

tacts Cl(1)···C(2) 3.31, Cl(1)···H(2) 3.05 and Cl(2)···O(2) 3.15 Å. Presumably the barrier to internal rotation around C(3)—C(4) permits the separation of diastereoisomers with opposite axial chirality. The compound examined would then have the absolute configuration (1*S*,6*S*,9*R*,1',4-*aR*). The ring system does not allow independent inversions at the 1 and 9 asymmetry centres; if one is *R* the other must be *S*.

The packing of the molecules is shown in Fig. 2. Adjacent molecules are connected along *x* by weak O(3)—H(O3)···O(4) hydrogen bonds of 2.845 (4) Å with O(3)—H(O3) 0.64 (4) and H(O3)···O(4) 2.28 (4) Å. The angle O(3)—H(O3)—O(4) is 150 (5)°. There are no other intermolecular distances significantly shorter than the sum of the van der Waals radii.

Acta Cryst. (1977). B33, 873–876

N-Benzylphenothiazine

BY SHIRLEY S. C. CHU

School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275, USA

AND DICK VAN DER HELM

Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069, USA

(Received 7 July 1976; accepted 9 September 1976)

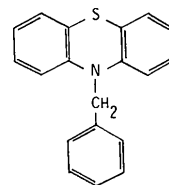
Abstract. C₁₉H₁₅NS, triclinic, $P\bar{1}$, $Z = 4$, $M_r = 289.40$, $a = 11.274$ (7), $b = 11.504$ (7), $c = 13.404$ (9) Å, $\alpha = 90.873$ (6), $\beta = 91.824$ (7), $\gamma = 120.484$ (6)°, $V = 1496.39$ Å³, $D_x = 1.284$, $D_m = 1.27$ g cm⁻³ (by flotation), $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 17.83$ cm⁻¹. Final residual $R = 0.048$.

Introduction. Samples of *N*-benzylphenothiazine (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 acetone solutions. The unit-cell parameters were obtained from the measurement of '+' and '-' 2θ values of 28 reflections and the intensity data were collected on a Nonius CAD-4 automatic diffractometer. An $\omega/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 5668 independent reflections with 2θ values below 140°, of which 4671 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, and no absorption corrections were applied.

Thanks are due to J. Trofast for providing the crystals.

References

- CAHN, R. S., INGOLD, C. & PRELOG, V. (1966). *Angew. Chem.* **78**, 413–447.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 TROFAST, J. & WICKBERG, B. (1977). *Tetrahedron*. In the press.



(I)

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 block-diagonal least-squares method with anisotropic temperature factors. All the H atoms were located by difference Fourier syntheses. The isotropic temperature factors were used for the H atoms in the refinement. The weight of the reflection was assigned as $1/[\sigma(F)]^2$ for observed reflections and zero for unobserved reflections, 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 0.048. The magnitude, $\{\Sigma w(F_o - F_c)^2 / (m - n)\}^{1/2}$, where m is the number of reflections and n is the number of parameters refined, was 1.11. The atomic scattering factors used for S, N, and C were those from *International Tables for X-ray Crystallography* (1962). For H, the values of Stewart, Davidson & Simpson (1965) were used. The final positional and H thermal parameters are given in Table 1.*

The computer programs used in this analysis were *ORFLS* (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 Bradfield Computing Laboratory at Southern Methodist University.

Discussion. The determination of the crystal structure of *N*-benzylphenothiazine is a continuation of the studies on a series of phenothiazine derivatives. The mechanism of the bromination of *N*-substituted phenothiazines has been studied extensively (Biehl, Chiou, Keepers, Kennard & Reeves, 1975; Chiou, Reeves & Biehl, 1976). The bromination occurs on the phenothiazine ring system with *N*-alkylphenothiazines and on the phenyl ring with *N*-phenylphenothiazines. However, in the case of *N*-benzylphenothiazine, debenzyla-tion occurs before bromination takes place on the

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

The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

Molecule A	x	y	z		Molecule B	x	y	z
S	181 (1)	8061 (1)	1551 (0)		S'	749 (0)	1992 (0)	2648 (0)
N	1748 (1)	6663 (1)	1055 (1)		N'	-1436 (1)	-265 (1)	3788 (1)
C(1)	4013 (2)	8680 (2)	1404 (2)		C'(1)	-1222 (2)	1186 (2)	5217 (1)
C(2)	4799 (3)	10018 (2)	1760 (3)		C'(2)	-604 (2)	2463 (2)	5681 (2)
C(3)	4180 (3)	10691 (2)	2125 (3)		C'(3)	332 (2)	3585 (2)	5199 (2)
C(4)	2764 (3)	10056 (2)	2105 (2)		C'(4)	679 (2)	3443 (2)	4250 (2)
C(6)	-1635 (2)	5535 (2)	2145 (2)		C'(6)	-984 (2)	450 (2)	1096 (2)
C(7)	-2128 (2)	4178 (2)	2238 (2)		C'(7)	-2077 (3)	-723 (3)	659 (2)
C(8)	-1352 (2)	3636 (2)	1947 (2)		C'(8)	-2947 (2)	-1735 (2)	1254 (2)
C(9)	-59 (2)	4446 (2)	1564 (2)		C'(9)	-2763 (2)	-1591 (2)	2285 (2)
C(11)	2573 (2)	8024 (2)	1390 (1)		C'(11)	-867 (2)	1018 (2)	4262 (1)
C(12)	1970 (2)	8750 (2)	1720 (2)		C'(12)	114 (2)	2167 (2)	3790 (1)
C(13)	-357 (2)	6362 (2)	1749 (1)		C'(13)	-757 (2)	587 (2)	2126 (1)
C(14)	458 (2)	5829 (2)	1458 (1)		C'(14)	-1665 (2)	-428 (2)	2739 (1)
C(15)	2371 (2)	6015 (2)	518 (1)		C'(15)	-2165 (2)	-1457 (2)	4388 (1)
C(16)	3063 (2)	5411 (2)	1142 (1)		C'(16)	-3650 (2)	-1910 (2)	4602 (1)
C(17)	3402 (2)	5716 (2)	2151 (1)		C'(17)	-4329 (2)	-1270 (2)	4247 (2)
C(18)	4049 (2)	5151 (2)	2677 (1)		C'(18)	-5689 (2)	-1732 (2)	4455 (2)
C(19)	4371 (2)	4285 (2)	2204 (2)		C'(19)	-6385 (2)	-2845 (2)	5032 (2)
C(20)	4026 (2)	3966 (2)	1203 (2)		C'(20)	-5726 (2)	-3500 (2)	5390 (2)
C(21)	3380 (2)	4524 (2)	678 (1)		C'(21)	-4362 (2)	-3033 (2)	5183 (1)

Hydrogen-atom coordinates ($\times 10^3$)									
Molecule A	x	y	z	B	Molecule B	x	y	z	B
H(1)	446 (2)	825 (2)	110 (2)	5.2 (5)	H'(1)	-190 (2)	45 (2)	555 (1)	4.4 (4)
H(2)	581 (3)	1038 (3)	174 (2)	10.2 (9)	H'(2)	-92 (2)	257 (2)	635 (2)	6.1 (6)
H(3)	479 (3)	1167 (3)	241 (2)	9.9 (9)	H'(3)	69 (3)	445 (2)	555 (2)	7.3 (6)
H(4)	223 (3)	1057 (3)	242 (2)	8.5 (7)	H'(4)	134 (2)	420 (2)	387 (2)	6.9 (6)
H(6)	-220 (2)	592 (2)	235 (2)	6.5 (6)	H'(6)	-35 (2)	117 (2)	70 (2)	5.4 (5)
H(7)	-301 (2)	364 (2)	252 (2)	5.9 (6)	H'(7)	-221 (3)	-79 (3)	-10 (2)	8.5 (7)
H(8)	-166 (2)	270 (2)	200 (2)	6.0 (6)	H'(8)	-374 (2)	-265 (2)	96 (2)	5.4 (5)
H(9)	50 (2)	400 (2)	130 (2)	5.3 (5)	H'(9)	-342 (2)	-230 (2)	268 (1)	5.1 (5)
H(15)1	164 (2)	530 (2)	11 (1)	4.5 (4)	H'(15)1	-206 (2)	-219 (2)	404 (2)	5.1 (5)
H(15)2	309 (2)	668 (2)	5 (2)	6.4 (6)	H'(15)2	-163 (2)	-126 (2)	505 (2)	4.9 (5)
H(17)	306 (2)	624 (2)	252 (1)	4.2 (4)	H'(17)	-383 (2)	-47 (2)	385 (1)	4.8 (5)
H(18)	428 (2)	545 (2)	337 (1)	4.8 (5)	H'(18)	-612 (3)	-120 (2)	423 (2)	7.0 (6)
H(19)	479 (2)	384 (2)	259 (2)	4.9 (5)	H'(19)	-740 (2)	-313 (2)	516 (2)	7.0 (6)
H(20)	428 (2)	332 (2)	85 (2)	6.7 (6)	H'(20)	-620 (2)	-431 (2)	583 (2)	6.4 (6)
H(21)	310 (3)	425 (2)	-3 (2)	7.2 (6)	H'(21)	-384 (2)	-352 (2)	543 (2)	6.2 (5)

phenothiazine ring. In addition, many phenothiazine derivatives are important antipsychotic (Zirkle & Kaiser, 1970) and antidepressant (Kaiser & Zirkle, 1970) agents. This work will also contribute to the basic understanding of the different substituents on the stereochemistry of the phenothiazine derivatives.

The stereoscopic view of the configuration of one 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 1.758 ± 0.002 Å and that of the four C–N bond lengths within the cen-

tral ring is 1.409 ± 0.003 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 ± 0.1 and $120.6 \pm 0.2^\circ$ respectively. The folding angles between the best planes of the two benzene rings of the phenothiazine ring system are 148.2 and 150.1° for the two crystallographically independent molecules *A* and *B* respectively.

All C–N–C angles are close to 120° , indicating that the three N–C bonds around the N atom are approximately planar in configuration. The torsion angles about N–C(15) and C(15)–C(16) bonds are shown in Fig. 3. The phenyl ring of the benzyl group is essentially coplanar with plane N–C(15)–C(16) in mole-

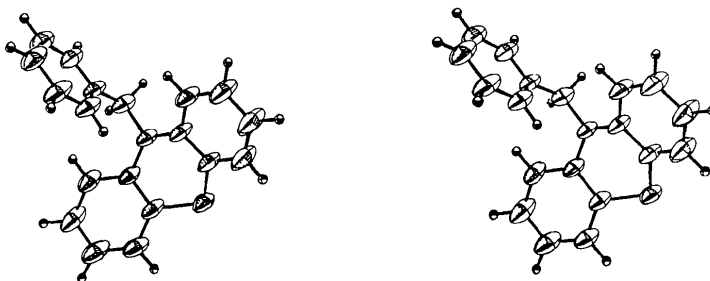


Fig. 1. The stereoscopic drawing of one of the two crystallographically independent molecules of *N*-benzylphenothiazine.

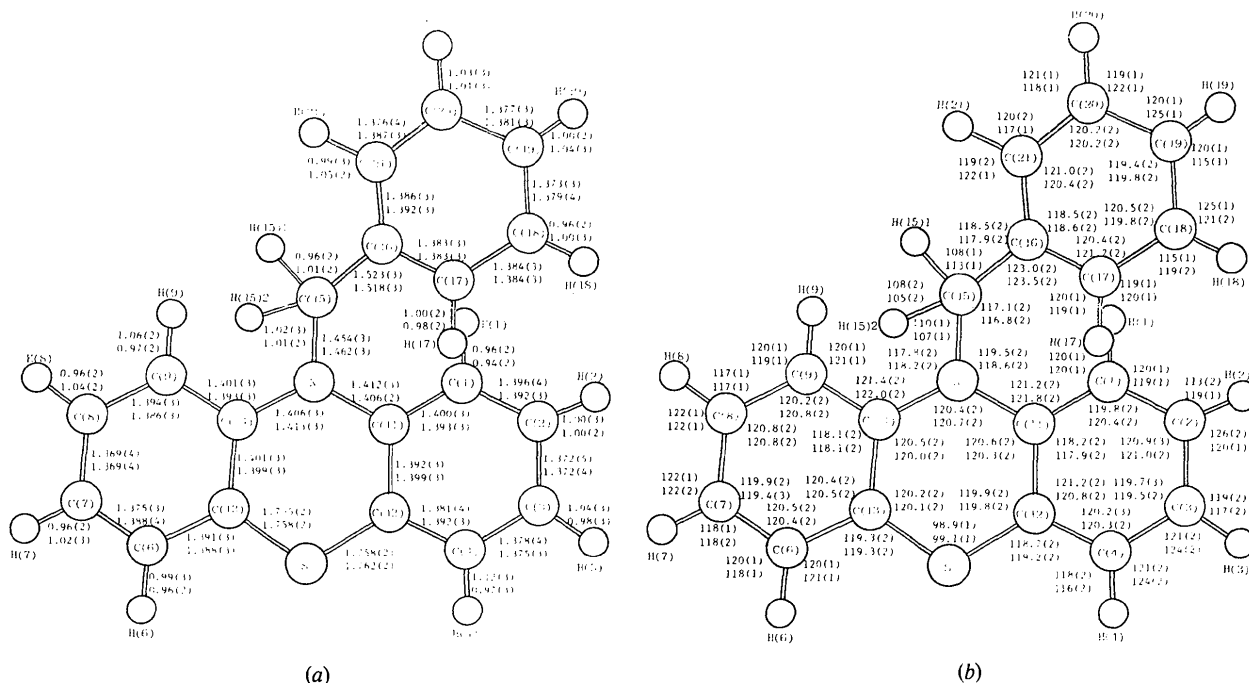


Fig. 2. (a) The bond lengths (Å) and (b) the bond angles ($^\circ$) of the two independent molecules. Upper numbers refer to molecule *A*, lower numbers to molecule *B*; e.s.d.'s are in parentheses.

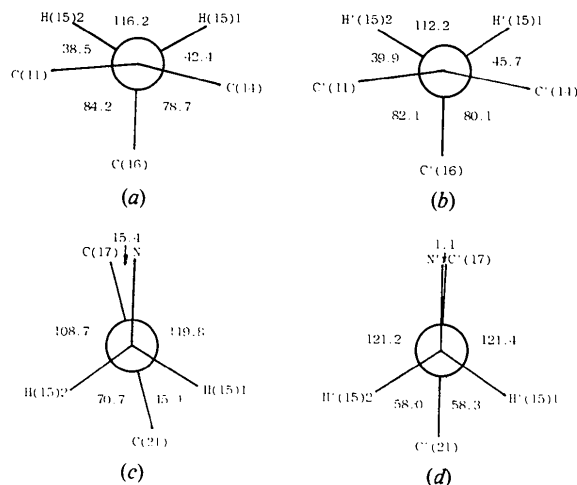


Fig. 3. The torsion angles ($^{\circ}$) about the (a) N—C(15), (b) N'—C'(15), (c) C(15)—C(16), and (d) C'(15)—C'(16) bonds in *N*-benzylphenothiazine.

cule *B*; however, the two planes make an angle of 15° in molecule *A*. The packing of the molecules in the crystal is determined by the van der Waals interaction. The closest intermolecular distances are 3.56 and 3.60 Å between C(8) and C(15) and between C(9) and C(15) respectively.

Acta Cryst. (1977). B33, 876–879

Ferrocenylmethylpyridinium Iodide*

By GEORGE M. BROWN AND LOWELL H. HALL†

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

(Received 28 June 1976; accepted 2 August 1976)

Abstract. $(C_5H_5)Fe(C_5H_4)CH_2(NC_5H_5)^+I^-$, monoclinic, $P2_1/c$, $a = 10.125(3)$, $b = 12.713(3)$, $c = 12.231(3)$ Å, $\beta = 98.24(2)^{\circ}$, $D_c = 1.727$ g cm $^{-3}$, $Z = 4$ [$23.5 \pm 1.0^{\circ}C$, $\lambda(Mo K\alpha) = 0.7107$ Å]. The cyclopentadienyl rings are within 1.2° of parallelism and about 4.2° from eclipse. The iodide ion is 3.73 Å from the N atom and 3.58 Å from an α -C atom of the pyridinium ring, in a position almost the same as that

The support of the Robert A. Welch Foundation to S. S. C. Chu is gratefully acknowledged. The authors wish to thank Dr Edward R. Biehl of Southern Methodist University for kindly providing the samples.

References

- BIEHL, E. R., CHIOU, H. S., KEEPERS, J., KENNARD, S. & REEVES, P. C. (1975). *J. Heterocycl. Chem.* **12**, 397–399.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
 CHIOU, H., REEVES, P. C. & BIEHL, E. R. (1976). *J. Heterocycl. Chem.* **13**, 77–82.
 CHU, S. S. C. (1973). *Structural Interpretation Programs*. Institute of Technology, Southern Methodist Univ.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
 KAISER, C. & ZIRKLE, C. L. (1970). *Medicinal Chemistry*, 3rd ed., edited by A. BURGER, Part II, pp. 1470–1497. New York: Wiley-Interscience.
 SHONO, R. (1971). Technical Report 49, Crystallography Department, Univ. of Pittsburgh.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 ZIRKLE, C. L. & KAISER, C. (1970). *Medicinal Chemistry*, 3rd ed., edited by A. BURGER, Part II, pp. 1410–1469. New York: Wiley-Interscience.

of the iodide ion relative to the pyridinium ring in 1-methylnicotinamide iodide.

Introduction. A crystal specimen of the dark amber material‡ with dimensions about $0.06 \times 0.5 \times 0.6$ mm was used to obtain all diffraction data. From the Laue symmetry, $2/m$, and the systematic absences, $h0l$ for odd l and $0k0$ for odd k , the space group was uniquely established to be $P2_1/c$. The cell parameters were calculated by the method of least squares from angle data for 12 Mo $K\alpha$ reflections in the 2θ range 35 to

* Research sponsored by the Energy Research and Development Administration under contract with the Union Carbide Corporation.

† Permanent address: Chemistry Department, Eastern Nazarene College, Wollaston, Massachusetts 02170, USA. Participation in the research supported by Oak Ridge Associated Universities.

‡ Kindly supplied by Professor Ted Bieber, Chemistry Department, Florida Atlantic University, Boca Raton, Florida.