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N-(*o*-Methoxyphenyl)phenothiazine

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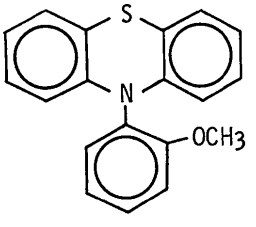
N-(*o*-Methoxyphenyl)phenothiazine, $C_{19}H_{15}NOS$, is monoclinic, $P2_1/a$, $Z=4$; M.W. 305·40; $a=13·379$ (1), $b=14·043$ (1), $c=8·960$ (1) Å, $\beta=115·42$ (1)°; $D_x=1·334$, $D_m=1·32$ g cm^{-3} (by flotation); λ(Cu $K\alpha$)$=1·5418$ Å, μ(Cu $K\alpha$)$=18·38$ cm^{-1}. Final residual $R=0·039$.

Introduction

Samples of *N*-(*o*-methoxyphenyl)phenothiazine (I) were obtained through the courtesy of Dr Edward R. Biehl of the Chemistry Department of Southern Methodist University. Single crystals in the form of clear prisms were grown from a trichloroethylene solution. The unit-cell parameters were obtained from the measurement of '+' and '−' 2θ values of 55 reflections. The space group, $P2_1/a$, was deduced from systematic absences ($h0l$ absent with h odd and $0k0$ absent with k odd). The intensity data were collected on a Nonius CAD-4 automatic diffractometer with a crystal approximately $0·17\times0·14\times0·38$ mm mounted along the c axis. A $\theta/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 3126 independent reflections with 2θ values below 150°, of which 2558 were considered as observed by the criterion $I>2·0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors; no absorption corrections were applied.



(I)

The structure was determined by the heavy-atom method. The refinement was carried out by the full-

Table 1. *Fractional atomic coordinates* ($\times10^4$, *except* $\times10^3$ *for hydrogens*) *and thermal parameters*

The estimated standard deviations are given in parentheses and refer to the last positions of respective values. The expression for the temperature factor exponent consistent with B values in Å^2 is:

$$-\tfrac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23}).$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	1031 (0)	2282 (0)	259 (1)	5·33 (2)	2·96 (1)	4·94 (2)	−0·57 (1)	2·26 (1)	−0·85 (1)
O	3521 (1)	4235 (1)	4858 (2)	4·05 (5)	4·51 (6)	4·45 (6)	0·77 (4)	0·89 (4)	0·52 (5)
N	1627 (1)	4202 (1)	2031 (2)	3·50 (5)	3·14 (5)	3·09 (5)	−0·49 (4)	1·41 (4)	−0·50 (4)
C(1)	2322 (2)	4854 (1)	123 (2)	5·20 (9)	3·64 (7)	4·40 (8)	−0·32 (6)	2·68 (7)	−0·19 (6)
C(2)	2508 (2)	4773 (2)	−1279 (2)	6·04 (10)	4·83 (9)	4·87 (9)	−0·16 (8)	3·28 (8)	0·23 (7)
C(3)	2190 (2)	3961 (2)	−2243 (2)	5·82 (10)	6·11 (11)	4·07 (8)	0·15 (8)	2·77 (8)	−0·32 (8)
C(4)	1698 (2)	3230 (1)	−1785 (2)	4·80 (8)	5·05 (9)	3·96 (7)	−0·20 (7)	1·95 (7)	−1·14 (7)
C(6)	−445 (1)	2322 (1)	1591 (2)	3·73 (7)	4·10 (8)	4·47 (8)	−0·76 (6)	0·75 (6)	0·33 (6)
C(7)	−863 (2)	2634 (2)	2670 (3)	3·80 (8)	5·60 (10)	5·40 (9)	−0·88 (7)	1·85 (7)	0·93 (8)
C(8)	−464 (2)	3470 (2)	3517 (3)	4·80 (9)	5·71 (11)	5·45 (10)	−0·51 (8)	2·84 (8)	0·29 (8)
C(9)	338 (2)	3997 (1)	3278 (2)	4·45 (8)	4·22 (8)	4·31 (8)	−0·32 (6)	2·31 (7)	−0·08 (6)
C(11)	1820 (1)	4122 (1)	602 (2)	3·21 (6)	3·18 (6)	3·01 (6)	0·27 (5)	1·08 (5)	−0·01 (5)
C(12)	1529 (1)	3291 (1)	−361 (2)	3·38 (6)	3·61 (7)	3·29 (6)	0·16 (5)	1·11 (5)	−0·35 (5)
C(13)	393 (1)	2815 (1)	1404 (2)	3·38 (7)	3·23 (7)	3·10 (6)	−0·12 (5)	0·67 (5)	0·37 (5)
C(14)	780 (1)	3681 (1)	2229 (2)	3·01 (5)	3·15 (6)	2·98 (6)	−0·07 (5)	0·81 (5)	0·37 (5)
C(15)	1983 (1)	5066 (1)	2968 (2)	3·36 (6)	2·96 (6)	2·98 (6)	−0·36 (5)	1·42 (5)	−0·31 (5)
C(16)	1366 (1)	5890 (1)	2434 (2)	4·11 (7)	3·45 (7)	4·10 (7)	0·33 (6)	1·53 (6)	0·09 (6)
C(17)	1698 (2)	6728 (1)	3334 (3)	5·81 (10)	3·14 (7)	5·50 (9)	0·32 (6)	2·87 (8)	−0·19 (6)
C(18)	2650 (2)	6728 (1)	4779 (2)	6·59 (11)	3·64 (7)	4·97 (9)	−1·35 (8)	3·18 (8)	−1·29 (7)
C(19)	3278 (2)	5912 (1)	5337 (2)	4·63 (8)	4·86 (9)	3·32 (7)	−1·35 (7)	1·38 (6)	−0·75 (6)
C(20)	2954 (1)	5071 (1)	4433 (2)	3·26 (6)	3·65 (7)	3·11 (6)	−0·40 (5)	1·51 (5)	0·04 (5)
C(21)	4526 (2)	4211 (2)	6342 (3)	4·17 (9)	7·55 (14)	5·09 (10)	0·69 (8)	0·98 (7)	2·01 (10)

Table 1 (*cont.*)

	x	*y*	*z*	*B*
H(1)	249 (2)	544 (2)	73 (3)	3·5 (5)
H(2)	286 (2)	534 (2)	−159 (3)	4·0 (6)
H(3)	234 (2)	386 (2)	−323 (3)	4·1 (6)
H(4)	151 (2)	262 (2)	−242 (3)	3·5 (5)
H(6)	−68 (2)	176 (1)	94 (2)	3·0 (5)
H(7)	−144 (2)	227 (2)	279 (3)	4·6 (6)
H(8)	−80 (2)	370 (2)	429 (3)	3·7 (5)
H(9)	59 (2)	460 (2)	382 (3)	3·4 (5)
H(16)	64 (2)	586 (2)	142 (3)	4·1 (6)
H(17)	130 (2)	731 (2)	288 (3)	4·1 (6)
H(18)	289 (2)	732 (2)	536 (3)	4·7 (6)
H(19)	394 (2)	589 (2)	639 (3)	4·5 (6)
H(21)1	440 (2)	431 (2)	736 (3)	4·9 (6)
H(21)2	501 (2)	476 (2)	638 (3)	3·8 (5)
H(21)3	480 (2)	362 (2)	634 (3)	6·1 (7)

matrix least-squares method with isotropic temperature factors and the block-diagonal least-squares method with anisotropic temperature factors. All the hydrogen atoms were located on a difference Fourier synthesis. The isotropic temperature factors were used for hydrogen atoms in the final refinements. The weight of the reflection was assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was calculated from counting statistics. The quantity $\sum w(||F_o|-|F_c||)^2$ was minimized. The final R $(\sum||F_o|-|F_c||/\sum|F_o|)$ was 0·039. The magnitude of $[\sum w(F_o-F_c)^2/(m-n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 1·75. The atomic scattering factors used for sulfur, oxygen, nitrogen, and carbon atoms were those from *International Tables for X-ray Crystallography* (1962), and for hydrogen, the values given by Stewart, Davidson & Simpson (1965).The final positional and thermal parameters are given in Table 1.*

The computer programs used in this analysis were the *ORFLS* program (Busing, Martin & Levy, 1962), the block-diagonal least-squares program (Shiono, 1971), the Zalkin Fourier synthesis program modified by Dr R. Shiono of the University of Pittsburgh, and a number of structure interpretation programs (Shiono, 1971; Chu, 1973). All calculations were carried out on a CDC CYBER 72 computer in the Computing Laboratory at Southern Methodist University.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31654 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The determination of this crystal structure is a continuation of studies on a series of phenothiazine derivatives. The mechanism of bromination of *N*-substituted phenothiazines has been studied using *N*-alkyl- and *N*-arylphenothiazines. It has been found that the bromination occurs on the phenothiazine ring system with *N*-alkylphenothiazines and on the phenyl ring with *N*-phenylphenothiazines (Biehl, Chiou, Keepers, Kennard & Reeves, 1975; Biehl, 1975). This indicates that the charge delocalization occurs in the phenyl ring of *N*-phenylphenothiazines and that there is no mutual electronic interaction between the two ring systems. The purpose of these studies is to explain the difference in the reactivity of the different *N*-substituted phenothiazines.

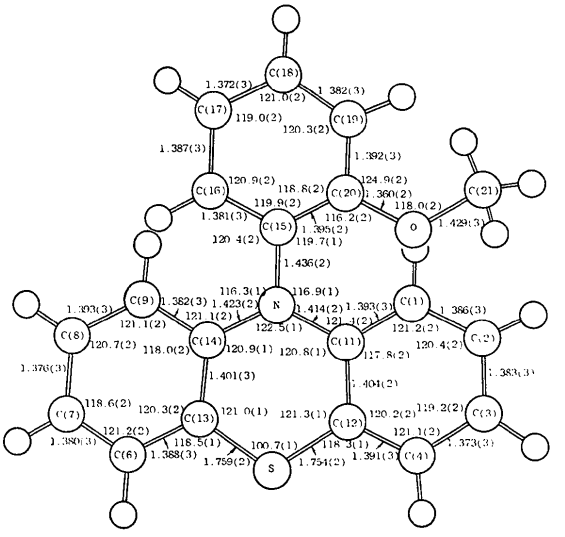


Fig. 2. Bond lengths (Å) and bond angles (°) of *N*-(*o*-methoxyphenyl)phenothiazine with e.s.d.'s in parentheses.

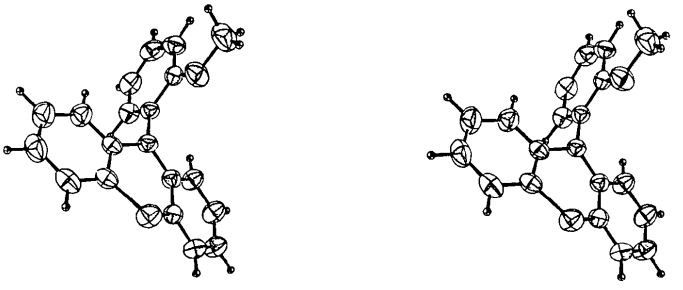


Fig. 1. Stereoscopic drawing of one molecule of *N*-(*o*-methoxyphenyl)phenothiazine.

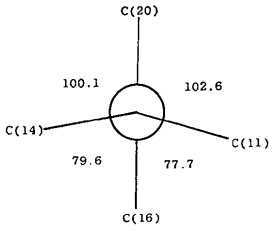


Fig. 3. The torsion angles (°) about the N–C(15) bond in *N*-(*o*-methoxyphenyl)phenothiazine.

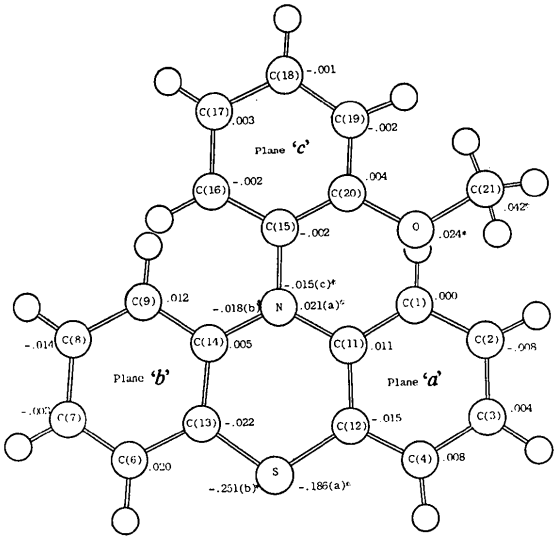


Fig. 4. Deviations from least-squares planes in Å units. The equations for the planes are:

Plane '*a*' $-5{\cdot}668x+7{\cdot}089y-4{\cdot}456z=1{\cdot}169$
Plane '*b*' $-9{\cdot}867x+5{\cdot}594y-1{\cdot}575z=0{\cdot}405$
Plane '*c*' $11{\cdot}018x+3{\cdot}518y-7{\cdot}286z=1{\cdot}806$.

Dihedral angles between the least-squares planes: '*a*' and '*b*' 157·5, '*a*' and '*c*' 103·3, '*b*' and '*c*' 99·2°. An asterisk indicates atoms excluded from the calculation of the least-squares planes. The lettering in parentheses indicates the deviation from that plane.

A stereoscopic view of the configuration of an *N*-(*o*-methoxyphenyl)phenothiazine molecule is shown in Fig. 1 (Johnson, 1965). The identification of the atoms and the bond lengths and bond angles with their standard deviations are shown in Fig. 2. The mean value of the two C–S bond lengths is 1·757 (2) Å, and the C–S–C bond angle is 100·7 (1)°. The mean value of the two C–N bond lengths within the central ring is 1·419 (2) Å, and the C–N–C bond angle within the central ring is 122·5 (1)°. The folding angle between the least-squares planes of the two benzene rings is 157·5°. Both the C–S and C–N bond lengths are in good agreement with those of other phenothiazine derivatives (Chu & van der Helm, 1975). However, the C–S–C and C–N–C bond angles agree with those found in phenothiazine (Bell, Blount, Briscoe & Freeman, 1968) and methoxypromazine (Marsau & Gauthier, 1973) since they all have similar folding angles. In all other *N*-substituted phenothiazines, the *N*-substituents are extended to the convex side of the phenothiazine ring, the folding angles as well as the C–S–C and C–N–C bond angles are smaller than those in phenothiazine (Chu & van der Helm, 1975). The reason for the large folding angle in *N*-(*o*-methoxyphenyl)phenothiazine is that the *N*-phenyl substituent extends both to the concave and convex side of the tricyclic ring. This is illustrated by the torsion angle about the N–C(15) bond in Fig. 3. Nevertheless, all C–N–C angles are close to 120°, indicating that the three N–C bonds around the nitrogen atom are approximately planar in configuration.

The C–H bond lengths range from 0·91 to 1·03 Å with a mean value of 0·98 Å and a r.m.s. standard deviation of 0·02 Å. The C–C–H bond angles involving the benzene rings range from 115 to 124° with a mean value of 120°, and the O–C–H and H–C–H bond angles involving tetrahedral carbon atoms range from 103 to 117° with a mean value of 110°. The r.m.s. standard deviation of these bond angles is 2°.

The phenyl ring is planar and is nearly perpendicular to the central ring of the phenothiazine. The dihedral

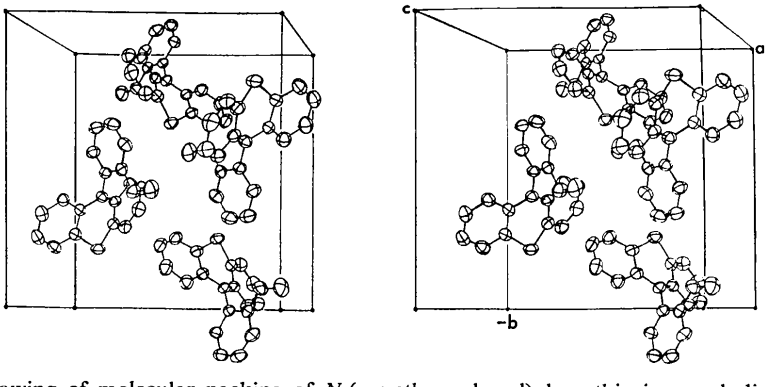


Fig. 5. Stereoscopic drawing of molecular packing of *N*-(*o*-methoxyphenyl)phenothiazine, excluding hydrogen atoms, in the unit cell.

angle between the least-squares planes of the phenyl ring and the central ring [C(11), C(12), C(13) and C(14)] is 91·1°. This can be seen from the torsion angle about the N–C(15) bond in Fig. 3. The O and C(21) atoms of the methoxy group are nearly coplanar with the phenyl ring. The deviations of the atoms from the two benzene rings and the phenyl ring are shown in Fig. 4.

The packing of the molecules in the crystal is shown in the stereoscopic drawing in Fig. 5. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distances are 3·58 and 3·59 Å between O and C(7) and between C(2) and C(8) respectively.

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The Crystal Structure of $Bi_{12}O_{15}Cl_6$

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The structure of $Bi_{12}O_{15}Cl_6$ has been determined by symbolic addition and Fourier methods and refined to $R=0{\cdot}094$ for 1083 independent counter intensities. The crystals are orthorhombic, space group *Pnma*, with $a=40{\cdot}532$ (8), $b=3{\cdot}8688$ (4), $c=15{\cdot}487$ (3) Å, $Z=4$. The Bi atoms are of two types, one coordinated by four O atoms, the other by five. The Bi–O distances lie between 2·03 and 2·69 Å. The fourfold coordination can be described as a square pyramid with the lone pair of electrons of Bi at its apex, and the five-coordination as an octahedron with the lone pair at one corner. The coordination polyhedra are linked by sharing edges and corners to form infinite layers parallel to [010]. Between the nets are parallel trigonal prisms of Cl^- ions.

Introduction

The present study is part of an investigation of the systems Bi_2O_3–BiOCl and Bi_2O_3–BiOF–BiOCl. The intention is to prepare compounds of complex compositions but predictable structures. The investigation was started with the latter system where the structure of $Bi_6O_7FCl_3$ has been reported (Hopfgarten, 1975).

Experimental

For the preparation of $Bi_{12}O_{15}Cl_6$ a mixture of Bi_2O_3 and BiOCl in the mole ratio 1:2 was heated in a sealed gold capsule for 24 h at 860 °C. The product consisted of colourless needle-shaped crystals, elongated along **b**. Weissenberg photographs indicated orthorhombic symmetry with the systematic absences $0kl$ and $hk0$ for $k+l$ and h odd respectively, indicating the space groups *Pnma* (No. 62) or $Pn2_1a$ (No. 33).† The photographs also showed that the $Bi_{12}O_{15}Cl_6$ modification prepared had an *OD* structure, since there were intensity streaks along [100]. Several crystals prepared at different temperatures were tried. All the photographs showed streaks with more or less pronounced maxima corresponding to disorder along the [100] direction. The intensity distribution on the

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† Orientation different from that given in *International Tables for X-ray Crystallography* (1965).