Table 1. *Fractional atomic coordinates* (×10⁴) *of the non-*H *atoms for models* (1) *and* (2) *and equivalent isotropic thermal parameters* (Å² ×10³) *for model* (1) *with e.s.d.'s in parentheses*

Model (1) coordinates correspond to equivalent positions as listed in *International Tables for X-ray Crystallography* (1952); for model (2) one must change $\frac{1}{4}-x, \frac{1}{4}+y, \frac{1}{4}-z$ to $\frac{1}{4}+x, \frac{1}{4}+y, \frac{3}{4}+z$, *etc.*

	x	y	z (1)	z (2)	$\lvert\Delta z\rvert/\sigma_z(1)$	U_{eq}*
O(1)	3027 (2)	5012 (2)	0	0	—	80 (2)
C(2)	3673 (2)	5031 (2)	−1416 (7)	1429 (7)	1·9	49 (2)
O(3)	4209 (2)	4501 (1)	−1948 (7)	1946 (7)	0·3	49 (1)
C(4)	4967 (2)	4633 (2)	−3662 (6)	3674 (6)	2·0	40 (2)
C(5)	4009 (2)	5582 (1)	−2787 (8)	2802 (8)	1·9	49 (2)
C(6)	4606 (3)	4309 (2)	−5760 (9)	5774 (9)	1·6	65 (2)

* $U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha + 2U_{12}aba^*b^*\cos\gamma]$.

Table 2. *Bond distances* (Å) *and valence angles* (°) *with e.s.d.'s in parentheses for models* (1) *and* (2)

	(1)	(2)	$\Delta l/[(\sigma_{l_1})^2 + (\sigma_{l_2})^2]^{1/2}$
O(1)—C(2)	1·206 (4)	1·211 (4)	0·88
C(2)—O(3)	1·343 (5)	1·343 (4)	0·00
O(3)—C(4)	1·463 (5)	1·469 (5)	0·15
C(4)—C(4ⁱ)	1·526 (6)	1·527 (5)	0·13
C(4ⁱ)—C(5)	1·506 (4)	1·507 (4)	0·18
C(5)—C(2)	1·482 (5)	1·482 (5)	0·00
C(4)—C(6)	1·517 (6)	1·518 (6)	0·12
O(1)—C(2)—O(3)	120·6 (4)	120·2 (3)	
O(1)—C(2)—C(5)	129·3 (4)	129·5 (3)	
O(3)—C(2)—C(5)	110·0 (3)	110·3 (3)	
C(2)—O(3)—C(4)	111·7 (3)	111·4 (3)	
O(3)—C(4)—C(4ⁱ)	103·0 (3)	103·0 (2)	
O(3)—C(4)—C(5ⁱ)	107·1 (3)	106·9 (3)	
O(3)—C(4)—C(6)	107·8 (3)	108·1 (2)	
C(6)—C(4)—C(4ⁱ)	117·4 (3)	117·4 (3)	
C(6)—C(4)—C(5ⁱ)	116·2 (3)	116·1 (3)	
C(4)—C(4ⁱ)—C(5)	104·2 (2)	104·1 (2)	
C(4ⁱ)—C(5)—C(2)	103·5 (2)	103·5 (2)	

Symmetry code: (i) $1-x, 1-y, z$.

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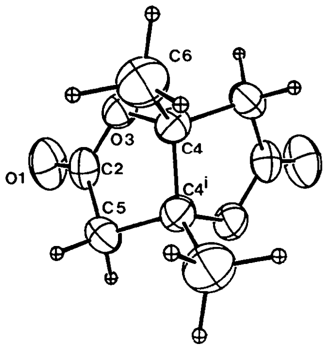

Fig. 1. Perspective view of the molecule along [001]. Thermal ellipsoids of the non-H atoms are drawn at the 50% probability level with *ORTEP*II (Johnson, 1971).

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Acta Cryst. (1984). C**40**, 500–502

3,3′,5,5′-Tetrabromophenolsulfonphthalein (Bromphenol Blue),* $C_{19}H_{10}Br_4O_5S$

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Abstract. $M_r = 670{\cdot}02$, monoclinic, $C2/c$, $a = 31{\cdot}003\ (4)$, $b = 11{\cdot}037\ (2)$, $c = 21{\cdot}183\ (3)$ Å, $\beta = 143{\cdot}7\ (1)°$, $V = 4291{\cdot}2$ Å³, $D_m = 2{\cdot}06$, $D_x = 2{\cdot}07$ Mg m⁻³, $Z = 8$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 7{\cdot}45$ mm⁻¹, $F(000) = 2560$, $T = 293$ K, $R = 0{\cdot}061$ for 1697 observed reflections. The bromphenol blue molecule consists essentially of three planar groupings: the sulfonphthalein ring system and two dibromophenol rings attached to the tetrahedral C atom of the five-membered ring of the sulfonphthalein system. The dibromophenol rings are inclined with respect to each

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* 4,4′-(3*H*-2,1-Benzoxathiol-3-ylidene)bis[2,6-dibromophenol] *S*,*S*-dioxide.

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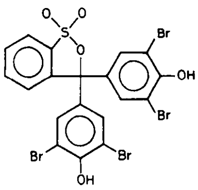
other at 73° whereas they make angles of 85 and 68° with respect to the sulfonphthalein system. The molecules aggregate into helical columns with the non-polar regions of the molecules in the interior and the polar regions on the surface. The columns are held together by a network of hydrogen bonds.

Introduction. Phenolsulfonphthalein dyes like bromphenol red (BPR) and bromphenol blue (BPB) are extensively used as indicators in biochemical studies on proteins (Weber & Osborn, 1969). We have been attempting to use these dyes for characterizing a possible additional binding site in lysozyme (Krishna Murthy, Vijayan & Gurnani, 1981). It is of interest in this context to determine the molecular geometry of these dyes, and here we report the crystal structure of bromphenol blue (I).



(I)

Experimental. Crystals (Sigma Chemical Co.) grown by slow evaporation of a solution in a mixture of acetone and acetic acid. Density by flotation in a mixture of bromoform and benzene. Unit-cell dimensions initially determined from X-ray diffraction photographs and subsequently refined using 19 reflections in the θ range 12 to 19°. Crystal $0\cdot1 \times 0\cdot25 \times 0\cdot38$ mm. CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta_{\max} = 23°$, ω–2θ scan, h 0 to 34, k 0 to 12, l −23 to 23. Two standard reflections, variations less than 6%. 3053 reflections measured; 1697 unique with $I > 2\sigma(I)$ used for structure solution and refinement. Data corrected for absorption using program *SHELX* (Sheldrick, 1976); max. and min. values of transmission factors 0·49 and 0·18. $R_{\rm int} = 0\cdot033$ for $0kl$ and $0k\bar{l}$ reflections. Structure solved by heavy-atom method and refined using the full-matrix least-squares program *SHELX* (which uses F magnitudes). Non-hydrogen atoms assigned anisotropic thermal parameters. Eight H atoms, with positions determined from geometrical considerations, included in the final SFLS cycles; their positional coordinates and isotropic temperature factors, assumed to be the same as the equivalent isotropic temperature factors (Hamilton, 1959) of the C atoms to which they are attached, were not refined. Refinement converged at $R = 0\cdot061$, $wR = 0\cdot063$, $S = 1\cdot327$, $(\Delta/\sigma)_{\max} = 0\cdot008$; $w = 1\cdot25/[\sigma(|F_o|)^2 + 0\cdot00001 \times |F_o|^2]$. Form factors in *SHELX*. The most prominent feature in the final $\Delta\rho$ map was a peak of height $2\cdot2$ e Å^{-3} in the neighbourhood of a Br atom; this did not make chemical sense and may be due to ripples or insufficient allowance for anisotropic thermal vibrations; remaining features had density varying between $-1\cdot2$ and $0\cdot9$ e Å^{-3}; most of the strong features were again in the neighbourhood of Br atoms.

Discussion. The final positional parameters and the equivalent isotropic temperature factors of the non-hydrogen atoms are given in Table 1.*

A perspective view of the molecule is given in Fig. 1. The molecule consists essentially of three planar groupings: the sulfonphthalein ring system (*A* in Fig. 1) and two dibromophenol rings (*B* and *C* in Fig. 1) attached to the tetrahedral C atom in the five-membered ring of the sulfonphthalein system. All the atoms except O(3) in the sulfonphthalein system form a plane. O(3) deviates from this plane towards the side of C(2) by 0·28 (1) Å. The two dibromophenol rings lie on opposite sides of the plane. The geometry of the molecule is best described in terms of the orientations of the dibromophenol rings with respect to the sulfonphthalein system. Dibromophenol rings *B* and *C*, which

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* (*Hamilton,* 1959) *of the non-hydrogen atoms*

Estimated standard deviations are given in parentheses.

	x	y	z	$B_{\rm eq}$(Å^2)
Br(1)	4233 (1)	8517 (1)	2272 (1)	4·5 (1)
Br(2)	1320 (1)	9600 (2)	−572 (1)	5·5 (1)
Br(3)	4132 (1)	2477 (2)	1965 (2)	5·8 (1)
Br(4)	4738 (1)	3141 (2)	5267 (1)	6·4 (1)
S(1)	1324 (2)	4097 (3)	123 (3)	2·8 (1)
C(1)	2500 (6)	5357 (11)	1471 (9)	1·9 (5)
C(2)	2613 (6)	6619 (10)	1286 (9)	1·7 (5)
C(3)	3268 (6)	6913 (12)	1786 (10)	2·4 (5)
C(4)	3342 (7)	8056 (13)	1585 (10)	2·9 (5)
C(5)	2775 (7)	8842 (11)	893 (10)	2·7 (6)
C(6)	2115 (7)	8501 (12)	396 (10)	2·8 (5)
C(7)	2041 (6)	7412 (11)	607 (9)	2·3 (5)
C(8)	3151 (7)	4526 (11)	2206 (10)	2·3 (5)
C(9)	3323 (7)	4008 (11)	1831 (11)	2·8 (5)
C(10)	3909 (8)	3251 (12)	2491 (12)	3·7 (6)
C(11)	4364 (8)	3009 (14)	3525 (11)	3·9 (6)
C(12)	4183 (7)	3538 (12)	3893 (10)	3·1 (5)
C(13)	3588 (7)	4285 (11)	3247 (10)	2·6 (5)
C(14)	2181 (7)	5481 (12)	1753 (10)	2·5 (5)
C(15)	2441 (7)	6149 (11)	2558 (10)	3·0 (6)
C(16)	2077 (8)	6092 (12)	2708 (11)	3·4 (6)
C(17)	1469 (9)	5431 (14)	2057 (14)	4·3 (7)
C(18)	1178 (8)	4760 (13)	1224 (12)	3·6 (6)
C(19)	1552 (7)	4835 (10)	1088 (10)	2·3 (5)
O(1)	2820 (6)	9950 (7)	653 (7)	3·8 (4)
O(2)	4952 (6)	2266 (11)	4186 (8)	6·3 (5)
O(3)	1914 (4)	4797 (7)	410 (6)	2·2 (3)
O(4)	1499 (6)	2850 (8)	350 (8)	4·4 (5)
O(5)	633 (5)	4407 (10)	−927 (7)	4·9 (5)

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* List of structure factors, anisotropic thermal parameters, bond lengths and angles and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39023 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

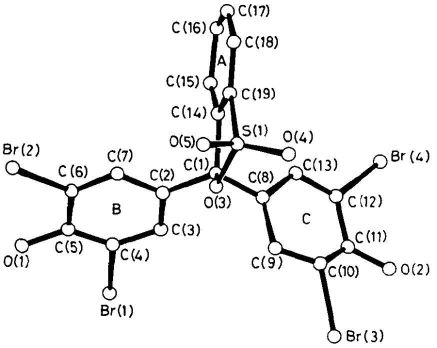

Fig. 1. A perspective view of the molecule.

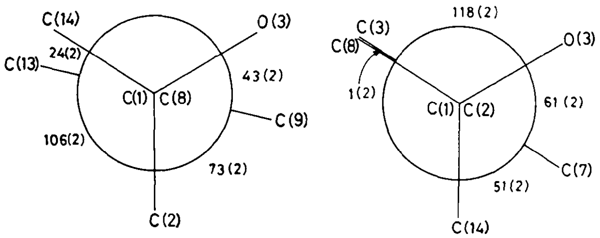

Fig. 2. Conformation of the molecule about the C(1)—C(2) and C(1)—C(8) bonds. The relevant torsion angles (°) are indicated.

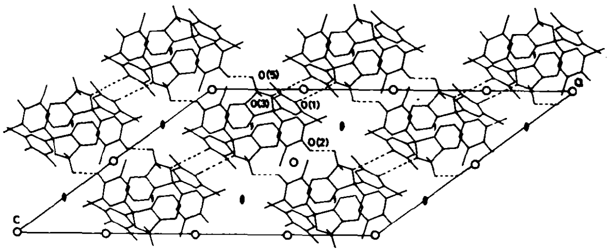

Fig. 3. The crystal structure as seen along the *b* axis. The broken lines represent hydrogen bonds. Only atoms involved in hydrogen bonds are numbered.

are inclined with respect to each other at 73°, are oriented with respect to the sulfonphthalein system at 85 and 68° respectively. The dispositions of the rings are controlled by rotations about the C(1)—C(2) and C(1)—C(8) single bonds. The conformations about these bonds are given in Fig. 2. The orientations of the two rings are clearly different. One lies in a plane defined by C(2), C(1) and C(8) while the other lies approximately in the plane of C(14), C(1) and C(8).

The crystal structure of the compound is shown in Fig. 3. The molecules aggregate into helical columns around 2_1 screw axes. These columns are presumably stabilized by van der Waals interactions. It is interesting to note that the interior of each column is made up of the non-polar regions of the molecules whereas the polar regions consisting of O and Br atoms are distributed on its surface. This arrangement is reminiscent of hydrophobic association in macromolecular systems. The columns which run parallel to the *b* axis are held together by a network of O—H···O hydrogen bonds. The hydroxyl O atoms belonging to the dibromophenol rings are the donors in the two crystallographically non-equivalent hydrogen bonds. The acceptor atom in one of the hydrogen bonds is the ring O atom O(3) while that in the other is O(5). The O(1)···O(3) and O(2)···O(5) distances are 2·97 (3) and 2·96 (3) Å respectively. The dimerization of the molecules across inversion centres facilitated by the O(1)···O(3) hydrogen bond and its symmetry equivalent is somewhat similar to that found in the crystal structures of some carboxylic acids (Leiserowitz, 1976).

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The Structure of *transoid*-(1*RS*, 3*SR*, 6*RS*, 9*RS*)-7-Hydroxyimino-9-methyl-1-(2-methylpropyl)tricyclo[4.2.1.$0^{3,9}$]nonan-8-one, $C_{14}H_{21}NO_2$

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Abstract. $M_r = 235{\cdot}33$, monoclinic, $P2_1/c$, $a = 7{\cdot}3367\,(9)$, $b = 7{\cdot}9791\,(9)$, $c = 23{\cdot}298\,(2)$ Å, $\beta = 103{\cdot}207\,(7)°$, $V = 1327{\cdot}8\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}172\,(3)$, $D_x = 1{\cdot}177$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}732$ cm^{-1}, $F(000) = 128$, $T = 298$ K, $R = 0{\cdot}0647$ for 1254 independent reflections with $F^2 > 3\sigma(F^2)$. The crystal structure determines the configuration of an intermediate in an ongoing formal total