The Molecular and Crystal Structure of
3,7-Dimethyl-1,5-dioxa-3,7-diazacyclo-octane-2,4,6,8-tetraspirocyclopropane*

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The cell constants of the monoclinic crystals of 3,7-dimethyl-1,5-dioxa-3,7-diazacyclooctane-2,4,6,8-tetraspirocyclopropane, the structural formula of which was not known, are $a=8 \cdot 382$, $b=23 \cdot 999$, $c=7 \cdot 320$ Å and $\beta=111 \cdot 48°$, $Z=4$, space group $P2_1/n$. The molecular symmetry is 2; this twofold axis has no relation to the space group symmetry. The cyclo-octane ring is in a crown-like conformation with the cyclopropane groups in two planes perpendicular to the plane of the cyclo-octane ring. The methyl groups are in the axial position.

Introduction

A condensation reaction of bis-*N,N*-(1-hydroxycyclopropyl)-methylamine 1, which results in a compound 2 with approximately twice the molecular weight of 1, was carried out by van Tilborg (1968). From spectroscopic data (nuclear magnetic resonance, infrared, mass) it could be concluded that 2 consists of four cyclopropane rings, two methyl groups connected to nitrogen atoms and a cyclo-octane ring containing four carbon, two nitrogen and two oxygen atoms. However it could not be established whether the eight-membered ring was a 1,3-dioxa-5,7-diazacyclo-octane or a 1,5-dioxa-3,7-diazacyclo-octane. From our crystal structure determination it follows that the second formula is the true one, so that throughout this communication we

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refer to the compound as ONON, thus indicating the sequence of the oxygen and nitrogen atoms in the ring.
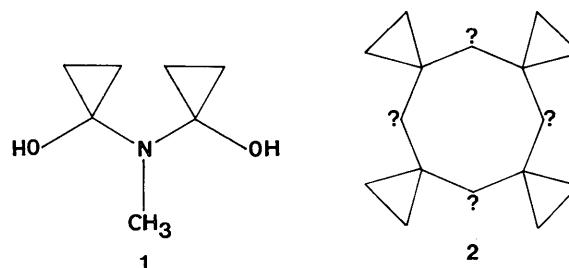
Crystal and intensity data

Crystals of ONON are monoclinic. The axes have been chosen such that the space group is $P2_1/n$. The cell constants, obtained by means of calibrated zero-layer Weissenberg diagrams, are $a=8 \cdot 383$ (2), $b=23 \cdot 999$ (3), $c=7 \cdot 320$ (1) Å and $\beta=111 \cdot 48$ (1), $Z=4$.

Table 1. *Final parameters and their e.s.d.'s*

The positional parameters x, y and z are given in fractions multiplied by 10^4. The thermal parameters, based on the expression $\exp(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{31}lh)$, have been multiplied by 10^5.

	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
N(1)	8542 (2)	4084 (1)	4793 (2)	1326 (25)	159 (3)	1929 (34)	20 (13)	42 (16)	1028 (49)
N(2)	5399 (2)	3159 (1)	2709 (2)	1815 (30)	124 (3)	2001 (36)	−6 (14)	6 (15)	1118 (54)
O(1)	7548 (2)	3268 (1)	6002 (2)	1680 (24)	134 (2)	1979 (30)	37 (12)	124 (13)	731 (44)
O(2)	6346 (2)	3985 (1)	1516 (2)	1619 (23)	158 (2)	1741 (27)	−143 (12)	−58 (12)	1193 (42)
C(1)	7912 (2)	3847 (1)	6177 (3)	1626 (33)	140 (3)	1718 (38)	18 (16)	−9 (17)	1004 (58)
C(2)	5889 (3)	3090 (1)	4755 (3)	1695 (34)	134 (3)	2109 (45)	−78 (17)	109 (18)	1110 (64)
C(3)	5000 (2)	3692 (1)	1820 (3)	1409 (30)	144 (3)	1921 (39)	−52 (16)	68 (18)	778 (57)
C(4)	7420 (2)	4331 (1)	3035 (3)	1557 (31)	133 (3)	1810 (39)	−62 (15)	4 (17)	1145 (58)
C(5)	9979 (3)	3781 (1)	4612 (3)	1580 (36)	248 (5)	2876 (57)	190 (21)	57 (27)	1733 (76)
C(6)	6190 (4)	2783 (1)	1724 (4)	3170 (59)	170 (4)	2828 (59)	263 (25)	−220 (25)	2220 (98)
C(7)	8801 (3)	4021 (1)	8264 (3)	2640 (50)	213 (5)	1868 (47)	−176 (24)	−96 (22)	998 (79)
C(8)	6997 (3)	4212 (1)	7102 (3)	2576 (47)	173 (4)	2691 (55)	84 (23)	−114 (23)	2818 (87)
C(9)	5441 (4)	2545 (1)	5418 (4)	2922 (55)	187 (4)	2930 (62)	−342 (25)	356 (26)	1475 (98)
C(10)	4553 (3)	3072 (1)	5662 (4)	2278 (47)	255 (5)	3068 (62)	−365 (25)	169 (29)	2554 (92)
C(11)	3370 (3)	3737 (1)	0088 (4)	1765 (40)	247 (5)	2893 (59)	−190 (23)	396 (29)	−146 (78)
C(12)	3557 (3)	4012 (1)	2011 (4)	1666 (38)	204 (4)	4065 (73)	208 (21)	385 (29)	2235 (88)
C(13)	8165 (3)	4791 (1)	2237 (3)	2309 (45)	173 (4)	2471 (51)	−313 (22)	165 (23)	1561 (79)
C(14)	6809 (3)	4918 (1)	3065 (3)	2359 (46)	129 (3)	2626 (52)	54 (19)	37 (21)	1378 (82)

The intensity data were collected with a Nonius automatic single-crystal diffractometer with Cu $K\alpha$ radiation. The intensities were scanned by the moving-crystal moving-counter method up to a maximum θ of 68·5°. Very high intensities were reduced by attenuation filters. In the course of the measurements the reference intensities decreased by 60% and a correction for this effect was applied. The absorption correction was ignored; 2536 reflexions were measured and of these 1968 were significantly above zero.

Structure determination and refinement

The carbon, oxygen and nitrogen atom positions were located with the help of automatic computer programs (Schenk, 1969) based on the symbolic addition method (Karle & Karle, 1966).

The positions of the atoms were refined by a block-diagonal least-squares program using the atomic scattering factors from *International Tables for X-ray Crystallography* (1962) and the weighting scheme of Cruickshank (1961). At the stage $R = 10\%$ a difference synthesis revealed all hydrogen atoms; their peak heights ranged from 0·3 to 0·6 e.Å^{-3}.

The last least-squares cycles were carried out with refinement of all positional parameters, anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the hydrogen atoms. A number of reflexions, which apparently suffered from extinction, were omitted. The final R value was 4·4%. The last difference synthesis showed a residual density between +0·15 and −0·15 e.Å^{-3}.

Table 1 lists the positional and thermal parameters of the heavy atoms and Table 2 those of the hydrogen atoms. The estimated standard deviations are those given by the block-diagonal least-squares procedures.

Table 2. *Parameters of the hydrogen atoms with their e.s.d.'s in brackets*

x, y and z values are given in fractions $\times 10^3$, B values in Å^2.

	x	y	z	B
H(1)	964 (3)	345 (1)	383 (4)	4·6 (0·6)
H(2)	051 (4)	400 (1)	384 (4)	5·7 (0·7)
H(3)	081 (4)	371 (1)	595 (4)	5·5 (0·7)
H(4)	542 (5)	279 (2)	028 (5)	7·2 (0·9)
H(5)	742 (4)	289 (1)	184 (5)	7·5 (0·8)
H(6)	625 (5)	244 (2)	215 (5)	9·1 (1·1)
H(7)	977 (3)	430 (1)	847 (3)	3·1 (0·5)
H(8)	888 (3)	372 (1)	924 (3)	2·9 (0·5)
H(9)	606 (4)	403 (1)	746 (4)	5·0 (0·7)
H(10)	682 (3)	458 (1)	661 (4)	3·1 (0·5)
H(11)	626 (3)	243 (1)	670 (4)	4·0 (0·6)
H(12)	475 (4)	227 (1)	430 (4)	5·4 (0·7)
H(13)	488 (3)	321 (1)	703 (3)	2·9 (0·5)
H(14)	333 (4)	310 (1)	478 (4)	4·4 (0·6)
H(15)	333 (3)	399 (1)	898 (4)	3·5 (0·6)
H(16)	273 (4)	338 (1)	973 (4)	4·5 (0·6)
H(17)	363 (4)	441 (1)	202 (4)	4·9 (0·6)
H(18)	300 (4)	386 (1)	286 (4)	4·8 (0·7)
H(19)	782 (3)	482 (1)	082 (3)	2·5 (0·5)
H(20)	939 (3)	490 (1)	295 (4)	3·7 (0·6)
H(21)	716 (3)	511 (1)	429 (3)	2·1 (0·4)
H(22)	564 (3)	503 (1)	207 (4)	3·8 (0·6)

Discussion

Molecular symmetry

Within the limits of accuracy ONON displays twofold symmetry with the twofold axis perpendicular to the cyclo-octane ring (see for instance Fig. 2). From Fig. 1(a) it is seen that the differences between bond lengths related by the twofold axis are of the order of magnitude of the e.s.d.'s. Bond lengths which are chemically equivalent and not related by the twofold axis deviate somewhat more, but most of the deviations are not significant either.

Fig. 1. (a) Bond lengths and (b) bond angles in ONON with the e.s.d.'s in brackets.
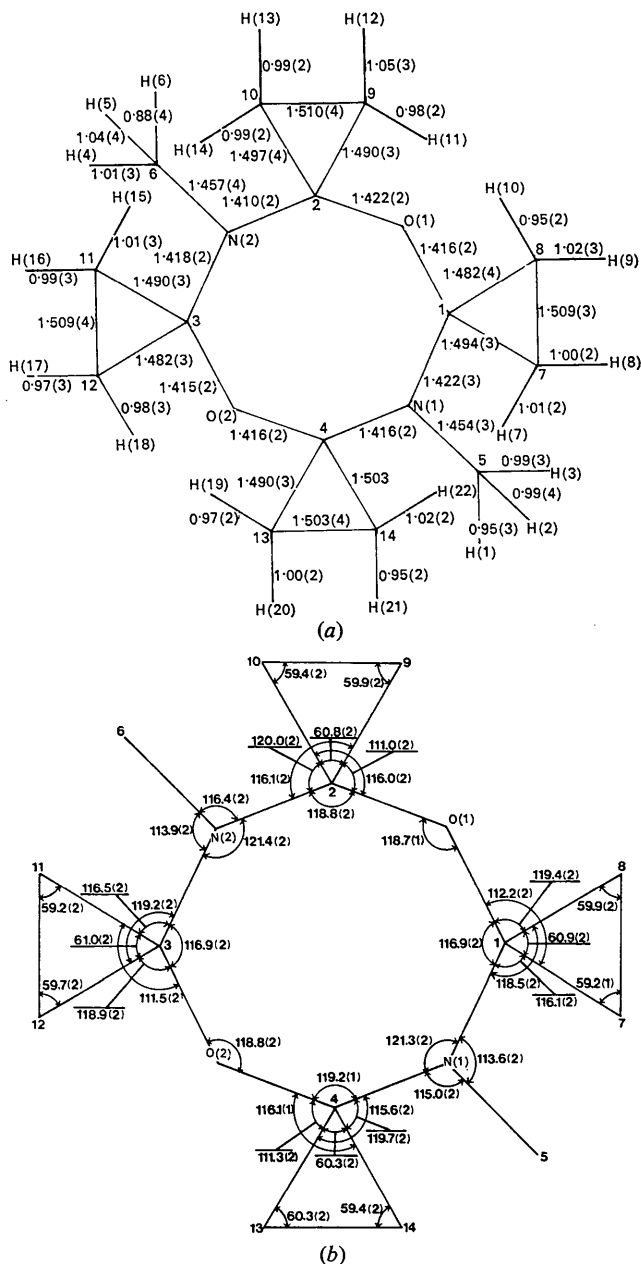
The four cyclopropane rings of one molecule, considered by themselves, display the symmetry *mm2*; the mirror planes pass through the cyclopropane rings with deviations smaller than 0·03 Å. The N–CH₃ groups and the oxygen atoms of course do not comply with this symmetry.

Bond lengths

All bond lengths are normal except the four endocyclic C–N bonds which are about 0·05 Å shorter than the average value of 1·472 ± 0·005 Å for the paraffinic and saturated heterocyclic C–N bond (Sutton, 1965). This is the more remarkable since the endocyclic C–O bonds are quite normal (in dimethyl ether the C–O bond is 1·416 Å; Sutton, 1965).

Bond angles

The bond angles involving an 'axial' cyclopropane carbon atom [C(8), C(10), C(12) and C(14)], a ring carbon atom and a nitrogen or oxygen atom are three or more degrees larger than the corresponding angles involving the 'equatorial' cyclopropane carbon atoms [C(7), C(9), C(11) and C(13)] as is shown in Fig. 1(*b*). This is caused by the steric interactions between the hydrogen atoms bonded to the carbon atoms C(8), C(10), C(12) and C(14). The relevant distances are 2·17 [H(9)–H(13)], 2·22 [H(10)–H(21)], 2·26 [H(14)–H(18)] and 2·23 Å [H(17)–H(22)], which are appreciably shorter than the accepted van der Waals distance of 2·40 Å.

The *endo* angles of the cyclooctane ring are appreciably larger than the corresponding angles in saturated amines and ethers. As a result of this the ring is fairly planar. The distances of the ring atoms from the best plane of the ring are given in Fig. 2.

Valence angles involving hydrogen atoms are given in Table 3.
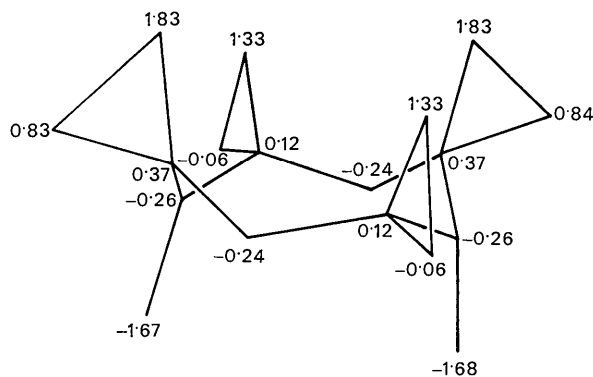

Fig. 2. A perspective view of the ONON molecule. The distances of the atoms from the best plane through the cyclooctane ring, calculated by the method of Schomaker, Waser, Marsh & Bergman (1959), are indicated. The equation of this plane is $0.783x - 0.563y - 0.266z + 2.044 = 0$, in which x, y and z are coordinates relative to the orthogonal standard axes (Cruickshank, 1961).

Table 3. *Valence angles involving hydrogen atoms*

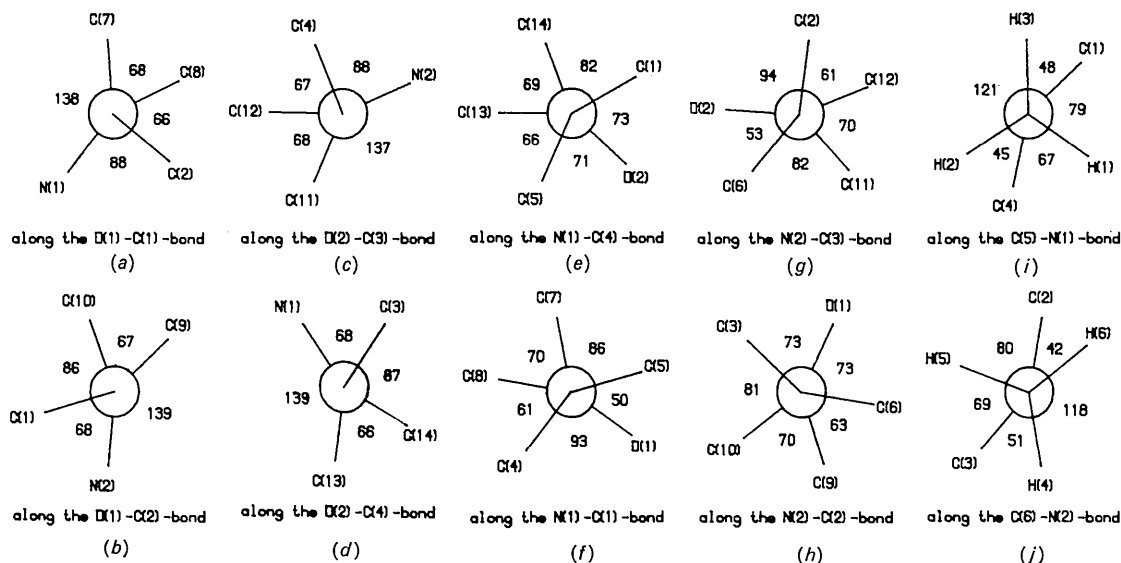|						
N(2)—C(10)—H(4)	106 (2)°	C(7)—C(16)—H(17)	117 (2)°	C(8)—C(18)—H(21)	118 (1)°	
N(2)—C(10)—H(5)	115 (2)	C(7)—C(16)—H(18)	118 (2)	C(8)—C(18)—H(22)	119 (1)	
N(2)—C(10)—H(6)	113 (3)	C(15)—C(16)—H(17)	115 (1)	C(17)—C(18)—H(21)	117 (1)	
H(4)—C(10)—H(5)	108 (3)	C(15)—C(16)—H(18)	114 (2)	C(17)—C(18)—H(22)	116 (2)	
H(4)—C(10)—H(6)	108 (3)	H(17)—C(16)—H(18)	118 (2)	H(21)—C(18)—H(22)	116 (2)	
H(5)—C(10)—H(6)	106 (3)					
C(6)—C(14)—H(13)	113 (2)°	C(7)—C(15)—H(15)	113 (2)°	C(8)—C(17)—H(19)	118 (1)°	
C(6)—C(14)—H(14)	110 (2)	C(7)—C(15)—H(16)	116 (2)	C(8)—C(17)—H(20)	119 (2)	
C(13)—C(14)—H(13)	108 (2)	C(16)—C(15)—H(15)	109 (2)	C(18)—C(17)—H(19)	116 (2)	
C(13)—C(14)—H(14)	113 (2)	C(16)—C(15)—H(16)	118 (2)	C(18)—C(17)—H(20)	121 (2)	
H(13)—C(14)—H(14)	110 (2)	H(15)—C(15)—H(16)	124 (2)	H(19)—C(17)—H(20)	113 (2)	
N(1)—C(9)—H(1)	113 (2)°	C(5)—C(12)—H(9)	116 (2)°	C(5)—C(11)—H(7)	114 (1)°	
N(1)—C(9)—H(2)	110 (2)	C(5)—C(12)—H(10)	115 (2)	C(5)—C(11)—H(8)	114 (1)	
N(1)—C(9)—H(3)	108 (2)	C(11)—C(12)—H(9)	116 (1)	C(12)—C(11)—H(7)	118 (1)	
H(1)—C(9)—H(2)	101 (3)	C(11)—C(12)—H(10)	119 (1)	C(12)—C(11)—H(8)	114 (1)	
H(1)—C(9)—H(3)	113 (2)	H(9)—C(12)—H(10)	118 (2)	H(7)—C(11)—H(8)	121 (2)	
H(2)—C(9)—H(3)	110 (2)					

Fig. 3. Newman projections along the bonds of the cyclooctane ring and along both methyl–nitrogen bonds.

Molecular geometry

The ONON molecule has a crown-like conformation. Both N–CH₃ groups and the oxygen atoms are situated on one side of the cyclo-octane ring and the centres of the cyclopropane rings on the other. The methyl groups are found in the axial positions with respect to the octane ring (see Fig. 2). Both methyl groups are attached in the staggered conformation [see Fig. 3(i), (j)] and as a result of this the inter-methyl distance between H(1) and H(5) is only 2·33 Å (Table 4).

Table 4. *Short non-bonded hydrogen–hydrogen distances*

The accepted van der Waals radius of hydrogen is 1·20 Å. The first atom mentioned belongs to the original molecule.

	Position of the second atom			Distance
H(1)—H(5)	(x	y	z)	2·33 Å
H(2)—H(20)	(x	y	z)	2·35
H(2)—H(18)	(1+x	y	z)	2·47
H(4)—H(13)	(x	y z−1)		2·47
H(6)—H(12)	(x	y	z)	2·38
H(7)—H(10)	(x	y	z)	2·44
H(7)—H(20)	(2−x 1−y 1−z)			2·42
H(8)—H(9)	(x	y	z)	2·36
H(8)—H(12)	(½+x ½+y ½+z)			2·48
H(9)—H(13)	(x	y	z)	2·17
H(10)-H(21)	(x	y	z)	2·22
H(11)-H(13)	(x	y	z)	2·26
H(12)-H(14)	(x	y	z)	2·42
H(14)-H(18)	(x	y	z)	2·26
H(15)-H(17)	(x	y	z)	2·37
H(16)-H(18)	(x	y	z)	2·49
H(17)-H(22)	(x	y	z)	2·23
H(19)-H(22)	(x	y	z)	2·37
H(20)-H(21)	(x	y	z)	2·33

Starting with the N(1)–C(1) bond the dihedral ring angles along the successive cyclo-octane bonds are −93, +88, −68, +73, −94, 88, −68 and 73° respectively [see Fig. 3(a)–(h)]. Apparently the cyclopropane groups coupled to C(1) and C(3) are tilted appreciably higher out of the cyclooctane plane than the other cyclopropane groups (see Fig. 2).

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