eine Bindungslänge von 1,84 Å. Der mittlere P—C-Abstand im $(C_6H_{11})_4P_2$-Molekül liegt damit sowohl etwas über dem Paulingschen Wert als auch über dem typischen P—C-Abstand von 1,83 Å in aliphatischen Verbindungen (Corbridge, 1974), ist aber in guter Übereinstimmung mit dem P—C-Abstand in Verbindungen, in denen Phosphor an eine Cyclohexylgruppe gebunden ist (Tabelle 5).

Die Bindungswinkel am dreibindigen P-Atom sollten bei einer sp^3-Hybridisierung auf Grund der Platzbeanspruchung des freien Elektronenpaars weniger als 109,5° betragen. Die experimentell ermittelten Werte entsprechen dieser Erwartung (Tabelle 4). Bei einer Betrachtung der P—P—C-Winkel fällt auf, dass an beiden P-Atomen in guter Übereinstimmung jeweils ein kleinerer (Mittelwert 101,2°) und ein grösserer Winkel (Mittelwert 107,7°) vorliegen. Dabei sind die kleineren Winkel den angenähert parallel zueinander und senkrecht zur P—P-Achse ausgerichteten Cyclohexylgruppen, die auf Lücke stehen, zugeordnet. Die Winkelaufweitung bei den beiden anderen Cyclohexylgruppen ist auf die intramolekulare Abstossung zwischen den übereinander stehenden Ringen zurückzuführen.

Kristallstruktur

Fig. 5 zeigt die Anordnung der Moleküle im Kristall. Die aus Tabelle 6 zu entnehmenden intermolekularen H—H-Abstände gehen bis auf Werte hinunter, wie sie auch zwischen den verschiedenen Cyclohexylgruppen des gleichen Moleküls auftreten. Dies weist darauf hin, dass zu der beschriebenen Molekülgeometrie auch durch die Packung im Kristallgitter hervorgerufene sterische Effekte beitragen.
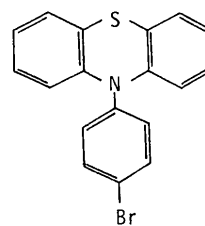
Die recht dichte Packung spiegelt sich in niedrigen isotropen Temperaturfaktoren wider. Die B_{iso}-Werte der P-Atome liegen bei 1,29 und 1,39 Å² und die der C-Atome zwischen 1,59 und 3,99 Å².

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N-(p-Bromophenyl)phenothiazine

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$C_{18}H_{12}NSBr$, monoclinic, $P2_1/c$, $Z = 8$, $M_r = 354\cdot26$, $a = 9\cdot571$ (1), $b = 24\cdot154$ (3), $c = 13\cdot011$ (1) Å, $\beta = 91\cdot63$ (1)°, $D_x = 1\cdot565$, $D_m = 1\cdot55$ g cm⁻³ (by flotation), λ(Cu $K\alpha$) = $1\cdot5418$ Å, μ(Cu $K\alpha$) = $52\cdot66$ cm⁻¹. Final residual $R = 0\cdot040$. The two crystallographically independent molecules have the same conformation with the p-bromophenyl group planar.

Introduction

Samples of the compound (I) were obtained through the courtesy of Dr Edward R. Biehl, Chemistry Department, Southern Methodist University. Single crystals in the form of clear prisms were grown from a mixed acetone, methanol and trichloroethylene solution. The unit-cell parameters were obtained

from the measurement of '+' and '−' 2θ values of 32 reflections. The space group, $P2_1/c$, was deduced from systematic absences ($h0l$ absent with l odd and $0k0$ absent with k odd). The intensity data were collected on a Datex–Syntex automatic diffractometer at the Biophysics and Biochemistry Department, Texas A. & M. University, College Station, Texas. A crystal approximately 0·69 × 0·12 × 0·12 mm, was used for the data collection. A θ/2θ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 3083 independent reflections with 2θ values below 100°, of which 2642 reflections 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, and no absorption corrections were applied.

(1)

The structure was determined by the heavy-atom method. There are two crystallographically independent molecules in one asymmetric unit of the crystal. The refinement was carried out by the full-matrix least-squares method with isotropic temperature factors and the block-diagonal least-squares method with aniso-

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *and B values for* H

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

	x	y	z		x	y	z
Molecule A				Molecule B			
Br	2962 (1)	386 (0)	−2464 (0)	Br'	−1598 (1)	4446 (0)	10216 (0)
S	3166 (1)	2285 (1)	3477 (1)	S'	−1856 (1)	2873 (0)	3892 (1)
N	3804 (3)	1599 (1)	1623 (2)	N'	−1297 (3)	3456 (1)	5936 (2)
C(1)	3881 (5)	717 (2)	2582 (3)	C'(1)	−1440 (4)	4381 (2)	5171 (3)
C(2)	3826 (5)	439 (2)	3503 (3)	C'(2)	−1547 (5)	4726 (2)	4301 (3)
C(3)	3702 (5)	707 (2)	4420 (3)	C'(3)	−1605 (5)	4496 (2)	3320 (3)
C(4)	3537 (4)	1279 (2)	4397 (3)	C'(4)	−1622 (4)	3931 (2)	3211 (3)
C(6)	4833 (5)	3011 (2)	2479 (4)	C'(6)	−196 (5)	2102 (2)	4842 (3)
C(7)	5577 (5)	3197 (2)	1664 (4)	C'(7)	473 (5)	1869 (2)	5663 (4)
C(8)	5771 (5)	2856 (2)	845 (4)	C'(8)	600 (5)	2152 (2)	6584 (3)
C(9)	5204 (5)	2324 (2)	817 (3)	C'(9)	35 (4)	2682 (2)	6677 (3)
C(11)	3742 (4)	1296 (2)	2584 (3)	C'(11)	−1435 (4)	3809 (2)	5064 (3)
C(12)	3541 (4)	1570 (2)	3475 (3)	C'(12)	−1583 (4)	3590 (2)	4073 (3)
C(13)	4220 (4)	2491 (2)	2465 (3)	C'(13)	−811 (4)	2621 (2)	4928 (3)
C(14)	4411 (4)	2139 (2)	1623 (3)	C'(14)	−692 (4)	2920 (2)	5851 (3)
C(15)	3661 (4)	1318 (2)	653 (3)	C'(15)	−1327 (4)	3698 (2)	6938 (3)
C(16)	2444 (4)	1384 (2)	83 (3)	C'(16)	−2510 (4)	3632 (2)	7495 (3)
C(17)	2236 (4)	1107 (2)	−839 (3)	C'(17)	−2598 (4)	3857 (2)	8471 (3)
C(18)	3275 (5)	771 (2)	−1189 (3)	C'(18)	−1485 (4)	4145 (2)	8873 (3)
C(19)	4499 (5)	711 (2)	−652 (3)	C'(19)	−274 (4)	4207 (2)	8338 (3)
C(20)	4693 (4)	978 (2)	275 (3)	C'(20)	−194 (4)	3985 (2)	7361 (3)

	x	y	z	B		x	y	z	B
Molecule A					Molecule B				
H(1)	406 (4)	53 (2)	187 (3)	7·6 (12)	H'(1)	−135 (4)	455 (1)	590 (3)	5·4 (10)
H(2)	407 (4)	5 (2)	349 (3)	6·3 (10)	H'(2)	−161 (4)	520 (2)	444 (3)	9·0 (14)
H(3)	367 (4)	52 (2)	517 (3)	6·2 (11)	H'(3)	−171 (4)	473 (2)	263 (3)	7·8 (13)
H(4)	346 (4)	145 (2)	502 (3)	5·1 (10)	H'(4)	−164 (4)	378 (2)	249 (3)	5·2 (9)
H(6)	461 (4)	323 (2)	305 (3)	5·9 (10)	H'(6)	−30 (4)	191 (2)	413 (3)	6·3 (11)
H(7)	602 (4)	361 (2)	167 (3)	7·3 (12)	H'(7)	93 (5)	154 (2)	562 (4)	9·9 (15)
H(8)	625 (4)	295 (2)	27 (3)	5·6 (11)	H'(8)	108 (4)	200 (2)	723 (3)	6·0 (10)
H(9)	533 (3)	211 (1)	22 (2)	4·0 (8)	H'(9)	17 (4)	289 (1)	737 (3)	4·4 (9)
H(16)	175 (4)	161 (1)	35 (3)	4·5 (9)	H'(16)	−333 (4)	344 (1)	719 (3)	5·0 (9)
H(17)	138 (4)	116 (1)	−124 (3)	5·6 (9)	H'(17)	−346 (4)	381 (2)	878 (3)	6·0 (10)
H(19)	516 (4)	47 (1)	−92 (3)	5·1 (10)	H'(19)	53 (3)	440 (1)	867 (3)	4·1 (8)
H(20)	557 (3)	96 (1)	59 (2)	3·9 (8)	H'(20)	64 (4)	407 (1)	693 (3)	4·7 (9)

tropic temperature factors. All the H atoms were located by a difference Fourier synthesis. The isotropic temperature factors were used for H atoms in the final refinements. The weight of the reflections was assigned as $1/|\sigma(F)|^2$, where $\sigma(F)$ was calculated from counting statistics. The quantity $\Sigma w(||F_o| - |F_c||)^2$ was minimized. The final R index $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0·040. The magnitude of $[\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 0·97. The atomic scattering factors used for Br, S, N, and C atoms were those from International Tables for X-ray Crystallography (1962), and for H the values given by

Stewart, Davidson & Simpson (1965) were used. The final positional parameters are given in Table 1.*

The computer programs used in this analysis were ORFLS (Busing, Martin & Levy, 1962), a 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;
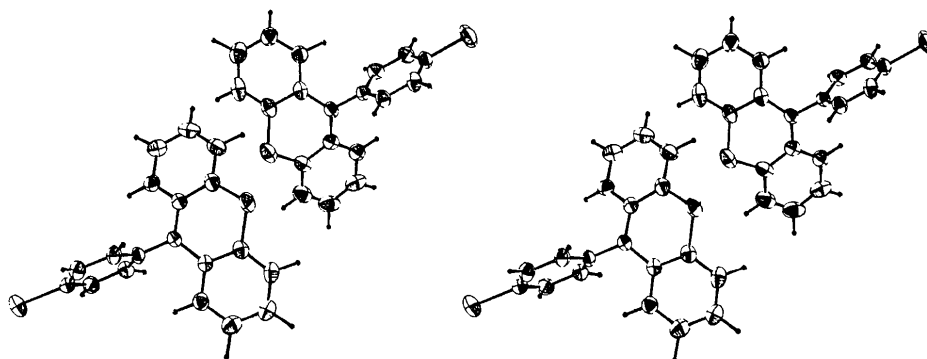
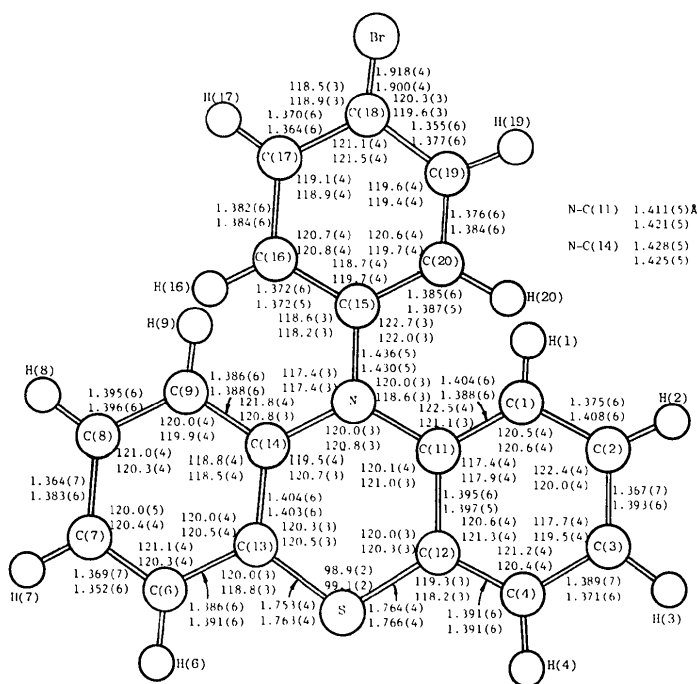Fig. 1. A stereoscopic drawing of the two crystallographically independent molecules.

Fig. 2. The bond lengths (Å) and the bond angles (°) of the two independent molecules. Upper numbers refer to molecule A, lower numbers refer to molecule B; e.s.d.'s are in parentheses.

Chu, 1973). All calculations were carried out on a CDC CYBER 72 computer in the Bradfield Computing Laboratory at Southern Methodist University.

Discussion

The purpose of this crystal structure determination is to confirm the title compound as the bromination product of N-phenylphenothiazine. It has been found that the bromination occurs on the N-phenyl ring, predominately at the *para* position, of N-phenylphenothiazines (Chiou, Reeves & Biehl, 1976). This work will also contribute to the basic understanding of the effect of different substituents on the stereochemistry of the phenothiazine derivatives.

A stereoscopic view of the configuration of the two crystallographically independent molecules is shown in Fig. 1 (Johnson, 1965). The two molecules have the same conformation. 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 four C—S bond lengths is 1.762 ± 0.004 Å and that of the four C—N bond lengths within the central ring is 1.421 ± 0.005 Å. The mean values of the two C—S—C bond angles and the two C—N—C bond angles within the central ring are 99.0 ± 0.2 and $120.4 \pm 0.3°$ respectively. These are in good agreement with values for other phenothiazine derivatives (Chu & van der Helm, 1975, 1976). The folding angle between the best planes of the two benzene rings of the phenothiazine ring system are 144.9 and $150.8°$ for the two crystallographically independent molecules A and B respectively.

The p-bromophenyl group is planar, and the angles between this phenyl ring and the two planes of the benzene rings are 115.4 and $99.7°$ in molecule A and 109.9 and $99.3°$ in molecule B. However, in N-(o-methoxyphenyl)phenothiazine (Chu, Yang & van der Helm, 1976), the phenyl ring nearly bisects the angle between the two benzene rings of the phenothiazine ring system. The packing of the molecules in the crystal

(Fig. 3) is determined by the van der Waals interactions. The closest interatomic distances are 3.50, 3.59, and 3.60 Å between C'(6) and C'(18), C(4) and C(8), and C(16) and C'(14), respectively.

The half-normal probability-plot analysis (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) was used to compare the two crystallographically independent molecules. The comparisons of the bond lengths and bond angles are shown in Fig. 4. Results derived from data containing a random normal distribution of errors would give a linear plot of zero intercept and unit slope. However, the slope of the least-squares line is 1.8, indicating that the bond lengths and bond angles of the two independent molecules do not agree as well as pre-
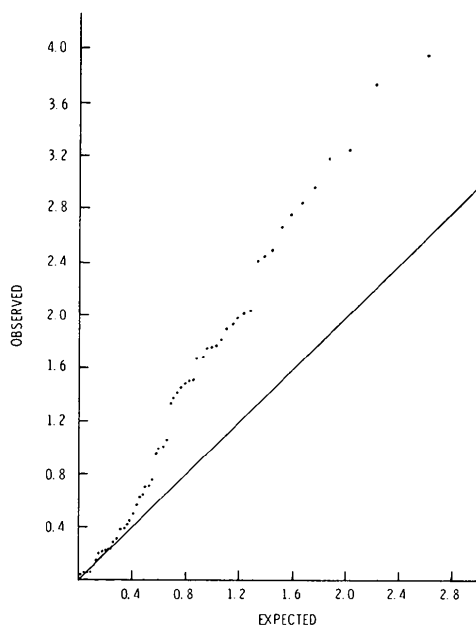

Fig. 4. Half-normal probability plot for the comparison of bond lengths and bond angles of the two crystallographically independent molecules (excluding hydrogen atoms). The solid line represents the unit slope.
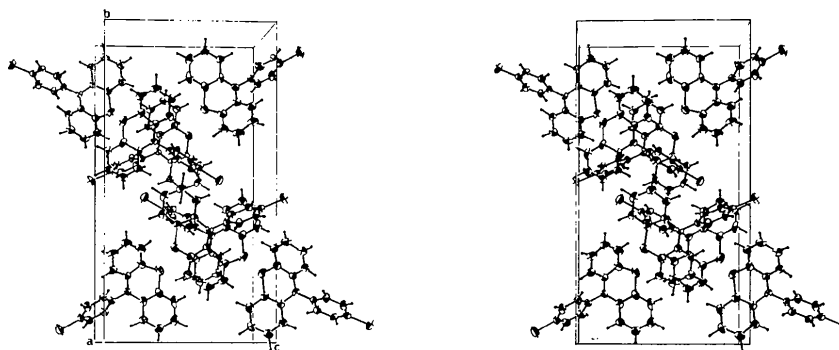

Fig. 3. A stereoscopic drawing of the molecular packing in the unit cell.

dicted on the basis of the e.s.d.'s in the positional parameters.

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Structure de Cu₂Mn₃O₈

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The crystal structure of $Cu_2Mn_3O_8$ was investigated by the photographic method. The crystals are monoclinic, space group $C2/m$, with $a = 9.695$ (7), $b = 5.635$ (3), $c = 4.912$ (4) Å, $\beta = 103.31$ (7)° and $Z = 2$. As in the $Co_2Mn_3O_8$ structure, a special feature is the presence of $[Mn_3O_8]_n^{4n-}$ sheets connected by Cu^{2+} ions. In each sheet the Mn atoms are surrounded by six O atoms forming an octahedron. These octahedra have practically the same features as those observed in β-MnO_2; the oxidation state of the Mn atoms in the sheets is four. The Cu ions possess only one coordination polyhedron. Each Cu atom has a distorted tetragonal-pyramidal environment of five O atoms. The four atoms closest to the Cu ion are situated in the basal plane of the pyramid: Cu–O(1) = 1.999 and Cu–O(1) = 1.982 Å. Cu^{2+} is displaced 0.54 Å out of the basal plane toward an apical coordinated O atom: Cu–O = 2.103 Å.

Introduction

Trois nouveaux oxydes doubles appartenant aux systèmes binaires $MnO_2.MO$ (*M étant un métal divalent*) *ont été mis en évidence récemment:* $Cu_2Mn_3O_8$, $Co_2Mn_3O_8$ *et* $Zn_2Mn_3O_8$ (*Lecerf, 1973, 1974*). *Une étude radiocristallographique de ces trois phases originales a montré que* $Co_2Mn_3O_8$ *et* $Zn_2Mn_3O_8$ *sont isotypes et possèdent une structure originale* (*Riou & Lecerf, 1975*). *Cette structure comporte en particulier des feuillets anioniques* $[Mn_3O_8]_n^{4n-}$ *reliés entre eux par les ions* Co^{2+}. *Ces ions possèdent deux coordinations différentes, l'une tétraédrique,*

l'autre octaédrique, mais l'ion divalent est très fortement déplacé en direction de l'une des faces de l'octaèdre.

La présente publication est consacrée aux détermination et étude structurales de $Cu_2Mn_3O_8$ qui d'après l'étude cristallographique préliminaire apparaît original.

Partie expérimentale

Les monocristaux de $Cu_2Mn_3O_8$ se présentent sous forme de plaquettes noires allongées suivant l'axe [010]. L'échantillon utilisé pour la détermination struc-