

The significant intramolecular distances are between H(2)–H(11), 2.13 Å, and H(42)–H(7), 2.22 Å, as illustrated in Fig. 3. Solely from a consideration of the intramolecular H–H contacts, the observed orientation of the benzene ring would seem to be the most favorable, since rotation about the C(3)–C(6) bond in either direction in order to relieve these intramolecular H–H repulsions would increase others, notably H(7)–H(7') and H(11)–H(41'). The shortest intermolecular contacts are H(2)–O(1), 2.44 Å, and H(9)–H(11), 2.46 Å, where O(1) is generated by $x, \bar{y}, \frac{1}{2}+z$, and H(11) by $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

As previously mentioned the dimerization of 3-phenyl-2-cyclopentenone also occurs in the crystalline state. The solution photodimer undergoes thermal and photochemical monomerization while the solid-state dimer resists such decomposition. A preliminary study in this laboratory of the packing of the monomer, 3-phenyl-2-cyclopentenone, favors the head-to-tail *cis-anti-cis* structure of the solid-state photodimer. The monomer structure is characterized by double bonds which are approximately 3.7 Å apart, across a crystallographic center of symmetry. For dimerization to be effective in the solid state the reacting centers are usually less than 4 Å apart (Cohen & Schmidt, 1964; Schmidt, 1971). Crystals of the solid-state dimer have been prepared and further analysis is in progress.

Computations were performed on the CDC 6600 computer at WPAFB using the X-RAY system (Stew-

art, Kundell & Baldwin, 1970). Stereoscopic drawings were prepared by the ORTEP program of Johnson (1965).

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Structural Studies of Dibenz[*c,f*]azocines. I. *N*-Methyl-5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine*

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Crystals of the title compound, C₁₆H₁₇N, are orthorhombic, *Pna*2₁, with $a=15.400$, $b=16.041$, $c=5.055$ Å, and $Z=4$. The crystal structure has been determined by the tangent formula, and refined by the least-squares method to $R=0.042$ for the 849 observed reflexions. The eight-membered azocine ring is in the rigid boat-chair conformation, and the molecule has a non-crystallographic plane of symmetry through the N...C diagonal of the ring. The N–CH₃ bond is in an off-axial position, and its length of 1.435 (7) Å is about 0.04 Å shorter than expected for a N(*sp*³)–C(*sp*³) bond. The endocyclic angle at N is 117.5 (3)° and the exocyclic angles are 114.0 (3) and 114.7 (3)°; the mean at N being 115.4°. The length of the N...C diagonal is 3.34 Å.

Introduction

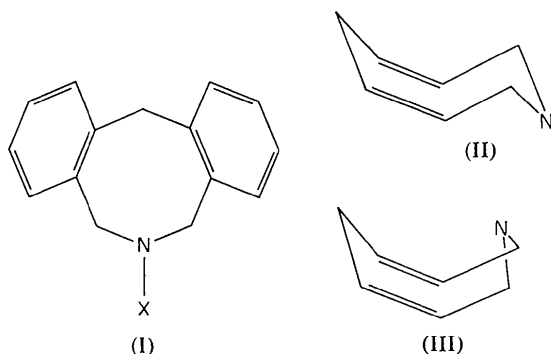
Several *N*-derivatives of 5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine (I), have been synthesized for pharmaco-

logical screening by Casadio, Pala, Crescenzi, Marazzi-Uberti, Coppi & Turba (1968), and by Pala, Mantegani & Zunga (1970). The conformational properties in solution of the *N*-methyl derivative have been determined by Renaud, Layton & Fraser (1973) from a study of its n.m.r. spectrum. The latter also plan to carry out further n.m.r. studies on different *N*-alkyl

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derivatives in order to provide information on the steric effects in these eight-membered ring systems. The azocine ring can be in one of two possible conformations: the rigid boat-chair (II) or the flexible twist-boat (III) conformation.



The *N*-methyl and the *N*-*t*-butyl derivatives have been subjected to an X-ray study in order to determine the conformations of the eight-membered azocine ring in the solid state and how it is affected by the size of the substituent on the N atom. Part I of this series describes the crystal and molecular structure of the *N*-methyl derivative and part II describes that of the *N*-*t*-butyl derivative and includes a comparison of the two structures.

Experimental

Crystal data

N-Methyl-5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine.
 $C_{16}H_{17}N$; F.W. 223.32.
 Source: R. N. Renaud; recrystallized from aqueous ethanol.
 Crystal habit: thin plate, colourless, m.p. 92.0°C.
 Crystal dimensions: 0.67 × 0.08 × 0.05 mm.
 Unit cell: orthorhombic, $Pna2_1$:
 $a = 15.400$ (4), $b = 16.041$ (1), $c = 5.055$ (1) Å,
 $V = 1248.7$ Å³, $Z = 4$, $D_x = 1.188$ g cm⁻³,
 $D_m = 1.178$ g cm⁻³ (floatation in KI solution, 22°C).
 Radiation: Cu $K\alpha$, Ni filter, $\lambda(K\alpha_1) = 1.54050$,
 $\lambda(K\alpha_2) = 1.54434$ Å, $\mu(\text{Cu}) = 5.60$ cm⁻¹.

Intensities

Automatic 4-circle diffractometer, crystal mounted along c^* , θ - 2θ scan at 2° min⁻¹, two background measurements per reflexion, $\sin \theta/\lambda \leq 0.588$. Number of reflexions scanned = 1187, number observed = 849, number unobserved = 338, number of observations per parameter = 3.9.

Corrections

(1) For crystal decomposition, empirically with the aid of one standard reflexion; (2) 1/Lp; (3) absorption by Gaussian integration (Ahmed, 1970), range of absorption correction to intensities = 1.028 to 1.063.

Table 1. $|E|$ statistics and starting phases

(a) The $|E|$ distribution compared with the expected values for centrosymmetric and non-centrosymmetric structures (Karle, Dragonette & Brenner, 1965)

	Observed	Centric	Acentric
$\langle E \rangle$	0.878	0.798	0.886
$\langle E ^2 \rangle$	0.982	1.000	1.000
$\langle E^2 - 1 \rangle$	0.770	0.968	0.736
$ E \geq 3.0$	0.08%	0.27%	0.01%
$ E \geq 2.0$	2.6	4.55	1.83
$ E \geq 1.0$	30.3	31.73	36.79

(b) Starting set of planes and phases

<i>h</i>	<i>k</i>	<i>l</i>	$ E $	Phase	
12	11	0	3.93	0	} Origin-defining
2	9	3	2.81	0	
7	3	2	2.55	0	
2	6	2	2.02	$\pi/4$	
2	1	0	2.09	$0, \pi$	
1	2	1	1.97	$\pm(\pi/4, 3\pi/4)$	

Structure determination

The $|E|$ distribution analysis shown in Table 1(a) clearly confirms that the space group is non-centrosymmetric. Phase determination by the tangent formula, Karle & Karle (1966) and Karle (1968), was restricted to the 204 planes with $|E| \geq 1.30$. Eight trial runs were carried out with the set of planes and phases listed in Table 1(b). Three of these had final R_K values of 0.186, 0.187, and 0.203, with the others in the range 0.34–0.40. The E maps for the phase sets with the two lowest R_K values gave all the non-hydrogen atoms, with each map showing one of the two enantiomorphs since the enantiomorph was not fixed in the starting set of phases. All the H atoms were located from a subsequent difference map.

Refinement

Block-diagonal least-squares minimizing $\sum w(\Delta F)^2$ where $w = 1/\{1 + [(|F_o| - 26)/35]^4\}$ and $2.5 \leq |F_o| \leq 100.5$; anisotropic for C and N, isotropic for H; and excluding all the unobserved reflexions. Mean $(\Delta/\sigma) = 0.11$ and maximum $(\Delta/\sigma) = 0.67$ in final cycle. For the observed reflexions the final R and $R_w = 0.042$, and all unobserved reflexions are calculated less than $1.5 \times$ their threshold amplitudes. In the final difference map the residual electron density is less than 0.2 e \AA^{-3} .

f curves

Hanson, Herman, Lea & Skillman (1964) for C and N; Stewart, Davidson & Simpson (1965) for H.

Computer programs

The N.R.C. Crystallographic Programs for the IBM/360 System by Ahmed, Hall, Pippy & Huber (1966).

Results

A perspective view of the molecular structure showing the conformation and the numbering system is presented in Fig. 1. The absolute configuration has not

been determined, and so could be the mirror image of that shown. The atomic parameters and their estimated standard deviations are listed in Table 2. The observed and calculated structure amplitudes are available.* The bond lengths and valency angles, not corrected for thermal vibration, are presented in Fig. 2.

Discussion

The n.m.r. studies of *N*-methyldibenzazocine by Renaud *et al.* (1973) established that the molecules in solution exhibit two conformations of the azocine ring, with 96.5% in the boat-chair and 3.5% in the twist-boat conformations. The present X-ray analysis has shown that in the solid state the azocine ring is in the boat-chair conformation.

The molecule as a whole has a non-crystallographic plane of symmetry passing through atoms C(12), H(12,1), H(12,2), N(6), C(17), and H(17,3). The boat-chair azocine ring may be described as consisting of four successive planes; *A*: through N(6), C(5), C(7); *B*: through C(5), C(7), C(15), C(14); *C*: through C(15), C(14), C(13), C(16); and *D*: through C(13), C(16), C(12); with interplanar dihedral angles of $\widehat{AB}=106.6$, $\widehat{BC}=146.1$, and $\widehat{CD}=110.4^\circ$. The six carbon atoms of each benzene ring are coplanar, $\chi^2=10.4$ and 0.5 for the two planes, and each plane forms a dihedral angle of $143.3 \pm 0.5^\circ$ with plane C. The dihedral angle between the planes of the two benzene rings is 114.3° .

The methyl substituent on N(6) is in an off-axial position as can be seen from the torsion angles C(17)-N(6)-C(5)-C(14) and C(17)-N(6)-C(7)-C(15) which are $49.9 \pm 0.1^\circ$, whereas the calculated values for the equatorial and axial positions are about 147 and 29° , respectively. Adoption of this off-axial position is necessary to keep the methyl group away from the π electron cloud of the benzene rings.

The bond lengths in this molecule are: 1.377–1.399 (6 or 7) Å for the twelve C–C aromatic bonds, mean = 1.391 Å; 1.515–1.516 (6) Å for the four C–C single bonds; 1.460 and 1.465 (5) Å for the two cyclic C–N bonds; and 0.95–1.13 (4 or 5) Å for the C–H bonds, mean = 1.06 Å. All these are in good agreement with the corresponding average values quoted by Sutton (1965). However, the remaining exocyclic N(6)–C(17) bond is of length 1.435 (7) Å which is significantly shorter than Sutton's value of 1.472 ± 0.005 Å for a N(sp^3)-C(sp^3) bond. The sp^3 hybridization state of N(6) is indicated by its deviation of 0.32 Å from the plane formed by its three adjoining carbon atoms. The 0.037 Å decrease in the N(6)–C(17) bond length is thus not due to donation from the nitrogen's lone pair, but could be attributed to more efficient

overlap of the bonding orbitals as indicated by the relatively large endocyclic C–N–C angle of 117.5° .

The shortest intramolecular H...H van der Waals contacts are 2.21 ± 0.05 Å for H(7,1)...H(8) and H(5,1)...H(4), whereas the H...H transannular contacts across the azocine ring are found to be 2.37 ± 0.02 Å. All the intermolecular distances are greater than the corresponding van der Waals contacts.

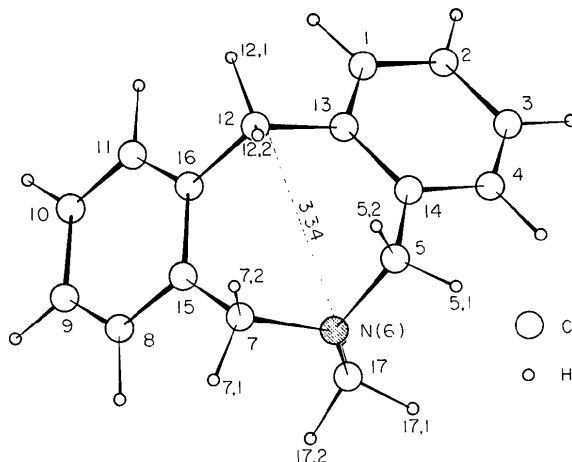


Fig. 1. Perspective view of the *N*-methyldibenz[*c,f*]azocine molecule.

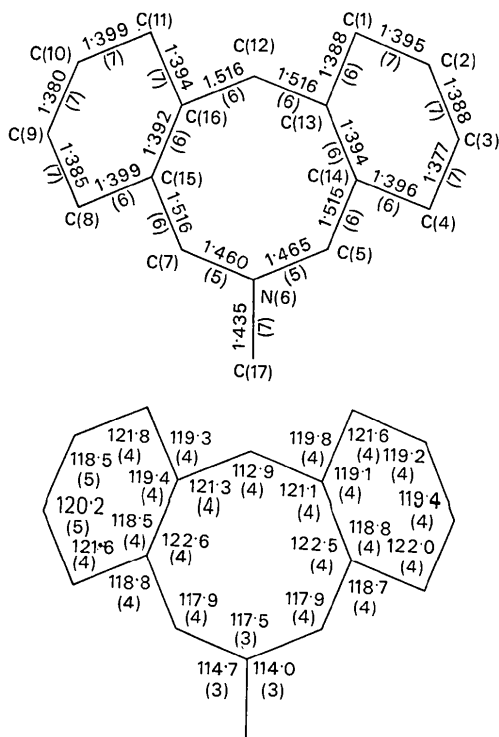


Fig. 2. Bond lengths (Å), valency angles ($^\circ$), and their estimated standard deviations in parentheses referred to the least significant digits.

* The structure-factor table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30407 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Fractional coordinates, vibration tensor components (\AA^2) for the expression $T = \exp[-2\pi^2(U_{11}a^*h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$, and their e.s.d.'s (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>	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
C(1)	3342 (3)	8604 (2)	-1313 (10)	714 (29)	478 (23)	522 (30)	-140 (51)	-45 (57)	324 (45)
C(2)	3898 (3)	9171 (3)	-2543 (11)	902 (34)	418 (23)	571 (31)	-41 (51)	-6 (59)	360 (50)
C(3)	4764 (3)	9198 (2)	-1783 (11)	841 (32)	356 (22)	623 (30)	-10 (50)	132 (65)	30 (44)
C(4)	5055 (3)	8665 (2)	158 (10)	656 (26)	351 (21)	564 (28)	-37 (47)	206 (56)	-38 (41)
C(5)	4877 (3)	7529 (3)	3516 (9)	639 (26)	463 (26)	405 (24)	-108 (48)	-136 (51)	19 (40)
N(6)	4978 (2)	6643 (2)	2893 (8)	497 (18)	434 (17)	460 (19)	99 (37)	-21 (39)	34 (33)
C(7)	4241 (3)	6096 (2)	3427 (9)	652 (28)	459 (22)	416 (26)	239 (45)	81 (52)	-1 (41)
C(8)	3498 (3)	5218 (3)	-2 (11)	620 (29)	537 (26)	648 (34)	-4 (54)	274 (56)	-309 (45)
C(9)	2883 (3)	5075 (3)	-1949 (12)	664 (30)	703 (30)	632 (33)	-313 (60)	291 (65)	-482 (49)
C(10)	2317 (3)	5701 (3)	-2683 (12)	514 (28)	958 (38)	675 (37)	-257 (66)	141 (57)	-509 (56)
C(11)	2375 (3)	6471 (3)	-1400 (11)	384 (23)	808 (33)	657 (34)	-12 (64)	-40 (54)	-154 (48)
C(12)	3007 (3)	7462 (3)	1933 (10)	493 (24)	639 (26)	559 (29)	-134 (57)	165 (52)	96 (46)
C(13)	3635 (3)	8065 (2)	639 (10)	533 (23)	401 (21)	414 (24)	-166 (44)	122 (48)	156 (39)
C(14)	4505 (3)	8093 (2)	1394 (9)	549 (23)	348 (20)	392 (23)	-142 (39)	-15 (46)	120 (39)
C(15)	3565 (3)	5989 (2)	1274 (9)	596 (28)	497 (25)	427 (27)	134 (45)	195 (48)	-190 (43)
C(16)	2985 (2)	6618 (3)	584 (10)	400 (20)	570 (23)	470 (24)	39 (49)	260 (47)	-89 (39)
C(17)	5414 (3)	6486 (3)	435 (11)	529 (24)	554 (26)	631 (31)	-117 (54)	165 (57)	70 (44)

	<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)	2708 (31)	8583 (27)	-1924 (122)	8.0 (1.4)	H(5,1)	5517 (24)	7760 (22)	3918 (89)	5.1 (1.0)
H(2)	3632 (28)	9604 (26)	-3790 (108)	6.6 (1.2)	H(5,2)	4595 (25)	7611 (25)	5170 (102)	5.8 (1.1)
H(3)	5209 (30)	9661 (26)	-2669 (120)	7.8 (1.4)	H(7,1)	4487 (23)	5507 (22)	3822 (86)	4.4 (1.0)
H(4)	5746 (29)	8637 (26)	794 (118)	6.9 (1.2)	H(7,2)	3937 (27)	6280 (26)	5381 (114)	6.8 (1.2)
H(8)	3951 (28)	4724 (26)	447 (120)	7.1 (1.3)	H(12,1)	2357 (27)	7713 (24)	1752 (98)	5.8 (1.1)
H(9)	2824 (27)	4486 (25)	-2925 (103)	6.8 (1.3)	H(12,2)	3106 (24)	7437 (23)	3914 (86)	4.6 (0.9)
H(10)	1843 (29)	5612 (28)	-4199 (129)	7.4 (1.3)	H(17,1)	6037 (27)	6825 (25)	260 (109)	6.4 (1.2)
H(11)	1944 (27)	6966 (25)	-1664 (119)	6.5 (1.2)	H(17,2)	5729 (34)	5884 (31)	303 (148)	10.5 (1.7)
					H(17,3)	5059 (37)	6588 (34)	-1394 (147)	12.6 (2.0)

The angles between the H(12,1) ··· H(12,2) vector and the normals to the two benzene rings are 82.9° and 84.7°, mean 83.8 ± 0.9°.

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