

These results remain insufficient to understand fully the interaction of MMNO with cellulose materials. More information about the nature and the geometry of the interactions between MMNO and, for example, a glucose residue or relevant model compounds, is required. The structural elucidation of such crystalline adducts would obviously enlighten the understanding, at a molecular level, of the process of cellulose dissolution and mesomorph formation. Further work along this line is in progress in our laboratory and will be reported later.

The authors thank Professor D. Gagnaire and Dr H. Chanzy for their continuous interest in this work, and Drs E. Dueé and A. Grand of the Département de Recherches Fondamentales, CEN, Grenoble, France, for kindly providing computational assistance. The data collections were performed within the 'Groupe Grenoblois de Diffractométrie'.

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Acta Cryst. (1981). **B37**, 1862–1867

The Structure of Dibenzoyldiazomethane*

BY MARTIN COWIE AND MICHELE D. GAUTHIER

Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

(Received 22 September 1980; accepted 10 March 1981)

Abstract

The structure of dibenzoyldiazomethane has been determined from three-dimensional X-ray diffraction data collected by counter methods. $C_{15}H_{10}N_2O_2$, $M_r = 250.26$, crystallizes in the space group $P2_1/n$ with $a = 9.5631$ (9), $b = 14.564$ (2), $c = 10.154$ (1) Å, $\beta = 118.184$ (9)°, $V = 1246.6$ Å³ and $Z = 4$. The observed and calculated densities are 1.32 (1) and 1.333 Mg m⁻³, respectively. A full-matrix least-squares refinement on 1471 unique observed reflections converged at $R = 0.036$ and $R_w = 0.052$. The dibenzoyldiazomethane molecule has an *s-trans-s-cis* confor-

mation which is skewed significantly owing to non-bonded contacts. When a riding-motion correction is applied to the N–N distance [1.113 (2) Å, uncorrected] a value of 1.151 (2) Å results which is intermediate between an N–N triple and double bond. Other metrical parameters in the molecule indicate some π delocalization over the carbonyl and diazomethylene groups.

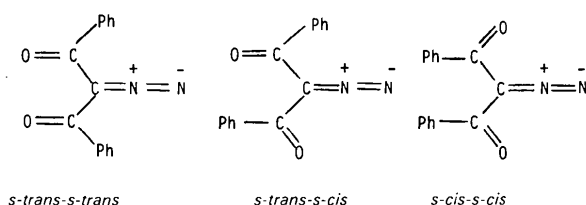
Introduction

Diazoalkane molecules have been the subject of investigation for many years owing, in part, to their utility as synthetic reagents (Fridman, Ismagilova,

* 2-Diazo-1,3-diphenyl-1,3-propanedione.

Zalesov & Novikov, 1972). Yet although their chemistry is well documented (Patai, 1978) very few structural studies have been carried out on free diazoalkane molecules, often because of the limited stability of these molecules. Dibenzoyldiazomethane [$C_6H_5COC(N_2)COC_6H_5$] is unusual in this regard, in that it may be isolated as a relatively stable, highly crystalline product.

In dibenzoyldiazomethane, a planar conformation of the molecule will be favored owing to the possibility of π delocalization over the molecular framework (Pauling, 1960, ch. 8.7). For such a planar molecule, three geometries are possible, having the carbonyl and diazomethylene functions either *cis* or *trans* relative to each other, about the C—C single bonds, as shown below.



Based on ESR studies of the carbene radical obtained through photolysis of the parent dibenzoyldiazomethane molecule, it was concluded (Murai, Torres & Strausz, 1980) that the *s-trans-s-cis* conformation was favored. In contrast, a study based on 1H NMR and dipole measurements (Nikolaev, Rodina & Korobitsyna, 1974) predicted the *s-cis-s-cis* conformation for a series of related, alkyl-substituted analogues, $RCOC(N_2)COR'$ [$R, R' = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3$]. The structural determination of the title species was therefore necessary to establish unambiguously its molecular conformation.

In addition, the chemistry of diazoalkanes with metal complexes has been of interest in recent years owing to the tremendous diversity of this chemistry (Herrmann, 1978). They can react as 1,3 dipoles or as nucleophiles through either the C or the terminal N atom, producing a variety of metal species, some containing the intact diazoalkane molecule, while others have only fragments of the parent species. Since part of our research interests involved the chemistry of dibenzoyldiazomethane with transition-metal complexes (Cowie & Gauthier, 1980a) the structural determination of this diazoalkane molecule was of importance to form a basis for structural comparisons within the coordinated species and to assist in understanding the metal chemistry of this species.

Experimental

Yellow crystals of dibenzoyldiazomethane, prepared by the reaction of $(C_6H_5CO)_2CH_2$ with *p*-toluenesulfonyl

Table 1. Summary of data and intensity collection for dibenzoyldiazomethane

Crystal dimensions	0.432 × 0.357 × 0.084 mm
Crystal volume	0.0130 mm ³
Crystal shape	Monoclinic prism with major faces of the forms {010}, {01 $\bar{2}$ }, {01 $\bar{1}$ }
Temperature	293 K
Radiation	Cu $K\alpha_1$ ($\lambda = 1.540562 \text{ \AA}$); Ni filtered
μ	0.7015 mm ⁻¹
Transmission factors	0.800–0.944
Take-off angle	2.75°
Scan speed	2° in 2 θ min ⁻¹
Scan range	0.90° below $K\alpha_1$ to 0.90° above $K\alpha_1$
Background counting time	10 s ($2\theta \leq 77.5^\circ$); 20 s ($77.5^\circ < 2\theta \leq 122.5^\circ$)
2 θ limits	3.0–122.5°
2 θ limits for centered reflections	50.0° ≤ 2 θ ≤ 70.0°
Final number of parameters varied	172
Unique data collected	2010
Unique data used [$F_o^2 \geq 3\sigma(F_o^2)$]	1471
Error in observation of unit weight	1.344 e
<i>R</i>	0.036
<i>R_w</i>	0.052

azide (Regitz, 1966) and recrystallized twice from ethanol were kindly supplied by Dr M. Torres and Professor O. P. Strausz (University of Alberta). A suitable crystal was mounted in air on a glass fiber, and precautions were taken to minimize the exposure of the crystal to light throughout the data collection.

Preliminary Weissenberg and precession photographs indicated the monoclinic space group $P2_1/c$. However, owing to an unfavorable β angle (*ca* 123°) the non-standard $P2_1/n$ setting with a somewhat more favorable β angle (118.18°) was chosen. Intensity-collection details are listed in Table 1.

Data were collected by the θ –2 θ scan method on a Picker four-circle automated diffractometer. Standard deviations in the intensities were calculated using a *p* factor of 0.05 (Doedens & Ibers, 1967). The intensities of three standard reflections were measured every 100 reflections. No significant change in these intensities was noted.

Structure solution and refinement

The structure was solved by direct methods, using the program *MULTAN* (Germain, Main & Woolfson, 1971), based on 231 reflections having $|E| > 1.40$. The *E* map corresponding to the solution with the best figures of merit revealed the positions of the 15-carbon-atom backbone. All other non-hydrogen atoms were located in a subsequent *E* map obtained by recycling *MULTAN* (Karle, 1968). All H atoms were located in subsequent electron density maps. Full-

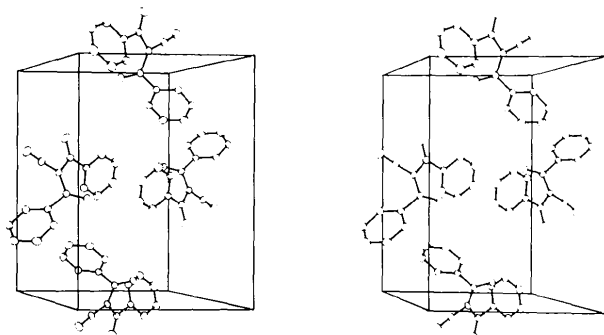


Fig. 1. A stereoview of the unit cell of dibenzoyldiazomethane. The *x* axis is into the page, the *y* axis runs from top to bottom and the *z* axis from left to right. 20% thermal ellipsoids are drawn.

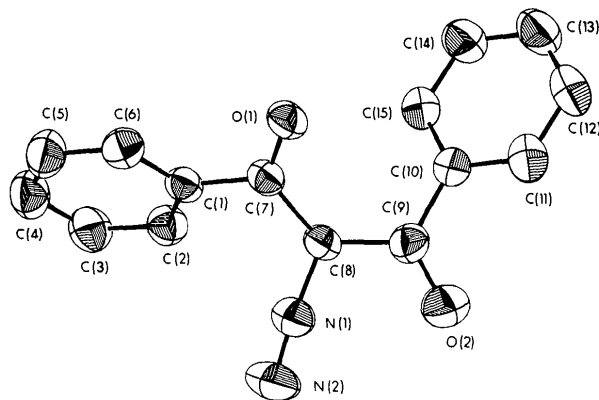


Fig. 2. A perspective view of dibenzoyldiazomethane showing the numbering scheme used. 50% thermal ellipsoids are drawn.

Table 2. Positional parameters ($\times 10^4$) and B_{eq} for the non-hydrogen atoms of dibenzoyldiazomethane

Estimated standard deviations in the least significant figure are given in parentheses in this and all subsequent tables.

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
O(1)	6694 (2)	10699.8 (9)	6156 (1)	4.27 (5)
O(2)	8448 (2)	8184 (1)	5629 (2)	5.72 (6)
N(1)	6460 (2)	9197 (1)	3457 (2)	4.39 (6)
N(2)	5817 (3)	8798 (2)	2404 (2)	6.55 (8)
C(1)	5869 (2)	11121 (1)	3644 (2)	3.34 (5)
C(2)	6368 (2)	11148 (1)	2557 (2)	4.06 (6)
C(3)	5663 (3)	11752 (1)	1366 (2)	4.75 (7)
C(4)	4449 (3)	12313 (1)	1235 (2)	5.06 (8)
C(5)	3952 (3)	12296 (1)	2309 (3)	4.98 (8)
C(6)	4674 (2)	11715 (1)	3522 (2)	4.06 (7)
C(7)	6614 (2)	10497 (1)	4954 (2)	3.34 (6)
C(8)	7267 (2)	9618 (1)	4776 (2)	3.62 (6)
C(9)	8454 (2)	9001 (1)	5904 (2)	3.91 (6)
C(10)	9680 (2)	9398 (1)	7333 (2)	3.71 (6)
C(11)	10351 (3)	8835 (2)	8583 (2)	4.77 (7)
C(12)	11528 (3)	9166 (2)	9921 (2)	5.77 (9)
C(13)	12058 (3)	10051 (2)	10017 (3)	5.85 (8)
C(14)	11428 (2)	10610 (2)	8779 (2)	5.20 (8)
C(15)	10233 (2)	10289 (1)	7441 (2)	4.25 (7)

Table 3. Selected interatomic distances (\AA) for dibenzoyldiazomethane

N(1)—N(2)	1.113 (2)	C(1)—C(2)	1.394 (2)
N(1)—N(2)*	1.151 (2)	C(2)—C(3)	1.386 (3)
N(1)—C(8)	1.338 (2)	C(3)—C(4)	1.373 (3)
C(7)—O(1)	1.222 (2)	C(4)—C(5)	1.380 (3)
C(7)—O(1)*	1.239 (2)	C(5)—C(6)	1.381 (3)
C(9)—O(2)	1.222 (2)	C(6)—C(1)	1.392 (3)
C(9)—O(2)*	1.252 (2)	C(10)—C(11)	1.388 (3)
C(1)—C(7)	1.486 (2)	C(11)—C(12)	1.379 (3)
C(7)—C(8)	1.472 (3)	C(12)—C(13)	1.372 (3)
C(8)—C(9)	1.476 (3)	C(13)—C(14)	1.376 (3)
C(9)—C(10)	1.485 (3)	C(14)—C(15)	1.380 (3)
		C(15)—C(10)	1.387 (3)

* Bond lengths corrected for riding motion, where the second atom is riding on the first.

Table 4. Selected bond and torsion angles ($^\circ$) for dibenzoyldiazomethane

N(2)—N(1)—C(8)	175.8 (2)	C(9)—C(10)—C(15)	122.5 (2)
N(1)—C(8)—C(7)	116.4 (2)	C(1)—C(2)—C(3)	120.1 (2)
N(1)—C(8)—C(9)	111.5 (2)	C(2)—C(3)—C(4)	120.2 (2)
O(1)—C(7)—C(1)	121.5 (2)	C(3)—C(4)—C(5)	120.2 (2)
O(1)—C(7)—C(8)	120.2 (2)	C(4)—C(5)—C(6)	120.2 (2)
O(2)—C(9)—C(8)	119.8 (2)	C(5)—C(6)—C(1)	120.2 (2)
O(2)—C(9)—C(10)	121.2 (2)	C(6)—C(1)—C(2)	119.1 (2)
C(1)—C(7)—C(8)	118.3 (1)	C(10)—C(11)—C(12)	120.3 (2)
C(7)—C(8)—C(9)	130.5 (1)	C(11)—C(12)—C(13)	120.0 (2)
C(8)—C(9)—C(10)	119.0 (2)	C(12)—C(13)—C(14)	120.3 (2)
C(7)—C(1)—C(2)	121.8 (2)	C(13)—C(14)—C(15)	120.1 (2)
C(7)—C(1)—C(6)	119.1 (2)	C(14)—C(15)—C(10)	120.2 (2)
C(9)—C(10)—C(11)	118.3 (2)	C(15)—C(10)—C(11)	119.1 (2)

C(1)—C(7)—C(8)—N(1)	-36.7 (2)
C(1)—C(7)—C(8)—C(9)	159.4 (2)
O(1)—C(7)—C(8)—C(9)	-20.5 (3)
C(7)—C(8)—C(9)—O(2)	154.5 (2)
C(7)—C(8)—C(9)—C(10)	-27.9 (3)
N(1)—C(8)—C(9)—C(10)	167.5 (2)
O(2)—C(9)—C(10)—C(15)	148.1 (2)
O(2)—C(9)—C(10)—C(11)	-28.4 (3)
C(8)—C(9)—C(10)—C(11)	154.2 (2)
C(8)—C(9)—C(10)—C(15)	-29.4 (3)
C(2)—C(1)—C(7)—C(8)	-30.4 (2)
C(2)—C(1)—C(7)—O(1)	149.4 (2)
C(6)—C(1)—C(7)—O(1)	-28.5 (2)
C(6)—C(1)—C(7)—C(8)	151.7 (2)
O(2)—C(9)—C(8)—N(1)	-10.0 (3)
O(1)—C(7)—C(8)—N(1)	143.4 (2)

matrix least-squares refinement techniques were used, with atomic scattering factors from the tabulation of Cromer & Waber (1974) used for all atoms except H, for which the values of Stewart, Davidson & Simpson (1965) were used. All non-hydrogen atoms were refined as individual atoms having anisotropic thermal parameters. The H atoms were included as fixed contributions in their idealized positions, with thermal parameters of 1 \AA^2 greater than the equivalent isotropic B for the corresponding C atom. Absorption corrections were applied to the data using Gaussian inte-

gration. In the final difference map, residual density was within $\pm 0.10 \text{ e } \text{Å}^{-3}$.

A stereoview of the unit cell is presented in Fig. 1. Fig. 2 shows the numbering scheme used in the molecule (hydrogens have the same number as their attached C atoms). The final positional parameters for the non-hydrogen atoms are in Table 2.* Relevant interatomic distances are listed in Table 3, while bond angles and torsion angles are in Table 4.

Description of structure and discussion

The unit cell of dibenzoyldiazomethane consists of four discrete molecules, with no unusually close intermolecular contacts. The molecule has an *s-trans-s-cis* configuration as initially proposed (Murai, Torres & Strausz, 1980) based on ESR results, but is in conflict with the *s-cis-s-cis* geometry proposed for the related diazoalkanes $\text{RCOC}(\text{N}_2)\text{COR}'$ [$R, R' = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3$] based on ^1H NMR spectra and dipole measurements (Nikolaev, Rodina & Korobitsyna, 1974). While there is likely *cis-trans* isomerization in solution, it is unlikely from steric arguments that the *s-cis-s-cis* geometry would predominate, except possibly for the smallest substituents (R, R'). In the present structure however, the *s-trans-s-cis* geometry is consistent with such steric arguments, in that in this geometry the two bulky phenyl groups have minimal contacts with each other. The third possible conformation, *s-trans-s-trans*, would also minimize non-bonded contacts between phenyl groups and in this regard, would seem to be the preferred conformation. For the *s-trans-s-trans* geometry, two carbonyl groups would have to be in close contact, whereas for the observed *s-trans-s-cis* conformation, one carbonyl and the much larger phenyl group are in close proximity. The observed geometry may therefore result from electronic factors (see below).

In the title compound, the close contacts between the carbonyl group and the phenyl ring, a consequence of the *s-trans-s-cis* geometry, result in significant deviations from planarity within the molecule. The molecule is twisted about the C(7)–C(8) and C(8)–C(9) bonds such that O(1) is thrust above the diazomethylene plane while O(2) falls below this plane. The resulting O(1)–C(7)–C(8)–N(1) and O(2)–C(9)–C(8)–N(1) torsion angles are $143.4(2)$ and $-10.0(3)^\circ$, respectively, with the *cis* carbonyl twisted less from the diazomethylene plane. These

* Lists of structure amplitudes, anisotropic thermal parameters, and idealized hydrogen parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35995 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecular twists oppose the tendency for the diazomethylene and ketone groups to be coplanar (Pauling, 1960, ch. 8.7) and therefore reduce the π delocalization somewhat. A tendency to maximize the delocalization probably keeps the molecule from deviating even more from planarity. The two phenyl rings are also twisted by *ca* 28° from the carbonyl groups, such that ring 1 [C(1)–C(6)] avoids the diazomethylene group and ring 2 [C(10)–C(15)] avoids the carbonyl C(7)O(1). This twisting also reduces the possible delocalization over the molecular framework. In the closely related molecule, benzoyl(phenyl)diazomethane, a similar skewing of the molecule was observed (Cowie & Gauthier, 1980b).

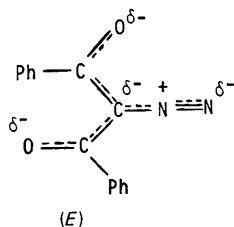
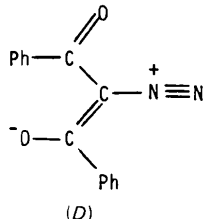
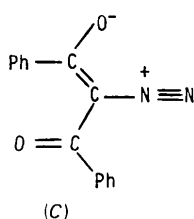
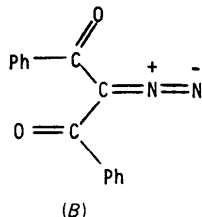
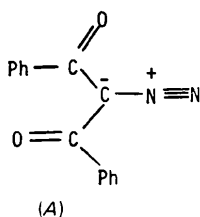
The C–C distances within both phenyl groups [average $1.384(8)$ and $1.380(6) \text{ Å}$] are as expected (Tamagawa, Iijima & Kimura, 1976). The C(1)–C(7) and C(9)–C(10) distances [$1.486(2)$ and $1.485(3) \text{ Å}$, respectively] are in excellent agreement and correspond to normal C–C single bonds between sp^2 -hybridized C atoms (Cotton & Wilkinson, 1972). On the other hand the C(7)–C(8) and C(8)–C(9) distances [$1.472(3)$ and $1.476(3) \text{ Å}$, respectively] are somewhat shorter, indicating partial double-bond character. A similar pattern of C–C bond lengths was observed in the analogous benzoyl(phenyl)diazomethane compound. Both carbonyl C–O distances [$1.222(2) \text{ Å}$ for C(7)–O(1) and C(9)–O(2)] are in good agreement with each other and indicate normal C=O double bonds (*International Tables for X-ray Crystallography*, 1968). If these bond lengths are corrected for riding motion,* however, the corrected values [$1.239(2)$ and $1.252(2) \text{ Å}$, respectively] indicate a bond order somewhat less than two, resulting from delocalization within the molecule. It should be noted that the corrected bond lengths are now significantly different. The *cis* carbonyl, which is more nearly coplanar with the diazomethylene group and which should therefore have more opportunity for π -delocalization with this group, is longer.

Within the diazomethylene part of the molecule, the C–N–N angle is virtually linear [$175.8(2)^\circ$], the C–N bond length [$1.338(2) \text{ Å}$] indicates a partial double bond (Kurland & White, 1957) and the N–N bond distance [$1.113(2) \text{ Å}$] is very close to the triple-bond values observed in dinitrogen and aromatic diazonium compounds (1.097 – 1.098 Å) (Wilkinson, 1957; Stoicheff, 1954; Rømming & Tjørnholm, 1968). All three parameters agree well with the values reported for six other diazoalkane molecules [C–N bond range $1.308(7)$ – $1.37(2) \text{ Å}$; N–N bond range $1.10(2)$ – $1.126(4) \text{ Å}$; N–N–C angle range $176.8(1)$ – $179.6(3)^\circ$] (Tulip, Corfield & Ibers, 1978; Hope &

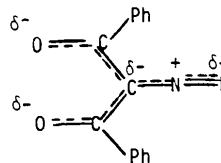
* Although the riding-motion correction is an approximation, we believe it gives a useful indication of the degree of shortening by thermal vibrations and therefore may give better descriptions of the bond lengths.

Black, 1972; Ansell, 1969; Presley & Sass, 1970; Abraham, Cochran & Rosenstein, 1971; Cox, Thomas & Sheridan, 1958). All N—N distances reported are unusually short, corresponding as they do to essentially triple bonds. On the basis of the C—N distances, which correspond to bond orders of *ca* 1.5, significantly longer N—N distances are to be expected. However, the distances in these terminal diazo groups are especially susceptible to an apparent shortening which results from thermal vibrations. A riding-motion correction to the N—N distance [N(2) riding on N(1)] gives the value of 1.151 (2) Å which corresponds closely to the expected bond order of 2.5, being intermediate between double- (Brown, 1966) and triple-bond values (*ca* 1.24 and 1.10 Å, respectively). A similar correction on the analogous molecule, benzoyl(phenyl)diazomethane (Cowie & Gauthier, 1980*b,c*) produced an almost identical corrected value of 1.152 (5) Å. Significantly, before correction the N—N distances in these two very similar compounds differed by 0.019 (5) Å. On the basis of the agreement of these thermally corrected distances with each other and with what we had expected from other parameters in the molecules, we maintain that they are more representative of the actual N—N distances in these molecules than are those previously reported, which we believe are artificially short.

In order to establish the preference of the *s-trans-s-cis* conformation over the sterically favored *s-trans-s-trans* geometry, it is worthwhile considering some of the canonical forms possible for the molecule in the observed conformation, as shown in structures (A) and (D).



As mentioned previously, significant delocalization over the molecular framework is possible if all atoms are coplanar and this is clearly seen from these canonical forms. The planarity of the molecule is opposed, however, by steric interactions which tend to suggest that the *s-trans-s-trans* conformation is more likely. However, the average structure (E) indicates an electrostatic stabilization for the observed conformation. This interaction results from the positive charge on N(1) and the negative charge on O(2). Consistent with this argument, the torsion angle involving the carbonyl *cis* to the diazo group, O(2)—C(9)—C(8)—N(1), is only 10° whereas for the *trans* carbonyl, where there is no such stabilizing electrostatic attraction, the torsion angle, O(1)—C(7)—C(8)—N(1), is 37°. For an *s-trans-s-trans* geometry, there would be no attractive interactions possible between carbonyl and diazo groups, and in fact a destabilizing, repulsive interaction would result between the two carbonyl groups, as illustrated below.



Electrostatically, the *s-cis-s-cis* conformation is favored, whereas based on steric arguments, the *s-trans-s-trans* geometry is most likely. The observed *s-trans-s-cis* geometry seems therefore to be a compromise between the electrostatic and steric forces within the molecule. The molecular parameters indicate that, in spite of the significant deviations from planarity, there is significant delocalization over the molecular framework.

Programs used

Besides local programs for the Amdahl V7 computer, the modified versions of the following were used: *FORDAP*, the Fourier summation program by A. Zalkin; *SFLS-5*, by C. J. Prewitt; *ORFFE*, by Busing, Martin & Levy (1964); *ORTEP*, by Johnson (1965); *AGNOST*, the Northwestern University absorption program which includes the Coppens—Leiserowitz—Rabinovich logic for Gaussian integration and the Tompa analytical method; and *MULTAN*, by Germain, Main & Woolfson (1971).

The authors thank the Natural Sciences and Engineering Council of Canada and the University of Alberta for financial support, and Dr M. Torres and Professor O. P. Strausz for supplying the crystals and for helpful discussions.

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The Structure and Energy Minimization of Two Benzothiazolium Iodides

BY DIETER ZOBEL AND GERHARD RUBAN

Institut für Kristallographie der Freien Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Federal Republic of Germany

(Received 17 July 1980; accepted 10 March 1981)

Abstract

The structures of 3-methyl-2-(2-thienylvinyl)benzothiazolium iodide ($C_{14}H_{12}NS_2^+ \cdot I^-$) (I) and 3,6-dimethyl-2-(2-thienylvinyl)thiazolo[4,5-*f*]benzothiazolium iodide ($C_{16}H_{13}N_2S_3^+ \cdot I^-$) (II) were determined by X-ray structure analysis. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 15.765$ (7), $b = 16.966$ (7), $c = 5.496$ (5) Å and $Z = 4$ for (I), and triclinic, space group $P\bar{1}$ with $a = 10.712$ (7), $b = 12.945$ (7), $c = 7.421$ (2) Å, $\alpha = 102.12$ (7), $\beta = 100.01$ (4), $\gamma = 99.14$ (5)° and $Z = 2$ for (II). The structures were solved by Patterson methods and refined by block-matrix least-squares

methods to R values of 5.3 and 6.2% for 1640 and 3211 reflexions, respectively. Disorder was found for (II) with respect to the terminal thiophene ring which was treated by group refinement. In addition, ethanol was found to be crystallized in the structure of (II). Energy minimization by variation of the torsion angle between the terminal thiophene ring and the rest of the structure led to results which are in good agreement with those obtained from the X-ray analysis.

Introduction

A large number of different monomeric and polymeric benzothiazolium systems containing π -electron systems