

## Structure of 1,1-Bis(bromomethyl)-1,2,3,4-tetrahydroacridine

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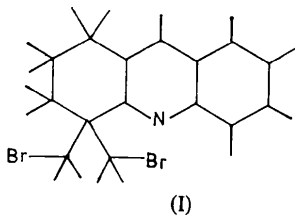
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### Abstract

$C_{15}H_{15}Br_2N$ ,  $M_r = 369.2$ , is triclinic,  $P\bar{1}$ , with  $a = 9.149$  (1),  $b = 13.258$  (1),  $c = 12.916$  (1) Å,  $\alpha = 114.6$  (1),  $\beta = 99.3$  (1),  $\gamma = 86.4$  (1)°,  $V = 1405.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.740$  Mg m<sup>-3</sup>. The structure has been determined by three-dimensional X-ray analysis and refined to  $R(F_o) = 0.067$  for 2314 reflections measured with a CAD-4 automated four-circle diffractometer. The unit cell contains two symmetrically independent molecules with different conformations of the 1,1-bis(bromomethyl)cyclohexene ring. The conformation of this ring is half-chair in molecule (I) and sofa in molecule (II) with asymmetry parameters  $\Delta C_2(I) = 0.7^\circ$ ,  $\Delta C_3(II) = 10.6^\circ$  and  $\Delta C_2(II) = 24.1^\circ$ . The molecular conformations suggest considerable steric strain in the 1,1-bis(bromomethyl)cyclohexene rings. The two bromomethyl groups in both molecules have analogous ( $\pm$ )*ap* and ( $\pm$ )*sc* conformations.

### Introduction

The title compound was obtained by Dr A. Sokolowska, Institute of Organic Chemistry of Łódź University, as an intermediate product in the synthesis of new derivatives of 1,2,3,4-tetrahydroacridine. It is characterized by the unexpected unreactivity of the two bromomethyl groups, which do not undergo the nucleophilic substitution reactions characteristic of alkyl bromides. This suggests that either the Br atoms are bonded as in an aromatic compound, or their unreactivity results from the particular molecular structure.



Single crystals of (I) were obtained by evaporation at room temperature from ethanol solution. From one such crystal, a small piece was cut and carefully ground

until it was approximately spherical with a diameter of 0.3 mm. The crystal system and approximate cell parameters were determined from oscillation and Weissenberg photographs using Cu  $K\alpha$  radiation. These parameters were refined and the intensities collected on a CAD-4 four-circle diffractometer at room temperature using Cu  $K\alpha$  radiation. Reflections were measured with a  $\theta/2\theta$  scan mode and the fluctuation in the intensity of a standard reflection was less than 2.5%. The intensities of 2418 independent reflections were measured, of which 104 had  $I < 3\sigma(I)$ . Lorentz, polarization and absorption corrections were applied. The density was measured by flotation in an aqueous solution of KI.

All calculations were performed on a RIAD-32 computer using the XRAY system (Stewart, Kundell & Baldwin, 1970). The distribution of the  $E$  values calculated during the data reduction showed the space group to be  $P\bar{1}$ . Hence, all the subsequent calculations were performed in the centrosymmetric space group.

The structure was solved by a combination of two traditional methods. Examination of the Patterson map allowed localization of the Br atoms. Direct methods with the *MULTAN* program (Germain, Main & Woolfson, 1970) confirmed the positions of Br atoms but the remaining heavy atoms were not found. They were located from an electron density map phased on the Br atoms. The structure was refined by the block-diagonal least-squares method, first with isotropic, then with anisotropic thermal parameters for the non-hydrogen atoms. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = [\sigma^2(F_o)]^{-1}$ . Atomic scattering factors for the non-hydrogen atoms were taken from Doyle & Turner (1968) and for H from *International Tables for X-ray Crystallography* (1962). Atomic scattering factors for Br were corrected for the real and imaginary components of anomalous dispersion using values of Cromer & Waber (1965). The H atoms were located from geometrical considerations ( $C-H = 1.00$  Å). The final  $R$  index,  $\sum |AF|/\sum F_o$ , was 0.067 for 2314 reflections. The H atoms were included, but not refined, in the last cycle of refinement, with isotropic temperature factors equal to those of the atoms to which they are bonded. The largest parameter shifts in the last cycle of refinement were less than 0.3

Table 1. Atomic parameters with the e.s.d.'s in parentheses ( $\times 10^4$  for positional parameters)

Positional parameters correspond to the anisotropic refinement.

	x	y	z	B ( $\text{\AA}^2$ )
Br(21)	3617 (1)	3708 (1)	3304 (1)	4.4 (1)
Br(1)	9100 (1)	4119 (1)	7891 (1)	4.3 (1)
Br(22)	6209 (2)	807 (1)	4569 (1)	4.6 (1)
Br(2)	14279 (2)	3683 (1)	6830 (1)	5.9 (1)
N(1)	10699 (9)	1430 (6)	7227 (6)	2.9 (5)
N(21)	6137 (9)	1754 (6)	1429 (6)	2.7 (5)
C(6)	11496 (11)	2184 (8)	8123 (8)	2.8 (6)
C(1)	12049 (12)	3162 (8)	7933 (8)	2.4 (6)
C(2)	12569 (12)	4123 (8)	9067 (8)	3.5 (7)
C(3)	13604 (13)	3743 (9)	9885 (9)	4.1 (7)
C(4)	12807 (13)	2976 (9)	10196 (8)	4.8 (8)
C(5)	11938 (12)	2091 (9)	9175 (8)	3.4 (6)
C(7)	11521 (13)	1130 (9)	9234 (9)	3.6 (7)
C(8)	10639 (12)	354 (8)	8320 (9)	3.4 (7)
C(9)	10145 (13)	-639 (9)	8353 (10)	4.3 (7)
C(10)	9279 (13)	-1380 (9)	7424 (11)	4.3 (7)
C(11)	8851 (14)	-1184 (9)	6410 (10)	4.8 (8)
C(12)	9336 (13)	-249 (9)	6375 (9)	5.1 (8)
C(13)	10205 (12)	516 (8)	7306 (9)	4.0 (7)
C(14)	10874 (12)	3495 (8)	7177 (8)	3.7 (7)
C(15)	13321 (13)	2655 (9)	7225 (9)	4.9 (7)
C(26)	6719 (10)	2476 (7)	2460 (8)	2.3 (6)
C(21)	6230 (11)	2402 (7)	3497 (8)	2.7 (6)
C(22)	6846 (12)	3309 (8)	4653 (8)	3.4 (7)
C(23)	8445 (13)	3612 (8)	4705 (8)	3.6 (7)
C(24)	8527 (13)	4086 (9)	3841 (9)	4.4 (8)
C(25)	7800 (12)	3271 (8)	2593 (8)	3.1 (6)
C(27)	8179 (11)	3294 (8)	1645 (8)	2.4 (5)
C(28)	7563 (11)	2579 (7)	566 (8)	2.5 (6)
C(29)	7880 (12)	2569 (8)	-482 (8)	3.2 (6)
C(210)	7250 (13)	1838 (9)	-1514 (8)	3.3 (6)
C(211)	6264 (13)	1028 (8)	-1582 (8)	3.8 (7)
C(212)	5912 (12)	1020 (8)	-599 (8)	3.6 (7)
C(213)	6535 (11)	1763 (8)	481 (8)	2.5 (6)
C(214)	4525 (12)	2368 (8)	3336 (8)	3.4 (6)
C(215)	6792 (12)	1241 (9)	3421 (8)	3.9 (7)

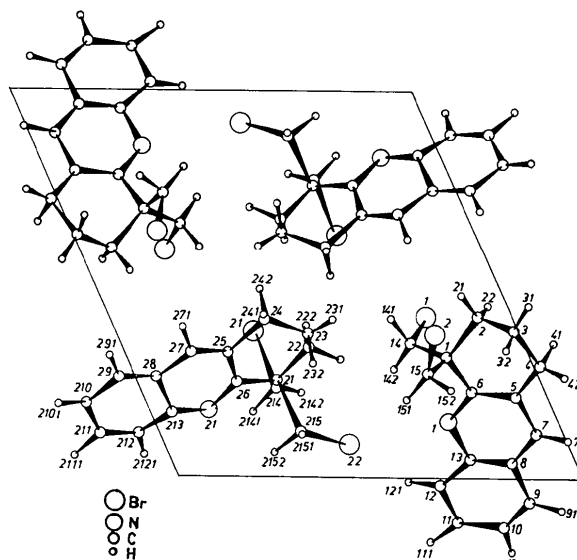
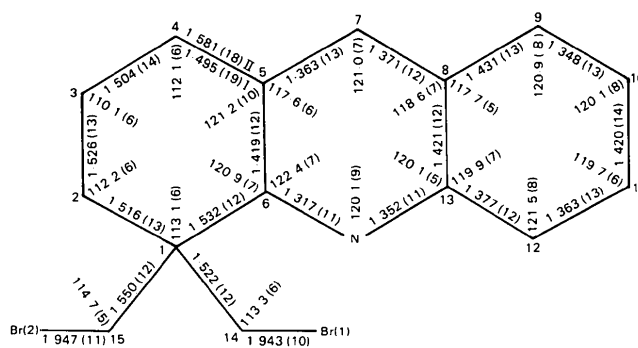


Fig. 1. Molecular packing.

Fig. 2. Average bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the two molecules.

of their e.s.d.'s. The atomic parameters are listed in Table 1.\* A final difference Fourier map indicated no unaccounted electron density.

### Discussion

The crystal structure consists of two conformationally different molecules. Their packing in the unit cell and the numbering scheme are shown in Fig. 1 (the numbering of heavy atoms in the first molecule is from 1 to 15, in the second from 21 to 215). Bond lengths

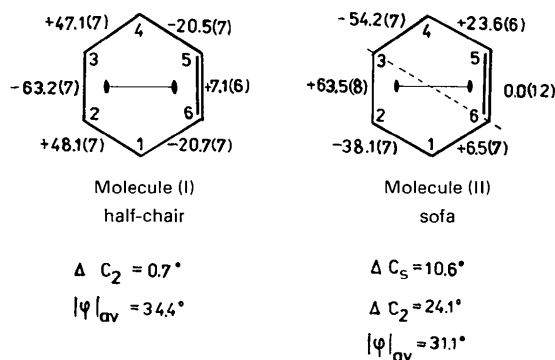
Table 2. Bond lengths ( $\text{\AA}$ ) with estimated standard deviations in parentheses

C(6)—C(1)	1.545 (18)	C(26)—C(21)	1.520 (17)
C(1)—C(2)	1.513 (18)	C(21)—C(22)	1.519 (18)
C(2)—C(3)	1.526 (19)	C(22)—C(23)	1.525 (17)
C(3)—C(4)	1.503 (21)	C(23)—C(24)	1.505 (19)
C(4)—C(5)	1.495 (19)	C(24)—C(25)	1.581 (18)
C(5)—C(6)	1.407 (17)	C(25)—C(26)	1.431 (17)
C(6)—N(1)	1.313 (16)	C(26)—N(21)	1.321 (15)
C(5)—C(7)	1.389 (19)	C(25)—C(27)	1.337 (17)
C(7)—C(8)	1.374 (18)	C(27)—C(28)	1.368 (16)
C(8)—C(13)	1.406 (18)	C(28)—C(213)	1.436 (17)
C(13)—N(1)	1.367 (16)	C(213)—N(21)	1.337 (15)
C(8)—C(9)	1.438 (19)	C(28)—C(29)	1.424 (17)
C(9)—C(10)	1.357 (19)	C(29)—C(210)	1.339 (17)
C(10)—C(11)	1.430 (21)	C(210)—C(211)	1.411 (19)
C(11)—C(12)	1.363 (20)	C(211)—C(212)	1.364 (17)
C(12)—C(13)	1.372 (18)	C(212)—C(213)	1.382 (17)
C(1)—C(15)	1.541 (18)	C(21)—C(215)	1.560 (17)
C(15)—Br(2)	1.940 (16)	C(215)—Br(22)	1.955 (15)
C(1)—C(14)	1.505 (18)	C(21)—C(214)	1.540 (15)
C(14)—Br(1)	1.962 (15)	C(214)—Br(21)	1.925 (14)

\* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34917 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond angles ( $^{\circ}$ ) with estimated standard deviations in parentheses

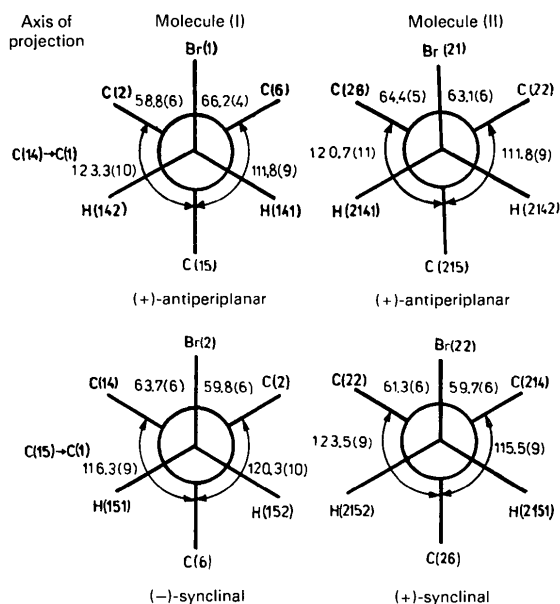
C(1)—C(2)—C(3)	111.8 (9)	C(21)—C(22)—C(23)	112.6 (8)
C(2)—C(3)—C(4)	110.5 (10)	C(22)—C(23)—C(24)	109.8 (9)
C(3)—C(4)—C(5)	113.1 (9)	C(23)—C(24)—C(25)	111.1 (9)
C(4)—C(5)—C(6)	122.7 (11)	C(24)—C(25)—C(26)	119.8 (9)
C(5)—C(6)—C(1)	120.4 (8)	C(25)—C(26)—C(21)	121.4 (7)
C(6)—C(1)—C(2)	111.4 (9)	C(26)—C(21)—C(22)	114.8 (8)
C(6)—C(5)—C(7)	116.8 (8)	C(26)—C(25)—C(27)	118.5 (8)
C(5)—C(7)—C(8)	120.2 (11)	C(25)—C(27)—C(28)	121.7 (10)
C(7)—C(8)—C(13)	119.7 (11)	C(27)—C(28)—C(213)	117.5 (10)
C(8)—C(13)—N(1)	119.6 (8)	C(28)—C(213)—N(21)	120.6 (7)
C(13)—N(1)—C(6)	119.8 (10)	C(213)—N(21)—C(26)	120.4 (9)
N(1)—C(6)—C(5)	123.6 (11)	N(21)—C(26)—C(25)	121.2 (10)
C(13)—C(8)—C(9)	118.0 (8)	C(28)—C(29)—C(210)	122.1 (11)
C(8)—C(9)—C(10)	119.8 (12)	C(29)—C(210)—C(211)	119.7 (11)
C(9)—C(10)—C(11)	120.6 (13)	C(210)—C(211)—C(212)	120.0 (8)
C(10)—C(11)—C(12)	119.4 (10)	C(211)—C(212)—C(213)	121.9 (11)
C(11)—C(12)—C(13)	121.1 (12)	C(212)—C(213)—C(28)	118.8 (10)
C(12)—C(13)—C(8)	121.0 (11)	C(213)—C(28)—C(29)	117.4 (7)
C(2)—C(1)—C(15)	112.2 (8)	C(214)—C(21)—C(26)	109.3 (8)
C(6)—C(1)—C(14)	110.2 (8)	C(215)—C(21)—C(22)	110.6 (8)
C(15)—C(1)—C(14)	106.4 (9)	C(215)—C(21)—C(214)	107.1 (9)
Br(1)—C(14)—C(1)	113.5 (8)	Br(22)—C(215)—C(21)	115.1 (7)
Br(2)—C(15)—C(1)	114.4 (8)	Br(21)—C(214)—C(21)	113.2 (8)

Fig. 3. Torsion angles ( $^{\circ}$ ) of the 1,1-bis(bromomethyl)cyclohexene rings.

and angles are shown in Tables 2 and 3. The average (for the two molecules) bond lengths and angles within  $3\sigma$  are shown in Fig. 2 on the schematic structural formula of the molecule.

Different conformations are observed for the 1,1-bis(bromomethyl)cyclohexene rings in the two symmetrically independent molecules. The torsion angles  $\varphi$ ,  $|\varphi|_{av}$  and the asymmetry parameters  $\Delta C_2$  and  $\Delta C_s$  (Duax & Norton, 1975) of these rings in molecules (I) and (II) are given in Fig. 3.

The ring in molecule (I) has a nearly ideal half-chair conformation with  $\Delta C_2(2-3) = 0.7^{\circ}$ . This ring in molecule (II) has a deformed-sofa conformation with  $\Delta C_s(3-6) = 10.6^{\circ}$  and  $\Delta C_2(2-3) = 24.1^{\circ}$ . Recently, analogous conformers of *p*-dithiacyclohexene rings have been observed in crystals of *N*-(2-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide (Bukowska-Strzyewska & Pniewska, 1979), where the conformations of this ring in the three symmetrically

Fig. 4. The conformations of the Br atoms and the  $\text{CH}_2\text{Br}$  groups down the C(1)—C(14) and C(1)—C(15) bonds, showing the relevant torsion angles ( $^{\circ}$ ).

independent molecules are: (a) symmetrical half-chair, (b) deformed intermediate sofa-half-chair, (c) converted half-chair form. The observed variety in the cyclohexene ring conformations indicates a small energy barrier between the conformers coexisting in solution and the possibility of the formation of a crystal containing different conformers.

Bond lengths in the cyclohexene rings are similar for both molecules. The typical differences between  $\text{C}(sp^3)\text{—C}(sp^3)$  and  $\text{C}(sp^3)\text{—C}(sp^2)$  bonds have not been observed.

The Newman projections along C(1)—C(15) and C(1)—C(14) are given in Fig. 4. According to Klyne & Prelog (1960) rules, the conformation of the Br(1) and Br(21) atoms is (+)-antiperiplanar, of Br(2) (–)-synclinal, and of Br(22) (+)-synclinal. The configuration of the Br atoms in relation to the main plane of the molecule is given in Fig. 5, which represents a projection of the cyclohexene ring perpendicular to this plane. The observed conformations of the bromomethyl groups lead to clear shortenings of the Br—H distances in both rings, independent of their sofa or half-chair conformation. The wedging of Br(2) between H(141) and H(21) and the covering of H(141) and H(142) of the C(14) $\text{H}_2\text{Br}$  group by the C(15) $\text{H}_2\text{Br}$  group can noticeably deactivate the nucleophilic substitution of the Br atoms. The Br—C bond lengths range from 1.925 (14) to 1.962 (15) Å and correspond to the typical length for this type of bond in paraffin hydrocarbons.

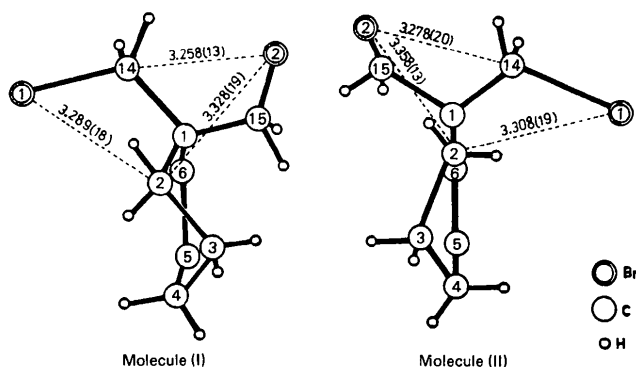


Fig. 5. Views of the 1,1-bis(bromomethyl)cyclohexene ring perpendicular to the C(1)–C(14)–C(15)–C(4) plane, showing some non-bonding short contacts (Å).

Table 4. *Least-squares planes of the quinoline rings and deviations (Å) of the atoms from the planes*

The equations of the planes are expressed in orthogonalized space as  $AX + BY + CZ = D$ . Atoms marked with an asterisk were not included in the least-squares-plane calculation. Equations of the planes are: for molecule (I),  $0.8610X - 0.4800Y - 0.1684Z = 4.9500$ ; for molecule (II),  $-0.7128X + 0.6369Y - 0.2936Z = -2.8187$ .

	(I)	(II)		(I)	(II)
C(6)	-0.004 (10)	0.032 (9)	C(13)	-0.007 (11)	-0.021 (10)
C(5)	-0.031 (11)	-0.013 (11)	N(1)	0.034 (8)	0.017 (8)
C(7)	0.014 (12)	-0.026 (10)	C(1)*	0.102 (11)	0.053 (10)
C(8)	0.002 (11)	-0.002 (10)	C(2)*	-0.334 (11)	0.178 (11)
C(9)	0.011 (12)	0.018 (11)	C(3)*	0.316 (12)	-0.614 (11)
C(10)	0.002 (12)	0.028 (12)	C(4)*	-0.117 (12)	-0.061 (12)
C(11)	-0.016 (12)	-0.017 (11)			
C(12)	-0.007 (12)	-0.016 (11)			
			$\chi^2 = 22.7$	$\chi^2 = 42.7$	
			$\alpha < 0.01$	$\alpha < 0.01$	

The quinoline rings in the molecules of the title compound are not perfectly planar. Table 4 gives the equations of their best planes, deviations of individual atoms from them, and  $\chi^2$  and  $\alpha$  values. The largest distances from this plane are observed in molecule (II)

for the atoms common to and neighbouring the cyclohexene ring. Both aromatic rings of molecule (II) are distinctly corrugated. The differentiation of the C–C and C–N bond lengths in both molecules is similar. As can be seen from Fig. 2, the average C–C bond lengths for the two molecules range from 1.348 (13) to 1.431 (13) Å and the C–N bond lengths from 1.317 (11) to 1.352 (11) Å. The intra-ring valency angles range from 117.6 (6) to 122.4 (7)° and a distinct pattern can be observed – the valency angle is larger if the bond lengths are shorter.

The molecular packing of the four molecules in the unit cell is given in Fig. 1. Interatomic contacts shorter than the sums of the van der Waals radii have not been observed.

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