Fig. 1. The shape and numbering of the molecule. Solid circles represent carbon atoms, circles oxygen atoms. The numbers correspond to those used in Table 1.

models). The bond lengths are normal, but although the angles in the nucleus are considerably larger than tetrahedral they are not unusual in this type of system (Murray-Rust, 1974; Murray-Rust & Murray-Rust, 1975; Murray-Rust & Smith, 1975).

Table 5. Intermolecular contact distances (Å) less than
3·60 Å (e.s.d. = 0·008 Å)

C(13)···O(3)	$\bar{x}$,	$\bar{y}$, 1−z		3·24
O(3)···C(1)	$\bar{x}$,	$\bar{y}$,	$\bar{z}$	3·31
C(4)···O(4)	$\bar{x}$−1, 1−y,		$\bar{z}$	3·55
O(4)···C(15)	$\bar{x}$−1,	$\bar{y}$,	$\bar{z}$	3·58
O(4)···C(5)	$\bar{x}$−1, 1−y,		$\bar{z}$	3·58
O(1)···C(5)	$\bar{x}$−1, 1−y,		$\bar{z}$−1	3·59

1970), but there are no structural data for the hydrocarbon. We have shown that an analogous molecule (III) adopts a shape with planar ethylene bridges but with very pronounced vibration of C(4) and C(5) perpendicular to the plane of the bridge, suggesting that the energies of the planar and twisted bridge systems in (I) may be very similar (Murray-Rust, 1974). The crystal structure of the 1,8-disubstituted derivative (II) was undertaken to investigate this [and also to confirm it as the product of synthesis (Henry, Moodie, Parker & Watt, 1975)].

The structure consists of discrete molecules with no unusually short intermolecular contact distances (Table 5), and it is reasonable to assume that the configuration observed is close to that of minimum energy. The homoadamantane nucleus has almost C_{2v} symmetry and the torsional angle in the ethylene bridge is only 2·0 (6)°. The thermal ellipsoids of the two atoms in this bridge, C(4) and C(5), do not show any unusual anisotropic motion perpendicular to the bridge (the vibration of the ester groups is more pronounced by comparison) and the C_{2v} conformation would thus appear considerably more stable than C_2 arrangements with a torsional angle of about 60° (as predicted from

References

Braun, P. B. & Hornstra, J. & Leenhouts, J. I. (1970). Acta Cryst. B26, 1802–1806.

Gleicher, G. J. & Schleyer, P. von R. (1967). J. Amer. Chem. Soc. 89, 582–593.

Henry, R. S., Moodie, W. T., Parker, W. & Watt, C. I. F. (1975). J. Chem. Soc. Perkin I. In the press.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

Liggero, S. H., Schleyer, P. von R. & Ramey, K. C. (1969). Spectrosc. Lett. 2, 197–199.

Main, P. (1971). LSAM system of crystallographic programs, Univ. of York.

Murray-Rust, J. & Murray-Rust, P. (1975). Acta Cryst. B31, 310–311.

Murray-Rust, P. (1974). J. Chem. Soc. Perkin II, pp. 1136–1141.

Murray-Rust, P. & Smith, I. (1975). Acta Cryst. B31, 587–589.

Powell, M. T. G. & Griffiths, A. (1969). CRYSTAL 69 programs, Portsmouth Polytechnic.

Schleyer, P. von R., Funke, E. & Liggero, S. H. (1969). J. Amer. Chem. Soc. 91, 3965–3967.

1,4-Dimethanodibenzo[d,i]-1,3,6,8-tetrazecine

By Peter Murray-Rust and Isobel Smith

Department of Chemistry, University of Stirling, Stirling, Scotland

Abstract. $C_{16}H_{16}N_4$, M = 264·33, orthorhombic, Pbcn, a = 10·57 (1), b = 7·46 (1), c = 16·93 (2) Å from precession photographs, refined by diffractometer. Z = 4, D_m = 1·33 (flotation), D_c = 1·316 g cm⁻³. The compound was crystallized from petrol as needle prisms. The structure, refined to R = 0·056, shows discrete molecules of almost D_{2d} symmetry with some angle strain in the heterocyclic rings.

Introduction. Systematic absences hk0 h+k=2n+1, h0l l=2n+1, 0kl k=2n+1 gave the space group as Pbcn. Data were collected for layers 0kl to 4kl and h0l to h7l with a Hilger–Watts linear diffractometer (Mo Kα radiation). 792 unique reflexions were recorded for which the intensity was greater than 3σ and the agreement between the two sets of data is shown in a merging R of 0·043 [$R = \sum|(F_1 − F_2)|/\frac{1}{2}\sum(F_1 + F_2)$].

Table 1. *Atomic positions and anisotropic temperature factors* ($\times 10^4$) *with e.s.d.'s in parentheses*

The expression used for the anisotropic temperature factor was $\exp\left(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]\right)$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	6132 (3)	273 (4)	2255 (2)	84 (3)	174 (6)	35 (1)	24 (4)	0 (2)	4 (2)
N(2)	4329 (3)	2960 (4)	1879 (2)	80 (3)	181 (6)	37 (1)	15 (4)	7 (2)	7 (2)
C(1)	6037 (3)	948 (5)	1459 (2)	68 (3)	164 (7)	36 (1)	−3 (4)	3 (1)	0 (3)
C(2)	5154 (3)	2258 (4)	1276 (2)	70 (3)	174 (7)	35 (1)	−9 (4)	1 (2)	−2 (3)
C(3)	5059 (3)	2898 (5)	501 (2)	84 (3)	203 (8)	40 (1)	−14 (5)	−4 (2)	16 (3)
C(4)	5844 (3)	2207 (6)	−81 (2)	100 (4)	259 (9)	29 (1)	−45 (5)	0 (2)	4 (3)
C(5)	6717 (3)	897 (6)	96 (2)	88 (4)	246 (9)	36 (1)	−23 (5)	4 (2)	−19 (3)
C(6)	6816 (3)	255 (5)	871 (2)	80 (4)	216 (8)	41 (1)	1 (5)	1 (2)	−17 (3)
C(7)	3414 (3)	1623 (5)	2174 (2)	60 (3)	229 (8)	38 (1)	2 (4)	−1 (2)	6 (3)
C(8)	5000 (*)	−723 (6)	2500 (*)	113 (6)	142 (10)	37 (2)	*	4 (3)	*
C(9)	5000 (*)	3970 (7)	2500 (*)	103 (6)	144 (9)	45 (2)	*	11 (2)	*
H(1)†	4388 (36)	3846 (57)	293 (22)	121	285	54	−39	−3	15
H(2)	5749 (37)	2622 (58)	−563 (23)	123	350	47	−72	1	−1
H(3)	7292 (30)	399 (47)	−308 (16)	73	222	17	−29	−1	−26
H(4)	7486 (39)	−646 (40)	1030 (19)	135	54	44	−17	7	−27
H(5)	2711 (25)	2319 (42)	2430 (24)	−7	119	90	4	−1	22
H(6)	3084 (25)	984 (47)	1676 (12)	26	329	−19	4	−1	22
H(7)	5227 (32)	−1496 (39)	2995 (16)	123	73	15	0	10	0
H(8)	4327 (35)	4786 (54)	2806 (22)	151	212	62	0	3	0

* Required by symmetry to be zero.

† Temperature factors for hydrogen atoms were estimated from those of the attached carbon atom and were not refined.

Lorentz and polarization corrections were applied (but none for absorption) and layer scales were obtained through common reflexions. The structure was solved by direct methods with the LSAM series of programs (Main, 1971) and refined by full-matrix least-squares calculations with our adaptation of the *PORFLS* program in the CRYSTAL 69 system of Powell & Griffiths (1968). Five cycles of refinement of positional and isotropic thermal parameters gave $R = 0.105$ [$R = \sum ||F_o| - |F_c|| / \sum |F_o|$] and a difference synthesis then provided all the hydrogen atom positions. Anisotropic temperature factors were introduced for the heavier atoms and the refinement, with the weighting scheme $w = 1/[1 + F_c^2]$, converged with $R = 0.056$.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Atomic parameters are given in Table 1, the numbering of the atoms in Fig. 1, bond lengths in Table 2, bond angles in Table 3 and some selected torsional angles in Table 4.

(I)
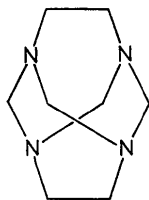
Discussion. The conformation of tricyclo[4,4,1,1^{3,8}]dodecane is of considerable interest as both S_4 and D_{2d}

Table 2. *Bond lengths* (Å) *between non-hydrogen atoms*
($e.s.d. = 0.005$ Å)

N(1)–C(1)	1·442	C(2)–C(3)	1·399
N(1)–C(8)	1·468	C(3)–C(4)	1·387
N(1)–C(7′)	1·476	C(4)–C(5)	1·376
N(2)–C(2)	1·441	C(5)–C(6)	1·401
N(2)–C(7)	1·476	C(7)–N(1′)	1·476
N(2)–C(9)	1·475	C(8)–N(1′)	1·468
C(1)–C(2)	1·386	C(9)–N(2′)	1·475
C(1)–C(6)	1·391		

Table 3. *Bond angles* (°) *involving non-hydrogen atoms*
($e.s.d. = 0.3°$)

N(1)–C(1)–C(2)	120·2	C(1)–C(2)–C(3)	119·9
N(1)–C(1)–C(6)	119·8	C(1)–C(6)–C(5)	119·9
N(1)–C(8)–N(1′)	119·2	C(2)–N(2)–C(7)	113·0
N(1)–C(7′)–N(2′)	118·0	C(2)–N(2)–C(9)	113·5
N(2)–C(2)–C(1)	120·3	C(2)–C(1)–C(6)	120·0
N(2)–C(2)–C(3)	119·7	C(2)–C(3)–C(4)	119·7
N(2)–C(7)–N(1′)	118·0	C(3)–C(4)–C(5)	120·6
N(2)–C(9)–N(2′)	118·7	C(4)–C(5)–C(6)	119·8
C(1)–N(1)–C(8)	112·6	C(7)–N(2)–C(9)	114·7
C(1)–N(1)–C(7′)	113·3	C(7)–N(1′)–C(8)	115·1

symmetries are possible. A nitrogen-substituted derivative (I) has been crystallized and analysed by X-ray crystallography (Murray-Rust, 1974) but doubt remained as to whether the molecule had D_{2d} symmetry (required by the space group) or was disordered in the crystal. We synthesized the title compound as an analogue [by the method of Bischoff (1898) using *o*-phenylenediamine] and recrystallized it from petrol. In this molecule the two-carbon bridges are constrained to be planar and this requires the nucleus to adopt D_{2d} symmetry. It was hoped that comparison of the bond angles in the two molecules might confirm the D_{2d} conformation of (I).

The structure consists of discrete molecules packed so that no intermolecular contact distance (between

Table 4. *Torsional angles in the tricyclic nucleus* (°) (*e.s.d.*=0·4°)

C(8)–N(1)–C(1)–C(2)	66·2		C(7)–N(2)–C(2)–C(1)	−67·2
C(7′)	C(2)	−66·7	C(9)	C(1)	65·7

C(1)–N(1)–C(8)–N(1′)	−78·7		C(2)–N(2)–C(7)–N(1′)	78·3
C(7′)	N(1′)	53·2	C(9)	N(1′)	−53·9

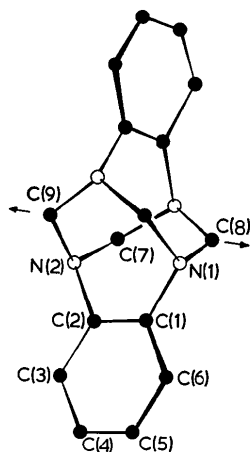| C(1)–N(1)–C(7′)–N(2′)	79·2		C(2)–N(2)–C(9)–N(2′)	−78·3
C(8)	N(2′)	−52·4	C(7)	N(2′)	53·7

N(1)–C(1)–C(2)–N(2)	0·3

Fig. 1. The geometry and numbering of the molecule. Primed atoms are generated by the action of the crystallographic diad shown.

non-hydrogen atoms) is less than 3·50 Å. Although the molecule lies on a crystallographic diad axis, its real symmetry is almost the expected D_{2d}. The bond lengths are all as expected [C–C(aromatic)=1·39 Å (av.); C(sp^2)–N=1·437, C(sp^3)–N=1·475 Å, the latter in good agreement with the corresponding value in (I) of 1·470

Å]. The bond angles in the tricyclic nucleus show the same sort of increases from the tetrahedral value as found in (I); the angles to be discussed have been averaged on the basis of D_{2d} symmetry and those for (I) are given in parentheses. The methylene bridges have an N–C–N angle of 118·6 (116·9°) but the other angle in the cyclooctane ring (114·8°) is considerably smaller than in (I) (119·3°). The geometry of the two-carbon bridges is very similar in the two molecules and the small differences can be explained by the different lengths of the C–C bonds. The torsional angles in the tricyclic system are also essentially the same in both molecules. We conclude therefore that the geometry found for (I) is not inconsistent with that required for a D_{2d} conformation, but naturally cannot dismiss the other possibilities put forward (Murray-Rust, 1974).

References

BISCHOFF, C. A. (1898). *Ber. dtsch. chem. Ges.* **31**, 3248–3260.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
MAIN, P. (1971). LSAM programs, Univ. of York.
MURRAY-RUST, P. (1974). *J. Chem. Soc. Perkin* II, 1136–1141.
POWELL, M. T. G. & GRIFFITHS, A. (1969). CRYSTAL 69 system of crystallographic programs, Portsmouth Polytechnic.

5,8-Di-t-butyl-3,3-dimethyl-9-isopropylidene-5,8-diaza-4,7-dioxabicyclo[4,2,1]nonan-2-one

BY JUDITH MURRAY-RUST AND PETER MURRAY-RUST

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

Abstract. $C_{18}H_{32}N_2O_3$, $M=324\cdot46$, orthorhombic, $Pna2_1$ (No. 33), $a=18\cdot13$ (2), $b=11\cdot56$ (2), $c=9\cdot45$ (2) Å, from precession photographs, refined by diffractometer (Mo $K\alpha$ radiation). D_m (flotation)=1·09 g cm^{-3}; for $Z=4$, $D_c=1\cdot09$ g cm^{-3}. The structure was solved by direct methods, and refinement converged at $R=$ 0·051; the molecule contains bridged five- and seven-membered rings, each of which contains a hydroxyl-amine group.

Introduction. Systematic absences $0kl$ $k+l=2n+1$, $h0l$ $h=2n+1$, indicated space groups $Pnam$ (No. 62)