

The Crystal and Molecular Structure of a Self-Complexing Molecule: 1-Phenyl-2-thiomethylethenyl 2, 4, 6-Trinitrobenzenesulfonate, (*E*)-

BY MICHELLE MEYERS AND KENNETH N. TRUEBLOOD

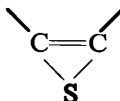
Department of Chemistry,* University of California, Los Angeles, California 90024, U.S.A.

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The title compound, $C_{15}H_{11}O_9N_3S_2$, was prepared by H. Cassey and G. Helmkamp and was originally believed (incorrectly) to be a thiirenium salt, containing an unsaturated three-membered ring that included a sulfur atom. It forms deep-red triclinic crystals belonging to space group *P*1, with $a_0 = 10.154$, $b_0 = 10.716$, $c_0 = 9.709$ Å, $\alpha = 118.33^\circ$, $\beta = 93.83^\circ$, and $\gamma = 99.05^\circ$. There are two formula units in the unit cell. The intensities of 3510 unique reflections were estimated from integrated equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least squares to $R = 0.105$. The most interesting structural features are: (1) the existence of what appears to be a weak charge-transfer or polarization-bonded complex involving the two symmetry-related molecules in the unit cell, with two identical and equivalent interactions per complex; and (2) considerable steric hindrance within the trinitrobenzenesulfonate group.

Introduction

The existence of thiirenes, which contain the grouping



(Carpino & McAdams, 1965; Paquette &

Wittenbrook, 1966), is of interest to theoretical chemists since these are the first compounds containing a three-membered heterocyclic ring with potential aromatic character. One of the products of the attempted synthesis (Cassey, 1967) of a thiirenium salt by the reaction of phenylacetylene with dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate was a deep-red crystalline material with empirical formula $C_{15}H_{11}O_9N_3S_2$ (I). Several possible structures were postulated, but the evidence was somewhat contradictory: nuclear magnetic resonance and conductivity data indicated that the compound was covalent in nature, but molecular-weight determinations by vapor-pressure osmometry with ethyl acetate and acetonitrile as solvents suggested that the compound was dissociated in solution and were thus more consistent with an ionic formulation. The present study was undertaken to establish unambiguously the structure of this compound. Although the molecule was found to be covalent and not to contain the thiirene ring system, the crystal structure is of interest because it contains a molecular complex formed from two identical molecules. Melloni, Modena & Scorrano (1967) have recently reported on the basis of spectroscopic and chemical evidence that similar reactions, such as the reactions of benzenesulfonyl trinitrobenzenesulfonates with tolanes, give rise to products with structures similar to that found for the present compound.

Experimental

Bright red parallelepipedal crystals of (I) were supplied by H. Cassey and G. Helmkamp. Oscillation and Weissenberg photographs showed no systematic extinctions or symmetry relations among intensities, other than Friedel's law, indicating that the unit cell was triclinic. Statistical analysis of the experimental intensity distribution (Howells, Phillips & Rogers, 1950) indicated that the space group was probably centrosymmetric and the structure was subsequently determined with the assumption that it was centrosymmetric. Initial cell axes were chosen, for convenience, in directions parallel to the crystal edges, but since one of the interaxial angles of this cell was acute, a more conventional cell was obtained by the Delaunay (1933) reduction. The direct-cell axes of these two unit cells are reversibly related by the transformation $(100/011/00\bar{1})$; we shall use capital letters (*H, K, L*) for indices relative to the initial unreduced cell and lower-case letters (*h, k, l*) for indices relative to the reduced cell. Precise cell dimensions were obtained by a least-squares refinement of 194 2θ measurements on *HOL*, *OKL*, and *HK0* Weissenberg photographs calibrated with superimposed quartz reflections; Cu $K\alpha$ radiation was used, with $\lambda = 1.5418$ Å and a_0 for quartz = 4.9131 Å. The unit-cell dimensions are

	Initial cell	Reduced cell
a_0	10.154 ± 0.002 Å	10.154 ± 0.002 Å
b_0	10.505 ± 0.003	10.716 ± 0.003
c_0	9.709 ± 0.002	9.709 ± 0.002
α	$116.11 \pm 0.02^\circ$	$118.33 \pm 0.02^\circ$
β	86.17 ± 0.03	93.83 ± 0.03
γ	102.83 ± 0.03	99.05 ± 0.02

*Contribution No. 2265.

Table 1. Observed and calculated structure factors

The columns are, respectively, h, |F_o|, and F_c. |F_o| values marked with U were below the minimum observable intensity; the |F_o| given is F_{min}/√3.

Table with multiple columns containing numerical data for structure factors. The table is organized into several vertical sections, each starting with a header like 'h, |F_o|, F_c' followed by rows of values. Some values are marked with 'U' or have a '3' as a multiplier. The data is presented in a grid-like format across the page.

The density of the crystals, determined by flotation in aqueous ZnI_2 , is 1.61 g. cm^{-3} ; that calculated for two molecules of $C_{15}H_{11}O_9N_3S_2$ per unit cell is 1.618 g. cm^{-3} , in good agreement with the experimental value.

Intensity data were collected on integrated equi-inclination Weissenberg photographs around the *B* and *C* axes of the unreduced cell, $K=0$ to 9 and $L=0$ to 2, using nickel-filtered $Cu K\alpha$ radiation. The intensities of 3510 unique reflections, about 85% of the Cu sphere, were estimated with a Baird-Atomic microdensitometer (model CB); of these, 2528 were above the minimum observable limit. Those too weak to be observed were assigned an intensity of $I_{\min}/3$ (Hamilton, 1955). The crystals used for collection of intensity data were small parallelepipeds; the dimensions of that mounted about **B** were 0.27 mm parallel to **B**, 0.21 mm along **C**, and 0.12 mm along **A**, while that mounted about **C** had dimensions 0.14 mm along **C**, 0.20 mm along **B** and 0.11 mm along **A**. Since the linear absorption coefficient of these crystals is 3.13 mm^{-1} , absorption errors were caused by the irregularity of the dimensions. However, the crystals were sufficiently small for the maximum such error to be only about 25 per cent in the relative values of the intensities and the average error was considerably smaller. No absorption corrections were made; consequently the apparent temperature factors found in this analysis cannot be deemed very significant. Lorentz, polarization, and Tunell corrections were applied and interlayer scale factors were refined by the method of Hamilton, Rollett, & Sparks (1965).

Structure determination and refinement

After an approximate scale factor and average temperature factor had been obtained by Wilson's (1942) method, the structure was solved by direct methods using a computer program, ACA (new) No. 2 (Long, 1965), based on the reiterative application of Sayre's (1952) equation. The signs of 331 normalized structure factors with magnitudes, $|E|$, greater than or equal to 1.5 were generated from a starting set which consisted of the seven reflections with the highest product of $|E|$ with the product-sum generated in Sayre's equation. Three of these signs were assigned arbitrarily to fix the origin, and all possible sign combinations were considered for the other four. An *E* map was computed with the set of signs having the second highest consistency index among the sixteen sets generated. (The completely consistent solution with all signs the same was rejected.) This *E* map displayed many recognizable features of the structure and successive Fourier syntheses resulted in an unambiguous and chemically reasonable solution (Meyers, 1968). It was realized at this point that the compound was not a thiirenum salt as originally believed, but rather a phenyl-thiomethyl-ethenyl sulfonate ester. However, attempts to refine the structure below an *R* value of about 0.30 resulted in divergence of observed and calculated structure factor values and oscillation of the values for the *y*-position

parameters. It was then discovered that the Lorentz-polarization-Tunell corrections had been incorrectly applied, so that there were large errors in the *E* values, averaging about 35 per cent. After the data had been properly corrected, and the scale factors for the different layers determined again as before, least-squares refinement progressed smoothly. The quick and unambiguous solution of the structure by Long's program is thus a tribute to the power of that direct method and that program.

In the early stages of refinement, the block-diagonal method was used; full-matrix techniques were employed in the last cycles. The program used was ACA (old) No. 317, modified (Gantzel, Sparks, & Trueblood, unpublished), which minimizes $\sum w(|F_o| - K|F_c|)^2$; the weights, *w*, were taken as inversely proportional to $\sigma^2(F_o)$, as estimated by the scaling program. The form factors used throughout this study were those of Hoerni & Ibers (1954) for C, N, and O, that of Dawson (1960) for S, and that of Stewart, Davidson & Simpson (1965) for H (bonded).

Plausible positions for the eleven hydrogen atoms were found from a difference map calculated near the end of the refinement. Attempts to refine these positions, with each hydrogen atom assigned an isotropic temperature factor which was not allowed to vary, led to unreasonable shifts in positions for five of the hydrogen atoms, presumably as a consequence of the absorption errors in the data alluded to above. The final *R* value for all observed data, calculated without these five erratic hydrogen atoms, was 0.105; that including the unobserved reflections as well was 0.131. The final observed and calculated structure factors are given in Table 1. The final shifts in position of the non-hydrogen atoms were all less than 0.7 estimated standard deviation in the final cycle; the average final shift was 0.2 e.s.d. The final positional parameters, and their e.s.d.'s, are listed in Table 2; the values shown in parentheses for the five hydrogen atoms were estimated from the difference map. Final thermal parameters and their e.s.d.'s are given in Table 3, but it must be emphasized again that there are doubtless systematic errors in these values because no absorption corrections were made. Consequently, no serious attempt at analysis of possible thermal motion of segments of this molecule in the crystal can be made from the present data. Rigid-body calculations (Shoemaker & Trueblood, 1968) for different portions of the molecule did indicate that the librational motions were not large, and consequently that the librational corrections to the C-C, C-S, and C-N bond distances would be small, averaging less than half the e.s.d. of these bonds, but no detailed discussion of the results is warranted. Corrections to the N-O bond lengths were estimated by the method of Busing & Levy (1964), assuming riding motion of the oxygen atoms relative to the nitrogen atoms. The average correction was 0.026 Å, which raises the average N-O bond length from 1.205 to 1.23 Å. Comparison of the root mean square displace-

ments of the oxygen atoms and nitrogen atoms normal to the plane of the nitro groups suggests that these nitro groups, like those in other nitroaromatic compounds, are undergoing significant torsional oscillation. The calculated r.m.s. librational amplitudes are 13° , 13° , and 11° for the nitro groups bound to C(2), C(4), and C(6) respectively (Fig. 1). The calculation was made in the same way as in the studies of 4-nitroaniline (Trueblood, Goldish & Donohue, 1961), where the amplitude was 13° , 3-nitroperchlorylbenzene (Palenik, Donohue, & Trueblood, 1968), with an amplitude of 14° , and 2-(2', 4'-dinitrobenzyl)pyridine (Seff & Trueblood, 1968), with an average amplitude of 9° .

Table 2. Final position parameters and their estimated standard deviations*

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$
C(1)	2983, 5	668, 5	267, 6
C(2)	3429, 5	2221, 5	1354, 6
C(3)	4182, 5	2782, 5	2801, 7
C(4)	4462, 5	1841, 5	3309, 7
C(5)	4039, 5	361, 5	2403, 6
C(6)	3303, 5	-169, 5	927, 6
S(7)	2299, 1	-35, 1	-1742, 2
O(8)	776, 3	-175, 4	-1567, 4
C(9)	-218, 5	-236, 5	-2754, 6
C(10)	-355, 5	1030, 6	-2547, 6
S(11)	-1557, 1	1426, 1	-3555, 2
C(12)	-1168, 8	3380, 7	-2398, 11
N(13)	3115, 5	3259, 5	854, 6
N(14)	5272, 4	2439, 4	4882, 6
N(15)	2828, 5	-1769, 4	36, 6
O(16)	2733, 4	1044, 4	-2170, 5
O(17)	2613, 4	-1414, 4	-2607, 5
O(18)	1940, 5	3254, 4	609, 6
O(19)	4028, 5	4083, 4	825, 6
O(20)	5798, 5	3721, 4	5571, 6
O(21)	5353, 5	1647, 4	5413, 5
O(22)	1623, 4	-2258, 4	-486, 5
O(23)	3689, 5	-2472, 4	-126, 7
C(24)	-933, 5	-1742, 6	-3922, 7
C(25)	-817, 6	-2896, 6	-3698, 8
C(26)	-1492, 7	-4309, 6	-4823, 9
C(27)	-2316, 7	-4563, 7	-6140, 9
C(28)	-2483, 7	-3433, 8	-6371, 9
C(29)	-1756, 6	-1984, 6	-5271, 7
H(5)	407, 5	-22, 5	293, 7
H(10)	27, 6	198, 6	-190, 7
H(12)	-134, 6	372, 6	-120, 8
H(12')	-27, 6	409, 6	-205, 8
H(25)	-24, 5	-278, 5	-303, 7
H(26)	-128, 6	-515, 6	-481, 8
H(3)	(0.46)	(0.39)	(0.32)
H(12'')	(-0.15)	(0.25)	(-0.24)
H(27)	(-0.26)	(-0.57)	(-0.74)
H(28)	(-0.19)	(-0.30)	(-0.64)
H(29)	(-0.24)	(-0.25)	(-0.53)

* Values given are $\times 10^4$ for C, N, O and S, and $\times 10^3$ for H. See Fig. 1 for the identities of the atoms. The values for the last five H atoms are taken from a difference map (see text) and are $\times 10^0$.

Molecular structure

The bond distances and angles are shown in Figs. 1 and 2, and the parameters of and deviations from least-

squares planes through various portions of the molecule are given in Table 4. The normals to the two aromatic rings deviate from one another by only about 7° ; all of the illustrations represent views of the molecule or the structure down the approximate average of these two normals. The molecular dimensions do not include corrections for thermal motion, but as indicated earlier, these would probably be significant only for the N-O bonds. The inverses of the diagonal elements of the matrix of the normal equations were used for estimating the standard deviations of the positions. The resulting e.s.d.'s of the bond distances vary from about 0.005 \AA for the S-O bonds to about 0.010 \AA for the C-C bonds; the e.s.d.'s of the bond angles vary from about 0.2° for O-S-O angles to about 0.6° for C-C-C and about 4° for C-C-H. However, the internal consistency of the distances within the aromatic rings is poor; although the average value is 1.39 \AA , it seems most unlikely that the extremes ($1.35, 1.44, 1.46 \text{ \AA}$) are as accurate as the above-mentioned random-error estimates imply. Those estimates are doubtless low, in part because the inverse matrix was not used (although the error from this cause is usually small) and also in part perhaps because of the absorption errors or other systematic errors; we did not feel it worthwhile to attempt to collect better data, but because of this internal evidence that the accuracy of the analysis is lower than the apparent precision by perhaps a factor of two or three, we also do not feel that extended discussion of minor variations in the geometry is warranted.

Except for the aforementioned fluctuations in the C-C distances in the aromatic ring, the bond distances and angles in the trinitrobenzenesulfonate portion of the molecule conform well with the values found in related compounds (*e.g.* Hanson, 1965, 1966; Cady, 1967; Gramaccioli, Destro & Simonetta, 1968; Seff & Trueblood, 1968). The endocyclic bond angles within the aromatic ring vary from 120° in the usual way, with the average angle at the nitro-substituted carbon atoms 124° and that at the other three carbon atoms 116° , in good agreement with the averages of 123 and 117° respectively, in a number of other nitroaromatics (Carter, McPhail & Sim, 1966; Palenik, Donohue & Trueblood, 1968). Carter *et al.* attribute this phenomenon to small changes in the hybridization at carbon atoms bonded to electron-withdrawing substituents, with increased *s*-character in the ring bonds.

The trinitrobenzenesulfonate group falls into the class of overcrowded compounds, recently reviewed by Avoyan, Struchkov & Dashevskii (1966). Although the aromatic ring itself is planar, the attached nitrogen atoms and (especially) the sulfur atom are displaced significantly from the plane (Table 4, Fig. 3). In addition, the *ortho* nitro groups are twisted about 53 and 61° out of the plane, in opposite directions (Fig. 2), while the *para* nitro group is twisted far less, only 11° , from the plane. (These angles actually represent the angles between the plane of the ring and the

planes of the different CNO₂ groups, and differ slightly from the angles of rotation about the C–N bonds because of the displacements of the nitrogen atoms from the ring plane.) The opposing out-of-plane displacements of the sulfonate sulfur atom and the *ortho* nitrogen atoms, and the rotations of the *ortho* nitro groups, seem quite clearly to result from intramolecular overcrowding. Some of the shortest variable contact distances between the sulfonate group and the adjacent nitro groups are illustrated in Fig. 3. These distances are for the most part slightly less than or equal to the sum of the van der Waals radii of the atoms involved, and would be appreciably smaller still were it not for the distortions from planarity mentioned above. One other apparent manifestation of the intramolecular overcrowding is the inequality of the two C–C–N angles at each of the *ortho* nitro groups; the C–N bonds are bent 2–3° away from the sulfonate group. The magnitude of nitro-group rotations in overcrowded aromatic compounds can be predicted (*e.g.* Dashevskii, Struchkov & Akopyan, 1966), at least in the absence of intramolecular hydrogen bonding or other strong non-bon-

ded attractions. The energy necessary to effect small rotations, *e.g.* that of the *para* nitro group in the present molecule, is less than about 0.4 kcal.mole⁻¹ (Dashevskii *et al.*, 1966) and thus small rotations can readily result from the influence of intermolecular packing forces.

The bond distances and angles within the sulfonate group itself generally agree well with those in other aromatic sulfonates, sulfonamides, and related species (Camerman & Trotter, 1965; MacDonald & Trotter, 1965; O'Connell & Maslen, 1967; Alléaume & Decap, 1965; Camerman, Camerman, & Trotter, 1965; Hall & Maslen, 1965; Sutherland & Young, 1963; Brown & Corbridge, 1966). The only significant exception is the O–S–C angle involving the esterified oxygen atom, O(8); the present value, 98°, is appreciably smaller than those reported for other sulfonate esters (102–109°). However, variability in angles in sulfonates and related species is not uncommon, presumably involving variations in both hybridization and intramolecular non-bonded repulsions, with the latter effect (Bartell, 1962) significant in so overcrowded a molecule.

Table 3. *Thermal vibration parameters and their estimated standard deviations**

	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
C(1)	66, 4	85, 4	81, 6	52, 7	2, 9	47, 7
C(2)	88, 5	85, 5	50, 5	28, 8	-43, 9	27, 7
C(3)	95, 5	70, 5	88, 7	34, 8	-27, 10	29, 8
C(4)	75, 4	93, 5	99, 6	31, 8	-47, 10	68, 8
C(5)	72, 4	94, 4	122, 6	18, 7	-33, 9	116, 7
C(6)	79, 4	76, 4	71, 6	31, 7	-17, 9	44, 7
S(7)	67, 1	100, 1	63, 1	40, 2	-10, 2	57, 2
O(8)	71, 3	118, 4	82, 4	59, 6	11, 7	85, 6
C(9)	62, 4	108, 5	90, 6	37, 7	5, 9	82, 8
C(10)	89, 5	125, 5	106, 6	47, 8	10, 10	139, 7
S(11)	91, 1	132, 1	162, 2	57, 2	-24, 3	173, 2
C(12)	150, 8	127, 7	275, 14	88, 12	51, 20	176, 14
N(13)	140, 6	74, 4	76, 6	52, 8	1, 10	29, 7
N(14)	88, 4	82, 4	68, 6	39, 7	-24, 9	3, 8
N(15)	113, 5	76, 4	92, 6	32, 8	-42, 10	27, 8
O(16)	86, 4	148, 4	125, 5	11, 7	-2, 8	136, 7
O(17)	110, 4	115, 4	76, 5	93, 7	69, 8	14, 8
O(18)	139, 5	151, 4	210, 7	121, 7	-18, 10	198, 7
O(19)	187, 7	131, 4	239, 8	54, 9	57, 13	220, 8
O(20)	137, 5	110, 5	149, 7	6, 8	-120, 11	52, 9
O(21)	152, 5	132, 4	130, 5	28, 8	-110, 9	122, 7
O(22)	117, 5	94, 4	96, 6	-6, 8	-15, 9	18, 8
O(23)	167, 6	104, 4	244, 10	95, 8	-104, 13	77, 10
C(24)	65, 4	116, 5	119, 7	25, 8	-16, 10	104, 9
C(25)	97, 6	120, 6	156, 8	7, 10	-21, 13	134, 10
C(26)	130, 7	98, 6	222, 11	51, 11	0, 16	137, 11
C(27)	125, 7	134, 8	158, 11	19, 13	21, 17	77, 15
C(28)	123, 8	183, 10	127, 9	-54, 15	-15, 16	100, 15
C(29)	100, 6	129, 6	83, 7	33, 10	-20, 12	69, 10
<i>B</i>						
H(5)	3.8 Å ²					
H(10)	4.5					
H(12)	5.5					
H(12')	5.5					
H(25)	4.2					
H(26)	5.5					

* Carbon, nitrogen, oxygen and sulfur temperature factor = $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. Values given are $\times 10^4$ for C, N, O and S. The values for the hydrogen atoms were assigned by adding 1.0 Å² to the approximate isotropic *B* of the atom to which they are attached; they were not refined. See Fig. 1 for the identities of the atoms.

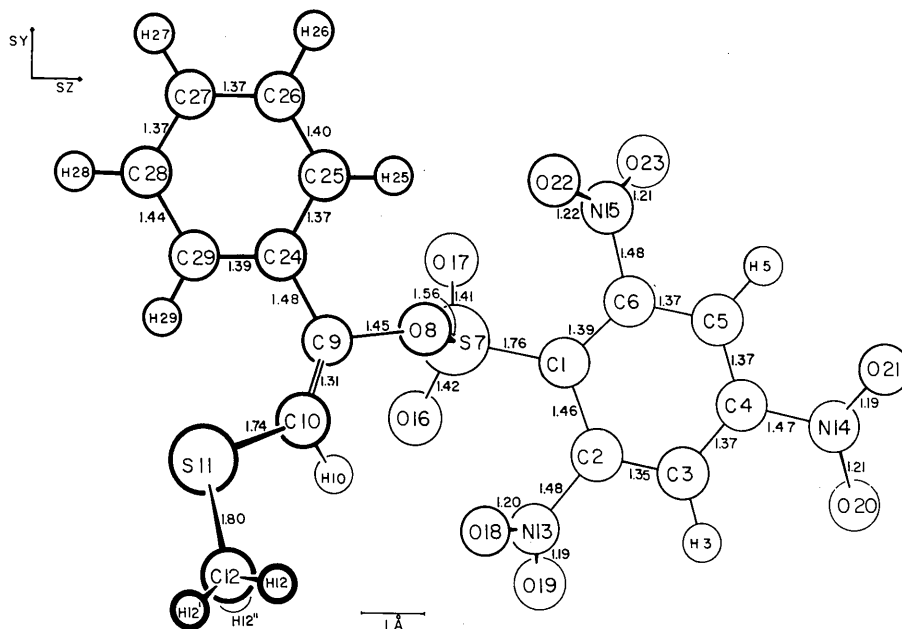


Fig. 1. Bond distances. The molecule is viewed along the approximate average of the normals to the least-squares planes of the aromatic rings. An orthogonal axial system was used, with SX measured along the average normal and SY, SZ perpendicular to it. The relationship of the fractional coordinates (x, y, z) to (SX, SY, SZ) , which are measured in Å, is

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -0.082 & -0.020 & 0.055 \\ 0.009 & -0.107 & 0.017 \\ 0.053 & -0.039 & 0.099 \end{pmatrix} \begin{pmatrix} SX \\ SY \\ SZ \end{pmatrix}.$$

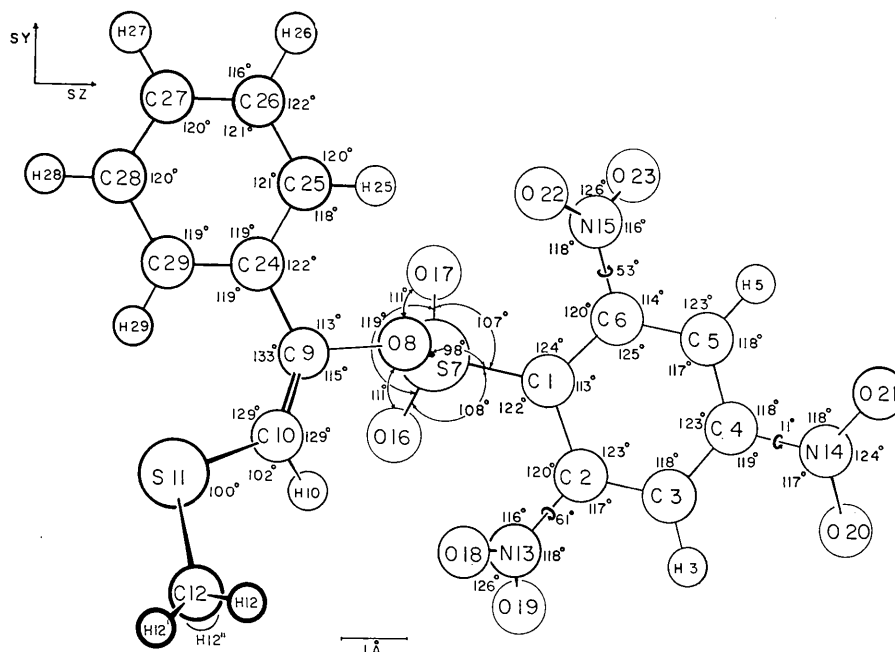


Fig. 2. Bond angles and angles of twist of the nitro groups. See Fig. 1 for definition of SY and SZ .

Table 4. *Some least-squares planes**

	I	II	III	IV	V	VI
$l_1 \times 10^4$	-9069	-1753	-9078	-2132	-8563	-7354
$l_2 \times 10^4$	-1713	2197	0129	-4830	-1330	-3206
$l_3 \times 10^4$	3849	9597	4193	8493	4991	5971
D (Å)	-1.749	-10.713	-3.266	-5.108	-4.123	-3.196
Deviations of atoms from plane (Å × 10 ²)						
C(1)	-2					
C(2)	3	1				
C(3)	-1					
C(4)	0		0			
C(5)	0					
C(6)	1			0		
S(7)	-31					
O(8)						5
C(9)					1	-3
C(10)						-6
S(11)						4
C(12)						15
N(13)	5	-2				
N(14)	-4		-1			
N(15)	8			1		
O(18)	102	1				
O(19)	-82	1				
O(20)	-24		0			
O(21)	16		0			
O(22)	96			0		
O(23)	-77			0		
C(24)					0	0
C(25)					2	
C(26)					-1	
C(27)					-1	
C(28)					2	
C(29)					-1	

* Bold-face deviations denote atoms used to define the plane. l_1, l_2, l_3 are direction cosines relative to an orthogonal set of axes parallel to $\mathbf{a}, \mathbf{c}^* \times \mathbf{a}$, and \mathbf{c}^* ; if the coordinates, in Å, in this system are X, Y , and Z , the equation of the plane is $l_1X + l_2Y + l_3Z + D = 0$. See Fig. 1 for identities of atoms.

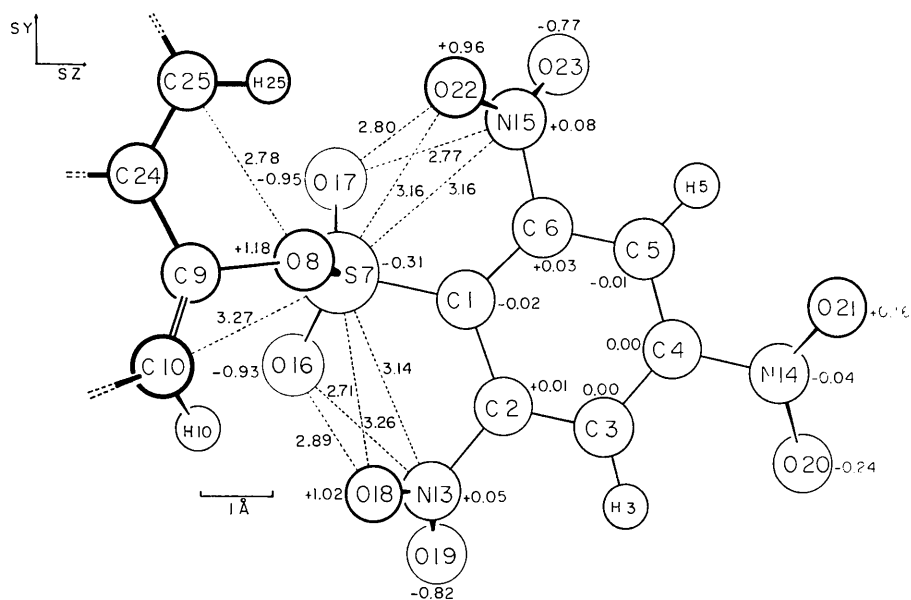


Fig. 3. Overcrowding in the trinitrobenzenesulfonate group: some short intramolecular non-bonded distances and deviations from the C(1)-C(6) ring plane.

The phenyl-thiomethylethenyl part of the molecule consists of two nearly planar groups (planes V and VI of Table 4), which are at 14° to one another. The methyl carbon atom, C(12), is only 0.15 \AA out of the plane of the ethenyl group and its immediately attached atoms, which comprise plane VI. Some of the deviations from planarity within plane VI, and the rotation of the phenyl group relative to the ethenyl group, seem attributable to a very short contact between H(29) and S(11). The estimated position of H(29) leads to a value of 2.4 \AA for this distance, and while this position is not reliable, it seems unlikely to be in error by as much as 0.5 \AA (it corresponds to reasonable C–C–H bond angles and a C–H distance of 1.08 \AA); thus this non-bonded S...H contact seems genuinely short, the sum of the van der Waals radii being about 2.9 \AA . The effect of this contact is manifested also in the unusually large C(24)–C(9)–C(10) and C(9)–C(10)–S(11) bond angles, which are enlarged by an average of about 6° from the value of around 125° which might be reasonable for them.

The bond angles and average bond distance (1.39 \AA) within the phenyl group are normal; the variations in the individual C–C distances in the ring seem explicable

only as statistical fluctuations, as mentioned earlier. The S(11)–methyl distance is also normal, as is the distance between the ethenyl and phenyl groups. The C(9)–C(10) formal double bond is short, about equal in length to the bond in allenes (Sutton, 1965), but the significance of this observation is nil. The C(10)–S(11) distance is also somewhat short, only about 0.03 \AA longer than the 1.71 \AA characteristic of typical carbon–sulfur double bonds (Sutton, 1965) and equal to that between the sulfur atom and the trigonal carbon atom in *S*-methylisothiourea sulfate (Stam, 1962); the latter bond presumably has, by resonance, some double-bond character. The bond distances in the phenylthiomethylethenyl system are, in general, consistent with the possibility that the electron density is extended over the entire phenyl-thioethenyl system. However, it was concluded by Degani, Mangini, Trombetti & Zauli (1967), on the basis of theoretical considerations and spectroscopic evidence, that sulfur vacant-orbital participation in π -bonding is uncommon, particularly in simple sulfides with resonance structures involving a negative charge on sulfur. They also point out that coplanarity is no criterion for testing valence-shell expansion, since appropriate orbitals exist for coupling

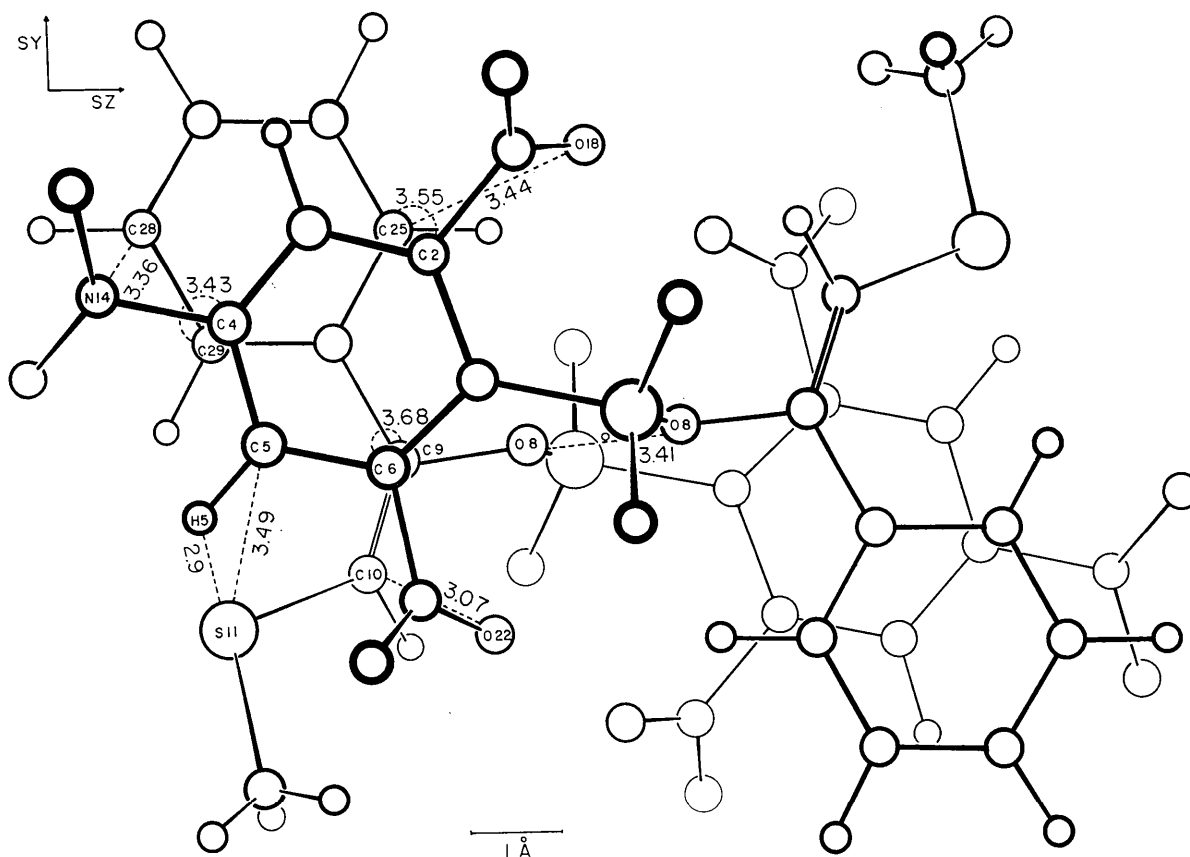


Fig. 4. The two symmetry-related molecules in the unit cell, viewed in the same direction as in Fig. 1. The shortest non-bonded intermolecular distances are shown. The center of symmetry is depicted as a small circle.

of sulfur with a π -system at any angle of twist. It is possible that the proximity to S(11) of the electronegative trinitrobenzene ring in the adjacent molecule (Fig. 4) results in polarization of the sulfur atom, increasing the likelihood of sulfur vacant-orbital participation. It is, moreover, reasonable to assume that the π -electrons associated with atoms C(24)–C(29), C(9) and C(10) are delocalized. The possibility that this portion of the PTME-TNBS molecule can function as an electron donor seems significant in the light of the molecular packing.

Intermolecular interactions

The present molecule is unusual in that it contains both an electron-accepting system (the trinitrobenzene group) and a possible electron-donating system (the phenyl-thiomethylethenyl residue). Consequently, the possibility exists for formation of a molecular complex between two identical molecules, with two equivalent interactions related by the crystallographic center of symmetry (Fig. 4). Molecular complexes, and in particular complexes involving trinitrobenzene as an electron-acceptor, have been extensively studied (Hanson, 1964, 1965, 1966; Brown, Wallwork & Wilson, 1964; Williams & Wallwork, 1966; Carter, McPhail & Sim, 1966; Prout & Wright, 1968). Wallwork (1961) divides molecular complexes into two categories: charge-transfer complexes, which involve overlapping of molecular orbitals, and polarization-bonded complexes, which

involve interactions between polar groups on one component and a polarizable second component. The nature of the interaction between the two molecules of PTME-TNBS in the unit cell could conceivably consist of either or both types of interaction. The non-bonded contact of the electron-poor atom C(5) with the polarizable S(11) could be indicative of a polarization-bonded type of interaction. (This distance is 3.49 Å (Fig. 4); the sum of the van der Waals radii is about 3.6 Å.)

The mutual dispositions of the two molecules of PTME-TNBS in the unit cell are depicted in Fig. 4. The substituted carbon atoms, C(2), C(4) and C(6), of the trinitrobenzene group nearly overlap C(25), C(29) and C(9) of the phenyl-thiomethylethenyl group. In all known complexes of *s*-trinitrobenzene, it is the non-substituted carbon atoms of *sym*-trinitrobenzene which are eclipsed by atoms of the donor component (Prout & Wright, 1968). However, according to Prout & Wright, the relative orientations of donor and acceptor molecules in a complex are determined by a combination of charge transfer interactions, dipole-induced dipole interactions, crystal packing requirements and dispersion forces. The relative importance of these interactions in determining the relative orientations of donor and acceptor molecules depends on the nature of the molecules involved.

Some of the shortest intermolecular distances are indicated in Fig. 4; as indicated earlier, the normals to

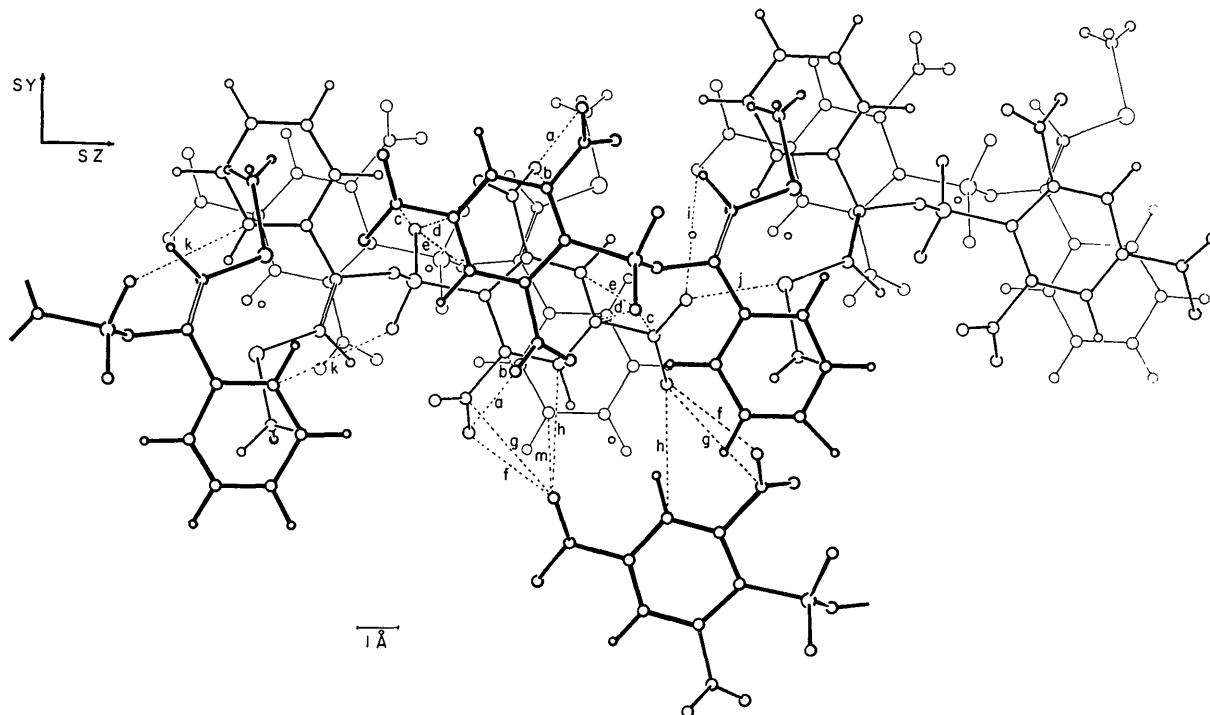


Fig. 5. The packing of molecules in the crystal. The direction of viewing is the same as in Fig. 1; centers of symmetry are depicted as small circles. All intermolecular interatomic distances smaller than 3.40 Å are shown; see Table 5. Symmetry-equivalent distances are denoted by the same small letter.

the two aromatic rings make an angle of 7° to one another. The average perpendicular separation of donor and acceptor components in the region of overlap is about 3.55 Å. In the related complexes mentioned above, the average perpendicular separation between donor and acceptor ranged from 3.2 to 3.35 Å. However, there seems to be little correlation between the shortness of the interplanar spacing and the importance of the charge-transfer contribution to the intermolecular bonding; rather, short interplanar spacings are associated with molecules in which dispersion forces assume the greatest importance (Prout & Wright, 1968). In the intensely red 1:2 complex of picrylazide with bis-8-hydroxyquinolino-Cu(II) (Bailey & Prout 1965), the average perpendicular separation is 3.45 Å. The molecules in the picrylazide complex, like those in the present crystals, are oriented favorably for good π -overlap. A charge-transfer band at $19,600\text{ cm}^{-1}$, polarized in a direction perpendicular to the molecular planes, was observed in the spectrum of the picrylazide complex (Bailey & Prout, 1965), confirming the suggested charge-transfer nature of the interaction. The spectrum of an $8 \times 10^{-4}\text{ M}$ solution of the present molecule in chloroform contains a peak at about $22,000\text{ cm}^{-1}$ which might be attributable to a charge transfer interaction, but further experiments are needed to demonstrate the significance of this observation. Such experiments, by Dr Joel Bernstein, are now in progress.

The molecular packing in the crystal is illustrated in Fig. 5. The shortest non-bonded intermolecular distances are listed in Table 5, together with the relationship between the molecules involved. There are no non-bonded distances as short as the sum of the usual van der Waals radii.

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Table 5. Intermolecular interatomic distances less than 3.40 Å

Symbol in Fig. 5	First atom*	Second atom*	Translations of second atom†	Distance
a	O(23), 1	O(19), 2	1, 0, 0	3.03 Å
b	O(23), 1	C(2), 2	1, 0, 0	3.25
c	O(17), 1	N(14), 2	1, 0, 0	3.13
d	O(17), 1	C(4), 2	1, 0, 0	3.15
e	O(17), 1	C(5), 2	1, 0, 0	3.37
f	O(20), 1	O(19), 2	1, 1, 1	3.13
g	O(20), 1	N(13), 2	1, 1, 1	3.38
h	O(20), 1	C(3), 2	1, 1, 1	3.30
i	O(21), 1	O(21), 2	1, 0, 1	3.17
j	O(21), 1	S(11), 1	1, 0, 1	3.31
k	C(29), 1	O(16), 2	0, 0, 1	3.25
m	C(26), 2	O(20), 2	1, 1, 1	3.36

* 1 indicates the atom is in the molecule at (x, y, z) of Table 2 or one translationally related to it; 2 denotes an atom in the molecule at $(-x, -y, -z)$ or one translationally related to it.

† Parallel to a, b, c respectively.

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Crystal Structure of *N*-Methyl-DL-leucylglycine Hydrobromide*

BY R. CHANDRASEKARAN† AND E. SUBRAMANIAN‡

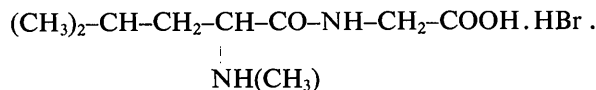
Centre of Advanced Study in Biophysics, University of Madras, Madras-25, India

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Crystals of *N*-methyl-DL-leucylglycine hydrobromide are orthorhombic, space group *Pbca*, with $a = 17.21$, $b = 17.80$ and $c = 8.41$ Å, $Z = 8$. The structure has been determined by the heavy atom method using three-dimensional photographic data collected with Cu $K\alpha$ radiation. All the hydrogen atoms in the molecule have been located from a difference-Fourier synthesis. The structure has been refined by full-matrix least-squares methods to a final R index of 0.103. The molecules in the crystal are stabilized by a network of hydrogen bonds. While the amino group is protonated, the carboxyl group appears to be in the non-ionized form. Surprisingly, the carbonyl oxygen atom in this group does not participate in hydrogen bonding even as an acceptor. The conformational features of the molecule are discussed.

Introduction

As part of a major work on the study of amino acids and simple peptides in this laboratory, an X-ray crystal structure analysis of the dipeptide *N*-methyl-DL-leucylglycine hydrobromide was carried out. The chemical formula of the compound is



Experimental

Crystals of the compound suitable for X-ray analysis were obtained by evaporating a solution of *N*-methyl-DL-leucylglycine in 30% hydrobromic acid at room temperature. Preliminary photographs taken with

Cu $K\alpha$ radiation established the crystallographic data summarized below:

Molecular formula: $\text{C}_9\text{H}_{18}\text{N}_2\text{O}_3 \cdot \text{HBr}$; M.W. = 283.

Orthorhombic; $a = 17.21$, $b = 17.80$, $c = 8.41$ Å.

Systematic absences: $0kl$, k odd,

$h0l$, l odd,

$hk0$, h odd.

Space group: *Pbca*.

$U = 2576.3$ Å³,

$D_o = 1.47$ g.cm⁻³ (floatation in a mixture of benzene and bromoform),

$D_c = 1.472$ g.cm⁻³,

$Z = 8$.

Absorption coefficient for X-rays, $\mu(\text{Cu } K\alpha) = 46$ cm⁻¹.

A thin crystal elongated along c , and sealed in a Lindemann capillary tube, was used to collect photographic intensity data for hkl , $l = 0-6$. These intensities were recorded using Cu $K\alpha$ radiation and multiple-film equi-inclination Weissenberg techniques. Photographs about the a or b axis could not be taken since the crystals crushed on cutting.

Of the 2152 reflexions which were accessible in the various layers, only 1582 reflexions were of measurable

* Contribution No. 276 from the Centre of Advanced Study in Biophysics, University of Madras, Madras-25, India.

† Present address: Department of Biophysics, University of Chicago, Chicago, Illinois 60637, U.S.A.

‡ Present address: Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada.