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Molecular Geometry. IV. Structure of 3,4,10,11,-Dibenzo-1,8-diazacyclotetradeca-1,3,8,10-tetraene, a Compound Containing a 14-Membered Ring

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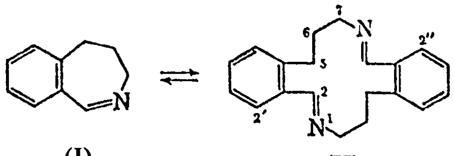
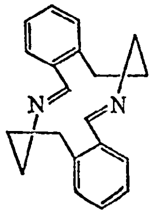
The structure of the title compound, $C_{20}H_{22}N_2$, has been determined for the purpose of elucidating the conformation of a large ring. 1098 three-dimensional intensities were measured on a Picker PDP 8/I diffractometer and the structure was refined to an R value of 0·65. The space group is $P2_1/c$ with $Z=2$ and $a=5·02$, $b=9·60$, $c=16·35$ Å, $\beta=96·5°$. The structure was solved by the symbolic addition method. In the 14-membered ring there are two *trans*-substituted double bonds. The C=N bond length is 1·257 Å.

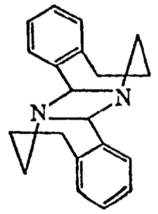
Goldman, Larson, Tretter & Andrews (1969) have recently shown that on standing 3,4-dihydro-5*H*-2-benzazepine (I) dimerizes to 3,4,10,11-dibenzo-1,8-diazacyclotetradeca-1,3,8,10-tetratene (II); the dimerization reaction is acid catalyzed and reversible. From mechanistic considerations a *trans,trans*'chair' structure (III) for (II) that placed the carbon–nitrogen double bonds in close proximity to facilitate formation of the assumed 1,3-diazetidine intermediate (IV) was postulated. A study of the crystal structure of (II) was initiated for the purpose of investigating the conformation of the 14-membered ring, since information pertaining to the structural aspects of large rings is scarce.



(I) (II)



(III)



(IV)

Experimental

Crystals of (II) were grown from hexane and a needle with dimensions 0·4 × 0·2 × 0·2 mm was selected for recording crystal and intensity data. Preliminary oscillation and Weissenberg photographs showed that the crystals are monoclinic and that (II) crystallizes in the space group $P2_1/c$ [$a=5·024(8)$, $b=9·598(2)$, $c=16·352(4)$ Å, $\beta=96·61°(2)$, $\varrho_c=1·218$ g cm^{-3}, $\varrho_{\rm obs}=1·225$ g cm^{-3}, $Z=2$].

The cell parameters were determined by least-squares fit to the settings for the four angles of eight reflections on a Picker FACS-I diffractometer (Cu $K\alpha$, $\lambda=1·54178$ Å). The crystal was mounted along the a axis. Data were collected with a Picker FACS-I system with monochromatic radiation and a θ–2θ scan technique. When the count rate exceeded 10000 c.p.s., attenuators were inserted. The diffracted intensities were measured with a scintillation counter equipped with a pulse-height analyzer. The scan rate was 2·0° min^{-1} with 10 s background measured at the two extremes of each scan. The scan range had a base width of 2·2°, with a dispersion factor allowing for α_1–α_2 splitting being applied at large 2θ values. One independent set of data was measured, which consisted of 1415 reflections of which 1098 were considered to be observed using the criterion that a reflection be greater than three times its standard deviation. One standard reflection was monitored every 100 measurements to check the crystal alignment and stability; no decrease in the intensity of the standard was observed. Lorentz and polarization corrections were applied to the data but no correction was made for absorption.

Structure determination and refinement

Normalized structure factors (E values) were calculated and the symbolic addition procedure for centrosymmetric crystals was used to obtain phases for 165 reflections with $E > 1·5$. An E map clearly revealed the benzene ring and a difference map located the remaining five atoms in the asymmetric unit. The initial R index ($R=\sum||F_o|-|F_c||/\sum|F_o|$) of 0·446 was reduced to 0·148 after four cycles of isotropic least-squares refinement. Two cycles of anisotropic refinement reduced the residual to 0·117. A difference map revealed the positions of all 11 hydrogen atoms and further refinement of coordinates using isotropic thermal parameters for hydrogens (these were set equal to the

Table 1. *Final positional and thermal parameters of dibenzodiazacyclotetradecatetraene (estimated standard deviations in parentheses)*

The temperature factor ($\times 10^4$) for non-hydrogen atoms is of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+\beta_{23}kl)]$. The hydrogen atoms were given isotropic temperature factors of the atoms to which they are attached.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−0·1502 (4)	0·0934 (3)	0·3005 (1)	312 (10)	120 (3)	34 (1)	−32 (4)	8 (2)	−9 (1)
C(2)	0·0639 (4)	0·1142 (3)	0·3607 (1)	282 (10)	108 (3)	38 (1)	3 (4)	9 (2)	0 (1)
C(3)	0·1239 (4)	0·2448 (2)	0·3947 (1)	162 (9)	109 (3)	−28 (1)	−11 (3)	10 (2)	2 (1)
C(4)	−0·0392 (4)	0·3585 (2)	0·3665 (1)	174 (9)	108 (3)	27 (1)	−19 (3)	10 (2)	5 (1)
C(5)	−0·2527 (4)	0·3353 (2)	0·3050 (1)	245 (10)	122 (3)	29 (1)	−9 (4)	−7 (2)	6 (1)
C(6)	−0·3075 (5)	0·2059 (3)	0·2730 (1)	291 (10)	144 (3)	26 (1)	−39 (4)	−12 (2)	−3 (1)
C(7)	0·0116 (4)	0·5016 (2)	0·3974 (1)	179 (9)	108 (3)	28 (1)	−13 (3)	−1 (2)	5 (1)
N	−0·1627 (3)	0·5961 (2)	0·3894 (1)	227 (8)	108 (2)	32 (1)	0 (3)	−6 (2)	1 (2)
C(9)	−0·0829 (4)	0·7360 (2)	0·4158 (1)	204 (9)	109 (3)	34 (1)	−8 (3)	4 (2)	4 (1)
C(10)	0·3566 (4)	0·2551 (2)	0·4619 (1)	124 (9)	113 (3)	39 (1)	1 (3)	−1 (2)	1 (1)
C(11)	0·2991 (4)	0·1894 (2)	0·5428 (1)	214 (9)	107 (3)	34 (1)	12 (4)	−12 (2)	2 (1)

Table 1 (*cont.*)

	x	y	z
H(1)	−0·1880 (48)	−0·0102 (25)	0·2762 (15)
H(2)	0·1898 (47)	0·0376 (24)	0·3819 (14)
H(5)	−0·3700 (42)	0·4171 (22)	0·2860 (13)
H(6)	−0·4489 (43)	0·1921 (20)	0·2319 (13)
H(7)	0·2028 (46)	0·5334 (22)	0·4243 (14)
H1(C9)	−0·0622 (46)	0·7845 (22)	0·3626 (14)
H2(C9)	0·0627 (46)	0·7329 (19)	0·4603 (14)
H1(C10)	0·5038 (45)	0·2011 (22)	0·4380 (13)
H2(C10)	0·4049 (44)	0·3494 (23)	0·4757 (13)
H1(C11)	0·2670 (41)	0·0872 (25)	0·5316 (13)
H2(C11)	0·4567 (46)	0·1931 (21)	0·5826 (13)

isotropic thermal parameters of the atoms to which they were attached) reduced the residual to 0·065. Refinement was terminated at this stage since the ratio of shifts to standard deviations was less than 0·3 for all parameters. The weighting scheme that was employed in the least-squares refinement was $\sqrt{w}=1/\sigma(F)$ where $\sigma(F)=0{\cdot}5\sigma(F^2)/F$. The scattering factors used throughout the work were those of Hanson, Herman, Lea & Skillman (1964). No correction was made for extinction.

Results and discussion

Table 1 summarizes positional and thermal parameters for the molecule and Tables 2 and 3 summarize bond distances and angles. Observed and calculated structure factors are shown in Table 4. The molecule has a center of symmetry and makes use of this symmetry in the space group $P2_1/c$. Bond distances and angles are normal and no significant deviations from accepted values were found. The estimated standard deviations in the C–C and C–N bond distances are 0·003 Å and in the C–H bonds are 0·02 Å. The bond angles involving the non-hydrogen atoms possess an average standard deviation of 0·2°, while those involving hydrogen atoms average 1·0°.

Table 2. *Bond lengths* (Å) *in the molecule (estimated standard deviations in parentheses*

C(1)—C(2)	1·387 (3)	C(1)—H(1)	1·07 (3)
C(2)—C(3)	1·390 (3)	C(2)—H(2)	0·99 (3)
C(3)—C(4)	1·409 (3)	C(5)—H(5)	1·00 (2)
C(4)—C(5)	1·401 (3)	C(6)—H(6)	0·94 (2)
C(5)—C(6)	1·365 (3)	C(7)—H(7)	1·05 (2)
C(6)—C(1)	1·382 (3)	C(9)—H1(C9)	1·00 (2)
C(4)—C(7)	1·476 (3)	C(9)—H2(C9)	0·97 (2)
C(3)—C(10)	1·512 (3)	C(10)–H1(C10)	1·02 (2)
C(7)—N	1·257 (3)	C(10)–H2(C10)	0·96 (2)
N——C(9)	1·453 (3)	C(11)–H1(C11)	1·01 (3)
C(10)–C(11)	1·522 (3)	C(11)–H2(C11)	0·97 (2)
C(11)–C(9)′	1·524 (3)		

Table 3. *Bond angles* (°) *in the molecule (estimated standard deviations in parentheses)*

C(1)—C(2)—C(3)	121·9 (2)
C(2)—C(3)—C(4)	118·4 (2)
C(3)—C(4)—C(5)	118·7 (2)
C(4)—C(5)—C(6)	121·6 (2)
C(5)—C(6)—C(1)	120·2 (2)
C(6)—C(1)—C(2)	119·1 (2)
C(2)—C(3)—C(10)	117·6 (2)
C(4)—C(3)—C(10)	124·0 (2)
C(5)—C(4)—C(7)	118·4 (2)
C(3)—C(4)—C(7)	122·5 (2)
C(3)—C(10)–C(11)	113·4 (2)
C(10)–C(11)–C(9)′	113·0 (2)
C(4)—C(7)—N	123·0 (2)
C(7)—N——C(9)	118·0 (2)
C(2)—C(1)—H(1)	116·7 (1·0)
C(6)—C(1)—H(1)	124·1 (1·0)
C(1)—C(2)—H(2)	123·1 (1·1)
C(3)—C(2)—H(2)	115·0 (1·0)
C(4)—C(5)—H(5)	118·1 (0·9)
C(6)—C(5)—H(5)	120·2 (0·9)
C(5)—C(6)—H(6)	120·7 (1·0)
C(1)—C(6)—H(6)	119·1 (1·0)
C(4)—C(7)—H(7)	121·7 (1·0)
N——C(7)—H(7)	115·1 (0·9)
N——C(9)—H1(C9)	103·2 (1·0)
N——C(9)—H2(C9)	110·8 (1·0)
C(11)′–C(9)—H1(C9)	108·4 (1·0)
C(11)′–C(9)—H2(C9)	101·3 (1·0)
C(3)—C(10)–H1(C10)	102·8 (1·0)
C(3)—C(10)–H2(C10)	112·8 (1·0)
C(11)–C(10)–H1(C10)	109·9 (1·0)
C(11)–C(10)–H2(C10)	104·7 (1·0)
C(10)–C(11)–H1(C11)	106·8 (0·9)
C(10)–C(11)–H2(C11)	109·9 (1·0)
C(9)′—C(11)–H1(C11)	117·7 (1·0)
C(9)′—C(11)–H2(C11)	109·8 (1·0)

Table 4. *Observed and calculated structure factors*

The benzene ring is planar within the errors of determination. The substituent carbon atoms C(7) and C(10) are displaced from the plane of the aromatic ring by 0·024 and −0·037 Å while the nitrogen atom is −0·311 Å out of this plane. The torsion angles C(3)–C(4)–C(7)–N and C(5)–C(4)–C(7)–N are −161·7 and 20·5° respectively. The near coplanarity of the aromatic ring and the carbon–nitrogen double bond and the slight shortening of the bonds in the 14-membered ring is to be expected since it gives rise to an extended π-system. Table 5 summarizes the least-squares plane.

Table 5. *Displacements from the least-squares plane for dibenzodiazacyclotetradecatetraene*

The direction cosines of the plane relative to **a**, **b**, **c*** directions are 0·684, −0·181 and 0·706 Å; the origin to plane distance is −4·184 Å. Asterisks denote atoms included in the calculation of least-squares plane.

C(1)	−0·003*	H(1)	0·024
C(2)	0·002*	H(2)	0·035
C(3)	0·002*	H(5)	−0·013
C(4)	−0·005*	H(6)	0·017
C(5)	0·004*	H(7)	0·393
C(6)	0·000*	H1(C9)	0·703
C(7)	0·024	H2(C9)	−0·198
N	−0·311	H1(C10)	0·683
C(9)	−0·129	H2(C10)	0·116
C(10)	−0·037	H1(C11)	−1·5260
C(11)	−1·3789	H2(C11)	−1·3302
		r.m.s.Δ	0·003

In the 14-membered ring there are two *trans* substituted double bonds. The C=N has a length of 1·257 ± 0·004 Å. The C=N bond length in a spectrum of molecules is quite variable and is very sensitive to local environment. Table 6 shows some typical values that have been observed.

Table 6. C=N *bond distances* (Å) *in some other compounds*

		Reference*
1,2-Benzodithiol-3-oxime	1·309 ± 0·01	1
N-5-Chlorosalicylidene-aniline	1·27 ± 0·01	2
N-Methyl-2-methylsulphonyl-2-phenylsulphonylvinylidineamine	1·154 ± 0·017	3
N-Ethyl-2,2′-dimethylsulphonylvinylidineamine	1·165 ± 0·014	4
Firefly D(−)-luciferin	1·27 ± 0·01 1·30 ± 0·01	5
2-Keto-3-ethoxybutyraldehyde-bis(thiosemicarbazone)	1·284 ± 0·006 1·285 ± 0·006 1·294 ± 0·006 1·290 ± 0·006	6
Dimethylglyoxime	1·253 ± 0·011	7
Urea nitrate	1·297 ± 0·01 1·315 ± 0·01	8
Tricycloquinazoline	1·284 ± 0·007 1·281 ± 0·007 1·271 ± 0·007	9
anti-2,6-Dimethyl-4-chloro-*N*-methylbenzaldoxime	1·299 ± 0·007	10
Sinigrin	1·29 ± 0·01	11

* (1) Andreetti, Cavalca, Manfredotti & Musatti (1969). (2) Bergman, Leiserowitz & Osaki (1964). (3) Bullough & Wheatley (1957). (4) Daly (1961). (5) Dennis & Stanford (1973). (6) Gabe, Taylor, Glusker, Minkin & Patterson (1969). (7) Hamilton (1961). (8) Harkema & Feil (1969). (9) Iball & Motherwell (1969). (10) Jensen & Jerslev (1969). (11) Marsh & Waser (1970).

Goldman *et al.* (1970) had predicted the conformation of (II) to be either (III) (*trans–trans* chair) or (IV) (*cis–anti–cis*). Our results show that (II) has a

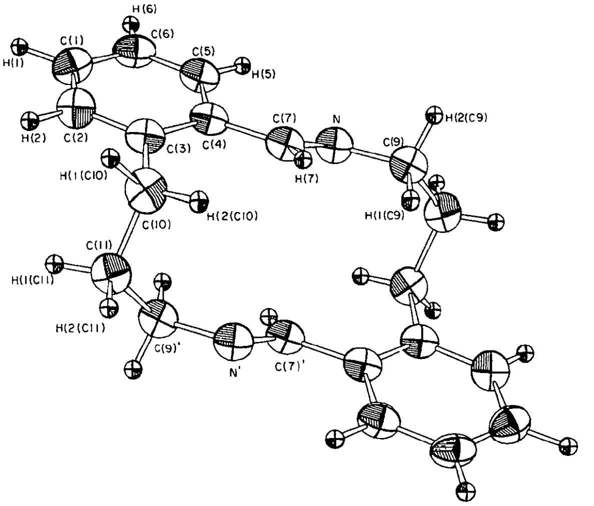


Fig. 1. Thermal ellipsoid plot of the molecule.

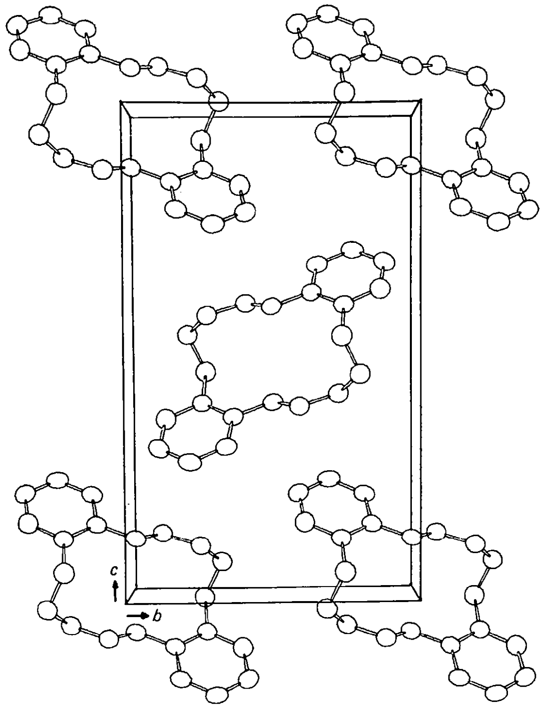


Fig. 2. View of the unit cell, *a*-axis projection.

trans–trans chair conformation. The two C=N bonds [C(7)–N′ and C(7)′–N] are parallel to each other. The C(7)–N′ and C(7)′–N distances are 3·60 Å. This shows that the structure can take the conformation shown in (IV) (*cis–anti–cis*) if two bonds move toward each other. Fig. 1 shows thermal ellipsoid plot of the molecule and Fig. 2 shows the view of the unit cell, *a*-axis projection. The intermolecular contacts are all greater than van der Waal's distances.

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The Crystal Structure of Phenmetrazine Hydrochloride

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The semi-rigid amphetamine analogue phenmetrazine crystallizes as the hydrochloride in both the orthorhombic and the monoclinic systems. Monoclinic crystals with $a=6{\cdot}11$, $b=29{\cdot}58$, $c=7{\cdot}19$ Å, $\beta=112{\cdot}4°$, space group *Cc* and four molecules of $C_{11}H_{15}ON.HCl$ in the unit cell were used for the investigation. The structure was determined from 1098 unique and significant counter-recorded reflexions within $\sin\theta/\lambda\le0{\cdot}65$ by the heavy-atom procedure and direct methods independently and was refined to an *R* index of 0·055. The conformation of the molecule was found to be almost identical with corresponding parts of amphetamine. The structure contains two strong NH···Cl hydrogen bonds with N···Cl distances of 3·09 and 3·07 Å which give rise to infinite layers of phenmetrazine and chloride ions. The layers are held together by van der Waals forces.

Introduction

Phenmetrazine (phenmetraline) is a semi-rigid analogue of amphetamine. Having a psychostimulating action like that of amphetamine (although weaker) it has been widely abused as a stimulating drug. Its main action, however, of decreasing appetite, has earlier made it a commonly used anorexic drug (Anorex, Preludin *etc.*).

The present study forms part of a research project