The Refinement of the Crystal Structure of N-Methylphenothiazine

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Abstract. $C_{13}H_{11}NS$, orthorhombic, M.W. 213·30, Ccm 2_1, $a = 14·642$ (3), $b = 11·315$ (2), $c = 6·672$ (1), $D_x = 1·281$, $D_m = 1·266$ g cm^{-3}, $Z = 4$. $\mu(Cu\ K\alpha) = 22·10$ cm^{-1}, $\lambda(Cu\ K\alpha) = 1·5418$ Å. The structure has been refined by the least-squares method with anisotropic temperature factors from new data obtained at room temperature with Cu $K\alpha$ radiation on an automatic diffractometer. The earlier structure result was confirmed; however, significant differences in bond lengths and bond angles were observed.

Introduction. Single crystals of N-methylphenothiazine were obtained through the courtesy of Dr Edward R. Biehl of the Chemistry Department of Southern Methodist University. The crystals are clear needle prisms with the c axis parallel to the needle axis. The unit-cell parameters were determined from measurements on the diffractometer. A crystal $0·18 \times 0·18 \times 0·80$ mm was used in the data collection on a Nonius-CAD 4 automatic diffractometer in the department of Chemistry of the University of Oklahoma, Norman, Oklahoma. A $\theta/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure the reflections of two different octants of the reciprocal lattice. The mean values were used in the refinement. Of the 663 independent reflections with 2θ values below 150°, 650 reflections were considered as observed. A reflection was considered as observed if its intensity was greater than $1·4\ \sigma(I)$, 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.

The structure of N-methylphenothiazine determined by Wakayama (1971) was confirmed, and his final co-ordinates were used as starting parameters for the refinement.* The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors. All the hydrogen atoms were located on difference Fourier synthesis. Their positional parameters were refined; however, their thermal parameters were assigned the same values as those of the atoms to which they are bonded. The $\sigma(F)$ determined from counting statistics was used for the weight of reflections, $\sqrt{w} = 1/\sigma(F)$. The quantity $\sum w\{||F_o| - |F_c||\}^2$ was minimized. The final R index ($\sum ||F_o| - |F_c|| / \sum |F_o|$) was 0·032. The final goodness-of-fit, $[\sum(F_o - F_c)^2/(m-n)]^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 1·19. The atomic scattering factors used were those in *International Tables for X-ray Crystallography* (1962). 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) and Zalkin Fourier Synthesis program modified by Dr R. Shiono of the University of Pittsburgh, and a number of struc-

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Table 1. *Fractional atomic coordinates and thermal parameters* (*all* $\times 10^4$)

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 β values is $(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	2569 (0)	0 (0)	0 (0)	46 (0)	96 (1)	302 (2)	0 (0)	40 (1)	0 (0)
N	1320 (2)	0 (0)	3557 (4)	49 (1)	93 (2)	198 (5)	0 (0)	9 (2)	0 (0)
C(1)	1849 (1)	1172 (2)	741 (4)	42 (1)	74 (1)	255 (5)	−9 (1)	4 (2)	−9 (2)
C(2)	1854 (2)	2211 (2)	−358 (5)	62 (1)	82 (1)	312 (6)	−23 (1)	3 (2)	14 (3)
C(3)	1361 (2)	3187 (2)	300 (6)	77 (1)	69 (2)	438 (9)	−17 (1)	−22 (3)	15 (3)
C(4)	841 (2)	3092 (2)	2010 (6)	69 (1)	72 (1)	456 (10)	1 (1)	−12 (3)	−41 (3)
C(5)	800 (1)	2040 (2)	3073 (5)	53 (1)	83 (2)	324 (6)	−2 (1)	5 (2)	−47 (3)
C(6)	1318 (1)	1062 (2)	2474 (3)	40 (1)	76 (1)	231 (4)	−6 (1)	−3 (2)	−21 (2)
C(7)	921 (4)	0 (0)	5554 (6)	89 (3)	134 (4)	201 (7)	0 (0)	27 (3)	0 (0)

Table 1 (cont.)

Coordinates are × 10³.

	x	y	z
H(C2)	218 (3)	228 (3)	−155 (6)
H(C3)	139 (2)	388 (3)	−50 (9)
H(C4)	47 (3)	377 (3)	241 (8)
H(C5)	45 (2)	200 (3)	419 (6)
H'(C7)	117 (3)	73 (4)	621 (7)
H"(C7)	9 (5)	0 (0)	534 (9)

Table 2. *Bond lengths* (Å) *and angles* (°) *(estimated standard deviations in parentheses with respect to the last place given)*

S——C(1)	1·764 (2)	C(2)–H(C2)	0·93 (4)
N——C(6)	1·402 (2)	C(3)–H(C3)	0·95 (4)
N——C(7)	1·455 (5)	C(4)–H(C4)	0·98 (4)
C(1)–C(2)	1·386 (3)	C(5)–H(C5)	0·91 (4)
C(1)–C(6)	1·399 (3)	C(7)–H'(C7)	1·01 (5)
C(2)–C(3)	1·390 (4)	C(7)–H"(C7)	1·22 (7)
C(3)–C(4)	1·377 (4)		
C(4)–C(5)	1·387 (4)		
C(5)–C(6)	1·400 (3)		

C(1)–S——C(1')	97·4 (1)	C(1)——C(2)–H(C2)	121 (3)
C(6)–N——C(6')	118·0 (2)	C(3)——C(2)–H(C2)	118 (3)
C(6)–N——C(7)	118·1 (3)	C(2)——C(3)–H(C3)	117 (3)
S——C(1)–C(2)	119·1 (2)	C(4)——C(3)–H(C3)	124 (3)
S——C(1)–C(6)	119·8 (2)	C(3)——C(4)–H(C4)	118 (2)
C(2)–C(1)–C(6)	121·0 (2)	C(5)——C(4)–H(C4)	121 (2)
C(1)–C(2)–C(3)	120·3 (2)	C(4)——C(5)–H(C5)	119 (2)
C(2)–C(3)–C(4)	119·2 (3)	C(6)——C(5)–H(C5)	120 (2)
C(3)–C(4)–C(5)	121·0 (3)	N———C(7)–H'(C7)	105 (3)
C(4)–C(5)–C(6)	120·6 (2)	N———C(7)–H"(C7)	107 (3)
N——C(6)–C(1)	120·0 (2)	H'(C7)–C(7)–H"(C7)	115 (4)
N——C(6)–C(5)	122·1 (2)	H'(C7)–C(7)–H'(C7')	110 (4)
C(1)–C(6)–C(5)	117·9 (2)		

ture interpretation programs (Shiono, 1971; Chu, 1971). All calculations were carried out on a CDC CYBER 72 computer in the Computing Laboratory at Southern Methodist University.

Discussion. The crystal structure was determined by Wakayama (1971) to an *R* value of 0·135 for three-dimensional data. This compound is of interest in correlating the effects of substituents on the configuration and conformation of tricyclic sulfur compounds. However, the data reported by Wakayama are not of sufficient accuracy. New data were therefore measured for the refinement of the structure.

The identification of atoms in *N*-methylphenothiazine and the illustration of the thermal ellipsoids (John-

Fig. 1. The structure of one molecule of *N*-methylphenothiazine.

son, 1965) are shown in Fig. 1. The bond lengths and bond angles with their standard deviations are listed in Table 2. The dihedral angle between the least-squares planes of the two benzene rings is 143·7° as compared with 153·3° in phenothiazine (Bell, Blount, Briscoe & Freeman, 1968). The S–C bond length agrees with that in other tricyclic compounds (Chu & Chung, 1973) where the coordination number of the sulfur atom is two. Apart from the changes in bond lengths and bond angles, the structure is unchanged from that reported previously.

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