

The Crystal and Molecular Structure of 3-Ethyl-2-methyl-6-nitrobenzothiazolium Tetrafluoroborate

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Crystals of 3-ethyl-2-methyl-6-nitrobenzothiazolium tetrafluoroborate are orthorhombic, space group $Pbc2_1$, with four molecules in a unit cell of dimensions $a = 10.377$ (5), $b = 16.679$ (6), $c = 7.759$ (8) Å, $V = 1342.91$ Å³, $D_c = 1.52$, $D_o = 1.50$ g cm⁻³. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The final R index was 0.06 for 1002 independent reflexions collected on a diffractometer with Cu $K\alpha$ radiation. In the tetrafluoroborate ion the F(3) atom occupies two different positions distributed on a statistical basis, and the B–F(4) bond (1.28 Å) is significantly shorter than the mean value of the B–F bonds. The conformation of the benzothiazolium molecule is in good agreement with that found in the position-6-unsubstituted molecule. The C(2)–N(3) bond is, however, 2.5σ longer in the 6-nitro derivative.

Introduction

It has been reported (Ferré, Vincent, Larivé & Metzger, 1973) that the physico-chemical properties and chemical reactivity of 2,3-dimethylbenzothiazolium are dependent on the nature of the substituent introduced in position 5 or 6.

The results of semi-empirical quantum-mechanical calculations indicate that the order of decrease of the net π charge on the C(2) atom is: 6-NO₂ > unsubstituted in position 6 > 6-OCH₃. The crystal structure analyses of 3-ethyl-2-methylbenzothiazolium tetrafluoroborate (Miler Srenger, 1974) and its 6-nitro and 6-methoxy derivatives have been undertaken, in order to establish the extent of the structural transformations the benzothiazolium molecule undergoes when substituted either by an electron-withdrawing or by an electron-releasing group.

The molecular structure of 3-ethyl-2-methyl-6-nitrobenzothiazolium tetrafluoroborate is reported here.

Experimental

Crystals were kindly prepared by Dr R. Dennialauler of the Kodak Pathé Laboratories.

The cell constants were calculated from the least-squares fit to 2θ values ($2\theta > 73^\circ$) of 11 reflexions measured manually on a diffractometer using Cu $K\alpha$ radiation. The single-crystal Weissenberg photographs showed systematic extinctions for reflexions with k odd for Ok_l and l odd for $h0l$, suggesting space group $Pbcm$

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or $Pbc2_1$. The structure determination confirmed the latter.

The crystal used for data collection was $0.2 \times 0.2 \times 0.1$ mm. The intensities for hkl and $\bar{h}\bar{k}l$ were measured on a Nonius CAD-3 automatic diffractometer by the θ - 2θ scan method up to $2\theta \leq 132^\circ$ (Cu $K\alpha$ radiation, $\mu = 25.85$ cm⁻¹). Two check reflexions were monitored every 40 reflexions. Their intensity fluctuations were random with a maximum variation of 2%. Each intensity was assigned an observational variance based on: $\sigma^2(I) = S + B_1 + B_2 + (pI)^2$, where S , B_1 and B_2 are the total integrated and background counts, I is the net intensity and p was taken to be 0.02. The equivalent intensities were averaged when both the values I_{hkl} and $I_{\bar{h}\bar{k}l}$ satisfied the condition $I \geq 2\sigma(I)$. Of 2544 measured reflexions, 1002 independent intensities were obtained; thus 5.3 observations per parameter were refined. The net counts were corrected for Lorentz and polarization factors. Absorption effects were considered negligible and were ignored.

Structure determination and refinement

The distribution statistics of the normalized structure factors (Table 1) were rather ambiguous when com-

Table 1. Statistical averages and distribution of normalized structure factors

	Experimental	Centrosymmetric	Noncentrosymmetric
$\langle E^2 \rangle$	0.9999	1.0000	1.0000
$\langle E^2 - 1 \rangle$	0.863	0.968	0.736
$\langle E \rangle$	0.816	0.798	0.886
$ E \geq 3.0$	0.1%	0.3%	0.01%
$ E \geq 2.0$	3.8	5.0	1.8
$ E \geq 1.0$	35.3	32.0	37.0

pared with the values derived by Karle, Dragonette & Brenner (1965) for centrosymmetric and noncentrosymmetric space groups.

In the first trials of the multiresolution technique of Germain, Main & Woolfson (1971) the centrosymmetric space group, *Pbcm*, was adopted. However, least-squares refinement of positional parameters of 13 atoms revealed on the *E* map failed.

The correct structure was found in *Pbc2₁*. From the *E* map computed from 210 reflexions with $E \geq 1.4$, 11 atoms of the benzothiazolium molecule as well as the B and F(1) atoms were recognized. Three cycles of least-squares refinement yielded an *R* of 0.32. The remaining heavy atoms were located in subsequent Fourier and difference syntheses. The atomic positions were refined by the full-matrix least-squares program *SIRIUS* (a local version of *ORFLS*, Busing, Martin & Levy, 1962), first with isotropic ($R = 0.17$) and then anisotropic thermal parameters, until the *R* factor dropped to 0.095. At this stage a difference synthesis clearly revealed the positions of the eleven H atoms. Their isotropic temperature factors were assumed to be equal to those of the heavy atoms to which they were bonded. The refinement was then restarted with the heavy atoms treated anisotropically, keeping the H atoms fixed. The weighting scheme was chosen so that the averages of $w\Delta F^2$ were constant for different ranges of $|F_o|$. The refinement converged to an *R* value of 0.081.

The F atoms having high temperature factors, difference syntheses were calculated for each F atom separately. Two distinct peaks were observed on the difference Fourier map calculated for F(3). Tem-

perature factors and occupancy parameters of F(3) and F(3') were refined in alternating cycles yielding occupancy factors of 0.57 for F(3) and 0.43 for F(3'). The *R* factor at this stage was 0.074.

In the last least-squares cycles all the atomic parameters, except the occupancy factors of F(3) and F(3'), were allowed to vary. The final *R* ($= \sum |F_o| - |F_c| / \sum |F_o|$) was 0.06, and the weighted residual $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum wF_o^2 \}^{1/2}$ was 0.08. The parameter shifts of the heavy atoms were less than 0.1σ , except for F(2), F(3) and F(3'), where the maximum variation attained 0.27σ . The standard deviation of an observation of unit weight, $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, was 1.01 for $m = 1002$ observations and $n = 188$ refined parameters. The scattering factors for the heavy atoms were from Cromer & Waber (1965); for the H atoms those of Stewart, Davidson & Simpson (1965) were used. On the final difference map only one peak exceeded $0.3 e \text{ \AA}^{-3}$; this was close to F(2).

The final atomic parameters with their e.s.d.'s are given in Table 2 for the heavy atoms and in Table 3 for the H atoms.*

Results and discussion

A perspective view of the molecule and the atomic numbering are illustrated in Fig. 1(a). The bond lengths and bond angles are given in Fig. 1(b) and (c). The estimated standard deviations of bond distances and angles are: S—C, 0.008; N—C, 0.009; N—O, 0.011; C—C, 0.012; B—F, 0.016; C—H, 0.07 Å; and C—S—C, S—C—N and N—C—C, 0.65; C—C—C, 0.8; O—N—O and F—B—F, 1; C—C—H, 3°.

Table 2. Final atomic fractional coordinates ($\times 10^4$)

The estimated standard deviations in parentheses apply to the last significant digit.

	x	y	z
S	1080 (2)	4902 (1)	6976 (0)
C(2)	2655 (7)	5151 (4)	6998 (14)
N(3)	2871 (5)	5926 (3)	6673 (8)
C(4)	1643 (8)	7185 (5)	6087 (14)
C(5)	425 (8)	7495 (5)	5878 (14)
C(6)	-644 (8)	7004 (5)	5944 (13)
C(7)	-590 (7)	6191 (5)	6315 (12)
C(8)	633 (7)	5889 (4)	6578 (12)
C(9)	1737 (7)	6363 (5)	6452 (11)
C(10)	3700 (8)	4546 (5)	7200 (16)
C(11)	4164 (7)	6307 (5)	6554 (11)
C(12)	4538 (9)	6735 (6)	8202 (15)
N	-1921 (7)	7349 (5)	5587 (16)
O(1)	-2031 (9)	8062 (4)	5410 (27)
O(2)	-2855 (7)	6923 (5)	5440 (18)
B	7315 (7)	4402 (5)	6968 (16)
F(1)	6637 (6)	3746 (3)	7527 (10)
F(2)	8201 (15)	4187 (8)	5777 (28)
F(3)	8401 (10)	4509 (10)	7918 (18)
F(3')	6956 (32)	4967 (10)	8212 (20)
F(4)	6708 (9)	4948 (6)	6130 (21)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33037 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Positional parameters ($\times 10^3$) for the hydrogen atoms with the estimated standard deviations in parentheses

	x	y	z
H(C4)	240 (4)	752 (3)	574 (8)
H(C5)	17 (5)	813 (3)	546 (7)
H(C7)	-133 (4)	587 (3)	653 (6)
H1(C10)	474 (9)	462 (5)	759 (14)
H2(C10)	325 (9)	422 (5)	821 (14)
H3(C10)	397 (5)	449 (3)	587 (8)
H1(C11)	410 (7)	663 (4)	545 (10)
H2(C11)	473 (6)	594 (4)	633 (9)
H1(C12)	426 (8)	633 (5)	936 (11)
H2(C12)	549 (8)	701 (5)	801 (12)
H3(C12)	383 (8)	694 (5)	857 (13)

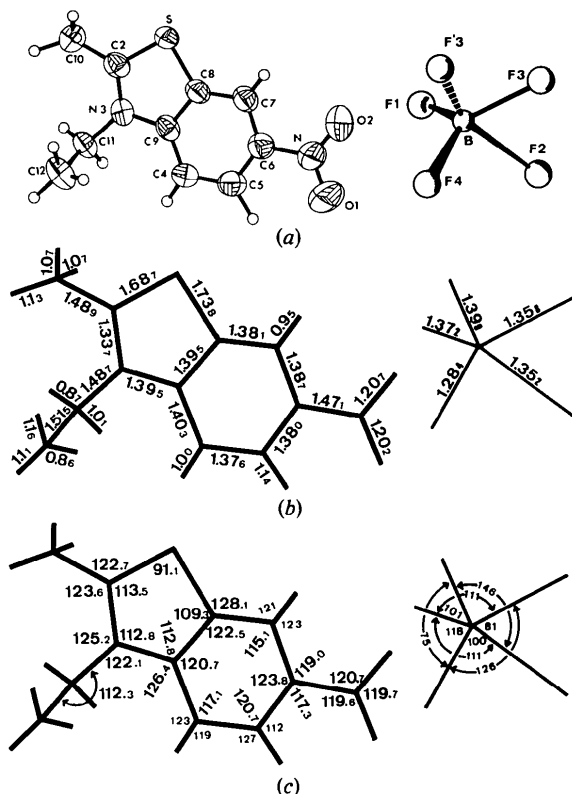


Fig. 1. (a) Perspective view of the molecule and atomic numbering. (b) Bond lengths (Å). (c) Bond angles (°).

Table 4. Equation of the least-squares plane and deviations of atoms from this plane

Equation of the least-squares plane
 $0.0532X - 0.1856Y - 0.9812Z + 6.7691 = 0$

Distances (Å) of atoms from the least-squares plane

S*	-0.000 (0)	C(6)	0.039 (10)
C(2)*	-0.008 (10)	C(8)	-0.028 (9)
N(3)*	0.011 (7)	C(10)	0.083 (13)
C(9)*	-0.018 (9)	C(11)	0.056 (8)
C(4)*	0.000 (11)	C(12)	-1.311 (12)
C(5)*	-0.004 (11)	N	0.134 (13)
C(7)*	0.012 (9)	O(2)	0.326 (14)
		O(1)	0.042 (21)

* Atoms included in the least-squares calculation.

The observed bond lengths and bond angles are in good agreement with those obtained for the 3-ethyl-2-methylbenzothiazolium ion (Miler Srenger, 1974). The only significant difference is observed for the C(2)–N(3) bond which is 2.5σ longer in the 6-nitro derivative (1.337 Å) than in the 3-ethyl-2-methylbenzothiazolium (1.313 Å) and *N*-benzyl-4-methylthiazolium (1.308 Å) (Power, Pletcher & Sax, 1970) ions, and thiamine chloride monohydrate (1.311 Å) (Pletcher, Sax, Sengupta, Chu & Yoo, 1972).

The equation of the least-squares plane of the benzothiazolium molecule as well as the deviations of the atoms from that plane, with corresponding e.s.d.'s, are given in Table 4. The best least-squares plane passes through S, C(2), N(3), C(4), C(5), C(7) and C(9); C(6) and C(8) are 3σ out of this plane.

The dihedral angle between the thiazolium part of the molecule and the benzene ring is 1.85° .

The N–O bond lengths (1.202 and 1.207 Å) as well as the C(6)–N bond (1.471 Å) agree, within the limits of error, with the values usually observed in aromatic nitro compounds.

The internal angle at C(6) is 123.8° . The increase of the internal angle at the C atom to which an electron-withdrawing substituent is attached is a common structural feature of aromatic compounds. The small value of the bond angle at C(7) (115.1°) compensates for the widening of the adjacent angles. A close intramolecular approach of 2.28 (5) Å is observed between H(5) and O(1) of the nitro group. This attraction between H(5) and O(1), suggested also by the C(6)–C(5)–H(5) angle of 112° , is probably due to the polarization of the C(5)–H(5) bond by the adjacent electron-withdrawing substituent. Such a short O...H distance was also found by Harlow, Simonsen, Pfluger & Sames (1974) in 2,4-dinitrobenzyl *p*-tolyl sulphone, where there is a close contact of 2.22 Å between the methylene H and the O of the *ortho* nitro group.

The plane passing through C(6), N, O(1) and O(2) forms an angle of 8.6° with the benzene ring.

The BF₄⁻ ion is rather ill defined, F(3) occupying two different positions on a statistical basis. The B–F(1) (1.372 Å), B–F(2) (1.352 Å), B–F(3) (1.358 Å) and B–F(3') (1.399 Å) interatomic distances equal, within the limits of error [$\sigma(\text{B–F}) = 0.016$ Å], the calculated B–F bond length (1.37 Å) when corrected for the partial ionic character of the bond, which arises from the differences in electronegativity of the atoms involved. The B–F(4) bond (1.28 Å) is significantly shorter than the calculated value, although disorder has

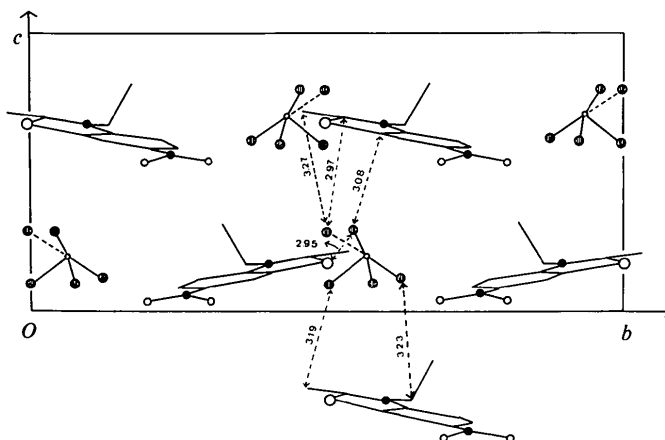


Fig. 2. The molecular packing as viewed along the *a* axis.

not been observed on the difference synthesis calculated for this atom.

The molecular packing is illustrated in Fig. 2. The shortest intermolecular contacts between the tetrafluoroborate and the benzothiazolium molecule range between 2.95 and 3.27 Å. Some nonbonded interactions are reflected in the short contacts between either S and F(3), 2.95 (1) Å, or C(2) and F(3'), 2.97 (2) Å, as well as between the methyl C(10) and F(4), 3.19 (2) Å. If we adopt the values of 1.85, 1.35, 1.70 and 2.00 Å for the van der Waals radii of S, F, C and the methyl group, the sum of the van der Waals radii for the S—F contact is 3.20 Å, for C—F is 3.05 Å and for the methyl—F contact is 3.35 Å.

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The Structure of Chaetoglobosin A: A Novel Use of Quartet Invariants

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The mycotoxin, chaetoglobosin A, crystallizes in space group $P2_12_12_1$ with four formula units, $C_{32}H_{36}N_2O_5 \cdot H_2O$, in a unit cell with dimensions $a = 10.036$ (1), $b = 16.888$ (1) and $c = 17.092$ (2) Å. The structure was determined by direct methods, making use of a technique which uses the reflections occurring most often in the negative quartets as a starting set in the multi-solution approach, and refined to $R = 0.033$ using 3207 reflexions measured with an automatic diffractometer. The absolute configuration has also been determined by means of the anomalous scattering of oxygen and proves to be the same as that of the 11-cytochalasins.

Introduction

A brief communication by Silvertton, Akiyama, Kabuto, Sekita, Yoshihira & Natori (1976) reported the structure of chaetoglobosin A (I) and gave

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references to previous chemical work on chaetoglobosins (A–F). The basic reasons for attempting the structure determination were to prove the structure and to determine the absolute configuration. The structure of another compound of this class, chaetoglobosin C (CHETC) (II), was determined independently by Springer, Clardy, Well, Cole, Kirksey, MacFarlane and Torgerson (1976).