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Structural Studies of Dibenz[*c,f*]azocines.III. 3-Bromo-*N*-methyl-5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine*†

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This X-ray study has shown that the compound C₁₆H₁₆NBr is 3-bromo-*N*-methyl-dibenzazocine. The crystals are monoclinic, *P*₂₁, with *a* = 16.398, *b* = 5.063, *c* = 8.038 Å, β = 92.07° and *Z* = 2. The structure has been determined from a Patterson map, and refined by least-squares calculations to *R* = 0.038 for the 1461 observed reflexions. The eight-membered azocine ring is in the rigid boat-chair conformation, with the N-CH₃ bond in an off-axial position. The dihedral angle between the planes of the two benzene rings is 114.5°. Substitution of Br in place of H on one of the benzene rings has increased the endocyclic C-C(Br)-C angle by 2.1°. The shortest Br...Br contact is 3.797 (1) Å. All the molecules in the crystal are of the same absolute configuration.

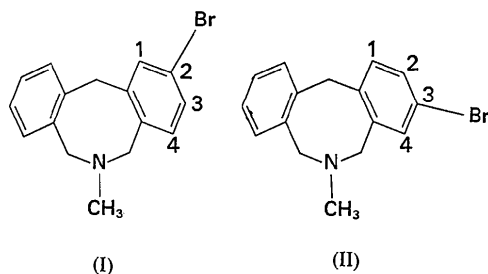
Introduction

The crystal structure of *N*-methyl-dihydro-dibenzazocine was described by Hardy & Ahmed (1974), as part I of this series. Its bromo derivative has been synthesized

by Renaud & Bovenkamp (1974) for the n.m.r. studies that they are conducting on the azocine system. The X-ray determination of the crystal structure has been undertaken in order to find out whether the compound is the 2-bromo (I) or the 3-bromo derivative (II). It was essential for the n.m.r. studies that the Br atom be *para* to the bridgehead methylene group.

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Suitable crystals for X-ray work were grown from absolute ethanol. The crystals were transparent and colourless flat needles.

Experimental

Crystal data

Formula	$C_{16}H_{16}NBr$	M.W.	302.21
Space group	$P2_1$	Z	2
a	16.398 (3) Å	V	666.91 Å ³
b	5.063 (7)	D_x	1.505 g cm ⁻³
c	8.038 (2)	D_m	1.499 g cm ⁻³
β	92.07 (5)°	$\mu(\text{Cu})$	44.59 cm ⁻¹

All X-ray measurements were carried out on a four-circle diffractometer, with Cu radiation, and a crystal fragment 0.15 × 0.17 × 0.20 mm. The cell dimensions were based on the angular settings of the axial reflexions and the density was measured by flotation in KI solution at 23°C.

Intensity data

The intensities were measured by the θ - 2θ scan method at a take-off angle of 3°, up to a limit of $2\theta=155^\circ$. The background was measured separately for every reflexion on the white radiation streak through it, and the intensity of the 600 reflexion was recorded every 30–40 reflexions for scaling purposes. 1589 reflexions were scanned, and 1461 (91.9%) observed above threshold, thus producing 6.5 observations per parameter.

Lp corrections were applied to the net counts. Near the end of the refinement, the observed structure amplitudes were corrected for absorption by the Gaussian integration method. These corrections were in the range 1.23 to 1.38.

Structure determination

The positions of the non-hydrogen atoms, except for the methyl carbon, were determined from a sharpened Patterson map. R for this trial structure was 0.23, assuming $B=3.5 \text{ \AA}^2$ for all atoms. A subsequent electron-density map revealed the position of the methyl carbon, and confirmed the positions of the other atoms.

The atomic parameters were refined by block-diagonal least-squares calculations, the quantity $\sum w(\Delta F)^2$ being minimized and only the observed reflexions included. The weights were calculated from $w=1/\{1+$

$[(|F_o|-25)/22]^4\}$, where $1.7 \leq |F_o| \leq 92.5$. All H atoms were located unambiguously from a difference map with peak heights 0.3–0.6 e Å⁻³, and were included in the refinement with isotropic parameters.

Absolute configuration

At the stage where R was 0.048, the absorption corrections and the anomalous component $\Delta f''(\text{Br})$ were introduced. One cycle of refinement was computed for the assumed model and for its enantiomorph. The agreement among the observed and calculated data for the two models, before and after refinement, are listed in Table 1. According to Hamilton's (1965) test, for 1461 observations and 226 parameters, the differences between the two models are significant and the enantiomorph model can be rejected at the 0.01 level or lower. It is noteworthy that the difference between the two models was more significant before than after the refinement cycle (see Table 1).

Table 1. Effect of anomalous dispersion on the agreement (1) for the accepted model, (2) for the enantiomorph

	Before refinement		After one cycle	
	(1)	(2)	(1)	(2)
$\sum F_o $	16985	16985	17121	17138
$\sum F_c $	17014	17020	16994	17010
$\sum \Delta F $	745	766	666	676
$\sum w(\Delta F)^2$	455	474	359	362
$R\%$	4.38	4.51	3.89	3.94
$R_w\%$	4.21	4.30	3.72	3.73
$\mathcal{R} = R(2)/R(1)$	1.0297		1.0128	
$\mathcal{R}_w = R_w(2)/R_w(1)$	1.0214		1.0027	

The absolute configuration is not particularly important for this structure since it applies only to the particular crystal under consideration and does not exclude the possible existence of the other enantiomorph.

Refinement was terminated after one more cycle where $\langle \Delta/\sigma \rangle = 0.3$, $(\Delta/\sigma)_{\text{max}} = 0.7$, $R = 0.038$, and $R_w = 0.037$ for the observed reflexions. The residual electron density in the final difference map was within $\pm 0.33 \text{ e \AA}^{-3}$. The f curves were those of Hanson, Herman, Lea & Skillman (1964) for C, N and Br, and Stewart, Davidson & Simpson (1965) for H. $\Delta f'$ and $\Delta f''(\text{Br})$ were taken from *International Tables for X-ray Crystallography* (1962).

Results

The refined parameters are listed in Table 2. Two orthogonal projections of this molecule are presented in Fig. 1.* The only reflexion with high discrepancy is 201 which is very strong and is probably affected by extinction. The bond lengths, valency angles and tor-

* The table of structure amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30595 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

sion angles, not corrected for thermal vibration, are given in Fig. 2. The C–H lengths are in the range 0.93–1.10 Å, and their mean is 1.00 Å.

Discussion

This study has confirmed that the Br atom is substituted at C(3). The conformation is very similar to that of the unsubstituted analogue reported by Hardy & Ahmed (1974). In both molecules, the azocine ring has the rigid boat–chair conformation, and the methyl group is in the off-axial position (Fig. 1). Also, both

compounds form needle-shaped crystals with non-centrosymmetric unit cells which have a short axial length of 5.059 ± 4 Å along the needle axis. All molecules in a given crystal are of the same absolute configuration, which may be a requirement for efficient packing. However, examination of the crystals' morphology could not confirm or disprove that the material is a racemic mixture.

Averaging the equivalent bond lengths and valency angles in the two halves of the *N*-methyl-dihydrodibenzazocine molecule, and comparing them with those of the 3-bromo analogue shows that the only significant

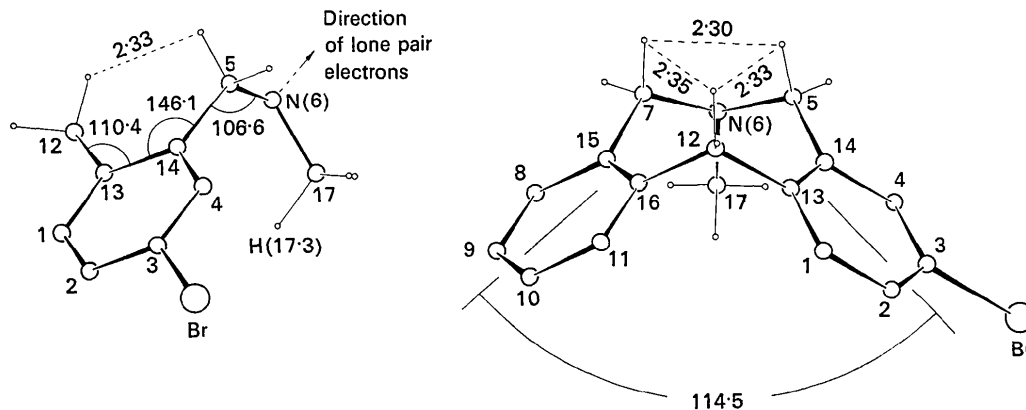


Fig. 1. Two orthogonal projections of the molecule, showing its conformation and the interplanar dihedral angles ($^{\circ}$) of the azocine ring. The figure on the left shows only half of the molecule since the two halves very nearly overlap in this view. The H atoms of the benzene rings are excluded for clarity. The H \cdots H contacts are in Å.

Table 2. Fractional coordinates, vibration tensor components (\AA^2) for the expression $T = \exp[-2\pi^2(U_{11}a^*h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$, all quantities $\times 10^4$

The isotropic temperature factors of the H atoms are in \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	2 <i>U</i> ₂₃	2 <i>U</i> ₁₃	2 <i>U</i> ₁₂
Br(1)	4453 (0)	0 (0)	1322 (1)	587 (3)	827 (4)	566 (3)	-30 (9)	381 (4)	446 (8)
C(1)	3808 (3)	1862 (12)	6115 (6)	356 (23)	512 (32)	435 (24)	118 (52)	-126 (37)	-110 (49)
C(2)	4171 (3)	686 (11)	4769 (6)	315 (20)	453 (38)	592 (26)	12 (50)	60 (37)	53 (43)
C(3)	3966 (3)	1616 (12)	3203 (6)	368 (23)	531 (33)	488 (25)	-52 (55)	102 (39)	-87 (50)
C(4)	3403 (3)	3584 (12)	2947 (6)	413 (23)	423 (28)	433 (25)	106 (48)	38 (39)	5 (47)
C(5)	2406 (3)	6920 (11)	3953 (6)	495 (27)	376 (29)	493 (26)	83 (51)	59 (42)	123 (50)
N(6)	1549 (2)	6281 (9)	4217 (5)	437 (20)	406 (24)	432 (20)	-147 (39)	11 (31)	53 (38)
C(7)	1248 (3)	6728 (12)	5883 (6)	478 (26)	420 (31)	537 (27)	-134 (54)	113 (43)	200 (51)
C(8)	625 (3)	3240 (13)	7653 (6)	446 (26)	610 (37)	470 (26)	-232 (56)	147 (42)	34 (55)
C(9)	655 (3)	1256 (12)	8855 (6)	559 (29)	613 (36)	446 (25)	-215 (55)	197 (43)	-76 (56)
C(10)	1388 (3)	489 (14)	9544 (5)	742 (31)	487 (41)	383 (22)	-123 (54)	84 (41)	-33 (63)
C(11)	2095 (3)	1725 (12)	9073 (6)	587 (29)	522 (34)	386 (24)	-247 (53)	-64 (42)	25 (57)
C(12)	2862 (2)	5081 (16)	7432 (5)	475 (23)	523 (29)	459 (22)	-475 (71)	-67 (36)	-82 (73)
C(13)	3240 (3)	3886 (11)	5916 (6)	361 (22)	394 (27)	426 (24)	-124 (44)	-45 (36)	-66 (42)
C(14)	3023 (2)	4781 (14)	4308 (5)	303 (18)	418 (29)	484 (22)	-20 (60)	90 (31)	5 (53)
C(15)	1330 (3)	4506 (10)	7154 (5)	471 (23)	347 (34)	409 (22)	-325 (45)	105 (35)	42 (44)
C(16)	2074 (3)	3769 (11)	7889 (5)	488 (26)	432 (28)	340 (22)	-264 (45)	42 (37)	58 (48)
C(17)	1273 (3)	3897 (12)	3422 (6)	472 (26)	553 (35)	496 (27)	-263 (53)	-160 (43)	7 (51)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	3990 (22)	1163 (83)	7233 (45)	2.0 (0.8)	H(9)	128 (25)	293 (151)	9150 (48)	4.1 (1.0)
H(2)	4533 (22)	-1011 (82)	4883 (46)	1.9 (0.8)	H(10)	1400 (23)	-876 (85)	10462 (45)	2.8 (1.0)
H(4)	3292 (30)	4343 (125)	1915 (60)	4.7 (1.2)	H(11)	2611 (29)	1111 (110)	9535 (58)	4.5 (1.2)
H(5.1)	2417 (30)	7479 (126)	2829 (60)	4.4 (1.2)	H(12,1)	3283 (23)	5244 (141)	8380 (47)	3.6 (0.9)
H(5.2)	2499 (30)	8611 (121)	4594 (60)	4.8 (1.3)	H(12,2)	2738 (30)	6943 (129)	7270 (61)	5.5 (1.3)
H(7,1)	665 (29)	7067 (122)	5734 (59)	4.6 (1.2)	H(17,1)	1430 (34)	3913 (130)	2246 (67)	5.6 (1.4)
H(7,2)	1439 (30)	8468 (122)	6383 (60)	4.7 (1.2)	H(17,2)	653 (35)	3791 (134)	3402 (70)	7.6 (1.8)
H(8)	107 (29)	3922 (108)	7141 (58)	4.4 (1.2)	H(17,3)	1526 (30)	2140 (127)	4048 (61)	5.2 (1.3)

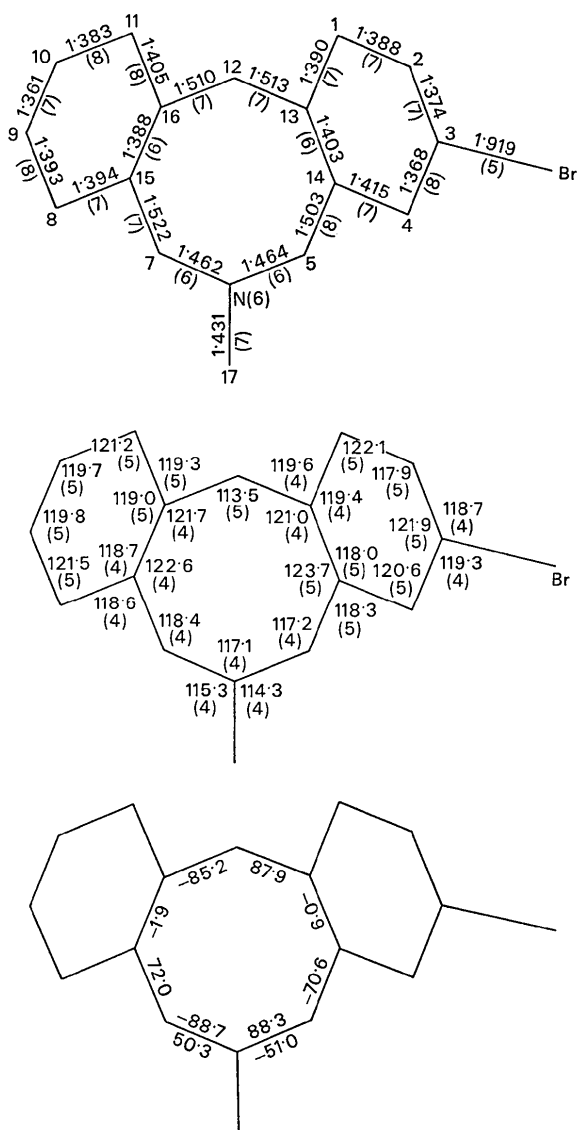


Fig. 2. Bond lengths (Å), valency angles (°), and torsion angles (°). The estimated standard deviations are given in parentheses.

difference is in the C(2)–C(3)–C(4) angle. It has an average value of 119.8 (3)° in the former structure and is observed as 121.9 (5)° in the latter, and the difference of 2.1° is significant. Two of the bonds show differences which are possibly significant. These are C(4)–C(14) and C(9)–C(10) which have mean values of 1.397 (3) and 1.384 (5) Å in the former, 1.415 (7) and 1.361 (7) Å in the latter. The discrepancies in the other bond lengths and angles are within experimental error. The N(6)···C(12) diagonals across the azocine rings

of the two compounds are 3.343 (6) and 3.358 (6) Å, respectively.

The folding of the azocine ring in the 3-bromo compound is described by the interplanar dihedral angles given in Fig. 1. C(1), C(2), C(3), C(4), C(14) and C(13) of benzene (1) are coplanar with $\chi^2=8.4$, and similarly C(8), C(9), C(10), C(11), C(16) and C(15) of benzene (2) are nearly coplanar with $\chi^2=13.2$. The dihedral angle between the mean planes of these two rings is 114.5°.

The plane through C(13), C(12) and C(16) makes dihedral angles of 88.1 and 85.7° with the mean planes of benzene (1) and (2), whereas the corresponding values for the non-substituted analogue are 87.8 and 87.3°, respectively. The large difference of 2.4° between the two dihedral angles in the 3-bromo compound is possibly significant, and could represent some strain in the half of the molecule furthest from the Br atom.

The packing of the molecules seems to be governed by van der Waals interactions. The only intermolecular contact shorter than the sum of the corresponding van der Waals radii is between the two Br atoms which are related by the 2_1 symmetry. The distance between them is 3.797 (1) Å, thus giving the van der Waals radius of Br as 1.90 Å instead of the 1.95 Å calculated by Pauling (1960). The shortest H···H intermolecular contact is 2.43 (8) Å between H(5,2) at (x,y,z) and H(17,3) at $(x,1+y,z)$, *i.e.* between adjacent molecules along the crystal's needle axis.

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