Fig. 1. A perspective view of the cation and anion of (1). H atoms, except for H(1), are omitted for clarity.
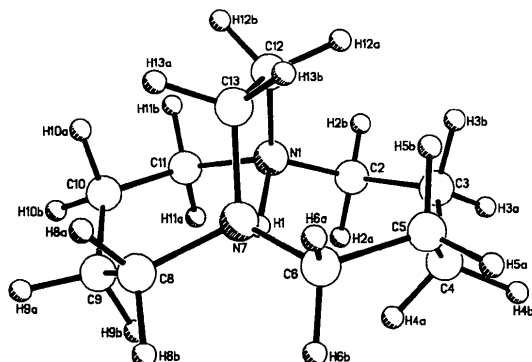

Fig. 2. Molecular structure of the cation of (1) showing methylene hydrogens.

Carboo, von Deuten, Kopf & Dreissig, 1986) and the inside-protonated salts of the [5.4.3]-, [5.5.2]- and [6.5.3]diamines (White *et al.*, 1988a,b,c), but contrasts with the bridge conformations observed in the inside-protonated [5.5.4]diamine (White *et al.*, 1988d) which display a local axis of symmetry.

The four-carbon bridge has the typical sequence of torsion angles having an approximate local axis of symmetry (Alder *et al.*, 1983, 1985, 1988; White *et al.*, 1988a,b). The two-carbon bridge is slightly twisted away from an eclipsed geometry [torsion angle = 13·5 (6)°]. The inside proton is essentially equidistant from the two bridgehead nitrogens [N(1)—H(1) 1·37 (7), N(7)—H(1) 1·47 (7) Å], the N—H—N angle is 132 (6)° and the N···N distance is 2·474 (7) Å. This N···N distance is the shortest observed in our series of inside-protonated ions.

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observed increase in the C—C—C bond angles is probably related to the large anisotropic displacement parameters observed for the C atoms (average isotropic $U = 0.074$ Å^2; see Table 1) indicating slight disorder or high thermal motion. The conformation of the five-carbon bridge is characterized by the $g^+g^-g^+g^-$ sequence of torsion angles, and has an approximate local plane of symmetry; this is similar to the five-carbon bridge conformations observed in the inside-diprotonated [1.1.1]cryptand (Knochel, Brugge,

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Conformation of 1,3,5-Tricyclohexyl-1,3,5-triazacyclohexane

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Abstract. $C_{21}H_{39}N_3$, $M_r = 333.6$, triclinic, $P\bar{1}$, $a = 19.322$ (3), $b = 10.076$ (2), $c = 5.291$ (2) Å, $\alpha = 77.81$ (2), $\beta = 84.48$ (2), $\gamma = 85.69$ (2)°, $V = 1001$ (1) Å^3, $Z = 2$, $D_x = 1.11$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 372$, $T = 293$ K, $R = 0.058$ for 3641 independent observed reflections. The triazacyclohexane ring adopts a chair conformation with diequatorial–axial orientation of the cyclohexyl groups. The torsion angles around the N—C bonds in the triazacyclohexane ring are 55·8–61·4 (2),

mean 59·3°, the N—C ring bonds are 1·447—1·476 (2), mean 1·461 Å, and the exocyclic N—C bonds are 1·473–1·484 (2), mean 1·479 Å. The torsion angles in the cyclohexane rings are 52·7–57·3 (2), mean 55·4°.

Introduction. Non-bonding electrons have appreciable conformational effects in heterocyclic chemistry (Riddell, 1980). In the case of the 1,3,5-trialkyl-1,3,-5-triazacyclohexanes (1) (hexahydro-s-triazines) the heterocyclic nucleus is expected to adopt a chair conformation and four distinct patterns of substituent orientation have to be considered, *eee, eea, eaa* and *aaa*, where *e* = equatorial and *a* = axial, with each of the conformers having axial repulsions involving the substituents or lone pairs of electrons on the N atoms. Several 1,3,5-trialkyl derivatives have been investigated in solution by NMR spectroscopy and by dipole-moment measurements and the results interpreted in terms of the *eee* conformer (Farmer & Hamer, 1968; Gutowsky & Temussi, 1967; Lehn, Riddell, Price & Sutherland, 1967), the *eea* conformer (Bushweller, Lourandos & Brunelle, 1974; Baker, Ferguson, Katritzky, Patel & Rahimi-Rastgoo, 1978), and varying amounts of the *eee, eea* and *eaa* conformers (Duke, Jones, Katritzky, Scattergood & Riddell, 1973). An X-ray crystallographic study of the 1,3,5-tribenzyl compound (1; $R = CH_2Ph$) at several temperatures has established that below *ca* 250 K there is a single conformation *eaa* and at higher temperatures there is an overall increase in the equatorial component (Sim, 1987).

(1)
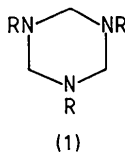
The 1,3,5-tricyclohexyl derivative (1; $R = C_6H_{11}$) is a solid at room temperature (Smolin & Rapoport, 1959; Stefaniak, Urbanski, Witanowski & Januszewski, 1969) and an X-ray diffraction study was undertaken to provide details of the conformation in the solid state.

Experimental. The title compound was obtained by reaction of cyclohexylamine with formaldehyde and was crystallized from ethanol. Crystal dimensions 0·6 × 0·6 × 0·8 mm. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, generator settings 50 kV, 20 mA. Cell dimensions from setting angles of 25 reflections with θ 14–20°; 4159 reflections surveyed in range θ 1·5–27·5°; h −24→24, k −12→12, l 0→6; 3641 independent reflections with $I > 2·5\sigma(I)$. Two reference reflections monitored periodically showed no significant variation in intensity. Corrections applied for Lorentz–polarization effects, assuming an ideally imperfect monochromator crystal. Structure deter-

mined by direct phasing using *MITHRIL* (Gilmore, 1984). H atoms located in difference Fourier syntheses. Full-matrix least-squares calculations on F with anisotropic thermal parameters for C and N atoms, and isotropic for H atoms. Isotropic extinction coefficient (Larson, 1967) included in final calculations, $g = 7·5$ (5) $\times 10^{-3}$. Convergence at $R = 0·058$, $wR = 0·084$, $S = 4·58$ for 438 parameters, $\Delta/\sigma < 0·04$, $w = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max. 0·27, min. −0·20 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations on a SEL 32/27 computer with the *GX* (Mallinson & Muir, 1985) system of programs.

Discussion. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Fig. 1, drawn with *ORTEP* (Johnson, 1965), illustrates the molecular structure.

The molecule adopts the *eea* conformation in the solid state, in contrast to the *eaa* conformation of the 1,3,5-tribenzyl compound at low temperature (Sim, 1987). These results suggest that diaxial repulsions increase in the order CH_2Ph/CH_2Ph < lone-pair/lone-pair < C_6H_{11}/C_6H_{11}, consistent with the greater steric requirements of cyclohexyl in comparison with benzyl. All three cyclohexyl rings have the C—N exocyclic bond equatorial.

The N atoms have distinctly pyramidal geometry, the N—C(cyclohexyl) bond being inclined at 52·2 (2), 46·7 (2) and 46·1 (2)° to the CH_2—N—CH_2 plane at N(1), N(3) and N(5), respectively. The average out-of-plane angle, 48·3°, is close to the corresponding angle in the tribenzyl derivative, 48·1°.

In the triazacyclohexane ring, the C—N torsion angles are in the range 55·8 (2)–61·4 (2), mean 59·3°. The C—C torsion angles in the cyclohexyl rings are rather smaller, 52·7 (2)–57·3 (2), mean 55·4°, with no distinction between axial (mean 55·8°) and equatorial (mean 55·3°) rings.

The C—N bond lengths are 1·447 (2)–1·484 (2), mean 1·467 Å, similar to those in the 1,3,5-tribenzyl compound which are 1·445 (2)–1·480 (2), mean 1·463 Å. The C—N ring bonds are slightly shorter than the exocyclic bonds and those at the equatorial sites N(1) and N(5) are slightly longer than those at the axial site N(3). The CH_2—N—CH_2 angles are 106·9 (2)–109·1 (2), mean 107·9°, and the N—CH_2—N angles are 110·5 (2)–112·9 (2), mean 111·6°.

In the cyclohexyl rings the C—C—C angles range from 109·1 (2) to 113·2 (2), mean 111·2°. The smallest

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

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
N(1)	0·31527 (5)	0·11951 (10)	0·18423 (21)	0·040
C(2)	0·32737 (8)	0·00881 (13)	0·03888 (29)	0·048
N(3)	0·26901 (6)	−0·07695 (10)	0·07175 (21)	0·044
C(4)	0·20977 (8)	0·00968 (13)	−0·02545 (27)	0·047
N(5)	0·19316 (5)	0·11655 (10)	0·12387 (20)	0·038
C(6)	0·25268 (7)	0·20071 (13)	0·09542 (27)	0·041
C(7)	0·37576 (7)	0·20528 (13)	0·14606 (25)	0·042
C(8)	0·44122 (8)	0·12233 (17)	0·24029 (43)	0·072
C(9)	0·50400 (8)	0·20782 (19)	0·21783 (38)	0·070
C(10)	0·48874 (9)	0·32225 (21)	0·36073 (37)	0·071
C(11)	0·42571 (9)	0·40883 (18)	0·26328 (47)	0·082
C(12)	0·36224 (7)	0·32356 (16)	0·28468 (35)	0·060
C(13)	0·25642 (7)	−0·15746 (12)	0·33960 (25)	0·041
C(14)	0·31838 (8)	−0·25665 (18)	0·40720 (32)	0·057
C(15)	0·30649 (9)	−0·34530 (19)	0·67898 (34)	0·062
C(16)	0·24155 (9)	−0·42262 (16)	0·70508 (38)	0·061
C(17)	0·17931 (9)	−0·32445 (18)	0·63816 (39)	0·064
C(18)	0·19111 (8)	−0·23464 (18)	0·36986 (35)	0·058
C(19)	0·12796 (7)	0·19867 (13)	0·06806 (24)	0·041
C(20)	0·06448 (8)	0·11618 (16)	0·17488 (31)	0·051
C(21)	−0·00313 (8)	0·20454 (19)	0·14370 (34)	0·061
C(22)	−0·00974 (9)	0·27593 (19)	−0·13526 (36)	0·066
C(23)	0·05370 (9)	0·35586 (18)	−0·24575 (38)	0·063
C(24)	0·12094 (8)	0·26646 (15)	−0·21705 (28)	0·051
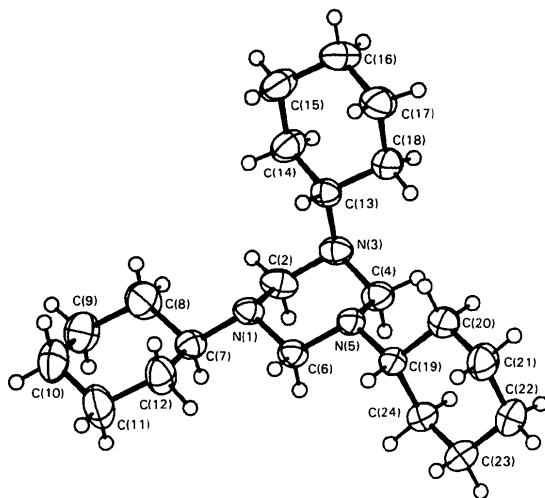
Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids of the C and N atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0·1 Å.

angles, 109·1, 109·6, 109·7°, are at the cyclohexyl positions directly bonded to the triaza heterocycle [*i.e.* C(7), C(13), C(19)], indicating that a steric effect is involved. Though the H—C—H angles of the cyclohexyl groups, 102·7 (17)–110·3 (19)°, are subject to fairly large errors, the mean value of 107·0° is undoubtedly significantly smaller than tetrahedral. The C—C bond lengths are 1·504 (3)–1·533 (2), mean 1·520 Å. The 33 C—H bonds of the cyclohexyl groups range from 0·90 (2) to 1·04 (3) Å and the mean length, 0·98 Å, is the customary 0·1 Å shorter than C—H internuclear distances determined by spectroscopy or neutron diffraction methods.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

N(1)—C(2)	1·476 (2)	N(1)—C(6)	1·467 (2)
N(1)—C(7)	1·479 (2)	C(2)—N(3)	1·447 (2)
N(3)—C(4)	1·453 (2)	N(3)—C(13)	1·484 (2)
C(4)—N(5)	1·465 (2)	N(5)—C(6)	1·457 (2)
N(5)—C(19)	1·473 (2)	C(7)—C(8)	1·528 (3)
C(7)—C(12)	1·521 (3)	C(8)—C(9)	1·521 (3)
C(9)—C(10)	1·504 (3)	C(10)—C(11)	1·510 (3)
C(11)—C(12)	1·532 (3)	C(13)—C(14)	1·520 (3)
C(13)—C(18)	1·510 (3)	C(14)—C(15)	1·531 (3)
C(15)—C(16)	1·506 (3)	C(16)—C(17)	1·518 (3)
C(17)—C(18)	1·521 (3)	C(19)—C(20)	1·528 (3)
C(19)—C(24)	1·533 (2)	C(20)—C(21)	1·527 (3)
C(21)—C(22)	1·512 (3)	C(22)—C(23)	1·518 (3)
C(23)—C(24)	1·525 (3)		

C(2)—N(1)—C(6)	107·8 (2)	C(2)—N(1)—C(7)	111·6 (2)
C(6)—N(1)—C(7)	110·7 (1)	N(1)—C(2)—N(3)	112·9 (2)
C(2)—N(3)—C(4)	106·9 (2)	C(2)—N(3)—C(13)	113·6 (2)
C(4)—N(3)—C(13)	114·7 (2)	N(3)—C(4)—N(5)	110·5 (2)
C(4)—N(5)—C(6)	109·1 (2)	C(4)—N(5)—C(19)	115·4 (2)
C(6)—N(5)—C(19)	112·0 (1)	N(1)—C(6)—N(5)	111·3 (1)
N(1)—C(7)—C(8)	111·3 (2)	N(1)—C(7)—C(12)	111·8 (2)
C(8)—C(7)—C(12)	109·1 (2)	C(7)—C(8)—C(9)	113·2 (2)
C(8)—C(9)—C(10)	111·3 (2)	C(9)—C(10)—C(11)	110·4 (2)
C(10)—C(11)—C(12)	111·4 (2)	C(7)—C(12)—C(11)	112·9 (2)
N(3)—C(13)—C(14)	109·8 (2)	N(3)—C(13)—C(18)	111·5 (2)
C(14)—C(13)—C(18)	109·6 (2)	C(13)—C(14)—C(15)	111·6 (2)
C(14)—C(15)—C(16)	111·4 (2)	C(15)—C(16)—C(17)	110·0 (2)
C(16)—C(17)—C(18)	111·6 (2)	C(13)—C(18)—C(17)	112·5 (2)
N(5)—C(19)—C(20)	111·1 (2)	N(5)—C(19)—C(24)	116·0 (2)
C(20)—C(19)—C(24)	109·7 (2)	C(19)—C(20)—C(21)	111·4 (2)
C(20)—C(21)—C(22)	111·8 (2)	C(21)—C(22)—C(23)	111·4 (2)
C(22)—C(23)—C(24)	111·7 (2)	C(19)—C(24)—C(23)	110·7 (2)

A few X-ray determinations of other types of 1,3,5-triazacyclohexanes have been reported. The 1,3,-5-triacetyl derivative has coplanar bonds at the N atoms and the topic of axial/equatorial orientation does not arise (Choi, Santoro & Marinkas, 1975). The 1,3,5-trinitro derivative has been studied both on its own (Choi & Prince, 1972) and in a complex with tetrahydrothiophene 1,1-dioxide (Haller, Brill & Rheingold, 1984); in both, two of the N atoms of the ring have pyramidal geometry with diaxial stereochemistry in the free compound and axial–equatorial stereochemistry in the complex, whereas the third N atom of the ring has planar geometry. The 1,3,5-tris(phenylsulfonyl) derivative has *eea* stereochemistry in the crystal (Rivero, Apredo, Castellano, Orazi & Corral, 1978) and the 1,3,5-triacetoxy derivative adopts the *aaa* conformation with O···O axial separations of 2·82–2·97 Å and an average ring torsion angle of 44° (Jerslev, Brehm & Gabrielsen, 1977). More directly pertinent, the 1,3,5-triphenyl derivative adopts the *aae* conformation, with an average ring torsion angle of 57·5° (Giumanini, Verardo, Randaccio, Bresciani-Pahor & Traldi, 1985).

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Substituent Effects on the Bicyclo[1.1.0]butane System. Structures of Bicyclo[1.1.0]butane Derivatives Substituted by Carbonyl and Carboxylate Groups

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Abstract. Structures of two bicyclo[1.1.0]butane derivatives substituted by methoxycarbonyl groups on the bridgehead carbon atoms C(1) and C(2) and linked on C(3) and C(4) by a ketal group (I) or by a carbonyl group (II). (I): $C_{11}H_{12}O_6$, $M_r = 240·21$, monoclinic, $P2_1/c$, $a = 11·546$ (1), $b = 12·141$ (2), $c = 8·319$ (2) Å, $\beta = 79·29$ (1)°, $V = 1145·8$ (5) Å^3, $Z = 4$, $D_x = 1·39$ Mg m^{-3}, λ(Mo Kα) = 0·71073 Å, $\mu = 0·11$ mm^{-1}, $F(000) = 504$, $T = 295$ K, $R = 0·043$ for 1782 unique observed reflections [$I > 3\sigma(I)$]. (II): $C_9H_8O_5$, $M_r = 196·16$, triclinic, $P\bar{1}$, $a = 5·726$ (1), $b = 7·033$ (1), $c = 10·734$ (1) Å, $\alpha = 88·48$ (1), $\beta = 88·18$ (1), $\gamma = 84·76$ (1)°, $V = 430·1$ (2) Å^3, $Z = 2$, $D_x = 1·51$ Mg m^{-3}, λ(Mo Kα) = 0·71073 Å, $\mu = 0·12$ mm^{-1}, $F(000) = 204$, $T = 295$ K, $R = 0·037$ for 2078 unique observed reflections [$I > 3\sigma(I)$]. The methoxycarbonyl groups at the bridgehead carbon atoms C(1) and C(2) of (I) give rise to a lengthening of the central bond [1·485 (2) Å] by 0·030 Å compared to the corresponding compound (III) which lacks π-accepting substituents. The corresponding central bond [1·453 (2) Å] of (II) is shortened compared with (I) by the effect of the CO group linking C(2) and C(3). By the same effect the remaining four bonds of the bicyclobutane system of (II) are lengthened by 0·012 Å [(I) 1·509 (3) Å; (II) 1·521 (5) Å].

Introduction. The central bond in bicyclo[1.1.0]butane derivatives is very sensitive to electronic effects of substituents and to changes of the dihedral angle between both three-membered rings (Irngartinger & Lukas, 1979; Allen, 1984). To obtain further information about the substituent effects, we investigated the structure of bicyclo[1.1.0]butane derivatives with equal dihedral angles. This angle is fixed by linking C(3) and C(4) (Fig. 1) with one carbon C(5) in order to find the pure substituent effects on the central bond without interference by steric influences. Our aim was to discover the effect of π-acceptor groups (*e.g.* the carbonyl group) on the bond lengths of bicyclo[1.1.0]butane, if the groups are substituted in different positions, and to determine their combined influence in polysubstituted systems. Therefore, we determined the structures of dimethyl spiro(1,3-dioxolane-2,3'-tricyclo[2.1.0.0^{2,5}]pentane)-1',5'-dicarboxylate (I) and dimethyl 3-oxotricyclo[2.1.0.0^{2,5}]pentanedicarboxylate