)	27(1)	2(1)	10(1)	16(1)
O(2)	43(1)	31(1)	24(1)	1(1)	8(1)	20(1)
O(3)	33(1)	17(1)	19(1)	-1(1)	8(1)	7(1)
O(4)	23(1)	33(1)	20(1)	-1(1)	6(1)	10(1)
O(5)	28(1)	32(1)	36(1)	8(1)	15(1)	11(1)

C(1)	20(1)	18(1)	20(1)	0(1)	9(1)	1(1)
C(2)	21(1)	20(1)	19(1)	-1(1)	10(1)	-1(1)
C(3)	22(1)	20(1)	19(1)	0(1)	8(1)	-1(1)
C(4)	27(1)	22(1)	22(1)	0(1)	11(1)	2(1)
C(5)	26(1)	27(1)	22(1)	1(1)	9(1)	1(1)
C(6)	26(1)	18(1)	20(1)	-2(1)	8(1)	5(1)
C(7)	19(1)	23(1)	20(1)	-1(1)	6(1)	3(1)
C(8)	22(1)	19(1)	18(1)	0(1)	8(1)	5(1)
C(9)	22(1)	19(1)	19(1)	-1(1)	7(1)	4(1)
C(10)	29(1)	33(1)	18(1)	-4(1)	5(1)	0(1)
C(11)	34(1)	20(1)	32(1)	-4(1)	13(1)	-3(1)
C(12)	43(1)	33(1)	48(1)	0(1)	22(1)	7(1)
C(13)	33(1)	41(1)	55(1)	12(1)	-1(1)	8(1)

Tab.18: $C_{13}H_{14}N_4O_5S$ (**32**): Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}).

	x	y	z	U(eq)
H(1)	5810(20)	8580(50)	5523(10)	25(5)
H(2)	7780(20)	2970(60)	5846(11)	32(6)
H(10A)	5720(30)	2750(70)	3112(14)	48
H(10B)	6810(30)	3440(70)	2937(14)	48
H(10C)	5930(30)	5530(60)	2829(14)	48
H(11A)	7160(30)	8650(70)	3459(14)	48

H(11B)	8100(30)	6530(70)	3595(14)	48
H(11C)	7710(30)	7860(70)	4092(14)	48
H(12A)	9110(30)	8060(70)	5172(15)	53(9)
H(12B)	10360(30)	7380(80)	5442(16)	62(10)
H(12C)	9470(30)	6040(70)	5679(14)	46(8)
H(13A)	10160(30)	7030(70)	6714(14)	49(8)
H(13B)	10610(30)	9750(60)	6960(13)	38(7)
H(13C)	11230(40)	8090(90)	6541(19)	73(12)

7.3.5 Crystal data for $C_{11}H_{17}N_3O_4$ (**35**).

Tab.19: $C_{11}H_{17}N_3O_4$ (**35**): Crystal data and structure refinement .

Empirical formula	$C_{11}H_{17}N_3O_4$
Formula weight	255.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	a = 9.9070(15) Å
	b = 16.064(3) Å
	c = 15.981(3) Å
Volume	2543.5(8) $Å^3$
Z	8
Density (calculated)	1.333 Mg/m^3
Absorption coefficient	0.103 mm^{-1}
F(000)	1088
Crystal size	0.35 x 0.45 x 0.35 mm^3
Theta range for data collection	2.42 to 27.52°.
Index ranges	-12<=h<=12, -20<=k<=20, -20<=l<=20
Reflections collected	22234
Independent reflections	3035 [R(int) = 0.0296]
Completeness to theta = 27.52°	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.2672 and 0.2351
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3035 / 0 / 250
Goodness-of-fit on F^2	1.877
Final R indices [I>2sigma(I)]	R1 = 0.0345, wR2 = 0.0880
R indices (all data)	R1 = 0.0376, wR2 = 0.0921

Extinction coefficient	0.0211(16)
Largest diff. peak and hole	0.306 and -0.188 e.Å^{-3}

Tab. 20: $C_{11}H_{17}N_3O_4$ (**35):** Selected bond lengths [Å] and angles [°] .

Anion A		Anion B	
O(1)-C(7)	1.235(1)	O(3)-C(12)	1.236(1)
O(2)-C(7)	1.385(1)	O(4)-C(12)	1.382(1)
O(2)-C(8)	1.430(1)	O(4)-C(13)	1.432(1)
C(6)-C(7)	1.401(1)	C(11)-C(12)	1.404(1)
C(8)-C(10)	1.514(2)	C(13)-C(14)	1.515(2)
C(8)-C(9)	1.521 (2)	C(13)-C(15)	1.517(2)
C(7)-O(2)-C(8)	116.4(1)	C(12)-O(4)-C(13)	116.3(1)
C(7)#1-C(6)-C(7)	121.4(1)	C(12)-C(11)-C(12)#1	121.4(1)
O(1)-C(7)-O(2)	114.4(1)	O(3)-C(12)-O(4)	114.9(1)
O(1)-C(7)-C(6)	128.3(1)	O(3)-C(12)-C(11)	128.1(1)
O(2)-C(7)-C(6)	117.3(1)	O(4)-C(12)-C(11)	116.9 (1)
O(2)#1-C(8)-O(2)	110.9 (1)	O(4)#1-C(13)-O(4)	110.8(1)
C(10)-C(8)-C(9)	113.0(1)	C(14)-C(13)-C(15)	112.0(1)

Cation

N(1)-C(1)	1.3439(13)	C(1)-N(1)-C(2)	108.28(9)
N(1)-C(2)	1.3959(14)	C(1)-N(2)-C(3)	108.48(9)
N(2)-C(1)	1.3439(13)	N(3)-C(1)-N(1)	126.65(9)
N(2)-C(3)	1.3971(13)	N(3)-C(1)-N(2)	125.09(9)
N(3)-C(1)	1.3362(12)	N(1)-C(1)-N(2)	108.19(8)
C(2)-C(3)	1.3360(19)	C(3)-C(2)-N(1)	107.74(9)
		C(2)-C(3)-N(2)	107.31(9)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

7.3.6 $C_{17}H_{27}BrN_2O_4$ (**37**) and $C_{17}H_{26}Br_2N_2O_4$ (**38**)

Tab.21: $C_{17}H_{27}BrN_2O_4$ (**37**) and $C_{17}H_{26}Br_2N_2O_4$ (**38**): Crystal data and structure refinement

	37	**38**
Empirical formula	$C_{17}H_{27}BrN_2O_4$	$C_{17}H_{26}Br_2N_2O_4$
Formula weigt [g/mol]	403.32	482.22
Crystal size [mm^3]	0.60 * 0.20 * 0.15	0.45 * 0.45 * 0.30
Temperature [K]	233	273
Crystal system	Monoklin	monoklin
Space group	P2(1)/n	C2/c
a [Å]	8.200(2)	25.180(7)
b [Å]	17.328(4)	13.704(3)
c [Å]	13.456(3)	13.023(9)
β [°]	91.72(39	109.59(4)
Volume [Å^3]	1911(1)	4234(3)
Z	4	8
μ(Mo-K$_\alpha$) [mm^{-1}]	2.173	3.851
Theta range for data collection	3.03 – 25.98	4.32 – 27.50
Solution and refinement	SHELXTL V5.1 (NT)	
Largest difference peak and hole [e. Å^3] (min, max)	+0.311, -0.422	+0.757, -0.830
Reflections collected	4541	7535
Independent reflections	3731	3898
Observed [I>2σ(I)]	2368	2738
Number of variables	326	235
R1 [I>2σ(I)]	0.0421	0.0453
wR2 [all data]	0.1187	0.1137

Tab.22: $C_{17}H_{27}BrN_2O_4$ (**37**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(2)	12319(1)	6994(1)	4405(1)	41(1)
N(1)	224(4)	3780(2)	-16(3)	31(1)
N(2)	308(4)	3781(2)	1590(2)	28(1)
O(1)	8937(4)	7805(2)	4319(3)	45(1)
O(2)	7399(4)	6816(2)	3835(2)	37(1)
O(3)	11236(4)	5454(2)	3364(2)	41(1)
O(4)	8557(4)	5643(2)	3351(2)	37(1)
C(1)	-647(5)	3652(2)	787(3)	29(1)
C(2)	1847(5)	3992(2)	1291(3)	30(1)
C(3)	1801(5)	3992(2)	281(3)	32(1)
C(4)	-203(5)	3679(3)	2637(3)	32(1)
C(5)	-2023(6)	3804(3)	2704(4)	41(1)
C(6)	306(8)	2894(3)	3006(4)	47(1)
C(7)	3232(6)	4154(3)	1995(4)	41(1)
C(8)	3122(7)	4145(4)	-417(4)	46(1)
C(9)	-385(6)	3666(3)	-1060(3)	36(1)
C(10)	-2194(7)	3840(3)	-1150(4)	43(1)
C(11)	7(8)	2862(3)	-1391(4)	52(1)
C(12)	10234(5)	6605(2)	4071(3)	30(1)
C(13)	8911(5)	7122(2)	4102(3)	33(1)

C(14)	10126(5)	5880(2)	3606(3)	30(1)
C(15)	7241(5)	5988(3)	3863(3)	34(1)
C(16)	5716(6)	5785(3)	3272(4)	46(1)
C(17)	7197(8)	5711(4)	4917(4)	52(1)

Tab.23: $C_{17}H_{26}Br_2N_2O_4$ (**38**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2675(1)	1512(1)	8581(1)	52(1)
Br(2)	1760(1)	6013(1)	2615(1)	46(1)
N(1)	3644(1)	564(3)	10026(3)	31(1)
N(2)	2861(1)	-208(3)	9850(3)	31(1)
O(1)	2055(1)	7789(3)	1434(3)	43(1)
O(2)	1188(1)	8259(3)	490(3)	49(1)
O(3)	456(1)	5997(3)	1384(3)	58(1)
O(4)	388(1)	7377(2)	483(3)	49(1)
C(1)	3083(1)	590(3)	9564(4)	35(1)
C(2)	3301(1)	-777(3)	10504(3)	28(1)
C(3)	3788(1)	-286(3)	10619(3)	30(1)
C(4)	2251(1)	-480(3)	9577(4)	37(1)
C(5)	1929(2)	309(4)	9964(5)	53(1)

C(6)	1982(2)	-746(4)	8397(4)	46(1)
C(7)	3214(2)	-1720(3)	10974(4)	38(1)
C(8)	4381(1)	-541(3)	11284(4)	39(1)
C(9)	4066(1)	1321(3)	9986(4)	36(1)
C(10)	4097(2)	1427(4)	8856(4)	51(1)
C(11)	3974(2)	2260(4)	10492(6)	58(1)
C(12)	1289(1)	6918(3)	1646(4)	35(1)
C(13)	1548(2)	7647(3)	1231(4)	35(1)
C(14)	707(2)	6704(3)	1213(4)	42(1)
C(15)	622(2)	8324(4)	501(5)	55(2)
C(16)	284(2)	8783(6)	-568(7)	80(2)
C(17)	613(2)	8882(5)	1495(7)	73(2)

Tab. 24: $C_{17}H_{27}BrN_2O_4$ (37) and $C_{17}H_{26}Br_2N_2O_4$ (38): Selected bond lengths [Å] and angles [°]

		37	**38**
Cation	Br(1) – C(1)	----	1.846(4)
	N(1) – C(1)	1.332(6)	1.336(4)
	N(1) – C(3)	1.391(5)	1.377(5)
	N(2) – C(1)	1.334(5)	1.337(5)
	N(2) – C(2)	1.385(5)	1.389(5)
	C(2) – C(3)	1.359(6)	1.362(5)

	C(1) – N(1) – C(3)	109.1(3)	108.4(3)
	C(1) – N(2) – C(2)	109.0(3)	107.8(3)
	N(1) – C(1) – N(2)	108.3(4)	109.3(4)
	C(3) – C(2) – N(2)	107.0(4)	107.13)
	C(2) – C(3) – N(1)	106.6(4)	107.3(3)
Anion	Br(2) - C(12)	1.880(4)	1.880(4)
	O(1) – C(13)	1.219(5)	1.230(4)
	O(2) – C(13)	1.386(5)	1.367(6)
	O(2) – C(15)	1.441(5)	1.433(5)
	O(3) – C(14)	1.225(5)	1.217(6)
	O(4) – C(15)	1.428(5)	1.422(6)
	C(12) – C(13)	1.408(6)	1.396(6)
	C(12) – C(14)	1.404(6)	1.413(5)
	C(13) – O(2) – C(15)	117.1(3)	117.2(3)
	C(14) – O(4) – C(15)	117.8(3)	117.7(3)
	C(13) – C(12) – C(14)	123.0(4)	123.4(4)
	O(2) – C(13) – C(12)	115.6(4)	115.3(3)
	O(4) – C(14) – C(12)	115.0(3)	115.1(4)
	O(4) – C(15) – O(2)	109.6(3)	110.5(4)
	C(17) – C(15) – C(16)	112.5(4)	114.6(6)

7.3.7 Crystal data for $[HN(C_2H_5)_3][C_{14}H_{15}O_8S]$ (**39**)

Tab.25: $[HN(C_2H_5)_3][C_{14}H_{15}O_8S]$ (**39**): Crystal data and structure refinement

Empirical formula	$[HN(C_2H_5)_3][C_{14}H_{15}O_8S]$
Formula weigt [g/mol]	445.52
Crystal size [mm^3]	0.50 * 0.25 * 0.15
Temperature [K]	293(2)
Crystal system	Triklin
Space group	P1
a [Å]	8.124(1)
b [Å]	9.333(2)
c [Å]	9.855(2)
α [°]	115.95(1)
β [°]	93.23(2)
γ [°]	113.74(2)
Volume [Å^3]	590.0(2)
Z	1
μ (Mo-K_α) [mm^{-1}]	0.180
D_x [g/cm^{-3}]	1.254
Theta range for data collection	3.16 – 27.90
Solution and refinement	Direct method (ShelXtl V5.1 (NT)
Largest difference peak and hole [e. Å^3] (min, max)	+0.552, -0.213
Reflections collected	5645
Independent reflections	5645
Observed (I>2σ(I))	3472
Number of variables	336
R1 [$I>2\sigma(I)$]	0.0650
wR2 [all data]	0.1654

Tab.26: $[HN(C_2H_5)_3][C_{14}H_{15}O_8S]$ (**39**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S	6880(2)	7056(1)	7976(1)	55(1)
O(11)	5685(4)	1428(4)	3134(3)	49(1)
O(12)	7274(4)	4058(4)	2981(3)	52(1)
O(13)	4267(4)	1377(4)	4942(4)	49(1)
O(14)	7507(5)	6672(4)	4694(4)	60(1)
O(21)	191(4)	2036(5)	5226(4)	63(1)
O(22)	1114(4)	4210(4)	7865(4)	49(1)
O(23)	1718(4)	2609(5)	3615(4)	59(1)
O(24)	3676(5)	6811(4)	8846(4)	63(1)
C(1)	5161(6)	5101(5)	6318(4)	36(1)
C(2)	9035(8)	6990(9)	7713(8)	69(2)
C(11)	5708(5)	4148(5)	4964(4)	37(1)
C(12)	5133(6)	2289(5)	4376(5)	37(1)
C(13)	6150(6)	2136(5)	2099(5)	47(1)
C(14)	6843(6)	5061(5)	4276(5)	42(1)
C(15)	4345(10)	1602(9)	1030(7)	70(2)
C(16)	7312(11)	1361(9)	1254(9)	67(2)
C(21)	3322(6)	4470(5)	6360(5)	37(1)
C(22)	1766(6)	2991(5)	4958(5)	43(1)

C(23)	271(7)	2311(6)	6793(6)	54(1)
C(24)	2791(6)	5275(5)	7774(5)	44(1)
C(25)	-1721(9)	1527(12)	6826(10)	86(2)
C(26)	1273(10)	1459(9)	7157(8)	66(2)
N	2780(7)	7656(6)	3239(6)	68(1)
C(31)	4220(13)	7269(9)	2579(10)	107(2)
C(32)	3716(15)	5363(10)	1718(11)	127(3)
C(41)	1976(11)	7095(8)	4327(9)	99(2)
C(42)	3381(8)	8169(9)	5954(8)	83(2)
C(51)	1052(13)	6886(12)	1856(12)	132(4)
C(52)	4(13)	7782(12)	2074(9)	110(3)

Tab. 27: $[HN(C_2H_5)_3][C_{14}H_{15}O_8S]$ (**39**): Selected bond lengths [Å] and angles [°].

S-C(1)	1.741(4)	O(22)-C(24)	1.362(5)
S-C(2)	1.805(6)	O(22)-C(23)	1.425(5)
O(11)-C(12)	1.355(5)	O(23)-C(22)	1.205(5)
O(11)-C(13)	1.432(5)	O(24)-C(24)	1.203(5)
O(12)-C(14)	1.377(5)	C(1)-C(21)	1.379(5)
O(12)-C(13)	1.426(5)	C(1)-C(11)	1.455(5)
O(13)-C(12)	1.228(5)	C(11)-C(14)	1.407(5)
O(14)-C(14)	1.226(5)	C(11)-C(12)	1.414(5)

O(21)-C(22)	1.352(5)	C(21)-C(24)	1.451(6)
O(21)-C(23)	1.444(6)	C(21)-C(22)	1.464(6)
		C(1)-S-C(2)	104.1(3)

C(12)-O(11)-C(13)	118.9(3)	O(12)-C(13)-O(11)	110.4(3)
C(14)-O(12)-C(13)	119.6(3)	O(14)-C(14)-O(12)	115.1(4)
C(22)-O(21)-C(23)	118.6(3)	O(14)-C(14)-C(11)	127.4(4)
C(24)-O(22)-C(23)	117.2(3)	O(12)-C(14)-C(11)	117.5(3)
C(21)-C(1)-C(11)	122.1(3)	C(1)-C(21)-C(24)	122.5(3)
C(21)-C(1)-S	118.4(3)	C(1)-C(21)-C(22)	122.0(3)
C(11)-C(1)-S	119.4(3)	C(24)-C(21)-C(22)	115.4(4)
C(14)-C(11)-C(12)	120.1(3)	O(23)-C(22)-O(21)	117.4(4)
C(14)-C(11)-C(1)	121.0(3)	O(23)-C(22)-C(21)	126.8(4)
C(12)-C(11)-C(1)	118.9(3)	O(21)-C(22)-C(21)	115.7(4)
O(13)-C(12)-O(11)	115.3(3)	O(22)-C(23)-O(21)	108.0(4)
O(13)-C(12)-C(11)	126.4(4)	O(24)-C(24)-O(22)	117.4(4)
O(11)-C(12)-C(11)	118.2(3)	O(24)-C(24)-C(21)	125.7(4)
		O(22)-C(24)-C(21)	116.8(3)

7.3.8 Crystal data for $C_{12}H_{12}O_8$ (**9**)

Tab. 28: $C_{12}H_{12}O_8$ (**9**): Crystal data and structure refinement

Empirical formula	$C_{12}H_{12}O_8$
Formula weigt [g/mol]	284.22
Crystal size [mm^3]	0.60 * 0.10 * 0.05
Temperature [K]	293(2)
Crystal system	Triklin
Space group	P -1
a [Å]	5.825(1)
b [Å]	7.333(2)
c [Å]	7.874(2)
α [°]	75.88(3)
β [°]	88.18(3)
γ [°]	74.29(3)
Volume [Å^3]	313.7(1)
Z	1
μ (Mo-K_α) [mm^{-1}]	0.129
D_x [g/cm^{-3}]	1.504
Theta range for data collection	4.43 – 32.83
Solution and refinement	direkte Methoden (ShelXtl V5.1 (NT))
Largest difference peak and hole [e. Å^3] (min, max)	+0.435, -0.216
Reflections collected	7303
Independent reflections	2081
Observed (I>2σ(I))	1542
Number of variables	116
R1 [$I>2\sigma(I)$]	0.0435
wR2 [all data]	0.1143

Tab.29: $C_{12}H_{12}O_8$ (**9**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2063(1)	4674(1)	6550(1)	27(1)
O(2)	4475(1)	2484(1)	8974(1)	27(1)
O(3)	-145(2)	7527(1)	6936(1)	32(1)
O(4)	4350(1)	3402(1)	11478(1)	31(1)
C(1)	934(2)	4834(2)	9479(1)	23(1)
C(2)	3362(2)	3497(2)	10122(1)	24(1)
C(3)	822(2)	5838(2)	7549(1)	24(1)
C(4)	3205(2)	2632(2)	7348(1)	25(1)
C(5)	1400(2)	1437(2)	7700(2)	33(1)
C(6)	5125(2)	1984(2)	6107(2)	35(1)

Tab. 30: $C_{12}H_{12}O_8$ (**9**): Selected bond lengths [Å] and angles [°].

O(1)-C(3)	1.3516(14)	O(3)-C(3)	1.1967(15)
O(1)-C(4)	1.4520(15)	O(4)-C(2)	1.2070(12)
O(2)-C(2)	1.3485(13)	C(1)-C(1)#1	1.347(2)
O(2)-C(4)	1.4651(12)	C(1)-C(2)	1.5064(16)
		C(1)-C(3)	1.5134(14)
C(3)-O(1)-C(4)	119.70(8)	O(4)-C(2)-C(1)	124.74(10)

C(2)-O(2)-C(4)	119.35(8)	O(2)-C(2)-C(1)	113.96(8)
C(1)#1-C(1)-C(2)	123.76(11)	O(3)-C(3)-O(1)	121.52(9)
C(1)#1-C(1)-C(3)	122.97(12)	O(3)-C(3)-C(1)	124.69(10)
C(2)-C(1)-C(3)	113.22(9)	O(1)-C(3)-C(1)	113.66(9)
O(4)-C(2)-O(2)	121.11(10)	O(1)-C(4)-O(2)	109.11(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+2

7.3.9 Crystal data for $C_{25}H_{23}O_4P$(**40**)

Tab. 31: $C_{25}H_{23}O_4P$(**40**): Crystal data and structure refinement

Empirical formula	$C_{25}H_{23}O_4P$	
Formula weight	418.40	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.130(2) Å	α= 90°.
	b = 13.389(6) Å	β= 117.974(11)°.
	c = 9.6192(18) Å	γ = 90°.
Volume	1038.5(5) $Å^3$	
Z	2	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	440	
Crystal size	0.35 x 0.25 x 0.25 mm^3	
Theta range for data collection	2.40 to 27.51°.	
Index ranges	-11<=h<=1, -17<=k<=17, -11<=l<=12	
Reflections collected	5453	
Independent reflections	4787 [R(int) = 0.0210]	
Completeness to theta = 27.51°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4787 / 1 / 364	
Goodness-of-fit on F^2	1.927	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0837	
R indices (all data)	R1 = 0.0347, wR2 = 0.0874	
Absolute structure parameter	-0.01(7)	
Extinction coefficient	0.030(5)	

Largest diff. peak and hole 0.267 and -0.294 e.Å^{-3}

Tab. 32:. $C_{25}H_{23}O_4P$ (**40**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	3835(1)	9143(1)	8900(1)	20(1)
O(1)	3369(2)	7210(1)	5633(2)	35(1)
O(2)	5947(2)	7170(1)	5987(2)	28(1)
O(3)	7927(2)	7505(1)	10663(2)	37(1)
O(4)	8229(2)	7253(1)	8526(2)	30(1)
C(1)	4372(2)	7821(1)	8860(2)	26(1)
C(2)	4846(2)	7341(1)	6569(2)	24(1)
C(3)	5514(2)	7613(1)	8169(2)	25(1)
C(4)	7232(2)	7481(1)	9211(2)	28(1)
C(5)	7607(2)	7530(1)	6909(2)	26(1)
C(6)	8643(3)	6975(2)	6310(3)	38(1)
C(7)	7666(2)	8655(1)	6750(2)	31(1)
C(8)	1932(2)	9514(1)	7237(2)	22(1)
C(9)	1216(2)	10417(1)	7357(2)	28(1)
C(10)	-196(2)	10771(2)	6059(2)	34(1)
C(11)	-877(2)	10236(2)	4664(2)	35(1)
C(12)	-191(2)	9335(2)	4546(2)	34(1)
C(13)	1227(2)	8964(1)	5836(2)	26(1)
C(14)	3557(2)	9293(1)	10621(2)	23(1)

C(15)	2330(2)	8708(1)	10708(2)	30(1)
C(16)	2170(3)	8720(2)	12083(3)	35(1)
C(17)	3219(3)	9309(1)	13341(2)	35(1)
C(18)	4412(3)	9908(1)	13249(2)	32(1)
C(19)	4577(2)	9908(1)	11878(2)	27(1)
C(20)	5460(2)	9932(1)	8974(2)	22(1)
C(21)	5147(2)	10633(1)	7784(2)	27(1)
C(22)	6448(2)	11194(1)	7815(2)	32(1)
C(23)	8053(2)	11065(1)	9027(2)	32(1)
C(24)	8372(2)	10371(1)	10213(2)	30(1)
C(25)	7080(2)	9796(1)	10181(2)	27(1)

Tab. 33: $C_{25}H_{23}O_4P$(**40**) Bond lengths [Å] and angles [°].

P(1)-C(8)	1.7937(16)	O(4)-C(5)	1.433(2)
P(1)-C(20)	1.7953(16)	C(1)-C(3)	1.502(2)
P(1)-C(14)	1.7993(15)	C(2)-C(3)	1.412(2)
P(1)-C(1)	1.8422(19)	C(3)-C(4)	1.421(2)
O(1)-C(2)	1.233(2)	C(5)-C(6)	1.513(2)
O(2)-C(2)	1.3809(19)	C(5)-C(7)	1.519(2)
O(2)-C(5)	1.433(2)	C(8)-C(13)	1.399(2)
O(3)-C(4)	1.234(2)	C(8)-C(9)	1.405(2)
O(4)-C(4)	1.386(2)	C(9)-C(10)	1.392(2)

C(10)-C(11)	1.384(3)	C(18)-C(19)	1.396(2)
C(11)-C(12)	1.388(3)	C(20)-C(25)	1.399(2)
C(12)-C(13)	1.399(2)	C(20)-C(21)	1.402(2)
C(14)-C(19)	1.397(2)	C(21)-C(22)	1.394(2)
C(14)-C(15)	1.402(2)	C(22)-C(23)	1.390(3)
C(15)-C(16)	1.397(2)	C(23)-C(24)	1.392(3)
C(16)-C(17)	1.384(3)	C(24)-C(25)	1.397(2)
C(17)-C(18)	1.388(3)		

C(8)-P(1)-C(20)	107.99(7)	O(3)-C(4)-O(4)	116.10(16)
C(8)-P(1)-C(14)	107.10(7)	O(3)-C(4)-C(3)	127.31(17)
C(20)-P(1)-C(14)	111.61(7)	O(4)-C(4)-C(3)	116.51(15)
C(8)-P(1)-C(1)	113.75(8)	O(4)-C(5)-O(2)	110.56(13)
C(20)-P(1)-C(1)	110.09(8)	O(4)-C(5)-C(6)	106.60(15)
C(14)-P(1)-C(1)	106.30(7)	O(2)-C(5)-C(6)	105.54(15)
C(2)-O(2)-C(5)	116.95(13)	O(4)-C(5)-C(7)	110.57(15)
C(4)-O(4)-C(5)	116.40(13)	O(2)-C(5)-C(7)	110.40(14)
C(3)-C(1)-P(1)	115.75(11)	C(6)-C(5)-C(7)	113.01(15)
O(1)-C(2)-O(2)	115.75(15)	C(13)-C(8)-C(9)	120.72(15)
O(1)-C(2)-C(3)	126.79(15)	C(13)-C(8)-P(1)	121.94(13)
O(2)-C(2)-C(3)	117.42(14)	C(9)-C(8)-P(1)	117.24(12)
C(2)-C(3)-C(4)	120.42(15)	C(10)-C(9)-C(8)	119.32(17)
C(2)-C(3)-C(1)	119.67(15)	C(11)-C(10)-C(9)	120.01(18)
C(4)-C(3)-C(1)	118.47(15)		

C(10)-C(11)-C(12)	120.92(16)	C(18)-C(19)-C(14)	119.62(17)
C(11)-C(12)-C(13)	120.13(16)	C(25)-C(20)-C(21)	119.70(15)
C(12)-C(13)-C(8)	118.90(16)	C(25)-C(20)-P(1)	119.24(12)
C(19)-C(14)-C(15)	120.31(15)	C(21)-C(20)-P(1)	120.91(12)
C(19)-C(14)-P(1)	122.52(12)	C(22)-C(21)-C(20)	119.87(16)
C(15)-C(14)-P(1)	117.02(12)	C(23)-C(22)-C(21)	120.24(17)
C(16)-C(15)-C(14)	119.45(17)	C(22)-C(23)-C(24)	120.20(16)
C(17)-C(16)-C(15)	119.81(18)	C(23)-C(24)-C(25)	119.99(16)
C(16)-C(17)-C(18)	121.05(16)	C(24)-C(25)-C(20)	119.99(16)
C(17)-C(18)-C(19)	119.71(18)		

Symmetry transformations used to generate equivalent atoms:

Tab. 34: $C_{25}H_{23}O_4P$ (**40**): Anisotropic displacement parameters ($Å^2$x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b*U^{12}

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	19(1)	23(1)	16(1)	1(1)	8(1)	-1(1)
O(1)	26(1)	40(1)	36(1)	-14(1)	13(1)	-5(1)
O(2)	27(1)	31(1)	28(1)	-5(1)	16(1)	-3(1)
O(3)	38(1)	44(1)	25(1)	9(1)	11(1)	10(1)
O(4)	24(1)	35(1)	30(1)	5(1)	12(1)	7(1)
C(1)	31(1)	23(1)	30(1)	3(1)	19(1)	2(1)
C(2)	25(1)	22(1)	29(1)	-2(1)	14(1)	-1(1)

C(3)	27(1)	24(1)	26(1)	2(1)	16(1)	1(1)
C(4)	29(1)	27(1)	28(1)	5(1)	14(1)	4(1)
C(5)	25(1)	27(1)	30(1)	1(1)	15(1)	1(1)
C(6)	36(1)	37(1)	49(1)	-1(1)	28(1)	6(1)
C(7)	32(1)	28(1)	39(1)	3(1)	21(1)	-1(1)
C(8)	18(1)	28(1)	19(1)	2(1)	7(1)	0(1)
C(9)	25(1)	29(1)	29(1)	1(1)	11(1)	0(1)
C(10)	27(1)	36(1)	39(1)	13(1)	16(1)	6(1)
C(11)	21(1)	51(1)	29(1)	15(1)	8(1)	3(1)
C(12)	25(1)	54(1)	20(1)	3(1)	7(1)	-3(1)
C(13)	21(1)	35(1)	21(1)	1(1)	10(1)	-1(1)
C(14)	25(1)	26(1)	20(1)	2(1)	11(1)	2(1)
C(15)	32(1)	32(1)	31(1)	-2(1)	20(1)	-5(1)
C(16)	45(1)	34(1)	42(1)	4(1)	33(1)	1(1)
C(17)	52(1)	35(1)	32(1)	6(1)	30(1)	9(1)
C(18)	44(1)	31(1)	23(1)	-1(1)	17(1)	5(1)
C(19)	33(1)	28(1)	22(1)	-1(1)	14(1)	-1(1)
C(20)	22(1)	25(1)	18(1)	-1(1)	9(1)	-2(1)
C(21)	26(1)	29(1)	22(1)	3(1)	9(1)	-2(1)
C(22)	34(1)	31(1)	30(1)	4(1)	15(1)	-6(1)
C(23)	31(1)	33(1)	34(1)	-4(1)	17(1)	-10(1)
C(24)	21(1)	36(1)	29(1)	-4(1)	7(1)	-4(1)
C(25)	26(1)	30(1)	22(1)	3(1)	8(1)	1(1)

Tab. 35: $C_{25}H_{23}O_4P$ (**40**): Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(1A)	4880(40)	7550(20)	9930(40)	37(7)
H(1B)	3330(40)	7460(20)	8300(40)	37(7)
H(6A)	9810(50)	7140(30)	6960(40)	52(8)
H(6B)	8560(40)	6290(30)	6480(40)	42(7)
H(6C)	8230(40)	7200(30)	5110(40)	50(8)
H(7A)	7190(40)	8830(30)	5570(40)	44(8)
H(7B)	8780(40)	8880(20)	7260(40)	39(7)
H(7C)	7040(30)	9000(20)	7130(30)	32(6)
H(9)	1730(40)	10800(20)	8400(30)	34(6)
H(10)	-670(40)	11380(20)	6210(30)	38(7)
H(11)	1920(40)	10480(20)	3730(40)	42(7)
H(12)	-660(40)	8920(20)	3550(40)	41(7)
H(13)	1650(30)	8380(20)	5750(30)	27(5)
H(15)	1510(40)	8320(20)	9750(40)	38(7)
H(16)	1320(40)	8420(20)	12030(40)	41(7)
H(17)	3190(40)	9260(30)	14340(40)	55(9)
H(18)	5150(40)	10290(30)	14150(40)	43(7)
H(19)	5350(40)	10330(20)	11820(40)	39(7)
H(21)	3940(40)	10710(20)	6890(30)	31(6)

H(22)	6180(40)	11670(30)	6990(40)	48(8)
H(23)	8930(40)	11410(30)	9010(40)	42(7)
H(24)	9430(40)	10260(20)	10970(30)	34(6)
H(25)	7340(30)	9270(20)	10970(30)	36(6)

7.3.10 Crystal data for $C_{18}H_{28}N_2O_4$ (**41**)

Tab. 36: $C_{18}H_{28}N_2O_4$ (**41**): Crystal data and structure refinement

Empirical formula	$C_{18}H_{28}N_2O_4$	
Formula weight	336.42	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.019(6) Å	α= 90°.
	b = 11.0484(13) Å	β= 122.518(14)°.
	c = 16.726(3) Å	γ = 90°.
Volume	3742.9(12) $Å^3$	
Z	8	
Density (calculated)	1.194 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	1456	
Crystal size	0.80 x 0.60 x 0.40 mm^3	
Theta range for data collection	3.10 to 27.96°.	
Index ranges	-1<=h<=31, 0<=k<=14, -22<=l<=18	
Reflections collected	4814	
Independent reflections	4505 [R(int) = 0.0188]	
Absorption correction	Psi-Scans	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4505 / 0 / 329	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1148	
R indices (all data)	R1 = 0.1077, wR2 = 0.1362	
Largest diff. peak and hole	0.178 and -0.162 e.$Å^{-3}$	

Tab. 37:. $C_{18}H_{28}N_2O_4$ (**41**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	0.0564(1)	0.1003(1)	0.4672(1)	48(1)
O(2)	0.1347(1)	-0.0103(1)	0.4552(1)	49(1)
O(3)	0.2354(1)	0.0610(1)	0.5129(1)	53(1)
O(4)	0.0806(1)	0.2742(1)	0.5452(1)	67(1)
N(1)	0.3342(1)	0.1696(1)	0.7346(1)	36(1)
N(2)	0.2639(1)	0.1778(1)	0.7781(1)	39(1)
C(1)	0.1834(1)	0.0738(2)	0.5097(1)	40(1)
C(2)	0.2728(1)	0.2033(2)	0.7075(1)	34(1)
C(3)	0.1679(1)	0.1665(2)	0.5514(1)	38(1)
C(4)	0.2209(1)	0.2565(2)	0.6139(1)	39(1)
C(5)	0.3651(1)	0.1204(2)	0.8258(1)	42(1)
C(6)	0.3213(1)	0.1256(2)	0.8525(1)	43(1)
C(7)	0.3655(1)	0.1971(2)	0.6801(1)	42(1)
C(8)	0.1024(1)	0.1870(2)	0.5253(1)	44(1)
C(9)	0.0806(1)	-0.0173(2)	0.4689(1)	45(1)
C(10)	0.2025(1)	0.2094(2)	0.7751(2)	53(1)
C(11)	0.4146(1)	0.2988(2)	0.7279(2)	57(1)
C(12)	0.1021(1)	-0.0809(2)	0.5609(2)	56(1)
C(13)	0.3937(1)	0.0870(3)	0.6604(2)	66(1)
C(14)	0.3326(2)	0.0901(3)	0.9464(2)	66(1)

C(15)	0.4340(1)	0.0729(3)	0.8821(2)	67(1)
C(16)	0.0261(1)	-0.0841(3)	0.3846(2)	70(1)
C(17)	0.1746(2)	0.1009(4)	0.7976(2)	85(1)
C(18)	0.2143(2)	0.3208(5)	0.8348(4)	109(1)

Tab. 38: $C_{18}H_{28}N_2O_4$ (**41**): Bond lengths [Å] and angles [°].

O(1)-C(8)	1.389(2)	C(1)-C(3)	1.398(3)
O(1)-C(9)	1.418(2)	C(2)-C(4)	1.501(2)
O(2)-C(1)	1.385(2)	C(3)-C(8)	1.408(2)
O(2)-C(9)	1.437(2)	C(3)-C(4)	1.506(3)
O(3)-C(1)	1.227(2)	C(5)-C(6)	1.346(3)
O(4)-C(8)	1.226(2)	C(5)-C(15)	1.493(3)
N(1)-C(2)	1.343(2)	C(6)-C(14)	1.496(3)
N(1)-C(5)	1.399(2)	C(7)-C(11)	1.510(3)
N(1)-C(7)	1.492(2)	C(7)-C(13)	1.512(3)
N(2)-C(2)	1.338(2)	C(9)-C(16)	1.504(3)
N(2)-C(6)	1.392(2)	C(9)-C(12)	1.508(3)
N(2)-C(10)	1.489(2)	C(10)-C(18)	1.513(4)
		C(10)-C(17)	1.516(4)
C(8)-O(1)-C(9)	117.01(13)	C(6)-C(5)-C(15)	127.29(19)
C(1)-O(2)-C(9)	116.70(14)	N(1)-C(5)-C(15)	125.57(19)

C(2)-N(1)-C(5)	108.54(14)	C(5)-C(6)-N(2)	107.28(15)
C(2)-N(1)-C(7)	124.07(14)	C(5)-C(6)-C(14)	127.2(2)
C(5)-N(1)-C(7)	126.90(14)	N(2)-C(6)-C(14)	125.4(2)
C(2)-N(2)-C(6)	108.94(14)	N(1)-C(7)-C(11)	109.62(16)
C(2)-N(2)-C(10)	123.00(15)	N(1)-C(7)-C(13)	113.57(18)
C(6)-N(2)-C(10)	127.97(15)	C(11)-C(7)-C(13)	113.56(19)
O(3)-C(1)-O(2)	115.63(17)	O(4)-C(8)-O(1)	115.86(16)
O(3)-C(1)-C(3)	126.84(17)	O(4)-C(8)-C(3)	127.80(19)
O(2)-C(1)-C(3)	117.47(15)	O(1)-C(8)-C(3)	116.30(17)
N(2)-C(2)-N(1)	108.11(14)	O(1)-C(9)-O(2)	110.11(15)
N(2)-C(2)-C(4)	124.56(15)	O(1)-C(9)-C(16)	106.84(19)
N(1)-C(2)-C(4)	127.29(15)	O(2)-C(9)-C(16)	106.51(17)
C(1)-C(3)-C(8)	121.11(17)	O(1)-C(9)-C(12)	111.03(17)
C(1)-C(3)-C(4)	118.51(15)	O(2)-C(9)-C(12)	110.17(16)
C(8)-C(3)-C(4)	119.72(17)	C(16)-C(9)-C(12)	112.0(2)
C(2)-C(4)-C(3)	112.53(15)	N(2)-C(10)-C(18)	109.7(2)
C(6)-C(5)-N(1)	107.13(16)	N(2)-C(10)-C(17)	111.6(2)
		C(18)-C(10)-C(17)	115.4(3)

Tab.39: $C_{18}H_{28}N_2O_4$ (**41**): Anisotropic displacement parameters (Å^{2}x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	28(1)	56(1)	47(1)	4(1)	13(1)	3(1)
O(2)	43(1)	65(1)	44(1)	-12(1)	27(1)	-10(1)
O(3)	43(1)	71(1)	57(1)	-7(1)	36(1)	-4(1)
O(4)	42(1)	59(1)	91(1)	-9(1)	30(1)	11(1)
N(1)	31(1)	42(1)	33(1)	1(1)	15(1)	-1(1)
N(2)	40(1)	44(1)	37(1)	-1(1)	23(1)	-6(1)
C(1)	37(1)	54(1)	32(1)	4(1)	20(1)	-1(1)
C(2)	33(1)	36(1)	36(1)	-1(1)	19(1)	-4(1)
C(3)	31(1)	45(1)	35(1)	6(1)	16(1)	3(1)
C(4)	34(1)	43(1)	39(1)	7(1)	20(1)	1(1)
C(5)	39(1)	43(1)	34(1)	2(1)	13(1)	-3(1)
C(6)	47(1)	44(1)	32(1)	0(1)	17(1)	-9(1)
C(7)	33(1)	59(1)	38(1)	2(1)	21(1)	0(1)
C(8)	34(1)	50(1)	41(1)	8(1)	16(1)	5(1)
C(9)	34(1)	56(1)	44(1)	-3(1)	21(1)	-3(1)
C(10)	43(1)	75(2)	50(1)	-8(1)	32(1)	-7(1)
C(11)	51(1)	64(2)	63(1)	-1(1)	35(1)	-11(1)
C(12)	54(1)	59(2)	63(1)	14(1)	37(1)	7(1)
C(13)	62(2)	75(2)	73(2)	-17(1)	45(2)	-3(1)
C(14)	76(2)	79(2)	39(1)	5(1)	29(1)	-18(2)

C(15)	44(1)	83(2)	56(2)	17(1)	14(1)	10(1)
C(16)	53(1)	86(2)	66(2)	-23(2)	28(1)	-20(1)
C(17)	64(2)	131(3)	71(2)	6(2)	43(2)	-30(2)
C(18)	83(2)	124(3)	136(4)	-60(3)	70(3)	-5(2)

Tab. 40: $C_{18}H_{28}N_2O_4$ (**41**): Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}).

	x	y	z	U(eq)
H(1)	2427(9)	2897(15)	5828(12)	36(5)
H(2)	2005(10)	3246(19)	6267(14)	47(5)
H(3)	3288(10)	2240(17)	6185(14)	47(5)
H(4)	655(13)	-900(2)	5726(17)	76(7)
H(5)	4509(13)	2720(2)	7917(18)	71(7)
H(6)	4319(11)	3190(2)	6910(17)	66(7)
H(7)	4327(14)	590(2)	7192(19)	78(8)
H(8)	4089(13)	1080(2)	6180(2)	89(8)
H(9)	1182(14)	-1580(3)	5620(2)	98(10)
H(10)	423(12)	-1600(3)	3760(18)	77(8)
H(11)	2990(14)	400(3)	9425(19)	91(9)
H(12)	1395(13)	-390(2)	6187(19)	82(8)
H(13)	1703(11)	2290(2)	7098(16)	64(7)
H(14)	-100(15)	-970(3)	3950(2)	100(9)

H(15)	103(14)	-390(3)	3260(2)	92(9)
H(16)	1983(17)	890(3)	8630(3)	125(13)
H(17)	3916(15)	3730(3)	7320(2)	97(9)
H(18)	3322(15)	1550(3)	9800(2)	106(11)
H(19)	4657(17)	1320(3)	8950(2)	123(13)
H(20)	3635(15)	190(3)	6380(2)	102(10)
H(21)	4408(15)	410(3)	9360(2)	104(10)
H(22)	3762(18)	640(3)	9860(2)	113(11)
H(23)	2427(19)	2940(3)	9030(3)	125(14)
H(24)	1308(18)	1270(3)	7780(2)	122(12)
H(25)	1719(19)	250(4)	7610(3)	152(16)
H(26)	1760(19)	3380(3)	8310(2)	121(12)
H(27)	4462(19)	190(4)	8510(3)	154(17)
H(38)	2330(2)	3860(5)	8170(4)	190(2)

7.3.11 Crystal data for $C_{20}H_{28}O_{10}S_2$ (**20**)

Tab. 41: $C_{20}H_{28}O_{10}S_2$ (**20**): Crystal data and structure refinement

Empirical formula	C20 H28O10 S2	
Formula weight	492.54	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.3430(14) Å	α= 76.495(17).
	b = 8.582(2) Å	β= 73.754(14)°.
	c = 10.2260(15) Å	γ = 78.360(18).
Volume	595.1(2) Å^3	
Z	1	
Density (calculated)	1.374 Mg/m^3	
Absorption coefficient	0.275 mm^{-1}	
F(000)	260	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.16 to 30.93°.	
Index ranges	-1<=h<=5, -12<=k<=12, -14<=l<=14	
Reflections collected	3093	
Independent reflections	2305 [R(int) = 0.0277]	
Completeness to theta = 30.93	60.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2305/ 0 / 169	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1256	
R indices (all data)	R1 = 0.0826, wR2 = 0.1439	
Largest diff. peak and hole	0.197 and -0.280 e.Å^{-3}	

Tab. 42: $C_{20}H_{28}O_{10}S_2$ (**20**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	557(1)	5281(1)	6045(1)	44(1)
O(2)	-1607(5)	8283(3)	3913(2)	51(1)
O(1)	1249(4)	8911(2)	3530(2)	44(1)
O(4)	3753(4)	4458(2)	3045(2)	61(1)
O(5)	3987(3)	6986(2)	2973(2)	47(1)
O(11)	9120(4)	13223(3)	-1261(2)	68(1)
C(2)	45(7)	7835(3)	3862(2)	35(1)
C(3)	919(5)	6054(3)	4160(2)	35(1)
C(4)	2990(5)	5724(3)	33657(2)	43(1)
C(6)	3234(6)	8424(3)	3563(3)	42(1)
C(12)	7486(7)	13242(8)	-149(4)	112(2)
C(13)	8088(9)	12755(7)	1153(4)	107(2)
C(14)	10133(10)	12429(6)	794(4)	102(2)
C(15)	10715(7)	12488(5)	-731(4)	79(1)
C(61)	4281(10)	9753(5)	2599(4)	66(1)
C(10)	10114(2)	8936(2)	13271(3)	34(1)
C(62)	3498(8)	8138(4)	5008(3)	49(1)

Tab. 43: $C_{20}H_{28}O_{10}S_2$ (**20**): Bond lengths [Å] and angles [°].

S(1)-C(3) #1	1.809(3)	O(11)-C(12)	1.404(5)
S(1)-C(3)	1.848(2)	C(2)-C(3)	1.528(4)
S(1)-S(1) #1	2.6626(14)	C(3)-C(4)	1.515(4)
O(2)-C(2)	1.186(4)	C(3)-S(1) #1	1.809(3)
O(1)-C(2)	1.328(4)	C(3)-C(3) #1	2.507(5)
O(1)-C(6)	1.441(4)	C(6)-C(61)	1.501(4)
O(4)-C(4)	1.191(3)	C(6)-C(61)	1.506(5)
O(5)-C(4)	1.350(4)	C(12)-C(13)	1.462(6)
O(5)-C(6)	1.442(3)	C(13)-C(14)	1.427(7)
O(11)-C(15)	1.400(5)	C(14)-C(15)	1.489(5)

C(3) #1-S(1)-C(3)	86.55(12)	C(2)-C(3)-C(3) #1	122.5(3)
C(3) #1 -S(1)-C(1) #1	43.85(7)	S(1) #1 -C(3)-C(3) #1	47.38(10)
C(3)-S(1)-S(1) #1	42.70(9)	S(1)-C(3)-C(3) #1	46.07(8)
C(2)-O(1)-C(6)	121.4(3)	O(4)-C(4)-O(5)	119.2(3)
C(4)-O(5)-C(6)	120.0(2)	O(4)-C(4)-C(3)	124.5(3)
C(15)-O(11)-C(12)	108.3(3)	O(5)-C(4)-C(3)	116.3(2)
O(2)-C(2)-O(1)	119.8(3)	O(1)-C(6)-O(5)	109.7(3)
O(2)-C(2)-C(3)	123.9(3)	O(1)-C(6)-C(62)	111.9(3)
O(1)-C(2)-C(3)	116.3(4)	O(5)-C(6)-C(62)	110.3(3)
C(4)-C(3)-C(2)	113.1(2)	O(1)-C(6)-C(61)	105.8(3)
C(4)-C(3)-S(1) #1	112.60(18)	O(5)-C(6)-C(61)	106.3(3)

C(2)-C(3)-S(1) #1	112.1(2)	C(62)-C(6)-C(61)	112.5(4)
C(4)-C(3)-S(1)	112.98(19)	O(11)-C(12)-C(13)	109.0(5)
C(2)-C(3)-S(1)	111.06(15)	C(14)-C(13)-C(12)	106.8(4)
S(1) #1 -C(3)-S(1)	93.45(12)	C(13)-C(14)-C(15)	106.1(4)
C(4)-C(3)-C(3) #1	124.4(2)	O(11)-C(15)-C(14)	107.6(4)

Symmetry transformations used to generate equivalent atoms:

Tab.44: $C_{20}H_{28}O_{10}S_2$ (**20**): Anisotropic displacement parameters (Å^{2}x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b*U^{12}

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	59(1)	49(1)	30(1)	-5(1)	-13(1)	-16(1)
O(2)	26(3)	57(1)	70(1)	-18(1)	-14(1)	0(1)
O(1)	26(2)	42(1)	65(1)	-2(1)	-18(1)	-5(1)
O(4)	56(2)	55(1)	65(1)	-20(1)	-12(1)	15(1)
O(5)	26(2)	63(1)	49(1)	-16(1)	-4(1)	-3(1)
O(11)	56(2)	102(2)	35(1)	-9(1)	-9(1)	2(2)
C(2)	25(4)	45(1)	36(1)	-8(1)	-8(1)	-2(2)
C(3)	34(3)	40(1)	31(1)	-6(1)	-9(1)	-2(1)
C(4)	43(3)	49(1)	35(1)	-7(1)	-12(1)	2(1)
C(6)	29(4)	48(1)	51(1)	-4(1)	-14(2)	-6(2)
C(12)	59(5)	225(6)	48(2)	-29(3)	2(2)	-29(4)
C(13)	101(6)	160(5)	46(2)	-11(2)	3(2)	-29(4)

C(14)	126(6)	123(3)	54(2)	-8(2)	-43(3)	6(3)
C(15)	79(4)	89(2)	60(2)	-15(2)	-18(2)	12(2)
C(61)	51(5)	70(2)	73(2)	7(2)	-15(2)	-21(2)
C(62)	47(4)	52(2)	54(2)	-11(1)	-19(2)	-7(2)

Tab. 44: $C_{20}H_{28}O_{10}S_2$ (**20**): Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}).

	x	y	z	U(eq)
H(12A)	6666	12493	-191	135
H(12B)	6748	14332	-203	135
H(13A)	7649	13626	1692	128
H(13B)	7549	11785	1711	128
H(14A)	10578	11358	1287	122
H(14B)	10678	13244	1036	122
H(15A)	11779	13116	-1159	95
H(15B)	11134	11391	-930	95
H(61A)	4090(6)	9840(4)	1690 (4)	67(10)
H(61B)	3670(6)	10760(5)	2890(4)	81(12)
H(61C)	5530(8)	9440(5)	2550(4)	84(18)
H(62A)	2910(5)	72708(4)	5590(3)	62(10)
H(62B)	2950(50)	9040(4)	5460(3)	56(9)
H(62C)	4870(6)	7860(4)	4970(3)	55(9)

7.3.12 Crystal data for $C_{24}H_{21}O_4PS$ (**42**)

Tab. 45: $C_{24}H_{21}O_4PS$ (**42**): Crystal data and structure refinement

Empirical formula	C24 H21 O4 P S	
Formula weight	436.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.2529(16) Å	α= 90°.
	b = 13.2721(17) Å	β= 118.209(10)°.
	c = 9.6779(15) Å	γ = 90°.
Volume	1047.3(3) Å^3	
Z	2	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	0.260 mm^{-1}	
F(000)	456	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.39 to 27.51°.	
Index ranges	-12<=h<=11, -17<=k<=17, -12<=l<=11	
Reflections collected	9483	
Independent reflections	4815 [R(int) = 0.0485]	
Completeness to theta = 27.51°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4815 / 1 / 356	
Goodness-of-fit on F^2	1.960	
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0797	
R indices (all data)	R1 = 0.0340, wR2 = 0.0831	
Absolute structure parameter	-0.05(6)	

Extinction coefficient	0.011(3)
Largest diff. peak and hole	0.282 and -0.224 e.Å^{-3}

Tab. 46: $C_{24}H_{21}O_4PS$ (**42**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5113(1)	8794(1)	8909(1)	19(1)
S(1)	4615(1)	7268(1)	9007(1)	26(1)
O(1)	2485(2)	7086(1)	10609(2)	36(1)
O(2)	123(2)	6886(1)	8449(2)	30(1)
O(3)	2125(2)	6826(1)	5595(2)	34(1)
O(4)	-70(2)	6817(1)	5932(2)	28(1)
C(1)	2489(2)	7176(1)	8146(2)	24(1)
C(2)	1779(2)	7073(1)	9175(2)	27(1)
C(3)	1589(2)	6951(1)	6517(2)	25(1)
C(4)	-812(2)	7184(2)	6838(2)	27(1)
C(5)	-961(3)	8322(2)	6711(3)	30(1)
C(6)	-2437(3)	6649(2)	6215(3)	38(1)
C(7)	7093(2)	8940(1)	10592(2)	22(1)
C(8)	7324(2)	9528(2)	11879(2)	26(1)
C(9)	8844(3)	9522(2)	13225(2)	31(1)
C(10)	10114(2)	8936(2)	13271(3)	34(1)
C(11)	9889(2)	8369(2)	11975(3)	34(1)
C(12)	8371(2)	8365(2)	10626(2)	30(1)

C(13)	5306(2)	9156(2)	7213(2)	22(1)
C(14)	6123(3)	10063(2)	7301(2)	28(1)
C(15)	6203(3)	10407(2)	5978(3)	34(1)
C(16)	5464(3)	9853(2)	4596(3)	37(1)
C(17)	4687(3)	8953(2)	4525(2)	36(1)
C(18)	4594(2)	8591(2)	5834(2)	27(1)
C(19)	3555(2)	9555(1)	8981(2)	21(1)
C(20)	3149(2)	9401(2)	10188(2)	25(1)
C(21)	1910(3)	9968(2)	10226(2)	29(1)
C(22)	1048(3)	10674(2)	9058(3)	31(1)
C(23)	1427(3)	10817(2)	7843(2)	32(1)
C(24)	2683(2)	10264(2)	7805(2)	25(1)

Tab. 47: $C_{24}H_{21}O_4PS$ (**42**): Bond lengths [Å] and angles [°].

P(1)-C(19)	1.7891(18)	C(7)-C(8)	1.397(3)
P(1)-C(7)	1.7956(18)	C(8)-C(9)	1.394(3)
P(1)-C(13)	1.7990(19)	C(9)-C(10)	1.392(3)
P(1)-S(1)	2.0893(7)	C(10)-C(11)	1.391(4)
S(1)-C(1)	1.7399(19)	C(11)-C(12)	1.394(3)
O(1)-C(2)	1.223(3)	C(13)-C(18)	1.395(3)
O(2)-C(2)	1.373(2)	C(13)-C(14)	1.402(3)
O(2)-C(4)	1.435(2)	C(14)-C(15)	1.393(3)

O(3)-C(3)	1.221(3)	C(15)-C(16)	1.391(4)
O(4)-C(3)	1.373(2)	C(16)-C(17)	1.379(4)
O(4)-C(4)	1.431(2)	C(17)-C(18)	1.395(3)
C(1)-C(3)	1.423(3)	C(19)-C(20)	1.400(2)
C(1)-C(2)	1.436(3)	C(19)-C(24)	1.401(2)
C(4)-C(6)	1.508(3)	C(20)-C(21)	1.386(3)
C(7)-C(12)	1.395(3)	C(21)-C(22)	1.393(3)
C(4)-C(5)	1.516(3)	C(22)-C(23)	1.390(3)
		C(23)-C(24)	1.389(3)

C(19)-P(1)-C(7)	113.52(9)	C(12)-C(7)-C(8)	120.87(17)
C(19)-P(1)-C(13)	108.30(8)	C(12)-C(7)-P(1)	116.90(14)
C(7)-P(1)-C(13)	107.46(8)	C(8)-C(7)-P(1)	121.98(14)
C(19)-P(1)-S(1)	110.27(6)	C(9)-C(8)-C(7)	119.47(19)
C(7)-P(1)-S(1)	102.49(6)	C(10)-C(9)-C(8)	119.7(2)
C(13)-P(1)-S(1)	114.82(7)	C(11)-C(10)-C(9)	120.60(19)
C(1)-S(1)-P(1)	105.65(7)	C(10)-C(11)-C(12)	120.1(2)
C(2)-O(2)-C(4)	117.34(16)	C(11)-C(12)-C(7)	119.2(2)
C(3)-O(4)-C(4)	117.99(15)	C(18)-C(13)-C(14)	121.11(18)
C(3)-C(1)-C(2)	121.83(17)	C(18)-C(13)-P(1)	121.57(15)
C(3)-C(1)-S(1)	118.84(15)	C(14)-C(13)-P(1)	117.23(15)
C(2)-C(1)-S(1)	117.34(14)	C(15)-C(14)-C(13)	119.2(2)
O(1)-C(2)-O(2)	116.81(19)	C(16)-C(15)-C(14)	119.6(2)

O(1)-C(2)-C(1)	127.70(19)	C(17)-C(16)-C(15)	120.93(19)
O(2)-C(2)-C(1)	115.39(18)	C(16)-C(17)-C(18)	120.5(2)
O(3)-C(3)-O(4)	116.21(18)	C(17)-C(18)-C(13)	118.6(2)
O(3)-C(3)-C(1)	127.66(18)	C(20)-C(19)-C(24)	119.80(17)
O(4)-C(3)-C(1)	116.07(17)	C(20)-C(19)-P(1)	119.25(14)
O(4)-C(4)-O(2)	110.79(16)	C(24)-C(19)-P(1)	120.86(14)
O(4)-C(4)-C(6)	105.74(18)	C(21)-C(20)-C(19)	119.59(18)
O(2)-C(4)-C(6)	106.23(18)	C(20)-C(21)-C(22)	120.51(19)
O(2)-C(4)-C(5)	110.37(17)	C(23)-C(22)-C(21)	120.07(19)
C(6)-C(4)-C(5)	113.67(18)	C(24)-C(23)-C(22)	119.96(19)
O(4)-C(4)-C(5)	109.91(17)	C(23)-C(24)-C(19)	120.05(18)

Symmetry transformations used to generate equivalent atoms:

Tab.48: $C_{24}H_{21}O_4PS$ (**42**): Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*U^{12}$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	18(1)	22(1)	18(1)	1(1)	9(1)	1(1)
S(1)	20(1)	23(1)	32(1)	4(1)	10(1)	3(1)
O(1)	38(1)	42(1)	27(1)	9(1)	14(1)	-1(1)
O(2)	27(1)	34(1)	32(1)	7(1)	16(1)	1(1)
O(3)	34(1)	39(1)	36(1)	-14(1)	21(1)	-5(1)
O(4)	22(1)	32(1)	30(1)	-7(1)	11(1)	-2(1)
C(1)	22(1)	22(1)	27(1)	1(1)	11(1)	1(1)

C(2)	29(1)	24(1)	29(1)	6(1)	15(1)	3(1)
C(3)	22(1)	22(1)	32(1)	-4(1)	13(1)	-1(1)
C(4)	23(1)	29(1)	29(1)	1(1)	12(1)	-1(1)
C(5)	27(1)	26(1)	38(1)	2(1)	16(1)	3(1)
C(6)	25(1)	36(1)	53(1)	-2(1)	18(1)	-5(1)
C(7)	20(1)	24(1)	20(1)	3(1)	8(1)	0(1)
C(8)	28(1)	27(1)	23(1)	1(1)	12(1)	-1(1)
C(9)	32(1)	28(1)	25(1)	1(1)	8(1)	-5(1)
C(10)	23(1)	34(1)	33(1)	6(1)	4(1)	-3(1)
C(11)	20(1)	33(1)	43(1)	5(1)	11(1)	3(1)
C(12)	27(1)	30(1)	32(1)	0(1)	14(1)	1(1)
C(13)	23(1)	28(1)	20(1)	3(1)	12(1)	3(1)
C(14)	31(1)	27(1)	29(1)	3(1)	17(1)	3(1)
C(15)	33(1)	37(1)	40(1)	13(1)	24(1)	7(1)
C(16)	33(1)	56(1)	30(1)	15(1)	20(1)	15(1)
C(17)	29(1)	57(1)	21(1)	3(1)	12(1)	8(1)
C(18)	21(1)	37(1)	22(1)	0(1)	9(1)	3(1)
C(19)	21(1)	22(1)	21(1)	0(1)	10(1)	2(1)
C(20)	28(1)	28(1)	21(1)	2(1)	14(1)	2(1)
C(21)	30(1)	34(1)	31(1)	-3(1)	20(1)	0(1)
C(22)	30(1)	31(1)	36(1)	-5(1)	18(1)	5(1)
C(23)	30(1)	31(1)	31(1)	3(1)	12(1)	7(1)
C(24)	28(1)	27(1)	22(1)	3(1)	13(1)	6(1)

Tab. 49: $C_{24}H_{21}O_4PS$ (**42**): Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}).

	x	y	z	U(eq)
H(5A)-1490(40)	8610(30)	7240(40)	41(8)	
H(5B)	0(40)	8640(20)	7060(30)	29(7)
H(5C)	-1650(50)	8510(30)	5530(50)	57(11)
H(6A)	-3020(50)	6800(30)	6850(50)	53(10)
H(6B)	-2230(40)	5940(30)	6350(40)	40(8)
H(6C)	-3230(40)	6850(30)	5110(40)	41(8)
H(8A)	6460(40)	9950(30)	11840(40)	34(7)
H(9A)	9010(50)	9950(30)	14060(50)	52(10)
H(10A)	11190(40)	8930(30)	14260(40)	41(8)
H(11A)	10700(40)	7950(20)	11980(30)	28(6)
H(12A)	8200(40)	7970(30)	9630(30)	31(7)
H(14A)	6610(40)	10410(30)	8290(40)	41(8)
H(15A)	6760(30)	11010(20)	6030(30)	24(6)
H(16A)	5640(50)	10080(30)	3720(50)	46(9)
H(17A)	4110(50)	8510(30)	3520(40)	50(9)
H(18A)	4080(40)	7980(30)	5830(40)	34(7)
H(20A)	3580(40)	8950(30)	10860(40)	34(7)
H(21A)	1660(40)	9890(30)	11120(30)	32(7)
H(22A)	230(40)	11100(30)	9120(40)	43(9)

H(23A)	790(50)	11340(30)	6920(40)	46(9)
H(24A)	3020(40)	10380(20)	7010(40)	31(7)

7.3.13 Crystal data for $C_{28}H_{50}N_4O_{17}S_4$ (**43**)

Tab. 50: $C_{28}H_{50}N_4O_{17}S_4$ (**43**): Crystal data and structure refinement

Empirical formula	$C_{28}H_{50}N_4O_{17}S_4$ (2·**43** · $C_4H_{10}O$)
Unit cell dimensions	a = 16.662(7)Å
	b = 16.662(7) Å
	c = 15.992(8) Å
Volume [$Å^3$]	4440(3)
Z	4
berechnete Dichte [$g{\cdot}cm^{-3}$]	1.282
Crastal system	Tetragonal
Space group	I4(1)/amd
Instrument	Siemens P4
Temperature [°K]	173(2)
Theta range for data collection	2.44 – 27.57
Abtastungsmodus	ω-Scan
Reflections Collected	10798
Independent reflections	1379 (R_{int} = 0.0886)
Structure's solution method	Direkte Methoden
Refinement method	Vollmatrix Least Squares on F^2
Number of the parameter	98
Solution and refinment programm	ShelXTL V5.1 NT
Final R indices [$I>2\sigma(I)$]	R1 = 0.0414, wR2 = 0.1119
R indices (all data)	R1 = 0.0489, wR2 = 0.1171
Largest diff. Peak and hole (e $Å^{-3}$)	0.469, -0.510

Tab. 51 $C_{28}H_{50}N_4O_{17}S_4$ (**43**): Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)		5605(1)	9771(1)	31(1)
N(3)	7849(2)	5000	10000	34(1)
O(1)	1415(1)	5529(1)	8528(1)	37(1)
O(2)	704(1)	5263(1)	7412(1)	41(1)
O(4)	10000	7500	6250	77(2)
C(1)	0	5436(2)	8697(1)	30(1)
C(2)	735(1)	5410(1)	8252(1)	32(1)
C(4)	0	4874(2)	7088(2)	44(1)
C(6)	0	5028(4)	6150(2)	75(1)
C(5)	0	3999(2)	7320(2)	57(1)
C(11)	9767(17)	7500	5451(10)	404(16)
C(12)	10000	7500	4731(5)	166(7)

Tab. 52: $C_{28}H_{50}N_4O_{17}S_4$ (**43**): Bond lengths [Å] and angles [°].

S(1)-C(1)	1.740(2)	C(1)-S(1)-S(1)#1	100.60(9)
S(1)-S(1)#1	2.1466(15)	C(2)-O(2)-C(4)	117.78(15)
O(1)-C(2)	1.231(2)	C(2)#5-C(1)-C(2)	119.6(2)
O(2)-C(2)	1.367(2)	C(2)-C(1)-S(1)	120.05(10)
O(2)-C(4)	1.436(2)	O(1)-C(2)-O(2)	114.63(14)
C(1)-C(2)	1.418(2)	O(1)-C(2)-C(1)	127.53(15)
C(4)-C(5)	1.504(5)	O(2)-C(2)-C(1)	117.80(15)
C(4)-C(6)	1.521(4)	O(2)#5-C(4)-O(2)	109.5(2)

O(2)-C(4)-C(5)	110.41(17)	C(5)-C(4)-C(6)	114.0(3
O(2)-C(4)-C(6)	106.2(2)		

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