The Crystal and Molecular Structure of
3-Ethyl-6-methoxy-2-methylbenzothiazolium Tetrafluoroborate

By E. Miler-Srenger* and C. Stora

Laboratoire de Cristallochimie, Tour 44, 11 quai Saint Bernard, Paris 75005, France

and Th. Avignon

Laboratoire de Chimie Organique A, Faculté des Sciences et Techniques de Saint Jérôme, rue Henri Poincaré, 13397 Marseille CEDEX 4, France

Crystals of $C_{11}H_{14}NOS.BF_4$ ($M_r = 295 \cdot 1$) are monoclinic, space group $P2_1/a$, with $Z = 8$, in a unit cell of dimensions $a = 13 \cdot 607$ (8), $b = 12 \cdot 581$ (6), $c = 16 \cdot 208$ (8) Å, $\beta = 97 \cdot 78$ (4)°, $V = 2749$ Å^3, $D = 1 \cdot 417$ g cm^{-3}, $\mu = 24 \cdot 60$ cm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The final R was $0 \cdot 072$ for 2911 independent reflections collected on a diffractometer with Cu $K\alpha$ radiation. The molecular structures of the 3-ethyl-2-methylbenzothiazolium and of its 6-nitro and 6-methoxy derivatives are compared and discussed with respect to the total net charge distribution in the molecule.

Introduction

The crystal structure analysis of the title compound was undertaken as a continuation of our study of the structural transformations the benzothiazolium molecule undergoes when substituted in position 6. The influence of an electron-releasing substituent, OCH_3, is described in the present paper.

Experimental

Crystals were kindly prepared by Dr Samat, of the Department of Chemistry, University of Brest.

The cell constants were calculated from the least-squares fit to the 2θ values of 11 reflexions measured manually on a diffractometer with Cu $K\alpha$ radiation. The crystal was assigned to the monoclinic system on the basis of Weissenberg photographs. The observed systematic extinctions for reflexions with h odd for $h0l$ and k odd for $0k0$ defined the space group as $P2_1/a$.

The crystal used for data collection was $0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 3$ mm. The intensities were measured on a Nonius CAD-3 automatic diffractometer by the θ–2θ scan method up to $2\theta = 132 \cdot 2°$ (Cu $K\alpha$ radiation). Two check reflexions were monitored every 40 reflexions. They showed a steady drop in intensity which reached 15% at the end of data collection. The intensities were corrected for this effect. Each intensity was assigned an observational variance based on the equation $\sigma^2(I) = S + B_1 + B_2 + (pI)^2$ where S, B_1 and B_2 are

---

* Present address: Laboratoire de Chimie des Métaux de Transition, 4 place Jussieu, 75230 Paris CEDEX 05, France.

the total integrated and background counts, I the net intensity and p was taken to be $0 \cdot 02$. Out of 4688 measured reflexions, 1777 had intensities less than $2\sigma(I)$. They were classed as unobserved and excluded from subsequent refinement. The net counts were corrected for Lorentz and polarization factors. Absorption effects were considered negligible and were ignored.

Structure determination and refinement

The structure was solved with the multisolution technique (Germain, Main & Woolfson, 1971). 500 E's $\geq 1 \cdot 5$ and 2000 Σ_2 relations were used to develop eight sets of phases. The E map calculated from the set of phases with the highest combined figure of merit ($2 \cdot 0$) showed 33 out of 38 non-hydrogen atoms of the two molecules in the asymmetric unit. Four cycles of least-squares refinement yielded an R of $0 \cdot 27$. The remaining heavy atoms were located in two subsequent difference syntheses. The structure was refined by the full-matrix least-squares program *SIRIUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962). After refinement of positional parameters, individual isotropic temperature factors and overall scale factor, the R factor was $0 \cdot 19$. The atomic positions and anisotropic thermal parameters of the two independent molecules were refined separately in alternate cycles, resulting in an R of $0 \cdot 12$. 28 H atoms were then revealed on a difference electron-density map. The isotropic temperature factor of each was assumed to equal that of the heavy atom to which it is bonded. The refinement was then restarted with the heavy atoms treated aniso-

Table 1. *Final atomic coordinates* ($\times 10^4$)

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

	x	y	z		x	y	z
S	1402 (1)	9359 (1)	86 (1)	C(7')	1318 (4)	9723 (4)	3770 (3)
C(2)	2395 (4)	10139 (4)	−35 (3)	C(8')	688 (4)	8910 (4)	3979 (3)
N(3)	2567 (3)	10172 (3)	−811 (2)	C(9')	98 (4)	8317 (4)	3394 (3)
C(4)	1921 (4)	9477 (4)	−2215 (3)	C(10')	−765 (6)	6836 (6)	5126 (5)
C(5)	1225 (4)	8810 (5)	−2647 (3)	C(11')	−1171 (5)	6836 (5)	3244 (4)
C(6)	555 (4)	8244 (4)	−2229 (3)	C(12')	−656 (6)	5887 (6)	2994 (5)
C(7)	527 (3)	8362 (4)	−1391 (3)	C(13')	2510 (7)	11284 (7)	3209 (7)
C(8)	1223 (3)	9054 (3)	−965 (3)	O'	1895 (4)	10625 (4)	2609 (3)
C(9)	1915 (3)	9573 (3)	−1365 (3)	B	−883 (4)	7157 (4)	287 (4)
C(10)	2996 (4)	10672 (5)	684 (3)	F(1)	−366 (5)	8041 (4)	425 (3)
C(11)	3424 (4)	10743 (5)	−1091 (4)	F(2)	−378 (4)	6475 (5)	−159 (3)
C(12)	3111 (5)	11766 (6)	−1460 (5)	F(3)	−1037 (4)	6696 (4)	991 (3)
C(13)	−649 (5)	6847 (6)	−2323 (4)	F(4)	−1721 (4)	7319 (5)	−244 (4)
O	−49 (3)	7576 (3)	−2731 (2)	B'	7093 (5)	9264 (6)	4167 (4)
S'	526 (1)	8512 (1)	4970 (1)	F(1')	6469 (5)	9248 (5)	4738 (4)
C(2')	−303 (5)	7571 (5)	4574 (3)	F(2')	6911 (6)	8630 (9)	3547 (7)
N(3')	−467 (3)	7569 (3)	3760 (3)	F(3')*	8076 (6)	9433 (13)	4373 (6)
C(4')	105 (4)	8503 (4)	2550 (3)	F(3")†	7692 (17)	8521 (16)	4528 (13)
C(5')	715 (5)	9279 (5)	2328 (3)	F(4')*	6734 (10)	53 (11)	3706 (8)
C(6')	1321 (5)	9886 (4)	2934 (4)	F(4")†	7524 (14)	240 (14)	4209 (10)

* Occupancy factor 0·67.
† Occupancy factor 0·33.

Table 2. *Positional* ($\times 10^3$) *and isotropic thermal parameters of the hydrogen atoms with estimated standard deviations in parentheses*

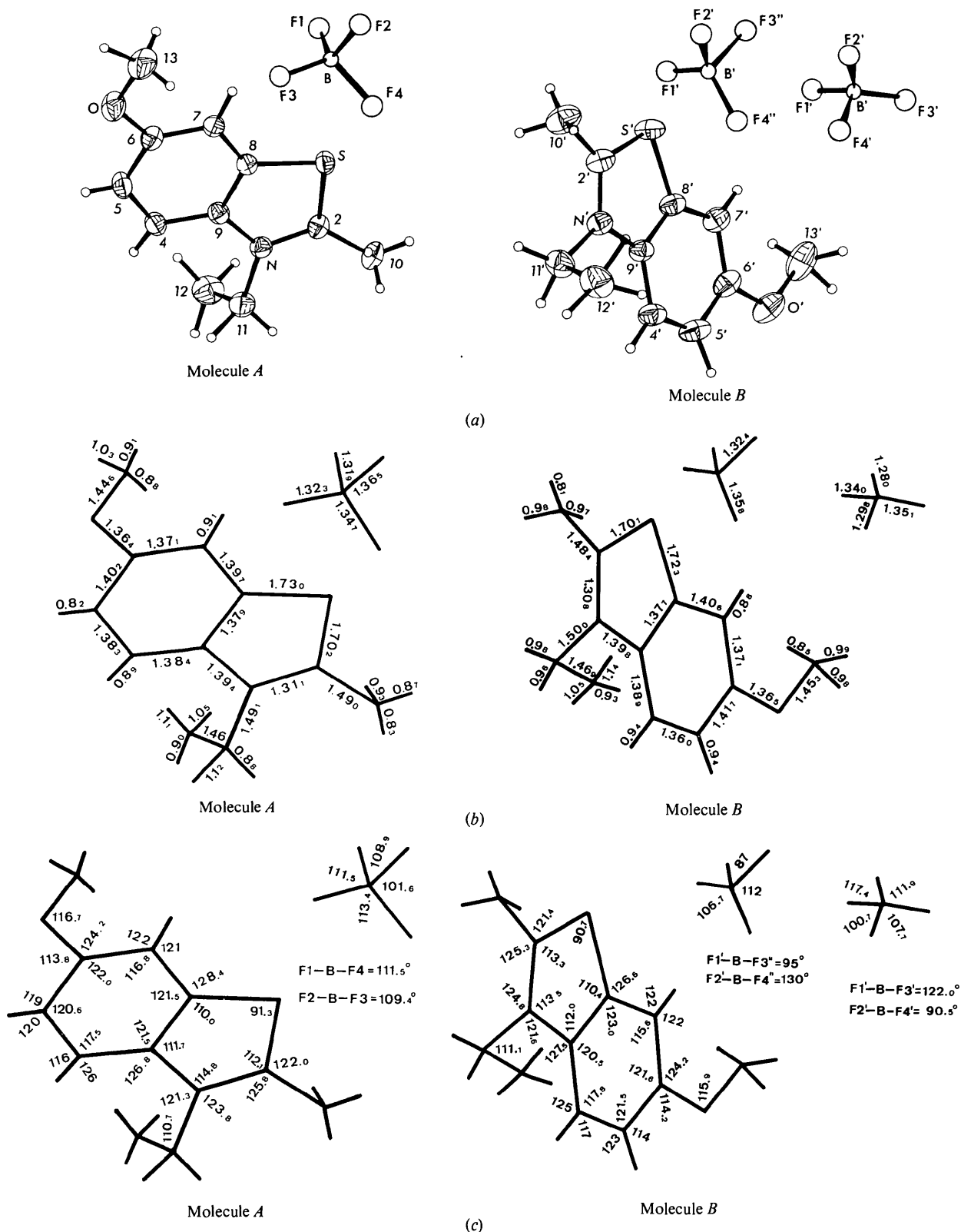|	x	y	z	$B(\text{Å}^2)$
H(4)	230 (3)	984 (4)	−252 (3)	4·6
H(5)	124 (5)	869 (5)	−314 (4)	8·9
H(7)	3 (3)	808 (4)	−113 (3)	4·7
H1(10)	293 (5)	1140 (5)	62 (4)	8·6
H2(10)	353 (4)	1036 (4)	77 (3)	5·6
H3(10)	287 (4)	1052 (4)	118 (3)	5·6
H1(11)	387 (3)	1031 (3)	−152 (2)	2·9
H2(11)	393 (6)	1074 (6)	−70 (5)	11·2
H1(12)	274 (6)	218 (7)	883 (5)	11·7
H2(12)	376 (5)	206 (6)	826 (4)	9·5
H3(12)	251 (6)	166 (6)	807 (5)	10·6
H1(13)	−22 (5)	646 (6)	−196 (4)	9·6
H2(13)	−113 (5)	720 (5)	−213 (4)	8·2
H3(13)	−101 (3)	645 (4)	−283 (3)	5·7
H(4')	−31 (4)	816 (4)	212 (3)	6·0
H(5')	86 (4)	937 (4)	178 (3)	6·5
H(7')	171 (3)	1009 (4)	415 (3)	5·3
H1'(10)	937 (5)	610 (7)	498 (4)	10·1
H2'(10)	853 (8)	700 (8)	497 (6)	13·8
H3'(10)	910 (6)	714 (7)	553 (6)	11·8
H1'(11)	844 (4)	705 (4)	273 (3)	6·3
H2'(11)	823 (5)	663 (6)	349 (4)	9·1
H1'(12)	881 (6)	548 (7)	259 (5)	12·0
H2'(12)	1000 (7)	594 (7)	282 (6)	14·1
H3'(12)	988 (6)	558 (7)	354 (5)	12·3
H1'(13)	316 (6)	91 (8)	333 (6)	12·8
H2'(13)	211 (4)	167 (4)	344 (3)	6·1
H3'(13)	290 (5)	165 (6)	283 (5)	10·0

tropically 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 factor of 0·086. At this stage, difference syntheses were calculated for each F atom separately. Two distinct peaks were observed for F(3') and F(4'). A subsequent refinement of the occupancy factors and isotropic temperature factors of F(3') and F(4') resulted in 0·67 for the occupancy factor of F(3') and F(4') and 0·33 for F(3") and F(4"). During the last least-squares cycles the positional and anisotropic thermal parameters of the heavy atoms of molecule A, molecule B and all the 28 H atom positions and isotropic thermal parameters were refined in alternate cycles. The final $R = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$ was 0·072 and the weighted residual $R_w = [(\Sigma w||F_o| - |F_c||^2)/\Sigma w|F_o|^2]^{1/2}$ was 0·10. The parameter shifts of the heavy atoms were less than 0·1σ. The standard deviation of an observation of unit weight, $S = [(\Sigma w||F_o| - |F_c||^2)/(m - n)]^{1/2}$, was 0·995 for $m = 2911$ observations and $n = 234$ refined parameters.

The scattering factors for the heavy atoms were from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). On the final difference synthesis three residual peaks of 0·4 e Å^{-3} were observed close to F(2), F(3) and F(4) and one peak of 0·5 e Å^{-3} close to F(2').

The final atomic parameters, along with the e.s.d.'s, are given in Table 1 for the heavy atoms and in Table 2 for the H atoms.*

Fig. 1. (a) Perspective view and atomic numbering of the two crystallographically independent molecules A and B. (b) Bond lengths (Å). (c) Bond angles (°). The two configurations of the disordered BF₄⁻ ion are represented separately, at arbitrary positions relative to the cation.

Results and discussion

A perspective view of the molecule with the atomic numbering is given in Fig. 1(a). The bond lengths and bond angles of the two crystallographically independent molecules (A and B) are given in Fig. 1(b) and (c). The estimated standard deviations of bond distances and bond angles are as follows: S—C 0·005; N—C and C—C(benzene) 0·007; C—CH$_3$ 0·01; C—O and B—F 0·008; B'—F' 0·013 and C—H 0·065 Å; C—S—C and S—C—N 0·4°; N—C—C 0·45°; C—C—C and F—B—F 0·5°; F'—B'—F' 0·95° and C—C—H 3·8°.

The bond lengths of the two crystallographically independent molecules are in good agreement. The bond-length distribution pattern of the benzene ring corresponds to that observed in 13 p-substituted alkoxybenzenes, as reported by di Rienzo, Domenicano, Portalone & Vaciago (1976): $a' =$ C(5)—C(6) (1·417 and 1·402 Å) > $a =$ C(6)—C(7) (1·371 Å molecules B and A), $b' =$ C(5)—C(4) (1·360 and 1·383 Å) < $b =$ C(7)—C(8) (1·406 and 1·397 Å), and $c' =$ C(4)—C(9) (1·389 and 1·384 Å) > $c =$ C(8)—C(9) (1·377 and 1·379 Å).

The nine atoms of the benzothiazolium molecule B lie in the same plane. Molecule A is slightly distorted. Its best least-squares plane passes through the five thiazolium ring atoms; C(4), C(6) and C(7) are more than 5σ out of this plane. The dihedral angle between the thiazolium and benzene rings is 2·4°.

The equations of the best least-squares planes of molecules A and B, as well as the deviations d_i of the atoms from these planes, with the corresponding e.s.d.'s, are given in Table 3.

In methoxy substituents a lengthening of the O—CH$_3$ bond, with respect to its calculated value of 1·42 Å, is usually observed (Merlino, 1971). In the present structure it amounts to 3σ, the O—CH$_3$ bonds being 1·446 Å in molecule A and 1·453 Å in molecule B. The O—CH$_3$ substituent is in a position cis to C(6)—C(7), the shorter adjacent benzene bond. A short intramolecular contact, 2·796 (A) and 2·777 Å (B) ($\bar{\sigma} =$ 0·009 Å), is thus observed between the methyl C(13) and C(7) giving rise to a bending of the C(6)—O bond. The C(7)—C(6)—O angle is 124° in both molecules.

The dihedral angle between the planes passing through C(6)—O—CH$_3$ and the benzene ring is 10·1° for molecule A and 1·9° for molecule B.

The B—F bond lengths of the two crystallographically independent BF$_4^-$ ions range from 1·280 to 1·365 Å. With the exception of the B—F(2) bond (1·365 Å) all the observed B—F distances are 2–6σ shorter than the corresponding calculated value of 1·37 Å. The F—B—F bond angles range from 87 to 130°. One of the BF$_4^-$ ions crystallizes in a twofold disordered fashion, the F(3') and F(4') atoms occupying two different positions on a statistical basis.

In the three crystal structures, 3-ethyl-2-methyl-benzothiazolium tetrafluoroborate (Miler-Srenger, 1974), its 6-nitro (Miler-Srenger & Robert, 1978) and 6-methoxy derivatives, the BF$_4^-$ ions appeared in different molecular-packing schemes. Disordered F atoms were observed when they were not involved in short intermolecular contacts and consequently had some freedom of motion. The worst resolution was observed for one of the two crystallographically independent tetrafluoroborate ions in the present structure. It did not have any obvious interaction with the molecules surrounding it.

The molecular packing is illustrated in Fig. 2. We adopted the values of 1·85, 1·35, 1·70 and 2·00 Å for

Table 3. *Equations of the least-squares planes and deviations of atoms from them*

Atoms included in the least-squares calculation of the planes are denoted by an asterisk for molecule A and a dagger for molecule B.

Equations of the planes
Molecule A: $-0·5905X + 0·7891Y - 0·1694Z - 8·1513 = 0$
Molecule B: $0·7456X - 0·6664Y - 0·0056Z - 2·6854 = 0$

Distances (Å) of atoms from the planes

	d_i (Molecule A)	d_i (Molecule B)
*†S	0·000 (1)	−0·000 (2)
*†C(2)	−0·005 (5)	0·017 (6)
*†N(3)	−0·001 (4)	−0·008 (4)
†C(4)	0·029 (5)	−0·003 (6)
†C(5)	−0·012 (6)	0·004 (7)
†C(6)	−0·096 (5)	0·006 (6)
†C(7)	−0·075 (5)	−0·006 (6)
*†C(8)	−0·008 (4)	0·001 (5)
*†C(9)	0·008 (5)	0·002 (5)
C(10)	−0·062 (6)	0·065 (8)
C(11)	−0·083 (6)	−0·021 (7)
C(12)	1·237 (7)	1·342 (8)
C(13)	−0·501 (7)	−0·009 (9)
O	−0·202 (4)	0·025 (5)

Table 4. *Total net charge distribution in 6-R-3-ethyl-2-methylbenzothiazolium*

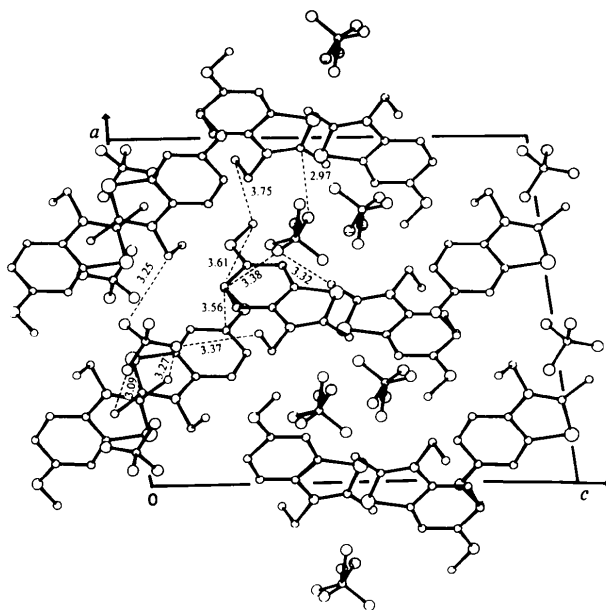|	$R =$ H	$R =$ NO$_2$	$R =$ OCH$_3$
S	0·050	0·090	0·005
C(2)	0·248	0·264	0·242
N(3)	0·002	−0·039	0·003
C(4)	−0·019	−0·001	0·018
C(5)	0·025	0·035	−0·033
C(6)	0·027	0·052	0·212
C(7)	0·022	0·030	−0·056
C(8)	0·039	−0·040	0·072
C(9)	0·078	0·103	0·064
C(10)	−0·333	−0·355	−0·325
C(11)	−0·312	0·106	0·120
C(12)	0·145	−0·043	0·029
N		0·483	
O(1)		−0·310	
O(2)		−0·314	
O			−0·198
C(13)			0·125

Fig. 2. The molecular packing as viewed along **b**.

the van der Waals radii of S, F, C and the methyl group. F$\cdots$H short contacts were not taken into consideration since their e.s.d.'s were usually significant.

Conclusion

The total net charges calculated by the semi-empirical CNDO/2 method for 3-ethyl-2-methylbenzothiazolium, as well as for its 6-nitro and 6-methoxy derivatives, are given in Table 4. The bond lengths of the three compounds are summarized in Table 5 and compared with the corresponding values observed in thiamine chloride monohydrate (Pletcher, Sax, Sengupta, Chu & Yoo, 1972).

The introduction of a nitro substituent in position 6 of the benzothiazolium molecule decreases the total net charge on C(7) and C(5). In the molecular structure, as a consequence, one observes a short intramolecular contact between H(5) and O(1) (2·28 Å), the distance between O(2) and H(7) (2·50 Å) being equal, in the

limits of error, to the sum of the van der Waals radii of the atoms involved.

The substitution of an electron-releasing, methoxy group in position 6 increases the total net charge on C(7) and C(5). Consequently there is a close contact of 2·78 Å between methyl C(13) and C(7).

The introduction of either an electron-releasing or electron-withdrawing substituent in position 6 of the benzothiazolium molecule affects mostly the molecular geometry of the benzene ring. Except for the slight lengthening (by 2·5σ) of the C(2)—N(3) bond in the 6-nitro derivative no significant modification is observed in the structure of the thiazolium ring.

However, we observe an out-of-plane bending tendency of the C(2) atom, the reactive centre of the molecule. The extent of the displacement of the C(2) atom from the plane formed by S, C(10) and N is a result of its positive total net charge and the direction and number of short-range interactions between the benzothiazolium molecule and the BF$_4^-$ ion. The out-of-plane bending of the C(2) atom is quite significant in the 6-nitro derivative and in one of the crystallographically independent molecules of the 3-ethyl-6-methoxy-2-methylbenzothiazolium, while the second molecule has no short contacts with the BF$_4^-$ ion and is consequently planar. The out-of-plane bending tendency of C(2) is less evident in 3-ethyl-2-methylbenzothiazolium where the deviation of the C(2) atom from the S, C(10), N plane does not exceed 1·5σ.

The total net charge q of the C(2) atom and its deviation from the plane formed by S, C(10) and N in 6-R-3-ethyl-2-methylbenzothiazolium is summarized in Table 6. As a reference, the corresponding value of d observed in the benzothiazoline part of the anhydro-

Table 6. *Total net charge q of the* C(2) *atom and its deviation d from the plane formed by* S, C(10), N *in* 6-R-3-*ethyl-2-methylbenzothiazolium*

R	$d(\text{Å})$	q
NO$_2$	−0·041 (11)	0·264
OCH$_3$	0·017 (5)	0·242
OCH$_3'$	−0·005 (6)	0·242
H	−0·009 (6)	0·248
Benzothiazoline	−0·580 (5)	

Table 5. *Bond lengths* (Å) *in* 6-R-3-*ethyl-2-methylbenzothiazolium*

	$R = H$	$R = NO_2$	$R = OCH_3$ molecule A	$R = OCH_3$ molecule B	Thiamine chloride monohydrate
S—C(2)	1·69$_8$	1·68$_7$	1·70$_2$	1·70$_1$	1·667
S—C(8)	1·73$_4$	1·73$_8$	1·73$_0$	1·72$_3$	1·731
C(2)—N(3)	1·31$_3$	1·33$_7$	1·31$_1$	1·30$_8$	1·311
N(3)—C(9)	1·39$_8$	1·39$_5$	1·39$_4$	1·39$_8$	1·392
N(3)—C(11)	1·48$_3$	1·48$_7$	1·49$_1$	1·50$_0$	1·496
C(11)—C(12)	1·51$_0$	1·51$_5$	1·45$_8$	1·46$_9$	
C—C$_{benzene}$	1·38$_7$	1·38$_7$	1·38$_6$	1·38$_7$	

base of benzothiazole is added. The C(2) atom is sp^3-hybridized in this compound (Miler-Srenger, 1969).

We wish to thank Dr Samat for providing the crystalline sample.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104–109.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.

MERLINO, S. (1971). Acta Cryst. B27, 2491–2492.

MILER-SRENGER, E. (1969). Bull. Soc. Chim. Fr. p. 3970.

MILER-SRENGER, E. (1974). Acta Cryst. B30, 1911–1914.

MILER-SRENGER, E. & ROBERT, F. (1978). Acta Cryst. B34, 585–588.

PLETCHER, J., SAX, M., SENGUPTA, S., CHU, J. & YOO, C. S. (1972). Acta Cryst. B28, 2928–2935.

RIENZO, F. DI, DOMENICANO, A., PORTALONE, G. & VACIAGO, A. (1976). Proceedings of the Yugoslav Centre of Crystallography, Suppl. to Vol. 11, pp. A102–104.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

The Crystal and Molecular Structure of 2-Acetamido-2,3-dideoxy-5,6-O-isopropylidene-D-threo-hex-2-enono-1,4-lactone, C11H15NO5

BY ŽIVA RUŽIĆ-TOROŠ

'Rudjer Bošković' Institute, PO Box 1016, 41001 Zagreb, Yugoslavia

AND I. LEBAN

Chemistry Department, University of Ljubljana, Murnikova 6, 61000 Ljubljana, Yugoslavia

2-Acetamido-2,3-dideoxy-5,6-O-isopropylidene-D-threo-hex-2-enono-1,4-lactone is monoclinic with $a = 5.218$ (1), $b = 22.703$ (3), $c = 10.138$ (1) Å, $\beta = 100.32$ (1)°, $Z = 4$, space group $P2_1$. The structure was solved by MULTAN and refined to an R of 0.048. The lactone group and ring in both independent molecules are planar within experimental error. The dioxolane rings are puckered. Two asymmetric molecules are connected by N–H⋯O (3.006 and 2.935 Å) hydrogen bonds forming dimers in the crystal lattice.

Experimental

The compound crystallizes as colourless prismatic rods. The unit-cell dimensions (Table 1) were determined from oscillation photographs with Cu $K\alpha$ radiation. The precise values were then deduced from zero-layer rotation patterns of single crystals (around a and b) taken in the asymmetric (Straumanis) position and indexed by means of corresponding Weissenberg photographs (Popović, 1974).

The space group was determined from Weissenberg photographs. The diffraction symmetry and space-group extinctions indicated $P2_1$ or $P2_1/m$; since the molecule is optically active the space group is necessarily $P2_1$. The intensities were collected on an automatic Enraf–Nonius CAD-4 four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation (ω–2θ mode, variable scan rate, $0 < 2\theta < 180°$). 3427 intensities were collected and the symmetrically related reflexions were averaged to 2478 independent reflexions. 489 of these were unobserved ($I \le 2\sigma$). The data were corrected for variations in the intensities of reference reflexions, and for Lorentz and polarization effects.

Table 1. Crystallographic and physical data

2-Acetamido-2,3-dideoxy-5,6-O-isopropylidene-D-threo-2-enono-1,4-lactone, C11H15NO5

FW	241.24	Z	4
Space group	$P2_1$	U	1181.56 Å³
a	5.218 (1) Å	D_c	1.357 g cm⁻³
b	22.703 (3)	μ(Cu $K\alpha$)	6.80 cm⁻¹
c	10.138 (1)	Crystal shape	Prismatic
β	100.32 (1)°		