cations. In the other compounds all the interlayers are occupied by cations but individual differences in their distributions lead to various symmetries.

We are indebted to Professor R. Nitsche for supplying the crystals and for helpful discussions. All numerical calculations were performed on the Univac-1106 of Rechenzentrum der Universität Freiburg.

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Stereochemistry of an Unusual Trialkyl Sulfonium Ion. The Crystal Structure of 2,3-Dimethyl-2-butenyl-1,1,2-trimethylpropyl-methylsulfonium 2,4,6-Trinitrobenzenesulfonate

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The nature and crystal structure of the product obtained from the reaction of methylsulfonium 2,4,6-trinitrobenzenesulfonate with two molecules of 2,3-dimethyl-2-butene has been determined by X-ray methods and the product was found to be the title trialkyl sulfonium salt. The triclinic ($P\bar{1}$) lattice parameters are $a=13{\cdot}128\pm0{\cdot}009$, $b=12{\cdot}100\pm0{\cdot}006$, $c=7{\cdot}992\pm0{\cdot}003$ Å, $\alpha=93{\cdot}94\pm0{\cdot}04^\circ$, $\beta=102{\cdot}00\pm0{\cdot}04^\circ$, and $\gamma=74{\cdot}95\pm0{\cdot}04^\circ$. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares calculations to an R value of 0·057 using 3504 observed reflections measured on a diffractometer. Knowledge of the structure of the trialkyl sulfonium ion has led to a suggested mechanism for its formation. The sulfonium ion is pyramidal and it is distorted from $3m$ symmetry. The C–S^+ bond distances are 1·799, 1·830 and 1·882 Å and increase with increasing bulkiness of the alkyl group on S^+. The *ortho* nitro groups of the trinitrobenzenesulfonate anion are twisted by 54 and 61° to the benzene plane while the *para* nitro group is twisted by only 2·5°. There are a number of intermolecular contacts shorter than 3·4 Å. The shortest contacts are between the trinitrobenzenesulfonate anions.

Introduction

In an attempt to synthesize another example of a stable episulfonium salt such as that obtained from the reaction of the olefin cyclooctene with methyl sulfenium trinitrobenzene sulfonate (Pettit & Helmkamp, 1963), the latter was reacted with excess 2,3-dimethyl-2-butene (Carbin & Helmkamp, 1970). Two molecules of 2,3-dimethyl-2-butene reacted to give a crystalline product whose structure resisted spectroscopic analysis (Carbin & Helmkamp, 1970). The present X-ray study has unequivocally established the structure of the product (I) and has also led to the proposal of a probable reaction mechanism for its formation. A paper on the details of the chemical work and a brief report on the X-ray structure have been published elsewhere (Carbin, Helmkamp, Barnes & Sundaralingam, 1972).

Experimental

Colorless crystals of (I) grown in nitromethane and ether were supplied by Carbin & Helmkamp. The crystal data are as follows: $C_{19}H_{29}N_3O_9S_2$, triclinic, $P\bar{1}$, $Z=2$; $a=13{\cdot}128\pm0{\cdot}009$, $b=12{\cdot}100\pm0{\cdot}006$, $c=7{\cdot}992\pm0{\cdot}003$ Å, $\alpha=93{\cdot}94\pm0{\cdot}04^\circ$, $\beta=102{\cdot}00\pm0{\cdot}04^\circ$, $\gamma=74{\cdot}95\pm0{\cdot}04^\circ$ (obtained by least-squares fit of eleven reflections measured on a diffractometer), $D_{\text{obs}}=1{\cdot}412$ g cm^{-3} (by flotation in CCl_4 and $C_2H_5P_2O$), $D_{\text{calc}}=1{\cdot}406$ g cm^{-3}. The crystal data are consistent with the presence of one formula unit of the complex, $(C_{13}H_{27}S)^+(C_6H_2N_3O_9S)^-$ in the asymmetric unit of the structure. The calculated linear absorption coefficient for Cu $K\alpha$ radiation is 24·2 cm^{-1}.

The crystal used for the data collection was a plate of approximate dimensions 0·25 × 0·05 × 0·7 mm. The intensities of 3990 independent reflections were measured on a Picker four-circle diffractometer using nickel-

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Table 1. *Observed and calculated structure factors*

The data are separated into groups having common k and l values. The three columns of each group list values of h, $10F_o$ and $10F_c$ in that order. An asterisk indicates a reflection less than $1\cdot5\sigma$, where σ is the standard deviation in the intensity.

Table 1 (*cont.*)

[illegible]

filtered copper radiation and a θ–2θ scan to a maximum 2θ of 128°. The scan width was 1·4° with background counts of 10 s on either side of the peak. 3504 reflections had an intensity (I) to standard deviation (σ) ratio of 1·5 and these were included in the final refinement. σ was derived from counting statistics (Stout & Jensen, 1968). After application of the usual Lorentz and polarization corrections, the overall scale factor and temperature factor were determined by Wilson's (1942) method. Absorption corrections were not considered warranted, as the major purpose of this investigation was to determine the chemical structure of the product in question.

Structure determination and refinement

The structure was determined by the heavy-atom technique. The positions of the two sulfur atoms were derived from a three-dimensional Patterson map. For economic reasons we initially used only the strongest 2697 reflections with an I/σ ratio greater than 15·5. Several successive difference Fourier syntheses provided the approximate positions for all of the nonhydrogen atoms. The conventional $R(=\sum||F_o|-|F_c||/\sum|F_o|)$ value at this stage for the 2697 reflections was 0·26 for all 33 nonhydrogen atoms included in the structure factor calculation. The nonhydrogen atoms of the structure were subjected to two cycles of isotropic least-squares refinement followed by two cycles of anisotropic refinement. The R value dropped to 0·05. The weighting scheme initially used was based on counting statistics. Each cycle of anisotropic refinement was carried out in two blocks, one for each ion of the structure. All the 29 hydrogen atoms were located by difference Fourier synthesis and were kept fixed with temperature factors of 4·0 Å^2 in the subsequent refinement of the nonhydrogen atoms. Two more cycles of anisotropic least-squares refinement were performed using all 3504 reflections greater than $1{\cdot}5\sigma$. As convergence had not been achieved an error curve ($|F_o-F_c|$ *versus* $|F_o|$) was plotted and the following weighting scheme was found suitable.

$$\frac{1}{\sqrt{w}}=4{\cdot}65 \text{ for } |F_{\text{obs}}|\le 57{\cdot}4,$$

$$\frac{1}{\sqrt{w}}=0{\cdot}084|F_{\text{obs}}|-0{\cdot}16 \text{ for } |F_{\text{obs}}|>57{\cdot}4\,.$$

Two final anisotropic cycles gave an R value of 0·057 for the 3504 reflections, and 0·062 for all 3990 measured

Table 2. *Atomic positional and thermal parameters*

Positional parameters of non-hydrogen atoms have been multiplied by 10^4 and those of hydrogen atoms, by 10^3. Anisotropic thermal parameters have been multiplied by 10^4. The anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$. Standard deviations refer to the least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−346 (2)	971 (2)	2495 (3)	59 (2)	58 (2)	85 (4)	−12 (2)	19 (2)	−1 (2)
C(2)	420 (2)	−76 (2)	2617 (3)	53 (2)	62 (2)	106 (4)	−11 (2)	14 (2)	0 (2)
C(3)	175 (2)	−1119 (2)	2499 (4)	63 (2)	58 (2)	125 (5)	−6 (2)	16 (2)	4 (3)
C(4)	−880 (2)	−1124 (2)	2268 (3)	70 (2)	59 (2)	104 (4)	−20 (2)	23 (2)	−8 (2)
C(5)	−1692 (2)	−137 (3)	2151 (4)	57 (2)	69 (2)	139 (5)	−20 (2)	23 (3)	−8 (3)
C(6)	−1396 (2)	886 (2)	2280 (4)	55 (2)	57 (2)	130 (5)	−6 (2)	25 (2)	−6 (3)
C(7)	−1526 (3)	−4747 (3)	4748 (5)	77 (3)	86 (3)	210 (7)	−13 (2)	54 (3)	−30 (4)
C(8)	−2926 (2)	−2718 (3)	5627 (4)	62 (2)	63 (2)	174 (6)	−17 (2)	27 (3)	9 (3)
C(9)	−4087 (3)	−2071 (3)	5475 (4)	62 (2)	66 (2)	203 (6)	−12 (2)	8 (3)	32 (3)
C(10)	−4802 (4)	−2234 (4)	3776 (6)	100 (3)	96 (3)	263 (9)	−16 (3)	−41 (4)	31 (4)
C(11)	−4439 (3)	−1372 (3)	6718 (5)	59 (2)	62 (2)	261 (8)	−5 (2)	34 (3)	29 (4)
C(12)	−5597 (3)	−744 (4)	6582 (7)	65 (3)	97 (4)	460 (14)	4 (2)	64 (5)	46 (6)
C(13)	−3744 (3)	−1125 (3)	8378 (5)	97 (3)	81 (3)	231 (8)	−10 (2)	41 (4)	−2 (4)
C(14)	−2557 (2)	−4839 (2)	7625 (4)	69 (2)	52 (2)	137 (5)	−15 (2)	7 (3)	4 (3)
C(15)	−2443 (3)	−6118 (3)	7291 (5)	95 (3)	53 (2)	213 (7)	−16 (2)	15 (4)	3 (3)
C(16)	−1535 (3)	−4606 (3)	8713 (5)	79 (3)	92 (3)	173 (6)	−24 (2)	−16 (3)	12 (3)
C(17)	−3564 (3)	−4238 (3)	8372 (4)	86 (3)	72 (3)	154 (6)	−21 (2)	43 (3)	4 (3)
C(18)	−4623 (3)	−4383 (4)	7305 (6)	75 (3)	121 (4)	273 (9)	−22 (3)	53 (4)	20 (5)
C(19)	−3430 (5)	−4621 (5)	10252 (5)	158 (5)	164 (5)	154 (7)	−49 (4)	60 (5)	15 (5)
N(1)	1576 (2)	−129 (2)	2947 (4)	55 (2)	80 (2)	179 (5)	−12 (2)	17 (2)	15 (3)
N(2)	−1164 (2)	−2233 (2)	2153 (3)	85 (2)	72 (2)	122 (4)	−32 (2)	22 (2)	−3 (2)
N(3)	−2294 (2)	1922 (2)	2269 (4)	62 (2)	68 (2)	241 (6)	−8 (2)	42 (3)	−11 (3)
O(1)	233 (2)	2727 (2)	4051 (3)	106 (2)	85 (2)	175 (4)	−38 (2)	31 (2)	−50 (2)
O(2)	−965 (2)	2983 (2)	1277 (4)	79 (2)	75 (2)	298 (6)	−16 (2)	−8 (3)	55 (3)
O(3)	893 (2)	1977 (2)	1473 (3)	79 (2)	81 (2)	154 (4)	−31 (1)	29 (2)	4 (2)
O(4)	2101 (2)	−720 (3)	1969 (4)	74 (2)	127 (3)	375 (8)	−23 (2)	85 (3)	−66 (4)
O(5)	1933 (2)	389 (2)	4201 (3)	68 (2)	125 (3)	168 (4)	−32 (2)	−16 (2)	11 (3)
O(6)	−2111 (2)	−2201 (2)	2012 (3)	91 (2)	98 (2)	220 (5)	−49 (2)	20 (3)	1 (3)
O(7)	−444 (2)	−3095 (2)	2202 (3)	109 (2)	55 (2)	198 (5)	−19 (2)	33 (3)	1 (2)
O(8)	−2264 (2)	2505 (2)	3572 (4)	106 (3)	96 (3)	336 (7)	−5 (2)	74 (3)	−77 (4)
O(9)	−3016 (2)	2078 (2)	1036 (4)	67 (2)	104 (3)	314 (7)	9 (2)	6 (3)	14 (3)
S(1)	−11 (1)	2312 (1)	2314 (1)	64 (1)	53 (1)	136 (1)	−18 (0)	11 (1)	0 (1)
S(2)	−2799 (1)	−4261 (1)	5411 (1)	55 (0)	61 (1)	127 (1)	−13 (0)	14 (1)	−3 (1)

Table 2 (*cont.*)

	x	y	z	β
H1(C18)	−522	−389	780	4·0
H2(C18)	−466	−410	611	4·0
H3(C18)	−461	−519	726	4·0
H4(C17)	−356	−465	941	4·0
H5(C19)	−268	−468	1087	4·0
H6(C19)	−395	−407	1084	4·0
H7(C19)	−358	−541	1019	4·0
H8(C16)	−133	−505	980	4·0
H9(C16)	−164	−377	899	4·0
H10(C16)	−93	−485	806	4·0
H11(C15)	−291	−622	615	4·0
H12(C15)	−167	−649	720	4·0
H13(C15)	−264	−646	821	4·0
H14(C7)	−99	−432	547	4·0
H15(C7)	−160	−457	353	4·0
H16(C7)	−123	−558	496	4·0
H17(C8)	−260	−246	474	4·0
H18(C8)	−250	−255	681	4·0
H19(C10)	−544	−155	350	4·0
H20(C10)	−506	−294	377	4·0
H21(C10)	−438	−232	280	4·0
H22(C12)	−600	−80	538	4·0
H23(C12)	−566	8	690	4·0
H24(C12)	−592	−108	739	4·0
H25(C13)	−393	−147	934	4·0
H26(C13)	−391	−26	859	4·0
H27(C13)	−298	−142	835	4·0
H28(C5)	−247	−12	198	4·0
H29(C3)	76	−183	258	4·0

reflections. The shift/σ ratios for the parameters were all less than one, the average being 0·17. The final standard deviation for an observation of unit weight was 0·78.

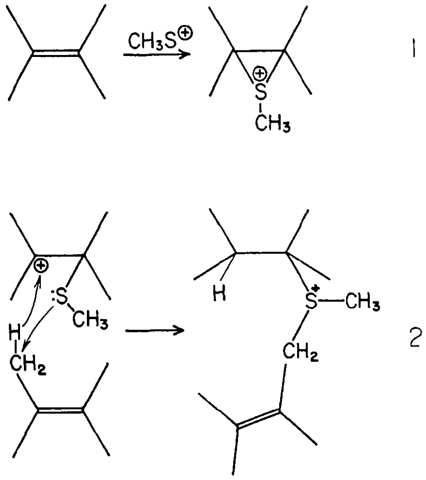
Table 1 lists the observed and calculated structure factors. Table 2 lists the positional coordinates and anisotropic temperature factors for the nonhydrogen atoms, and the positional coordinates for the hydrogen atoms. The standard deviations for these parameters have not been corrected to account for the two-part refinement.

Scattering factors used for C, N, O, and S were from Hoerni & Ibers (1954) and that for H was from Stewart, Davidson & Simpson (1965). The full-matrix least-squares refinement program used was that of Busing, Martin & Levy (1964), modified for the UNIVAC 1108 computer by Rao (1968).

Discussion of results

The determination of the structure of the final product has made it possible to suggest a reaction mechanism for its formation (scheme 1). In the initial step the episulphonium ion probably reacts with a molecule of

2,3-dimethyl-2-butene to form a three-membered sulphonium ion (1) which then undergoes further reaction with a second molecule of the olefin which involves a hydride shift to generate the cation 2,3-dimethyl-2-butenyl-1,1,2-trimethylpropyl-methyl sulfonium ion (2).



Molecular geometry and conformation of the cation

As expected the sulfonium ion exhibits a pyramidal geometry which is distorted from $3m$ symmetry in a way predictable from simple steric considerations. First the S–C bonds are found to increase (1·799, 1·830 and 1·882 Å) (Fig. 1) with increasing size of the alkyl group in the order methyl, butenyl, 1,1,2-trimethylpropyl. Secondly, the increase in the C–S–C angles (101·1, 105·1 and 107·5°) again follows the order of increasing steric interactions between the neighboring alkyl groups (butenyl, methyl > trimethylpropyl, methyl > trimethylpropyl, butenyl).

In the *S*-propyl group the C–C bond distances range from 1·519 to 1·564 Å. The significant increase of the C(14)–C(17) bond (1·550 ± 0·005 Å) from the normal paraffinic C–C bond distance (1·533 Å) is also expected from simple steric considerations. But, it is not apparent why the C(17)–C(19) bond is also significantly extended from the normal C–C distance. All of the C–C–

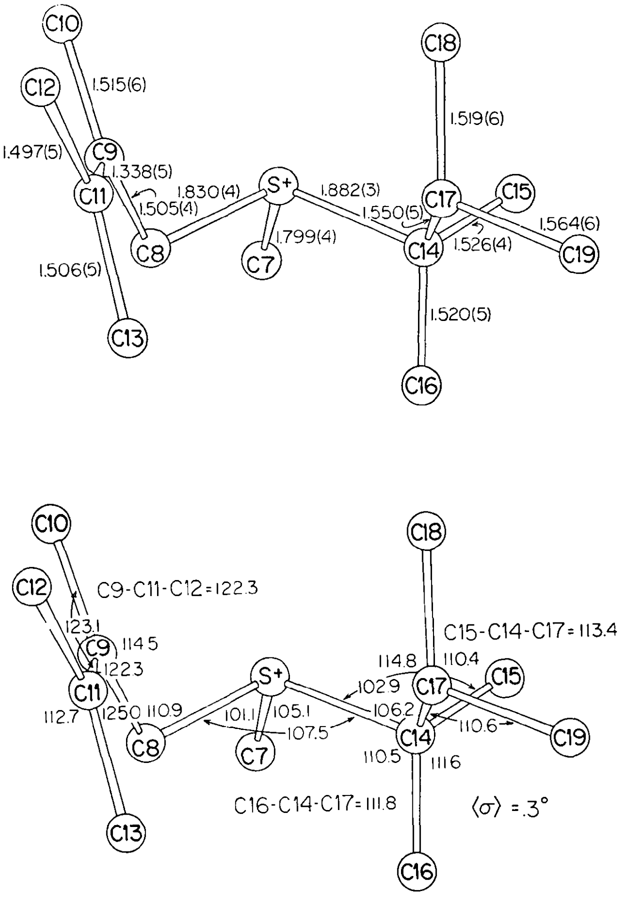


Fig. 1. Atom numbering, bond lengths, bond angles and molecular conformation of 2,3-dimethyl-2-butenyl-1,1,2-trimethylpropylmethyl sulfonium ion. The drawings were made with the *ORTEP* computer program (Johnson, 1965).

Table 3. *Selected torsion angles* (°)

The e.s.d.'s in torsion angles are about 0·4°.

Sulfonium cation			
C(12)–C(11)–C(9)–C(10)	−4·1	C(9)–C(8)—S^+——C(7)	157·0
C(12)–C(11)–C(9)–C(8)	+178·9	C(8)–S^+——C(14)–C(17)	−61·7
C(13)–C(11)–C(9)–C(10)	+175·8	C(8)–S^+——C(14)–C(16)	+59·7
C(13)–C(11)–C(9)–C(8)	−1·2	C(8)–S^+——C(14)–C(15)	178·9
C(11)–C(9)—C(8)–S^+	−121·6	S^+—C(14)–C(17)–C(19)	−177·8
C(9)—C(8)—S^+—C(14)	−93·1	S^+—C(14)–C(17)–C(18)	56·5
2,4,6-Trinitrobenzene sulfonate anion (TNBS)			
O(5)—N(1)—C(2)–C(1)	−54·3	O(7)–N(2)—C(4)—C(5)	−177·6
O(5)—N(1)—C(2)–C(3)	123·8	O(6)–N(2)—C(4)—C(3)	−177·27
O(4)—N(1)—C(2)–C(1)	+128·0	O(6)–N(2)—C(4)—C(5)	+2·1
O(4)—N(1)—C(2)–C(3)	−53·9	O(1)–S——C(1)—C(7)	+91·8
O(8)—N(3)—C(6)–C(1)	+61·3	O(1)–S——C(1)—C(6)	−97·6
O(8)—N(3)—C(6)–C(5)	−115·5	O(1)–S——C(1)—C(2)	−147·4
O(9)—N(3)—C(6)–C(1)	−123·2	O(2)–S——C(1)—C(6)	+23·1
O(9)—N(3)—C(6)–C(5)	+60·0	O(3)–S——C(1)—C(2)	−28·7
O(7)—N(2)—C(4)–C(3)	+2·9	O(3)–S——C(1)—C(6)	+141·9

C angles in the *S*-propyl group are significantly greater than the ideal tetrahedral value of 109°28′.

In the *S*-butenyl group the C–C 'single' bond distances agree with each other within the experimental errors. They range from 1·497 to 1·515 Å, with an average value of 1·506 Å. The angles facing the double bond range from 122·3 to 125·0° with an average value of 123·4°, while those opposite the double bond have an average value of 113·6°.

The atoms comprising the ethylenic system show slight but significant deviations from planarity (Fig. 3). Similar lack of planarity of ethylenic systems has also been observed previously (Sundaralingam, 1972). The sulfur atom deviates by 1·49 Å from the ethylene plane, torsion angle C(11)–C(9)–C(8)–S is 121·6°. Single bonds adjacent to double bonds typically show rotations of about 120° in a number of other hydrocarbon systems (Marteuscelli, 1969 and references therein; Craven & Cusatis, 1969; Sundaralingam, 1972).

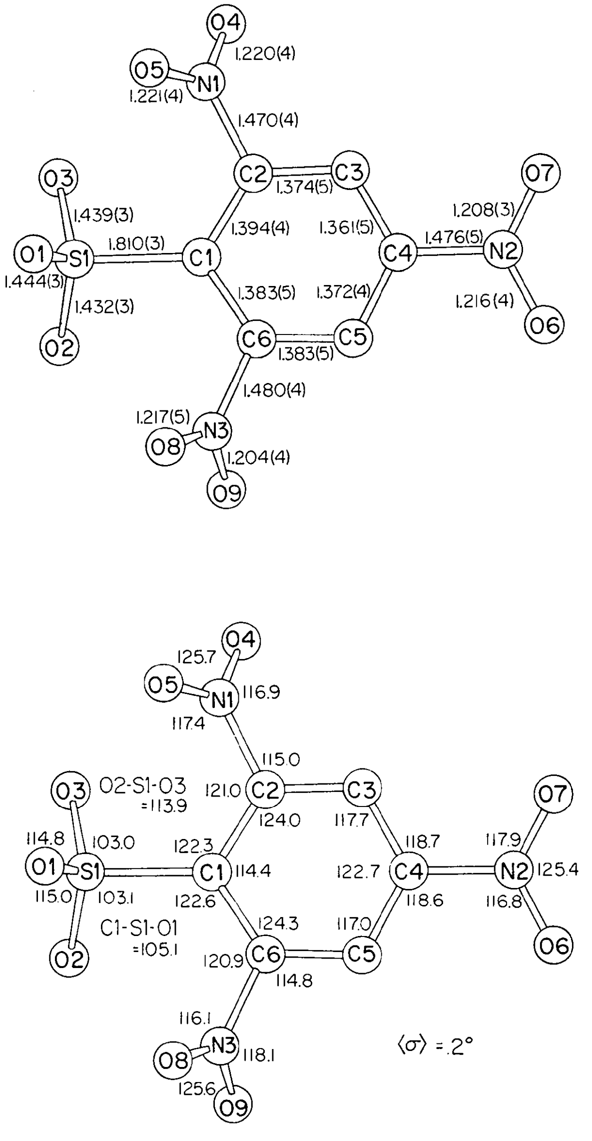


Fig. 2. Atom numbering, bond lengths, and bond angles of the 2,4,6-trinitrobenzene sulphonate anion.

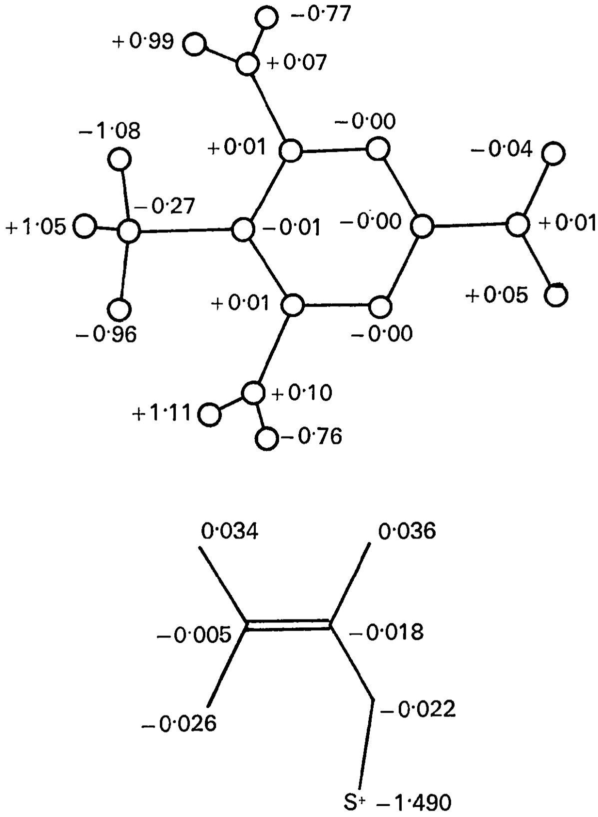


Fig. 3. Deviations (Å) of the atoms from the least-squares plane of the aromatic ring of the TNBS anion and from the least-squares plane of the ethylene group.

Molecular geometry and conformation of the TNBS anion

The structure of the trinitrobenzenesulfonate (TNBS) anion (Fig. 2) resembles closely that determined by Meyers & Trueblood (1969). However, the internal consistency of the bond distances of the aromatic ring appears to be much better in the present study. The average C–C bond distance is 1·380 Å, with extreme values of 1·361 and 1·394 ± 0·005 Å, the longer bonds are on the sulfonate side of the ring. This feature together with the observed trends in the internal ring angles are a manifestation of both the steric and electronic properties of the sulfonate and *ortho* nitro groups extensively discussed by Meyers & Trueblood (1969). In the sulphonate group the S–O bond distances are in excellent agreement with each other, their average value being 1·338 Å. The C–S–O angles are also close to each other and range from 103·0 to 105·1° (average 103·7°), while the O–S–O angles range from 113·9 to 115·0° (average 114·6°) and are considerably larger. The forced rotation of the *ortho* nitro groups by

54 and 61° (Table 3) out of the plane of the benzene ring was also found by Meyers & Trueblood (1969). The *para* nitro group is twisted only 2·5° out of the benzene plane compared with 11° found by the latter workers. This difference is attributable to the differences in the intermolecular packing in the two structures (see below).

The deviations of the atoms from the least-squares plane of the benzene ring are shown in Fig. 3. Despite the distortions from planarity of the substituents the benzene ring itself is planar. The sulfonate S atom shows the greatest displacement (0·27 Å) while the nitrogen atoms of the *ortho* nitro groups are displaced 0·07 and 0·10 Å on the opposite sides of it. In contrast the nitrogen atom of the *para* nitro group lies in the plane of the benzene ring. Apparently the amount of displacement of the nitrogen atoms from the benzene plane is related to the degree of twist of the nitro groups.

Crystal packing and interionic contacts

The negative charge on the trinitrobenzenesulfonate anion is expected to be more delocalized than the positive charge on the sulfonium ion which is certainly stabilized by induction from the three alkyl groups. The closest contact of 3·309 Å between the oppositely charged ions involves the methyl carbon atom C(7) of the sulfonium ion and the sulfonate oxygen atom O(1) (Fig. 4). Considerably shorter contacts are observed between the TNBS ions, the shortest being 2·963 Å, involving O(1) of the sulphonate and O(7) of the *para* nitro group of a symmetry-related ion. The latter contact is primarily responsible for keeping the *para* nitro groups close to the benzene plane. Adjacent benzene rings are held 3·95 to 4·01 Å apart by the sulphonate group and rotated *ortho* nitro groups. Intermolecular distances less than 3·4 Å are shown in Fig. 4.

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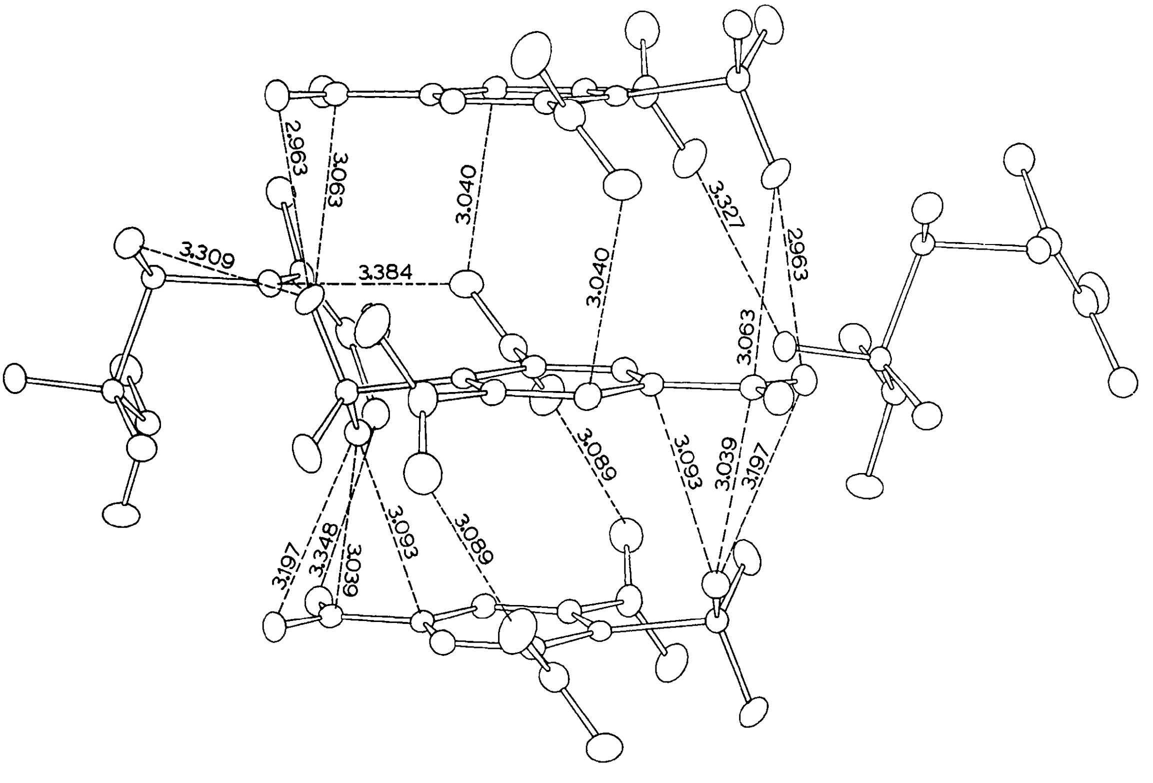

Fig. 4. A view along an arbitrary direction showing the arrangement of the ions and the intermolecular contacts less than 3·4 Å.

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The Crystal and Molecular Structure of Dimethyl *trans, trans*-2,5-Dichloromuconate

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The structure of dimethyl *trans,trans*-2,5-dichloromuconate, $C_8H_8O_4Cl_2$, was determined by single-crystal X-ray diffraction techniques. The unit cell is monoclinic, space group $P2_1/n$, with the following dimensions at 23 ± 2°C: $a = 3{\cdot}967\,(1)$, $b = 23{\cdot}339\,(5)$, $c = 5{\cdot}483\,(1)$ Å, $\beta = 95{\cdot}80\,(1)°$. There are two molecules in the unit cell; the molecules lie on centers of symmetry. The data were collected on an automated diffractometer. The structure was refined by full-matrix least-squares; the final value of the conventional R index is 0·041. The molecules lie in densely packed layers parallel to $(\bar{1}01)$. The carbonyl oxygen assumes the antiplanar conformation with respect to the β-carbon atom. Nonbonded intramolecular distances do not show a significant preference for one conformer over the other.

Introduction

The conformation of the carboxyl group, a representation of which is shown in Fig. 1, has been a subject of interest in a number of laboratories over the past few years. The preferred conformation at the carbon–carbon bond has been found to be the one which places the α, β carbon–carbon bond synplanar to the carbonyl (Leiserowitz & Schmidt, 1965). This preference is attributed by Leiserowitz and Schmidt to nonbonded interactions between the β-carbon and its hydrogen atoms, on the one hand, and the hydroxyl or carbonyl oxygen atoms, on the other. Chiefly due to the difference in carbon–carbon–carbonyl oxygen and -hydroxyl oxygen angles (characteristically about 122 and 114°, respectively), nonbonded β-carbon–oxygen and hydrogen–oxygen distances are 0·1 and 0·2 Å greater in the synplanar than in the antiplanar conformers.

This preference in conformation is amply confirmed for saturated acids, which are synplanar with only a few exceptions. However, the extension of this conformation to α,β-unsaturated acids on the basis of the same nonbonded interaction arguments is less satisfactory. Table 1 contains a list of α,β-unsaturated acids and esters whose structures are known, together with the respective conformations about the carboxyl carbon–carbon bond. Of the twenty-three crystallographically independent carboxyl groups represented in this table, nine are known to be antiplanar.

As Dunitz & Strickler (1968) point out, nonbonded interactions cannot be the sole factor determining conformations at the carbon–carbon bond in these compounds. They suggest that the bent-bond description of double bonds may be useful as a model of the interactions which produce the antiplanar conformation. If the carbonyl double bond is considered as two bent single bonds, then staggering about C–Cα in saturated acids leads to the synplanar conformation. However, in α,β-unsaturated acids, with two double bonds to be resolved into bent bonds, staggering about C–Cα gives the antiplanar conformation. In the latter case, the preference for the staggered conformation is in opposition to the steric factor and admits the possibility of antiplanar conformations.

While the bent-bond concept does rationalize the appearance of antiplanar conformations in unsaturated acids, it does not enable one to predict the conformations in such acids whose structures are not known.

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