

143 parameters
H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 1.3243P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.630 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.596 \text{ e } \text{\AA}^{-3}$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
C1	0.6364 (7)	0.3522 (10)	0.1554 (7)	0.0308 (14)
O1	0.4859 (5)	0.3028 (10)	0.1441 (6)	0.0466 (13)
C2	0.7005 (7)	0.3373 (11)	0.3097 (7)	0.035 (2)
C21	0.6357 (10)	0.1801 (15)	0.3877 (10)	0.054 (2)
C22	0.6624 (10)	0.4988 (19)	0.3962 (11)	0.063 (3)
C3	0.8705 (6)	0.3267 (10)	0.2817 (7)	0.0308 (13)
C31	0.9860 (7)	0.3119 (13)	0.3739 (7)	0.040 (2)
Br31	0.96608 (10)	0.3036 (2)	0.56683 (8)	0.0582 (3)
Br32	1.18650 (7)	0.30281 (14)	0.31561 (9)	0.0502 (3)
C4	0.8892 (7)	0.3438 (9)	0.1258 (7)	0.0308 (14)
C5	0.8448 (9)	0.5362 (12)	0.0905 (9)	0.047 (2)
C6	0.6726 (8)	0.5325 (11)	0.0996 (9)	0.043 (2)
C7	0.7521 (8)	0.2458 (11)	0.0702 (8)	0.038 (2)
Br71	0.72005 (10)	0.2633 (2)	-0.13079 (8)	0.0569 (3)
Br72	0.76657 (10)	-0.00079 (12)	0.10599 (10)	0.0507 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

C1—O1	1.393 (7)	C3—C4	1.515 (8)
C1—C6	1.532 (11)	C31—Br31	1.864 (7)
C1—C7	1.565 (9)	C31—Br32	1.884 (6)
C1—C2	1.575 (9)	C4—C7	1.521 (10)
C2—C22	1.543 (13)	C4—C5	1.575 (11)
C2—C3	1.544 (8)	C5—C6	1.537 (11)
C2—C21	1.547 (11)	C7—Br72	1.943 (9)
C3—C31	1.342 (9)	C7—Br71	1.945 (8)
O1—C1—C6	115.7 (6)	C3—C31—Br31	124.4 (5)
O1—C1—C7	117.3 (6)	C3—C31—Br32	121.5 (5)
C6—C1—C7	98.6 (5)	Br31—C31—Br32	114.1 (4)
O1—C1—C2	112.1 (5)	C3—C4—C7	101.2 (5)
C6—C1—C2	108.7 (6)	C3—C4—C5	105.1 (6)
C7—C1—C2	103.0 (5)	C7—C4—C5	101.7 (6)
C22—C2—C3	111.5 (6)	C6—C5—C4	102.4 (6)
C22—C2—C21	106.7 (7)	C1—C6—C5	104.8 (6)
C3—C2—C21	114.9 (7)	C4—C7—C1	95.0 (6)
C22—C2—C1	111.5 (7)	C4—C7—Br72	112.3 (5)
C3—C2—C1	99.9 (5)	C1—C7—Br72	117.8 (5)
C21—C2—C1	112.4 (6)	C4—C7—Br71	114.0 (5)
C31—C3—C4	123.7 (5)	C1—C7—Br71	113.5 (5)
C31—C3—C2	128.8 (6)	Br72—C7—Br71	104.5 (4)
C4—C3—C2	107.5 (5)		

Data collection: *KUMA KM4 Software* (Kuma Diffraction, 1991). Cell refinement: *KUMA KM4 Software*. Data reduction: *KUMA KM4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation* (Siemens, 1989). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,4,7-Triazatricyclo[5.2.1.0^{4,10}]decane at 100 K

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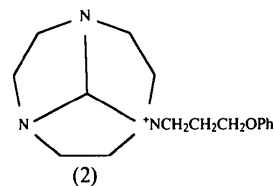
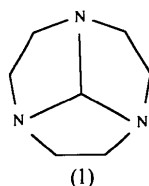
(Received 8 July 1994; accepted 16 August 1994)

Abstract

Molecules of C₇H₁₃N₃ possess non-crystallographic C₃ symmetry. Their structure may be visualized as three five-membered CNCCN rings: each is in a twist conformation and shares edges with the other two rings and a common pivot C atom.

Comment

1,4,7-Triazatricyclo[5.2.1.0^{4,10}]decane, (1), is a key intermediate in the synthesis of a range of N-substituted cyclonane ligands (Weisman, Vachon, Johnson & Gronbeck, 1987; Blake, Fallis, Parsons, Ross & Schröder, 1994). The homologous series of tricyclic trisaminomethanes has been the subject of a solution NMR study (Atkins, 1980), some of the conclusions from which are inconsistent with the results of the present crystal structure determination.



The molecule is saturated and the average values of its C—C and C—N bonds [1.523 (4) and 1.476 (4) Å, respectively] represent normal values. The C—N—C angles in the nine-membered ring [average 113.9 (2)°] are larger than those in the five-membered ring [average 105.0 (7)°] and the N—C—C angles [average 103.3 (10)°].

There is no disorder in the macrocyclic ring, which has C_3 symmetry within experimental error. This is shown strikingly by the in-ring torsion angles. Those about the C—C bonds average 38.5 (8)°; those about the C(9)—N(1), C(3)—N(4) and C(6)—N(7) bonds average -144.0 (9)°, while those at N(1)—C(2), N(4)—C(5) and N(7)—C(8) average 83.1 (9)°. The three five-membered rings have an almost pure twist conformation, with the twofold axis through C(10), and the other two C atoms 0.30 (3) Å above and below the plane defined by C(10) and the two N atoms. This allows partial staggering of the H atoms. The crystal is thus a racemate of two enantiomorphous conformations, with two distinct types of C atoms.

The presence of the central C(10) atom determines the disposition of the N lone pairs, which are directed away from the centre of the molecule. This has two consequences, the first being that the molecule is incapable of acting as a facially coordinating ligand. This contrasts with the analogous species containing C_3H_6 linkages (3), in which the N lone pairs are more inwardly directed (Seiler *et al.*, 1987), making possible the formation of complexes such as $Mo(3)(CO)_3$ (Van Kouwenberg *et al.*, 1989). The second consequence is that the lone pairs are likely to participate in the most significant packing interactions within the crystal: the smallest interatomic N...H—C separations are approximately 2.65 Å. Although all three N atoms in the molecule make equally plausible intermolecular contacts to three neighbouring molecules (Fig. 2), the fact that these do not conform to threefold symmetry may provide an explanation for the absence of trigonal crystallographic symmetry in the molecule.

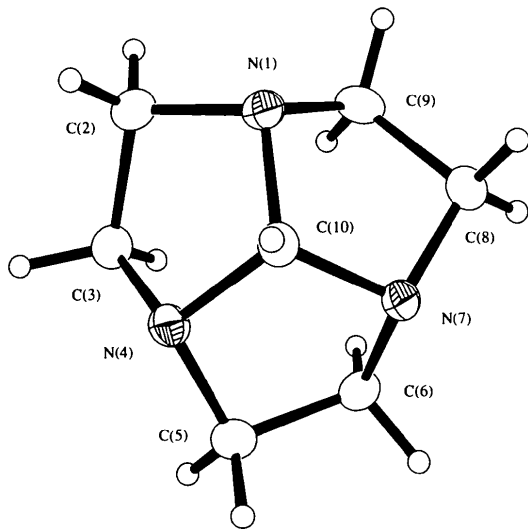


Fig. 1. A view of the molecule with the atom-numbering scheme which shows the non-crystallographic C_3 symmetry. Displacement ellipsoids enclose 50% probability surfaces.

The symmetric conformation of (1) contrasts with the highly distorted geometry of the related N^1 -(3-phenoxypropyl)-4,7-diaza-1-azoniatricyclo[5.2.1.0^{4,10}]-decane cation (2), the structure of which has been rationalized in terms of contributions from amidinium canonical forms (Farrugia, Lovatt & Peacock, 1993).

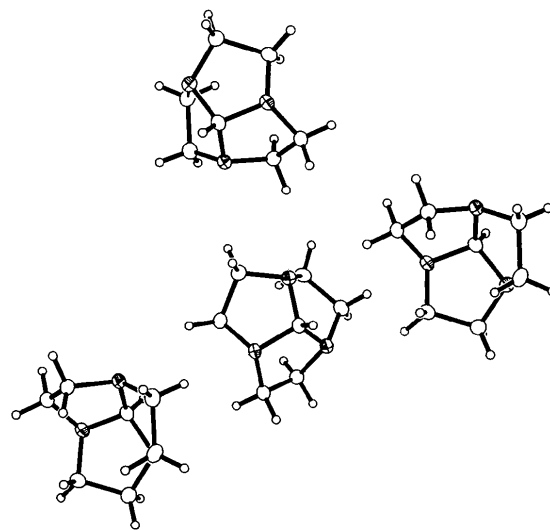
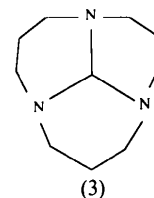


Fig. 2. A packing diagram illustrating the closest intermolecular contacts formed by each molecule.

Experimental

A clear oil was obtained by vacuum distillation from the reaction of 1,4,7-triazacyclononane with (MeO)₂CHNMe₂. A freshly distilled sample of (1) was sealed in a Pyrex capillary tube and mounted in a thermally insulating Tufnol pipe on a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986). Although the melting point of the sample was estimated to be 256–261 K, controlled crystallization in this temperature range was hampered by localized supercooling. Crystal growth was eventually achieved by freezing the sample in liquid nitrogen and then partially melting it by interrupting the cold stream. The liquid-solid phase boundary could then be controlled at 247 K, with the Cryostream nozzle-sample distance at 50 mm. This arrangement, which tended to maximize local temperature fluctuations in the sample, gave a region which exhibited extinction between crossed polars and was shown to be crystalline when investigated by diffractometry.

Crystal data

C₇H₁₃N₃M_r = 139.20

Monoclinic

P2₁/n

a = 6.027 (3) Å

b = 11.177 (3) Å

c = 10.715 (4) Å

β = 97.03 (4)°

V = 716.3 (5) Å³

Z = 4

D_x = 1.291 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 15 reflections

θ = 13–16°

μ = 0.082 mm⁻¹

T = 100.0 (2) K

Cylinder

0.30 × 0.30 × 0.30 mm

Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer

ω–2θ scans with on-line profile analysis (Clegg, 1981)

Absorption correction: none

1262 measured reflections

1262 independent reflections

927 observed reflections

[I > 2σ(I)]

θ_{max} = 25.01°

h = -7 → 7

k = 0 → 13

l = 0 → 12

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F²R[F² > 2σ(F²)] = 0.0607wR(F²) = 0.1578

S = 1.044

1253 reflections

144 parameters

All H-atom parameters

refined

w = 1/[σ²(F_o²) + (0.1173P)² + 0.5530P]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} = 0.020Δρ_{max} = 0.302 e Å⁻³Δρ_{min} = -0.302 e Å⁻³

Extinction correction:

F_c^{*} = kF_c[1 + (0.001F_c² × λ³/sin2θ)]^{-1/4}

Extinction coefficient:

0.017 (9)

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
N(1)	0.0024 (4)	0.7501 (2)	0.7766 (2)	0.0236 (6)
C(2)	-0.0625 (5)	0.6394 (2)	0.8383 (3)	0.0261 (7)
C(3)	0.0472 (4)	0.5392 (2)	0.7706 (3)	0.0227 (7)
N(4)	0.2631 (3)	0.5929 (2)	0.7498 (2)	0.0214 (6)
C(5)	0.3380 (5)	0.5590 (2)	0.6289 (3)	0.0245 (7)
C(6)	0.2195 (5)	0.6460 (2)	0.5342 (3)	0.0231 (7)
N(7)	0.2266 (4)	0.7592 (2)	0.6070 (2)	0.0199 (6)
C(8)	0.0254 (4)	0.8340 (2)	0.5790 (3)	0.0224 (7)
C(9)	-0.1406 (5)	0.7793 (3)	0.6587 (3)	0.0272 (7)
C(10)	0.2240 (4)	0.7232 (2)	0.7391 (2)	0.0199 (7)

Table 2. Selected geometric parameters (Å, °)

N(1)—C(10)	1.472 (3)	N(4)—C(10)	1.478 (3)
N(1)—C(9)	1.476 (4)	C(5)—C(6)	1.519 (4)
N(1)—C(2)	1.477 (3)	C(6)—N(7)	1.484 (3)
C(2)—C(3)	1.528 (4)	N(7)—C(10)	1.473 (3)
C(3)—N(4)	1.474 (3)	N(7)—C(8)	1.473 (3)
N(4)—C(5)	1.473 (3)	C(8)—C(9)	1.521 (4)
C(10)—N(1)—C(9)	105.4 (2)	N(7)—C(6)—C(5)	102.3 (2)
C(10)—N(1)—C(2)	104.5 (2)	C(10)—N(7)—C(8)	104.2 (2)
C(9)—N(1)—C(2)	114.2 (2)	C(10)—N(7)—C(6)	105.6 (2)
N(1)—C(2)—C(3)	104.3 (2)	C(8)—N(7)—C(6)	114.0 (2)
N(4)—C(3)—C(2)	102.4 (2)	N(7)—C(8)—C(9)	103.8 (2)
C(5)—N(4)—C(3)	113.6 (2)	N(1)—C(9)—C(8)	102.4 (2)
C(5)—N(4)—C(10)	104.3 (2)	N(1)—C(10)—N(7)	108.9 (2)
C(3)—N(4)—C(10)	106.1 (2)	N(1)—C(10)—N(4)	108.7 (2)
N(4)—C(5)—C(6)	104.7 (2)	N(7)—C(10)—N(4)	108.9 (2)
C(10)—N(1)—C(2)—C(3)	-31.4 (3)	N(7)—C(8)—C(9)—N(1)	39.6 (3)
C(9)—N(1)—C(2)—C(3)	83.2 (3)	C(9)—N(1)—C(10)—N(7)	11.3 (3)
N(1)—C(2)—C(3)—N(4)	37.8 (3)	C(2)—N(1)—C(10)—N(7)	131.9 (2)
C(2)—C(3)—N(4)—C(5)	-143.2 (2)	C(9)—N(1)—C(10)—N(4)	-107.2 (2)
C(2)—C(3)—N(4)—C(10)	-29.2 (3)	C(2)—N(1)—C(10)—N(4)	13.4 (3)
C(3)—N(4)—C(5)—C(6)	84.1 (2)	C(8)—N(7)—C(10)—N(1)	13.7 (3)
C(10)—N(4)—C(5)—C(6)	-31.0 (2)	C(6)—N(7)—C(10)—N(1)	-106.7 (2)
N(4)—C(5)—C(6)—N(7)	38.1 (2)	C(8)—N(7)—C(10)—N(4)	132.2 (2)
C(5)—C(6)—N(7)—C(10)	-30.0 (3)	C(6)—N(7)—C(10)—N(4)	11.7 (3)
C(5)—C(6)—N(7)—C(8)	-143.8 (2)	C(5)—N(4)—C(10)—N(1)	130.8 (2)
C(10)—N(7)—C(8)—C(9)	-32.6 (3)	C(3)—N(4)—C(10)—N(1)	10.6 (3)
C(6)—N(7)—C(8)—C(9)	82.0 (3)	C(5)—N(4)—C(10)—N(7)	12.3 (3)
C(10)—N(1)—C(9)—C(8)	-30.8 (3)	C(3)—N(4)—C(10)—N(7)	-107.9 (2)
C(2)—N(1)—C(9)—C(8)	-144.9 (2)		

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *CALC* (Gould & Taylor, 1985).

We thank SERC for the provision of a four-circle diffractometer.

Lists of anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Nitrobenzyl Trichloroacetimidate

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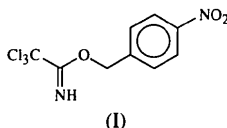
(Received 8 July 1994; accepted 19 September 1994)

Abstract

The imidate group in the title compound, $C_9H_7Cl_3N_2O_3$, is planar and approximately perpendicular to the *p*-nitrobenzyl group. The C=N bond is notably short for a double bond.

Comment

In connection with our interest in the use of alkyl trichloroacetimidates for the preparation of ethers and esters from alcohols and carboxylic acids, respectively (Armstrong, Brackenridge, Jackson & Kirk, 1988), we have prepared the title compound, (I), by the base-promoted addition of *p*-nitrobenzyl alcohol to trichloroacetonitrile.



Unlike most other trichloroacetimidates (Cramer, Pawelzik & Baldauf, 1958) (the only exception appears to be benzhydryl trichloroacetimidate), the product was

crystalline above ambient temperature (m.p. 356–358K), and the structure was therefore determined crystallographically in order to ascertain the geometry of the imidate group. Other benzyl trichloroacetimidates have been prepared, notably the parent compound (Wessel, Iversen & Bundle, 1985) and also *p*-methoxybenzyl trichloroacetimidate (Nakajima, Horita, Abe & Yone-mitsu, 1988).

A search of the Cambridge Structural Database (Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Mitchell, Smith & Watson, 1991) yielded three structures containing acyclic imidate functionalities. Coordinates were not available for two of these (Kolakowski, 1973, 1979), so detailed geometry can not be assessed. For the third structure (Nakano, Yokota, Igarashi & Sato, 1988), the imidate group is essentially planar with bond lengths and angles similar to those observed here. In the present structure, the C_3NO skeleton of the imidate group has an r.m.s. deviation from planarity of 0.006 Å. This group is approximately perpendicular to the aromatic ring [torsion angle C2—O1—C3—C4 80.3(2)°], with the nitro substituent essentially in the plane of the ring [O—N—C—C torsion angles –5.5(3), –6.5(3), 173.7(2) and 174.3(2)°]. The NH group is involved in a weak bifurcated hydrogen bond, intramolecular to C13 [H1···C13 2.52(5) Å, based on the freely refined position of H1] and intermolecular to O3 of the nitro group of an adjacent molecule [H1···O3($\frac{1}{2}-x, 1-y, z-\frac{1}{2}$) 2.49(9) Å], resulting in chains of hydrogen-bonded molecules running parallel to the *c* axis. The C=N bond is notably short for a double bond (typical values are in the range 1.27–1.32 Å), while the C—O bond lengths are typical for esters (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1992).

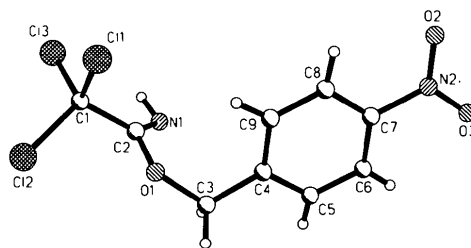


Fig. 1. The molecular structure of the title compound, showing the numbering scheme.

Experimental

The compound was prepared by slow addition of trichloroacetonitrile to a solution of *p*-nitrobenzyl alcohol in tetrahydrofuran to which sodium hydride (10 mol%) had been added. After complete reaction, the solvent was evaporated and the residue dissolved in ethyl acetate. Filtration and removal of the solvent from the filtrate yielded the title compound (95% yield). A suitable crystal was obtained directly from this evaporation.