

Tableau 6. Longueurs de liaisons en Å de la bis(diméthyl-2,3-benzothiazoline) et de l'anhydrobase du diméthyl 2,3 benzothiazole

Les écarts-types correspondants sont indiqués entre parenthèses.

	BDB	ADB
S(1)–C(2)	1,869 (3)	1,861 (9)
C(2)–N(3)	1,464 (4)	1,490 (9)
N(3)–C(4)	1,409 (4)	1,370 (9)
S(1)–C(9)	1,775 (3)	1,751 (8)
N(3)–C(11)	1,433 (4)	1,478 (9)
C(2)–C(10)	1,522 (6)	1,520 (10)
C—C	1,390 (6)	1,400 (11)
moyen du benzène		

Nous retrouvons dans les deux composés la même distance S(II)–C(sp³) anormalement longue, ce qui est une preuve que la déformation de cette liaison est propre à la molécule de la diméthyl-2,3 benzothiazoline.

Je suis reconnaissante à Mademoiselle C. Stora pour l'intérêt qu'elle a porté à ce travail. Je présente tous mes remerciements à M H. Larivé et à ses collaborateurs pour m'avoir proposé le sujet de ce travail et préparé des cristaux. Je tiens également à remercier Mademoiselle M. Poujade de l'aide qu'elle m'a apportée dans l'exécution des calculs.

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The Crystal Structure of Methylene Blue Thiocyanate

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The crystal structure of methylene blue thiocyanate comprises parallel planes 3·38 Å apart in which lie all atoms except the methyl hydrogens. Methylene blue molecules in adjacent planes are paired in anti-parallel fashion, the relative orientation being consistent with that suggested from n.m.r. and optical studies for the dimeric molecule in solution.

Spectroscopic studies of solutions containing polymers of planar, dipolar molecules like methylene blue (see Fig. 1) indicate a 'sandwich' structure in which aromatic planes are parallel and permanent dipole moments are opposed (Ballard & Park, 1970; Ballard & Gardner, 1971, Blears & Danyluk, 1967). We now report an X-ray study of methylene blue thiocyanate.

Experimental

Methylene blue thiocyanate was prepared by the addition of excess potassium thiocyanate to an aqueous solution

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of methylene blue (B.D.H. standard stain) at 22°C. Yellow-green crystals suitable for X-ray diffraction were obtained in the form of laths by the slow cooling of an ethanolic solution in a Dewar vessel over a period of two days.

A crystal of maximum dimension ~0·1 cm was mounted parallel to the *c* axis along its long edge. Using Cu K α radiation ($\lambda = 1\cdot5418$ Å) oscillation and precession photographs were obtained. The multifilm technique was employed to obtain integrated equi-inclination Weissenberg photographs for *hk* 0–3. The unit cell was found to be orthorhombic with the following dimensions at 22°C;

$$\begin{aligned} a &= 16\cdot83 \pm 0\cdot03 \text{ \AA} \\ b &= 14\cdot66 \pm 0\cdot03 \\ c &= 6\cdot75 \pm 0\cdot02 . \end{aligned}$$

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The error limits in the cell dimensions were estimated from the reproducibility of the measurements. The density determined by flotation was 1.350 g cm^{-3} ; with four $\text{C}_{17}\text{H}_{18}\text{N}_4\text{S}_2$ units the calculated density is 1.364 g cm^{-3} . From the systematic absences ($h0l$, $h=2n+1$; $0kl$, $k+l=2n+1$) it was deduced that the space group was either $Pna2_1$ or $Pnam$.

Intensities were measured visually with a calibrated film strip. Scale factors for each layer were obtained from reflexions common to the precession and Weissenberg photographs.

Lorentz and polarization corrections were applied in the usual way. No correction for absorption was made since $\mu=19.5 \text{ cm}^{-1}$. The total number of inde-

pendent reflexions measured was 1175; of these 747 were of non-zero intensity. Atomic scattering factors given in *International Tables for X-ray Crystallography* (1962) were used for all atoms.

Solution and refinement of structure

Normalized structure factors ($|E|$) were calculated (Hauptman & Karle, 1953) by means of the program NRC 4 forming part of the NRC Crystallographic System (Ahmed, Hall, Pippy & Huber, 1970) and adapted by Dr J. D. Lee for the ICL 1905 computer (Lee, 1971). The distribution of E 's was found to be centric hence the space group was $Pnam$.

The structure was solved by direct methods, phases being obtained for 173 reflexions with E lying between 4.295 and 1.502.

The coordinates of the heavy atoms obtained from the E map were refined by the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) in the version adapted for the ICL 1905 computer (Lee, 1971). Individual scale factors for each layer were varied during the refinement. After two cycles with isotropic temperature factors the conventional R value was 0.197. Inclusion of the six aromatic H atoms with a C-H bond distance 1.07 \AA and a further three cycles of refinement with anisotropic temperature factors gave $R=0.127$. The twelve H atoms of the methyl groups could not be located. The value of R after a final cycle

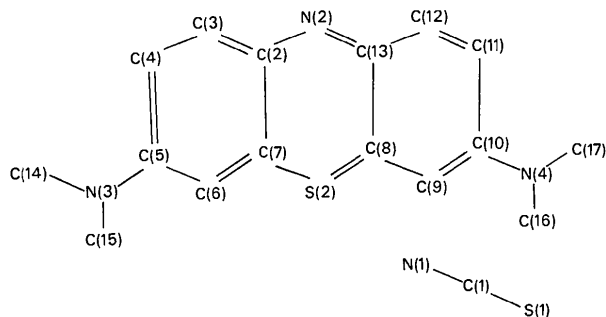


Fig. 1. Molecular structure of methylene blue showing the numbering of the heavy atoms.

Table 1. *Positional and thermal parameters*

Anisotropic temperature factors are defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11} \times 10^5$	β_{22}	β_{33}	<i>B</i>
C(1)	0.8357 (12)	0.5851 (19)	0.2500 (0)	372	684	2001	
C(2)	0.4192 (9)	0.4079 (11)	0.2500 (0)	261	280	2187	
C(3)	0.4042 (11)	0.3136 (14)	0.2500 (0)	302	479	2833	
C(4)	0.3301 (10)	0.2768 (12)	0.2500 (0)	382	281	3307	
C(5)	0.2620 (11)	0.3359 (12)	0.2500 (0)	341	389	2377	
C(6)	0.2765 (10)	0.4293 (13)	0.2500 (0)	289	319	3226	
C(7)	0.3504 (9)	0.4637 (10)	0.2500 (0)	276	247	2129	
C(8)	0.4629 (9)	0.5979 (12)	0.2500 (0)	202	360	2740	
C(9)	0.4878 (10)	0.6858 (13)	0.2500 (0)	267	396	1697	
C(10)	0.5689 (10)	0.7075 (12)	0.2500 (0)	323	441	1255	
C(11)	0.6242 (10)	0.6320 (12)	0.2500 (0)	265	398	879	
C(12)	0.5971 (10)	0.5456 (12)	0.2500 (0)	195	506	1719	
C(13)	0.5156 (10)	0.5239 (12)	0.2500 (0)	298	406	1513	
C(14)	0.1716 (9)	0.1977 (10)	0.2500 (0)				5.630
C(15)	0.1195 (10)	0.3661 (11)	0.2500 (0)				4.412
C(16)	0.5419 (10)	0.8770 (12)	0.2500 (0)				5.480
C(17)	0.6815 (9)	0.8189 (11)	0.2500 (0)				5.020
N(1)	0.8310 (11)	0.6640 (13)	0.2500 (0)	399	708	5010	
N(2)	0.4946 (9)	0.4348 (9)	0.2500 (0)	282	321	1929	
N(3)	0.1878 (9)	0.3015 (11)	0.2500 (0)	373	514	2425	
N(4)	0.5951 (8)	0.7919 (10)	0.2500 (0)	305	426	2008	
S(1)	0.8418 (6)	0.4767 (5)	0.2500 (0)	1247	575	5592	
S(2)	0.3607 (4)	0.5820 (9)	0.2500 (0)	197	273	3813	
H(3)	0.4565	0.2694	0.2500 (0)				3.000
H(4)	0.3238	0.2026	0.2500 (0)				3.000
H(6)	0.2283	0.4770	0.2500 (0)				3.000
H(9)	0.4486	0.7435	0.2500 (0)				3.000
H(11)	0.6881	0.6344	0.2500 (0)				3.000
H(12)	0.6417	0.4911	0.2500 (0)				3.000

of refinement was 0.115. Table 1 gives the final positional and thermal parameters.

Discussion of the structure

The structure comprises pairs of discrete cations $C_{16}H_{18}N_3S^+$ as shown in Fig. 2 lying in (110) planes at $z=0.25$ and $z=0.75$. These pairs form infinite columns parallel to the c axis. As expected from the optical studies the permanent dipole moments of the paired cations are in anti-parallel orientation.

A different result is reported for the chloride (Zhdanov, Zvonkova & Vorontsova, 1956) the orientation being parallel rather than anti-parallel. The distance (3.38 Å) between the planes is appropriate for the van der Waals separation of aromatic rings.

Bond distances and angles are summarized in Table 2. The linear SCN^- ions are coplanar with the aromatic rings and are not strongly bonded to single dye cations but are symmetrically surrounded by four coplanar dye cations as in Fig. 2.

Table 2. Interatomic distances (Å) and angles ($^\circ$)

(The significant figures of the standard deviations of the distances are in parentheses. The e.s.d. for the angles $\approx 1.2^\circ$.)

C(1)—N(1)	1.160 (15)	S(1)—C(1)—N(1)	179.75
C(1)—S(1)	1.592 (15)	C(3)—C(2)—C(7)	115.0
S(1)—N(1)	2.751 (15)	C(7)—C(2)—N(2)	127.5
C(2)—C(3)	1.411 (16)	C(2)—C(3)—C(4)	123.5
C(2)—C(7)	1.418 (22)	C(3)—C(4)—C(5)	119.7
C(2)—N(2)	1.329 (20)	C(4)—C(5)—C(6)	117.0
C(3)—C(4)	1.357 (15)	C(4)—C(5)—H(3)	120.9
C(5)—C(6)	1.391 (17)	C(5)—C(6)—C(7)	122.2
C(5)—N(3)	1.480 (23)	C(2)—C(7)—S(2)	119.5
C(6)—C(7)	1.341 (15)	C(6)—C(7)—C(2)	122.7
C(7)—S(2)	1.742 (16)	C(7)—S(2)—C(8)	103.45
C(8)—C(9)	1.356 (17)	C(13)—C(8)—S(2)	121.6
C(8)—C(13)	1.401 (24)	C(9)—C(8)—S(2)	115.8
C(8)—S(2)	1.736 (16)	C(8)—C(9)—C(10)	121.1
C(9)—C(10)	1.401 (16)	C(9)—C(10)—C(11)	117.0
C(10)—C(11)	1.447 (17)	C(10)—C(11)—C(12)	120.2
C(10)—N(4)	1.314 (22)	C(11)—C(12)—C(13)	122.8
C(11)—C(12)	1.346 (15)	C(12)—C(13)—C(8)	116.2
C(4)—C(5)	1.436 (17)	C(8)—C(13)—N(2)	125.6
		C(2)—N(2)—C(13)	122.4
		C(6)—C(7)—S(2)	117.8
C(12)—C(13)	1.409 (17)		
C(13)—N(2)	1.353 (22)		
C(14)—N(3)	1.546 (16)		
C(15)—N(3)	1.489 (15)		
C(16)—N(4)	1.536 (14)		
C(17)—N(4)	1.508 (14)		

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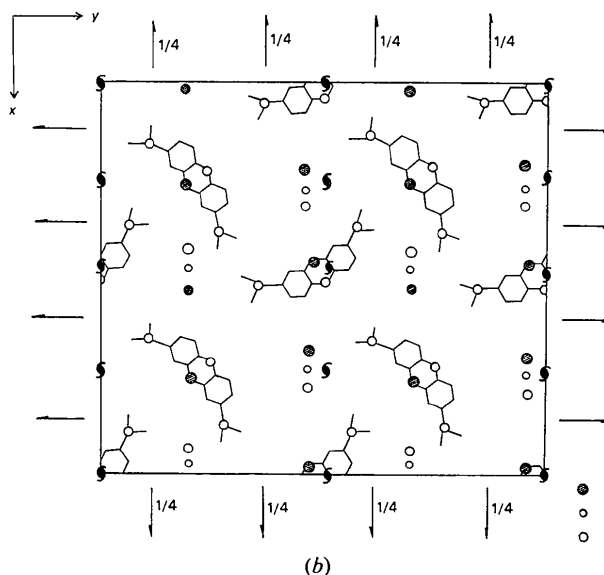
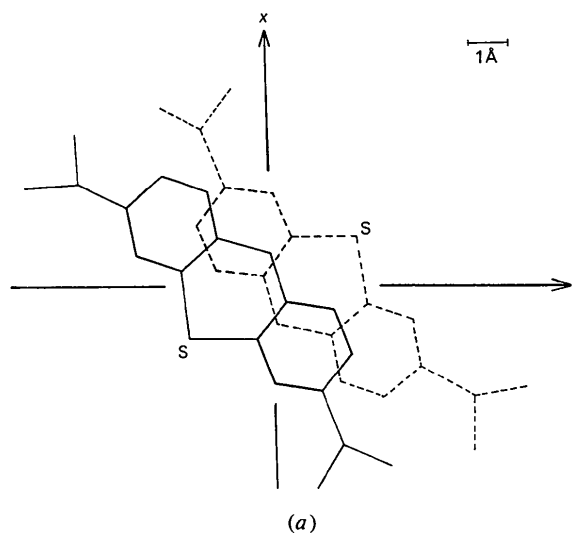


Fig. 2. (a) View down z showing the orientation of a pair of methylene blue cations. (b) View down z of four unit cells showing the heavy atoms at $z = \frac{1}{4}$.

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