negative atoms, N—O, the calculated values are 0·010 to 0·015 Å longer than the experimental values.

We ascribe these significant differences in agreement between theory and experiment to the effect of electron correlation in high-electron-density bonds, which is not accounted for adequately by extrapolation from higher-level calculations on simpler molecules, rather than to crystal-field effects.

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Structure of 6-{2-(3-Ethyl-2,3-dihydro-1,3-benzothiazol-2-ylidene)ethylidene}-2-methoxy-4-nitro-2,4-cyclohexadienone: A Model Compound for a Photomerocyanine

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Abstract

$C_{18}H_{16}N_2O_4S$ is monoclinic, space group $P2_1/c$, with $a = 13\cdot019$ (9), $b = 7\cdot696$ (8), $c = 16\cdot471$ (10) Å, $\beta = 91\cdot95$ (5)°, $V = 1649\cdot3$ Å^3, $D_c = 1\cdot44$ Mg m^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 0·225 mm^{-1}. The crystal structure has been determined from Mo $K\alpha$ data and refined to an R value of 0·062 for 1701 observed reflexions. In the solid state the polar zwitterionic form of the merocyanine is dominant. The molecular geometry of the thiazole ring approaches that of a thiazolium cation and the phenolate ring is the negatively charged moiety of the molecule. In the crystal lattice the molecules associate in pairs across centres of inversion. The slip angle is 55°.

Introduction

Colorless photochromic spiropyran compounds (*A*) transform, by the action of ultraviolet light, into strongly colored compounds. The structure of these colored forms was assigned on the basis of the

similarity of their solvatochromic behavior with that of the title compound (B) (Vandewyer, Hoefnagels & Smets, 1969).

(A)

(B)
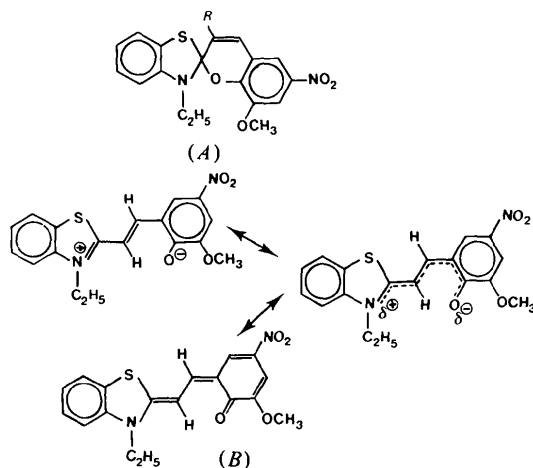
Guglielmetti and his collaborators concluded that the electronic structure of these colored photo-merocyanines is a delocalized one (Le Beuze, Samat, Botrel, Appriou & Guglielmetti, 1978). The results of NMR experiments (Samat, Martin & Guglielmetti, 1976), which are in favor of a polar zwitterionic form of the photomerocyanine, are attributed to the influence of Me_2SO, a polar solvent used in the measurements.

We report here the molecular structure of a model compound for a benzothiazole photomerocyanine, when crystallized from dimethylformamide.

Experimental

The cell constants were obtained from a least-squares fit to the setting angles of 13 reflexions measured on a diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å).

The observed systematic extinctions defined the space group as $P2_1/c$.

The crystal used for data collection was $0.1 \times 0.2 \times 0.4$ mm. The intensities were measured on a Philips PW 1100 diffractometer with graphite-mono-chromated Mo $K\alpha$ radiation by the θ–2θ scan method up to $2\theta = 54°$. Three check reflexions were monitored every 120 min. Their intensity fluctuations were random. 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 the total integrated and background counts, I the net intensity and p was taken to be 0.03. Out of 3264 measured reflexions 1563 had intensities less than $2\sigma(I)$. They were classed as unobserved and excluded from subsequent refinement. No correction was applied for absorption.

Structure determination and refinement

The structure was solved with the multisolution technique (Germain, Main & Woolfson, 1971).

Anisotropic full-matrix least-squares heavy-atom refinement gave an agreement index of 0.091. The H atoms were located from a difference map. The weighting scheme was chosen so that the averages of $w\Delta F^2$ were constant for different ranges of $|F_o|$. A full-matrix least-squares refinement of all the heavy atoms anisotropically and the H atoms isotropically yielded a final $R = (\sum ||F_o| - |F_c||)/\sum |F_o|$ of 0.062. The weighted residual $R_w = \{[\sum w(|F_o| - |F_c|)^2]/\sum wF_o^2\}^{1/2}$ is 0.071. The final prameter shifts of the heavy atoms were less than 0.1σ and the standard deviation of an observation of unit weight $S = [(\sum w||F_o| - |F_c||)^2/(m - n)]^{1/2}$ was 1.03 for $m = 1701$ observations and $n = 225$ refined parameters. The scattering factors for the heavy atoms were from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). The final difference map was essentially featureless, except for one peak of 0.6 e Å^{-3} located near the S atom.

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

* Lists of structure factors, anisotropic thermal parameters and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36722 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2)

The e.s.d.'s in parentheses apply to the last significant digit. The B_{eq} values were calculated with Hamilton's (1959) formula.

	x	y	z	B_{eq}
S(1')	3671 (1)	8821 (2)	6652 (1)	3.40
C(22')	3179 (3)	8028 (7)	5742 (3)	3.17
N(3')	2144 (3)	7911 (5)	5718 (2)	3.07
C(9')	1699 (3)	8515 (7)	6431 (3)	2.95
C(4')	657 (3)	8569 (8)	6595 (3)	3.93
C(5')	383 (4)	9187 (9)	7337 (4)	4.92
C(6')	1113 (4)	9771 (9)	7909 (4)	4.79
C(7')	2148 (4)	9693 (8)	7757 (3)	4.28
C(8')	2434 (3)	9062 (7)	7008 (3)	3.33
C(10')	1527 (3)	7322 (7)	5010 (3)	3.40
C(11')	1272 (4)	8773 (9)	4443 (4)	4.84
C(3)	3812 (3)	7499 (7)	5096 (3)	3.27
C(4)	4850 (3)	7516 (7)	5170 (3)	3.20
C(4a)	5589 (3)	7036 (6)	4581 (3)	2.96
C(5)	6635 (3)	7154 (6)	4824 (3)	3.10
C(6)	7385 (3)	6732 (6)	4287 (3)	3.11
C(7)	7143 (3)	6228 (7)	3486 (3)	3.49
C(8)	6141 (3)	6061 (7)	3235 (3)	3.24
C(8a)	5289 (3)	6438 (7)	3776 (3)	3.46
O(1)	4376 (2)	6203 (6)	3534 (2)	4.82
C(9)	6583 (5)	5156 (9)	1920 (3)	5.07
O(2)	5812 (3)	5555 (6)	2484 (2)	5.03
N	8440 (3)	6805 (6)	4559 (3)	3.91
O(3)	8666 (3)	7092 (6)	5281 (3)	5.05
O(4)	9111 (3)	6463 (7)	4064 (3)	6.22

Table 2. *Fractional atomic coordinates* (×10³) *and isotropic thermal parameters* (Å²) *for the* H *atoms*

The e.s.d.'s in parentheses apply to the last significant digit.

	x	y	z	B
H(4')	11 (3)	819 (6)	619 (3)	3·7
H(5')	−32 (3)	944 (6)	745 (3)	4·2
H(6')	86 (4)	1·030 (8)	842 (4)	7·5
H(7')	266 (3)	995 (6)	818 (3)	3·8
H(10'1)	89 (3)	663 (6)	523 (3)	3·4
H(10'2)	193 (3)	633 (5)	476 (2)	3·4
H(11'1)	184 (4)	937 (7)	429 (3)	5·4
H(11'2)	84 (3)	845 (6)	401 (3)	5·4
H(11'3)	85 (4)	985 (8)	480 (3)	5·4
H(3)	350 (3)	718 (5)	458 (2)	1·4
H(4)	516 (3)	773 (5)	569 (2)	2·2
H(5)	684 (3)	749 (6)	539 (2)	2·8
H(7)	768 (4)	594 (7)	310 (3)	5·2
H(91)	621 (4)	489 (7)	143 (3)	6·2
H(92)	707 (4)	623 (8)	184 (3)	6·2
H(93)	705 (5)	426 (8)	210 (4)	6·2

Results and discussion

The perspective view of the title compound with the atomic numbering is given in Fig. 1(a) and the bond lengths and bond angles in Fig. 1(b) and (c) respectively. A comparison of the molecular geometry of the benzothiazole group with that of the 3-ethyl-2-methylbenzothiazolium ion (Miler-Srenger, 1974) is given in Table 3. The considerable double-bond character of the C(22')–S(1'), C(9')–S(1') and C(22')–N(3') bonds in the thiazole ring indicate that the benzothiazole possesses some electronic character of the benzothiazolium ion.

The C(8a)–O(1) bond length of 1·254 Å is in good agreement with the values of 1·242–1·252 Å usually observed for ionized carboxyl groups, indicating a partial negative charge on the O(1) atom. The increased σ-electron-releasing character of O(1) is reflected in the small C(4a)–C(8a)–C(8) bond angle of 115·6°. It should be noted that in examples of monosubstituted benzene derivatives (Domenicano, Vaciago & Coulson, 1975) the smallest endocyclic angle (α = 114·1°) is observed in the tetraphenylborate anion (Sime, Dodge, Zalkin & Templeton, 1971) where the inherently low electronegativity of B is further lowered by the negative charge.

Table 3. *Comparison of bond distances* (Å)

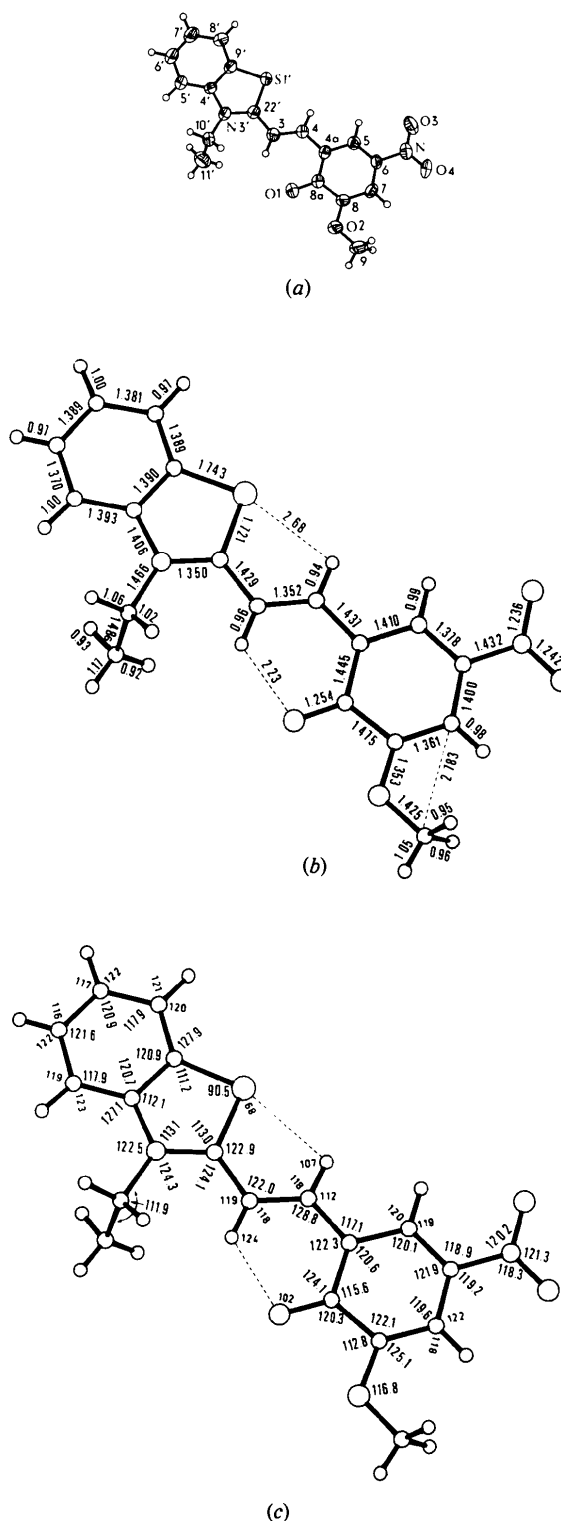|	Title compound	3-Ethyl-2-methyl-benzothiazolium ion
C(2')–S(1')	1·721 (5)	1·698
C(8')–S(1')	1·743 (5)	1·734
C(2')–N(3')	1·350 (6)	1·313
C(9')–N(3')	1·406 (6)	1·398
⟨C–C⟩_benzene	1·385	1·387

(a)

(b)

(c)

Fig. 1. (a) Perspective view and atomic numbering of the title compound. (b) Bond lengths (Å). The e.s.d.'s are 0·005 for S–C; 0·006 for O–C, N–C and N–O; 0·007 for C–C; and 0·05 Å for C–H. (c) Bond angles (°). The e.s.d.'s are 0·3 for C–S–C and S–C–N angles, 0·4 for C–C–N, C–C–O and C–N–O angles, 0·5 for C–C–C angles and 2·7° for C–C–H.

The geometry of the methoxy group is normal. The C(8)—O(2) bond has a marked bend in the plane, the C(7)—C(8)—O(2) and C(8)—O(2)—C(9) angles are 125 and 116·8° respectively. The dihedral angle between planes passing through C(8), O(2) and C(9) and the phenolate ring is 0·5 (5)°. Since the methyl C atom is coplanar with the ring system, the electron pair of O(2) would have a good overlap with the π orbitals of the ring.

The C(6)—N bond [1·432 (6) Å] is significantly shorter than the C—N bond length usually observed in aromatic nitro compounds (1·475 Å). The short C(6)—N bond is correlated with a smaller O(3)—N—O(4) bond angle and longer O—N bonds. Consequently the s character in the N-atom orbital pointing towards C(6) is increased (Williams, 1967) and a strong resonance interaction between NO_2 and the aromatic ring established.

The dihedral angle between the planes passing through C(6), N, O(3), O(4) and the phenolate ring is 5·8 (5)°, the mean observation for an unhindered NO_2 substituent being 6°.

The C(22')—C(3) (1·429 Å), C(3)—C(4) [1·352 (7) Å] and C(4)—C(4a) (1·437 Å) bonds are longer than the normal C—C double bond (1·34 Å) and shorter than the normal C_{sp^2}—C_{sp^2} single bond (1·48 Å). However, it should be noted that the C(3)—C(4) bond is only 2σ longer than the C—C double bond. The methinic chain's bond-angle values alternate about their mean value of 124·3°. The alternations of excess charges at the methinic chain's C atoms would be in the same sense as the alternations of their bond-angle values (Kulpe & Schulz, 1979).

The torsional angles are listed in Table 4.

With the exception of C(5') and C(22'), the atoms of the benzothiazole group lie in the same plane.

The phenolate ring is slightly distorted. Four of the six C atoms deviate by 3–3·5 σ from its least-squares

plane. The torsional angles of the C(6)—C(7) and C(4a)—C(8a) bonds are −3·4 and −2·9° respectively. Both the O(1) atom and the NO_2 group are bent out on the same side of the phenolate plane: O(1) is at −0·087 (4) Å and the N of NO_2 at −0·079 (5) Å. A similar trend has been observed in 3-methyl-4-nitro-pyridine N-oxide, where d_O is −0·028 and d_N −0·036 Å (Shiro, Masumi & Kubota, 1977).

The dihedral angle between planes passing through the benzothiazole and the phenolate ring is 5·2 (5)°.

The four atoms of the methinic chain, C(22'), C(3), C(4) and C(4a) are coplanar; the C(4)—C(3)—C(22')—S(1') torsion angle is 2·9° and that of C(3)—C(4)—C(4a)—C(5) 179·1°.

The slight molecular distortion from planarity and the widening of the bond angles at C(3), C(4), C(4a) and C(8a) increase the intramolecular distances between O(1) and H(3) as well as that between S(1') and H(4). Nevertheless the observed O(1)···H(3) and S(1')···H(4) distances [2·23 (3) and 2·68 (4) Å respectively] are significantly shorter than the sum of the van der Waals radii of the atoms involved.

The molecular packing is illustrated in Fig. 2. The molecules associate in pairs across centers of inversion so that adjacent molecules are reversed in orientation. Hence alternating layers of phenolate and thiazole ring planes are formed and piled in stacks along the b axis. The distances of N(3'), C(22') and S(1') to the phenolate ring's least-squares plane are:

	d^1 (Å)	d^{2i} (Å)
N(3')	3·391 (4)	3·927 (4)
C(22')	3·488 (5)	3·830 (5)
S(1')	3·615 (1)	3·703 (1);

Table 4. Torsional angles (°)

The e.s.d.'s are 0·6°.

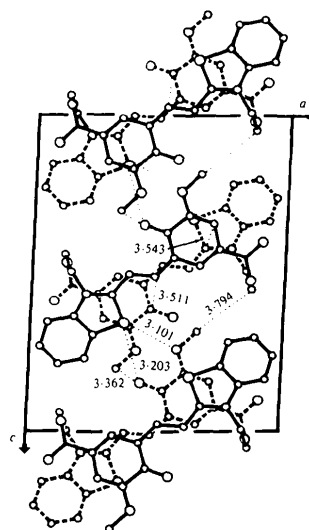|	
C(4)—C(3)—C(22')—S(1')	2·9
C(4)—C(3)—C(22')—N(3')	−174·9
C(22')—C(3)—C(4)—C(4a)	−179·8
C(3)—C(4)—C(4a)—C(5)	−179·1
C(3)—C(4)—C(4a)—C(8a)	0·3
C(4)—C(4a)—C(8a)—O(1)	−3·7
C(4a)—C(5)—C(6)—C(7)	2·0
C(5)—C(6)—C(7)—C(8)	−3·4
C(8)—C(8a)—C(4a)—C(5)	−2·9
O(3)—N—C(6)—C(5)	6·3
O(3)—N—C(6)—C(7)	−173·5
O(4)—N—C(6)—C(7)	2·0
O(4)—N—C(6)—C(5)	−178·3
C(9)—O(2)—C(8)—C(7)	0·5
C(9)—O(2)—C(8)—C(8a)	−179·8
O(1)—C(8a)—C(8)—O(2)	3·1

Fig. 2. Molecular packing of the title compound viewed along the b axis, showing crosslinking short contacts (Å) (e.s.d.'s range from 0·004–0·008 Å).

d^i refers to the $-x,-y,-z$ symmetry position and d^{2i} to that of $-x, 1-y, -z$; $b/2$ is equal to 3·848 Å. Further short contacts are established between O(3) and the ethyl C atom C(11'²ⁱ)[3·215 (8) Å] as well as between O(3) and one of the ethyl H atoms H(11'3²ⁱ) [2·44 (6) Å].

Within the centrosymmetric pair the molecules are laterally displaced with respect to each other. If the molecular long axis is taken along the methinic chain and the aggregate axis, the vector connecting the midpoints (A) of the C(3)—C(4) bonds, the slip angle C(4)···A···A^i is 55°.

The molecular stacks are crosslinked through the following short contacts:

	d (Å)		d (Å)
O(1)···C(9⁴ⁱ)	3·362 (8)	O(2)···S(1'³ⁱ)	3·101 (4)
O(1)···S(1'³ⁱ)	3·203 (4)	C(9)···C(11'⁴ⁱ)	3·794 (8);
O(1)···H(7'³ⁱ)	2·45 (4)		

3i and 4i correspond to $x, \frac{1}{2} - y, \frac{1}{2} + z$ and $-x, \frac{1}{2} + y, \frac{1}{2} - z$ symmetry operations respectively.

Conclusion

In the solid state the polar zwitterionic mesomeric form of the merocyanine is dominant. The molecular geometry of the thiazole ring approaches that of the thiazolium cation and the phenolate ring is the negatively charged moiety of the molecule. The presence of the electron-withdrawing NO_2 substituent in the phenolate ring enhances the delocalization of the negative charge on this part of the molecule and contributes to the stabilization of the polar structure of the merocyanine.

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Structure of 1-Fluoroadamantane, $C_{10}H_{15}F$, in its Plastic Phase

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Abstract

Single-crystal X-ray diffraction data were collected and interpreted for the plastic phase of 1-fluoroadamantane, $C_{10}H_{15}F$ at 293 K. The unit cell is face-centred cubic with $a = 9·535$ (4) Å, space group $Fm3m$, $Z = 4$. On the assumption of a rigid molecular skeleton, several types of orientational disorder were investigated: hindered reorientations between equally weighted orientations, free uniaxial rotation of the molecules about the C—F axis and decomposition of the atomic orientational average density on symmetry-adapted functions. With the first and the third models agreement between observed and calculated structure factors is found in which molecular (C—F) and lattice ([111]) threefold axes are aligned.