

7,7-Dichloro-1,6-dimethylbicyclo[4.1.0]heptane-*trans*-3,*trans*-4-dicarbonitrile*

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Abstract. $C_{11}H_{12}Cl_2N_2$, monoclinic, $P2_1/c$, $a = 13.206$ (7), $b = 6.936$ (4), $c = 12.906$ (7) Å, $\beta = 104.25$ (4)°, $Z = 4$, $D_c = 1.41$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 4.842$ mm⁻¹; final residual $R = 0.072$. The ring conformation is intermediate between half-chair and sofa; this is related to the non-bonded interaction between the *endo* Cl and the *cis*-3-axial H atoms, the remaining strain being quite strong. The molecular packing seems to be partly governed by the strong electrostatic attraction between the close equatorial cyano groups.

Introduction. Recent proton magnetic resonance studies have extended our structural knowledge of six-membered rings which *a priori* adopt a half-chair conformation: cyclohexenes (Aycard & Bodot, 1975; Lafrance, Aycard & Bodot, 1977), norcaranes (Pizzala, Bodot & Fruchier, 1977) and 1,2-epoxycyclohexanes (Pizzala, Aycard & Bodot, 1977a). The main purpose of these previous studies was to depict the structural evolution when the steric strain is increased; we have also investigated a series of 7,7-dichlorobicyclo[4.1.0]heptanes (Pizzala, Aycard & Bodot, 1977b); from their PMR coupling constants, we have established that the six-membered ring is not in a pure half-chair conformation.

In this new series of papers, our aim is to gain a better insight into the structures of model molecules and of compounds with original conformational features. The present paper refers to this kind of structure as the molecule examined here is thermodynamically more stable than its stereoisomer with two cyano groups in a *trans* relation (Pizzala *et al.*, 1977b).

* *trans* corresponds to the stereochemical relationship between a cyano group and the cyclopropane ring considered as substituents of the six-membered ring.

The synthesis of this compound has been reported elsewhere (Pizzala *et al.*, 1977b). The crystal was sealed in a Lindemann-glass capillary to prevent deterioration. All X-ray measurements were made at room temperature. X-ray oscillation and Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation indicated the monoclinic system. The intensities were collected on an automatic four-circle Enraf–Nonius CAD-4 diffractometer operating in the $\theta/2\theta$ scan mode and using Ni-filtered Cu $K\alpha$ radiation. Accurate cell parameters were determined by least-squares analysis from 15 middle reflections using a centering program. Of the 1857 independent reflections measured in the range $0 < \theta < 56^\circ$, 1586 with $I > 3\sigma(I)$ were regarded as observed. Only a Lorentz–polarization correction was applied.

The crystal structure was solved by the multi-solution procedure of *MULTAN* (Main, Woolfson,

Table 1. Final fractional coordinates ($\times 10^4$) with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
C(1)	7022 (3)	9262 (5)	8329 (3)	2.39 (6)
C(2)	7902 (3)	9321 (6)	7749 (3)	2.60 (7)
C(3)	8865 (3)	10536 (6)	8273 (3)	2.74 (8)
C(4)	8548 (3)	12401 (6)	8777 (3)	2.95 (8)
C(5)	8040 (3)	11824 (6)	9690 (3)	3.01 (8)
C(6)	7092 (3)	10548 (6)	9325 (3)	2.60 (7)
C(7)	7223 (3)	8395 (6)	9429 (3)	2.67 (7)
C(8)	5982 (3)	8929 (7)	7554 (3)	3.36 (9)
Cl(9)	6252 (1)	6982 (2)	9783 (1)	3.87 (3)
Cl(10)	8455 (1)	7371 (2)	10026 (1)	3.57 (3)
C(11)	9449 (3)	10969 (6)	7464 (4)	3.31 (8)
C(12)	7803 (4)	13533 (7)	7962 (3)	3.51 (9)
C(13)	6105 (3)	11445 (7)	9507 (4)	3.51 (9)
N(14)	9891 (3)	11304 (6)	6828 (3)	4.55 (9)
N(15)	7219 (4)	14348 (7)	7323 (4)	5.47 (10)

Lessinger, Germain & Declercq, 1974), based on 250 reflections with $E > 1.5$. The E map yielded all the non-hydrogen atoms.

The structure was refined by full-matrix least squares with *ORFLS* (Busing, Martin & Levy, 1962). After isotropic (three cycles) and anisotropic refinements (three cycles), a difference Fourier synthesis then revealed all the H atoms; their positions and isotropic thermal factors were introduced in the refinement procedure, but were not refined. To each H atom was assigned the mean isotropic thermal parameter of the atom to which it is bonded. Subsequent cycles reduced R to a final value of 0.072 with $R = \sum |KF_o - |F_c|| / \sum |KF_o|$.* Hughes's (1941) weighting scheme was used in the last two cycles: $w = 1/(a_w + b_w F_o + c_w F_o^2)$ if $F_o > F_w$ and $w = 1.57$ if $F_o < F_w$, with $a_w = 0.6389$, $b_w = 0.0336$, $c_w = 0.004$, $F_w = 1.01$.

The scattering factors were those of Doyle & Turner (1968) for heavy atoms, and those of Stewart, Davidson & Simpson (1965) for H atoms. The final atomic positions are listed in Table 1. All calculations were carried out on the 370/145 IBM computer of the Office Central de Mécanographie of Abidjan.

* Lists of structure factors, anisotropic thermal parameters and non-refined hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34575 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s to last digit quoted in parentheses

C(1)—C(2)	1.530 (5)	C(5)—C(6)—C(1)	118.2 (3)
C(2)—C(3)	1.537 (6)	C(6)—C(1)—C(2)	119.6 (3)
C(3)—C(4)	1.551 (6)	C(7)—C(1)—C(2)	119.6 (3)
C(4)—C(5)	1.545 (5)	C(8)—C(1)—C(2)	111.0 (3)
C(5)—C(6)	1.511 (6)	C(7)—C(1)—C(6)	59.1 (2)
C(6)—C(1)	1.549 (5)	C(8)—C(1)—C(6)	119.9 (3)
C(6)—C(7)	1.505 (6)	C(8)—C(1)—C(7)	119.1 (3)
C(6)—C(13)	1.514 (6)	C(1)—C(6)—C(7)	59.0 (2)
C(1)—C(7)	1.504 (5)	C(1)—C(6)—C(13)	119.2 (3)
C(1)—C(8)	1.505 (5)	C(5)—C(6)—C(7)	119.0 (3)
C(3)—C(11)	1.474 (6)	C(5)—C(6)—C(13)	113.0 (4)
C(4)—C(12)	1.477 (6)	C(7)—C(6)—C(13)	118.6 (4)
C(7)—Cl(9)	1.761 (4)	C(1)—C(6)—C(7)	62.0 (3)
C(7)—Cl(10)	1.769 (4)	C(1)—C(7)—Cl(9)	119.8 (3)
C(11)—N(14)	1.142 (6)	C(1)—C(7)—Cl(10)	120.1 (3)
C(12)—N(15)	1.132 (7)	C(6)—C(7)—Cl(9)	120.0 (3)
C(1)—C(2)—C(3)	116.5 (3)	C(6)—C(7)—Cl(10)	120.7 (3)
C(2)—C(3)—C(4)	111.3 (3)	Cl(9)—C(7)—Cl(10)	108.3 (2)
C(3)—C(4)—C(5)	108.5 (3)	C(3)—C(11)—N(14)	179.2 (5)
C(4)—C(5)—C(6)	113.3 (3)	C(4)—C(12)—N(15)	177.9 (5)

Discussion. The molecular structure is illustrated in Fig. 1. Bond lengths and angles are given in Table 2. The endocyclic torsion angles are listed in Table 3.

Relative to the C(5)C(6)C(1)C(2) plane (atoms are coplanar within 0.001 Å), C(3) is 0.14 Å above and C(4) is 0.64 Å below. In a half-chair ring conformation, these two atoms would be symmetrical relative to this plane. C(8), C(1), C(6) and C(13) are coplanar within 0.003 Å.

Ring conformation. From Table 3, it is obvious that the six-membered ring is intermediate between half-chair and sofa, the latter corresponding to a coplanar arrangement for five of the six ring atoms (Bucourt, 1974). The evolution from the half-chair to the experimental conformation is the best way for the molecule to minimize the strong Cl(10)⋯H(31) steric interaction, without too much of an increase in the Cl(10)⋯H(51) interaction.

Geometrical data. For the dichlorocyclopropane unit, comparisons may be made with the accurate data for similar molecules involving the tricyclo[9.1.0.0^{5,7}]-dodecane (Baker & Pauling, 1972) and the tricyclo[3.2.1.0^{1,5}]octane (Wilberg, Burgmaier, Shen, La Placa, Hamilton & Newton, 1972) skeletons. If we exclude the specific features of this last molecule ('inverted carbon'), larger differences are observed for the ring-junction dihedral angle which is 109, 107 and 115° respectively for molecules of the present compound [projection along C(6), C(1)], and of the dodecane and octane molecules. These modifications seem to be related to the relative strains of the fused

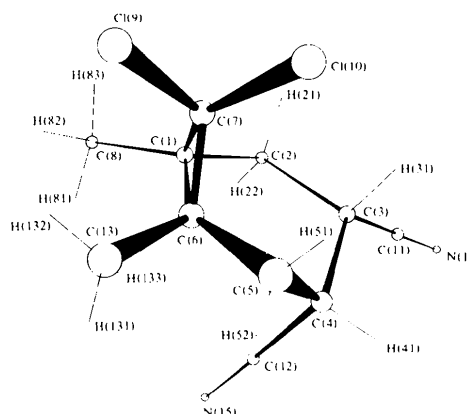


Fig. 1. A view of the molecule down the z axis showing the numbering of the atoms.

Table 3. Endocyclic torsion angles (°) with standard deviations in parentheses

	φ_{12}	φ_{23}	φ_{34}	φ_{45}	φ_{56}	φ_{61}
Experimental	-6.0 (5)	37.9 (5)	-64.2 (6)	58.3 (6)	-26.8 (5)	0.2 (5)
Half-chair	-15.0	46.0	-63.0	46.0	-15.0	0.0
Sofa*	0.0	28.0	-56.0	50.0	-27.0	0.0

* Cyclohexene (Bucourt, 1974).

rings which also induce the bond-angle [C(5)—C(6)—C(1) for our molecule] sequence: 118, 124 and 108°.

Non-bonded interactions. As we are dealing with a strained molecule, there are about 15 'short distances' ($< d_0$) between non-bonded atoms, d_0 corresponding to a zero value for the non-bonded energy as it is parametrized in the molecular-mechanics calculations (Allinger, 1976). The stronger steric interactions are associated with the Cl...H atom pairs ($d_0 = 3.08 \text{ \AA}$): Cl(10)...H(31) = 2.65, Cl(10)...H(51) = 2.57, Cl(9)...H(82) = 2.61, Cl(9)...H(132) = 2.66 Å.

There is an exact balance between these interactions acting on each side of the three-membered ring. Similar, but softer non-bonded interactions are observed in the tricyclo[3.2.1.0^{1,5}]octane molecule (Wilberg *et al.*, 1972) where the shortest Cl...H distances are 2.83 and 2.87 Å.

Among the attractive non-bonded interactions, we may select that acting between the C(13) methyl group and the axial C(12) cyano substituent; the corresponding C atoms are separated by 3.65 Å, which corresponds to the sum of the van der Waals radii (3.6 Å). The C(12)...H(131) and N(15)...H(131) distances, which are respectively 3.19 and 3.32 Å, also correspond to the sums of the van der Waals radii. These attractive interactions may counterbalance the *syn*-1,3-diaxial C(12)...H(22) interaction (2.81 Å $< d_0$), and even contribute to the energy stabilization of the present dicyano compound relative to its stereoisomer (see *Introduction*).

Molecular packing. As shown in Fig. 2, the main features of this molecular packing are the closeness of the equatorial cyano groups and their relative orientations; they are in parallel planes and their dihedral angle is about 160°. The distance between these groups is about 3.42 Å [C(11)...N(14)], which is less than the sum of the van der Waals radii ($\approx 3.70 \text{ \AA}$), as in the packing of *trans*-2-*tert*-butyl-4-oxocyclohexanecarbonitrile (Viani, Lapasset, Aycard, Lafrance & Bodot, 1978). The corresponding loss of attractive non-bonded energy may be counterbalanced by the strong electrostatic attraction between the large dipoles.

N(14) of this equatorial cyano group is also at a short distance from H(31) (2.81 Å) and H(41) (2.85 Å) of another molecule; so this N looks like a base ready to catch these H atoms which have an acidic character. But this closeness is not sufficient to change the hybridization of C(3) and C(4), since the sums of the three C—C(x)—C ($x = 3$ or 4) bond angles are typical of pure sp^3 hybridization (respectively 331 and 329°).

The observed geometrical adaptations to congestion are easily interpreted; but other structural data have to be collected to prove the generality of our observation. For this step, we are in agreement with the assumptions suggested by the previous PMR study.

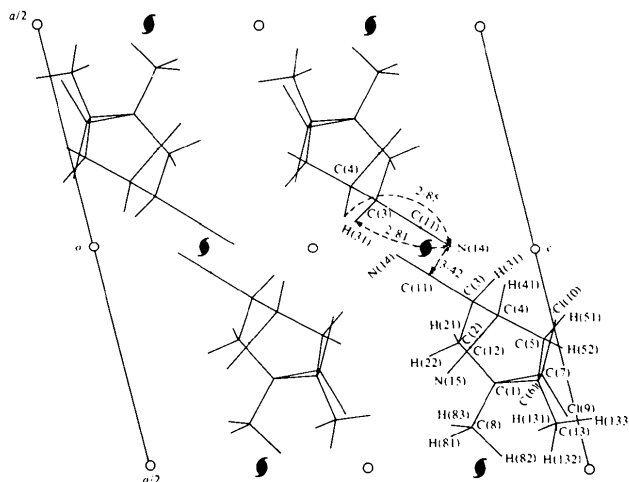


Fig. 2. The crystal structure viewed along the b axis showing the relative orientations of the cyano groups, and some short contacts (Å).

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