Acta Cryst. (1974). B30, 1674

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

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(*Received* 22 *February* 1974; *accepted* 8 *March* 1974)

Crystals of the title compound, $C_{19}H_{23}N$, are triclinic, $P\bar{1}$, with $a=10{\cdot}143$, $b=9{\cdot}863$, $c=9{\cdot}568$ Å, $\alpha=111{\cdot}38$, $\beta=116{\cdot}08$, $\gamma=91{\cdot}71°$, and $Z=2$. The crystal structure has been determined by the symbolic addition procedure and refined by the least-squares method to $R=0{\cdot}052$ for the 1993 observed reflexions. The azocine ring has the twist-boat conformation with half of the molecules left-handed and the other half right-handed, but otherwise the same degree of twist for all molecules. The endocyclic angle at N is 113·0 (2)° and the exocyclic angles are 115·1 (2) and 115·4 (2)°; mean = 114·5°. The length of the N· · ·C diagonal is 2·86 Å, indicating very weak transannular interaction across the azocine ring. Some preferred localization of electronic charge is observed in the benzene rings.

Introduction

The crystal structure of *N*-methyldihydrodibenzazocine has been described by Hardy & Ahmed (1974) as part I of this series. X-ray structural analysis of the title compound has been undertaken in order to determine the effect on the conformation of the azocine ring system when the bulky t-butyl group replaces the methyl group on the nitrogen atom.

Crystallization of *N*-t-butyldihydrodibenz[*c*,*f*]azocine from aqueous ethanol yielded small thin plate-like orthorhombic crystals of poor quality. Their X-ray diffraction pattern could not be fitted directly to any of the space groups. However, very slow crystallization from the same solvent yielded large well formed triclinic crystals of space group $P\bar{1}$. These were the crystals used for the structural details reported in this paper.

Experimental

Crystal data

N-t-Butyl-5,6-dihydro-7*H*,12*H*-dibenz[*c*,*f*]azocine.
$C_{19}H_{23}N$; F.W. 265·40
Source: R. N. Renaud; recrystallized from aqueous ethanol by slow evaporation.
Crystal habit: non-uniform hexagonal plate elongated about the *b* axis, colourless, m.p. 61–61·5°C.
Crystal dimensions: approximately 0·5 × 0·2 × 0·1 mm.
Unit cell: triclinic, $P\bar{1}$:
$a=10{\cdot}143$ (3), $b=9{\cdot}863$ (2), $c=9{\cdot}568$ (1) Å,
$\alpha=111{\cdot}38$ (4), $\beta=116{\cdot}08$ (3), $\gamma=91{\cdot}71$ (1)°,
$V=779{\cdot}7$ Å^3, $Z=2$, $D_x=1{\cdot}130$ g cm^{-3},
$D_m=1{\cdot}110$ g cm^{-3} (flotation in KI solution, 22°C).
Radiation: Cu $K\alpha$, Ni filter, $\lambda(K\alpha_1)=1{\cdot}54050$, $\lambda(K\alpha_2)=1{\cdot}54434$ Å, μ(Cu) = 4·96 cm^{-1}.

Intensities

Automatic 4-circle diffractometer, crystal mounted along **c***, θ–2θ scan at 2° min^{-1}, two background meas-

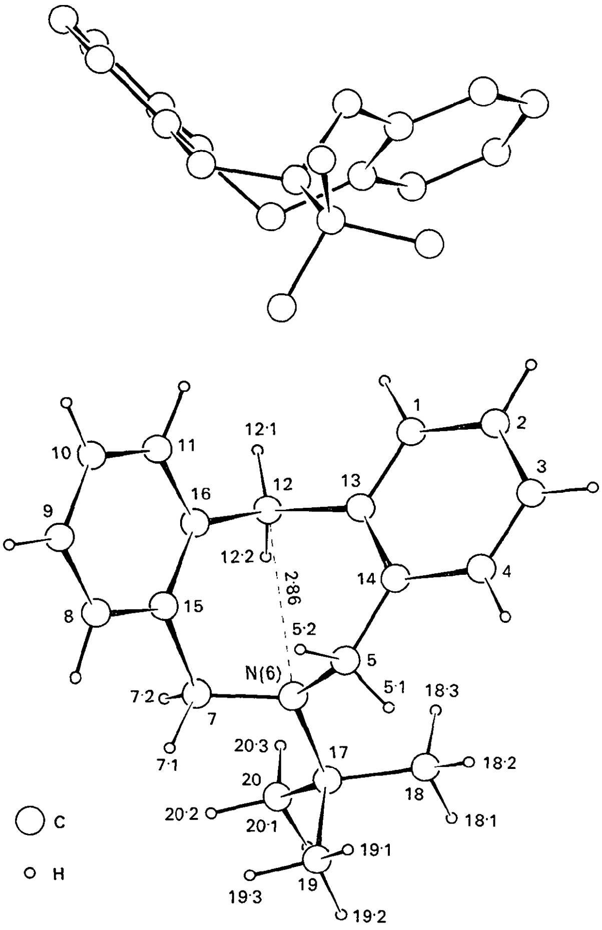

Fig. 1. Two orthogonal views of the molecule showing the twist-boat conformation of the azocine ring. The H atoms are omitted from the top view for clarity.

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* N.R.C. Publication No. 14043.
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urements per reflexion, $\sin\theta/\lambda \leq 0{\cdot}588$. Number of reflexions scanned = 2656, number observed = 1993, number unobserved = 663, number of reflexions per parameter = 7·3.

Corrections

(1) For crystal decomposition, empirically with the aid of one standard reflexion; (2) 1/Lp.

Structure determination

Symbolic addition; all C and N atoms located from E map with 321 reflexions having $|E| \geq 1{\cdot}5$; all H atoms from subsequent difference map.

Refinement

Block-diagonal least-squares minimizing $\sum w(\Delta F)^2$ where $w=1/\{1+[(|F_o|-14)/32]^4\}$ and $1{\cdot}0 \leq |F_o| \leq 82{\cdot}3$; anisotropic for C and N, isotropic for H; and excluding all the unobserved reflexions. Mean $(\Delta/\sigma) = 0{\cdot}2$ and maximum $(\Delta/\sigma) = 1{\cdot}08$ in final cycle. R and $R_w = 0{\cdot}052$ for the observed reflexions, and $|F_c| \leq 1{\cdot}5|F_{th}|$ for all the unobserved reflexions. The residual electron density, $|\Delta\varrho|_{\max} < 0{\cdot}2$ and $\sigma(\varrho) = 0{\cdot}04$ e Å^{-3}.

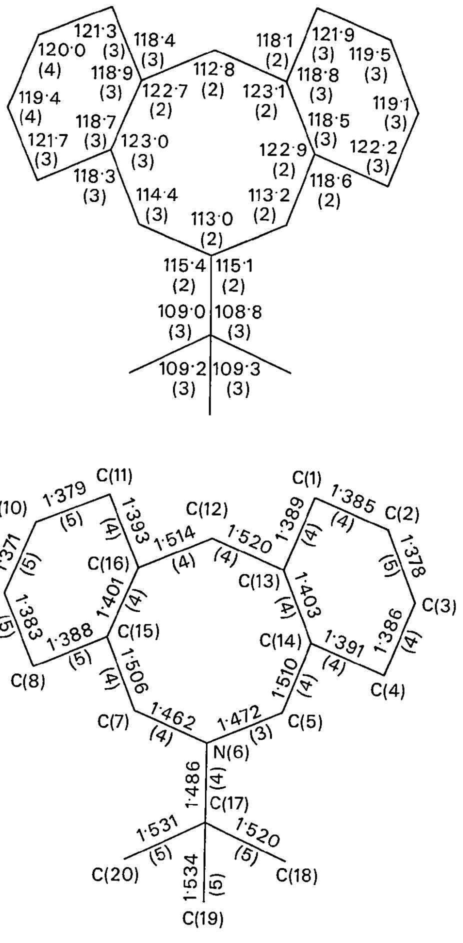

Fig. 2. Bond lengths (Å), angles (°), and their estimated standard deviations in parentheses. The angles C(18)–C(17)–C(20) and N(6)–C(17)–C(19) are 108·0 (3) and 112·3 (3)°, respectively.

f curves and computer programs

Same as for part I (Hardy & Ahmed, 1974).

Results

Two views of the molecular structure, showing the azocine ring in the twist-boat conformation, are presented in Fig. 1. The refined atomic parameters are listed in Table 1, and structure amplitudes are available.* The bond lengths and angles, not corrected for thermal vibrations, are shown on the schematic drawings in Fig. 2.

Discussion

The *N*-t-butyl dibenzazocine molecule, in the solid state, has its azocine ring in a twist–boat conformation. The degree of twist may be described by the torsion angles N(6)–C(7)–C(15)–C(16) and N(6)–C(5)–C(14)–C(13) which are estimated from a wire model of the molecule to be 0–10° for the untenable boat conformation and 60–80° for the maximum degree of twist. In this structure they have the values 41·3 and 42·3° respectively, the N(6)· · ·C(12) contact across the ring being 2·86 Å. Atom C(17) of the t-butyl group is in the equatorial position and is very nearly coplanar with atoms N(6), C(7), and C(15) of the azocine ring, where the torsion angle C(17)–N(6)–C(7)–C(15) is 179·5°. In the crystals, the azocine rings have the left-handed and right-handed forms of the twist-boat conformation in equal ratios, with an inversion centre of symmetry relating the two forms of the molecule.

Preliminary n.m.r. studies by Renaud, Layton & Fraser (1973*b*) of the *N*-t-butyl molecules in solution have shown that about 95% of the molecules have the azocine ring in a twist-boat conformation, and that the interconversion energy barrier between a pair of hand-related conformers is only 2–3 kcal mol^{-1}. The rocking motion from one conformer to the other is fast on the n.m.r. time scale and so gives rise to a time-averaged boat conformation.

The mean bond lengths are: 1·512 Å for C–C single (in the azocine ring), 1·528 Å for C–C single (in the t-butyl), 1·387 Å for C–C aromatic, 1·473 Å for C–N, and 1·06 Å for C–H. The aromatic bonds C(2)–C(3) and C(9)–C(10) are about 0·03 Å shorter than C(13)–C(14) and C(15)–C(16), indicating some peripheral localization of electronic charge in the molecule.

The χ^2 values for the weighted mean planes of the two benzene rings are 19·1 and 2·2, where both values

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30408 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

should be less than 11·3 if the six carbon atoms of each ring are to considered coplanar.

None of the intermolecular contacts in the crystal structure are significantly shorter than the appropriate van der Waals contacts.

Conclusions

From the crystallographic studies described in parts I and II of this series, the conformation of the azocine ring in the solid state has been found to be dependent on the size of the *N*-substituent. The conformation is boat–chair in *N*-methyldihydrodibenz[*c*,*f*]azocine, and twist-boat in the *N*-t-butyl analogue. Although the molecule is fairly flexible in the twist-boat conformation, the degree of twist is identical for all the molecules in the crystal where 50% are left-handed and the other 50 % are right-handed. The boat–chair and twist-boat conformations were found by Renaud *et al.* (1973*a*,*b*) from their n.m.r. studies of these molecules in solution, and they were also proposed by Dunitz & Waser (1972) for the two isomers of the related cycloocta-1,4-diene molecule.

Table 2. *Some torsion angles* (°) *in the azocine ring systems*

Hand (2) is the mirror image of the molecule shown in Fig. 1.

	$C_{16}H_{17}N$	$C_{19}H_{23}N$	
		Hand (1)	Hand (2)
C(14)-C(5)—N(6)—C(7)	−88·6	−115·5	−64·5
C(5)—N(6)—C(7)—C(15)	88·1	44·1	135·9
N(6)—C(5)—C(14)-C(13)	71·3	42·3	−42·3
N(6)—C(7)—C(15)-C(16)	−71·5	41·3	−41·3
C(12)-C(13)-C(14)-C(15)	0·3	−3·1	3·1
C(12)-C(16)-C(15)-C(7)	1·1	−2·8	2·8
C(16)-C(12)-C(13)-C(14)	−88·0	59·4	91·0
C(13)-C(12)-C(16)-C(15)	86·9	−91·0	−59·4
C(17)-N(6)—C(5)—C(14)	49·8	109·0	(±)179·5
C(17)-N(6)—C(7)—C(15)	−50·0	(±)179·5	−109·0

The torsion angles in the azocine rings of the two determined conformations are listed in Table 2. The torsion angles C(12)–C(13)–C(14)–C(5) and C(12)–C(16)–C(15)–C(7), which should be zero for no strain in the ring, are 1·1 and 0·3° in the *N*-methyl, and 3·1 and 2·8° in the *N*-t-butyl molecules. This is indicative of more strain in the latter despite the added flexibility of the twist-boat form of the azocine ring.

Table 1. *Fractional coordinates, vibration tensor components* (Å²) *for the expression* $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl + \ldots)]$, *and their e.s.d.'s* (*all quantities* × 10⁴)

The isotropic temperature factors of the H atoms are in Å².

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
C(1)	5184 (3)	3273 (3)	495 (3)	587 (17)	578 (17)	506 (16)	526 (28)	524 (28)	437 (28)
C(2)	3721 (3)	2451 (3)	−678 (3)	569 (18)	748 (21)	477 (16)	462 (30)	343 (28)	433 (31)
C(3)	3104 (3)	1370 (3)	−408 (3)	440 (16)	724 (20)	448 (16)	156 (29)	215 (26)	124 (28)
C(4)	3969 (3)	1119 (3)	1029 (3)	460 (15)	540 (16)	474 (15)	186 (25)	384 (25)	−6 (25)
C(5)	6328 (3)	1527 (3)	3696 (3)	459 (14)	427 (14)	455 (14)	329 (23)	402 (24)	−9 (22)
N(6)	7267 (2)	2838 (2)	5329 (2)	417 (11)	522 (13)	396 (11)	294 (20)	341 (19)	−40 (19)
C(7)	8881 (3)	2907 (3)	5984 (3)	456 (15)	784 (21)	467 (16)	502 (30)	256 (26)	4 (28)
C(8)	10453 (3)	1715 (3)	4714 (4)	402 (15)	587 (18)	823 (22)	614 (33)	385 (30)	170 (26)
C(9)	11001 (3)	1392 (4)	3564 (5)	455 (17)	665 (21)	1162 (29)	414 (39)	818 (37)	220 (30)
C(10)	10466 (4)	1914 (4)	2317 (5)	642 (20)	761 (22)	967 (26)	274 (38)	1102 (40)	125 (33)
C(11)	9393 (3)	2754 (3)	2216 (4)	537 (17)	633 (18)	616 (18)	326 (30)	648 (29)	−62 (28)
C(12)	7646 (3)	4009 (3)	3170 (3)	485 (15)	429 (14)	509 (15)	380 (24)	465 (25)	81 (23)
C(13)	6054 (3)	3049 (3)	1953 (3)	423 (13)	404 (13)	410 (13)	286 (22)	440 (23)	206 (21)
C(14)	5440 (3)	1932 (3)	2220 (3)	404 (13)	432 (14)	369 (13)	191 (22)	357 (22)	81 (21)
C(15)	9380 (3)	2566 (3)	4648 (3)	351 (13)	524 (16)	515 (15)	365 (26)	303 (24)	−18 (23)
C(16)	8837 (3)	3098 (3)	3371 (3)	361 (13)	424 (14)	482 (14)	260 (23)	381 (23)	−48 (21)
C(17)	6744 (3)	3158 (3)	6620 (3)	635 (18)	515 (16)	508 (16)	359 (26)	638 (28)	180 (27)
C(18)	5102 (4)	3250 (4)	5799 (4)	697 (20)	886 (24)	873 (24)	818 (40)	1030 (39)	547 (37)
C(19)	6901 (4)	1959 (4)	7313 (4)	1044 (26)	771 (22)	678 (20)	813 (36)	1104 (40)	559 (39)
C(20)	7666 (4)	4679 (4)	8113 (4)	975 (26)	662 (21)	672 (21)	−60 (34)	879 (40)	10 (37)

	x	y	z	B		x	y	z	B
H(1)	5631 (31)	4138 (31)	337 (35)	5·7 (0·7)	H(12,1)	7821 (29)	4759 (29)	2671 (33)	4·8 (0·6)
H(2)	3082 (35)	2733 (35)	−1728 (39)	7·2 (0·8)	H(12,2)	7740 (26)	4694 (26)	4325 (29)	3·7 (0·5)
H(3)	2002 (34)	753 (35)	−1279 (39)	7·0 (0·8)	H(18,1)	4704 (33)	3595 (33)	6666 (38)	6·7 (0·8)
H(4)	3530 (30)	311 (30)	1206 (34)	5·3 (0·7)	H(18,2)	4305 (39)	2179 (39)	4815 (44)	8·9 (1·0)
H(8)	10824 (34)	1296 (34)	5690 (39)	7·0 (0·8)	H(18,3)	4905 (40)	4007 (39)	5215 (45)	8·9 (1·0)
H(9)	11833 (35)	778 (35)	3681 (40)	7·3 (0·8)	H(19,1)	6326 (37)	856 (38)	6308 (42)	8·3 (0·9)
H(10)	10866 (37)	1723 (37)	1477 (41)	7·9 (0·9)	H(19,2)	6541 (38)	2187 (37)	8174 (42)	8·1 (0·9)
H(11)	8933 (35)	3126 (35)	1191 (39)	6·9 (0·8)	H(19,3)	8069 (38)	1920 (38)	8033 (43)	8·6 (0·9)
H(5,1)	5557 (27)	868 (27)	3800 (30)	4·0 (0·6)	H(20,1)	7209 (41)	5042 (41)	8956 (46)	9·7 (1·0)
H(5,2)	7029 (26)	821 (27)	3428 (30)	3·9 (0·6)	H(20,2)	8830 (37)	4638 (38)	8843 (42)	8·4 (0·9)
H(7,1)	9323 (33)	2181 (33)	6655 (37)	6·3 (0·7)	H(20,3)	7627 (37)	5507 (37)	7660 (41)	7·9 (0·9)
H(7,2)	9481 (34)	3986 (34)	6903 (38)	6·9 (0·8)					

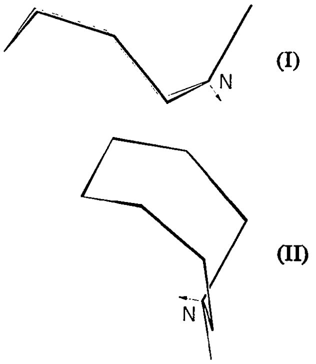

Fig. 3. Views of the azocine ring showing the nitrogen atom's lone pair of electrons in: (I) *N*-methyl, and (II) *N*-t-butyl dibenz[*c,f*]azocine.

The directions of the lone pair electrons for the two determined conformations are shown in Fig. 3. In the boat–chair conformation there is no indication of transannular interaction since the lone–pair electrons point away from the rest of the molecule, and the N(6)···C(12) and N(6)···H(12,2) distances are 3·344 and 3·19 Å, respectively. However, for the twist-boat conformation the lone-pair electrons point in towards the rest of the molecule, the N(6)···C(12) and N(6)···H(12,2) distances are 2·856 and 2·48 Å, and the C(12)–H(12,2)···N(6) angle is 101·1°. This may be indicative of slight interaction across the azocine ring, and could account for the observed peripheral localization of electronic charge in the benzene rings. In other compounds where transannular interaction has been postulated, the N···C(=O) distances are much shorter: 1·993 Å across the 8-membered ring of clivorine (Birnbaum, 1972), and 2·555 and 2·581 Å across the 10-membered rings of protopine and cryptopine (Hall & Ahmed, 1968*a,b*).

Grateful acknowledgement is made to Drs R. N. Renaud and R. B. Layton for supplying the crystals, and to Mrs M. E. Pippy for assistance with the computations.

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Acta Cryst. (1974). **B30**, 1677

Structure Cristalline et Moléculaire du Pipéridino-1 Benzyl-1 Cyclohexane

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(*Reçu le* 3 *mars* 1974, *accepté le* 12 *mars* 1974)

The crystal structure of 1-piperidino-1-benzylcyclohexane ($C_{18}NH_{27}$) has been determined by three-dimensional X-ray analysis. The crystals are monoclinic, $a=19\cdot491$, $b=6\cdot428$, $c=26\cdot164$ Å, $\beta=109\cdot10°$ and $Z=8$, space group $P2_1/c$. The structure was solved by direct methods and the final R index is 0·06.

Introduction

Cette étude a été entreprise afin de déterminer la configuration du carbone C(1) et la conformation de rotation des différents substituants portés par le cycle cyclohexanique.

Partie expérimentale

Les cristaux étudiés nous ont été fournis par le Laboratoire de M le Professeur Welvart. Les principales données expérimentales sont résumées dans le Tableau

Tableau 1. *Principales données expérimentales*

Formule brute: $C_{18}NH_{27}$
Masse moléculaire: 257
Système cristallin: monoclinique
Groupe spatial: $P2_1/c$
a = 19,491 (2) Å
b = 6,428 (2)
c = 26,164 (3)
β = 109,10°
V = 3082 Å^3
$F(000)$ = 1136 e
Nombre de réflexions indépendantes: 2901
Radiation utilisée, Mo $K\alpha$ = 0,7107 Å
Z = 8