

Structure of *r*-3-*tert*-Butyl-*c*-4,*t*-5-cyclohexenedicarbonitrile*

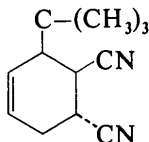
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Abstract. $C_{12}H_{16}N_2$, $M_r = 188.27$, m.p. 348 K, monoclinic, $C2/c$, $Z = 8$, $a = 21.631(8)$, $b = 6.127(3)$, $c = 16.995(6)$ Å, $\beta = 90.35(4)^\circ$, $V = 2252.4$ Å³, $d_m = 1.12(2)$, $d_x = 1.11$ Mg m⁻³, $\mu(Cu K\alpha) = 0.520$ mm⁻¹, $F(000) = 916$. The crystal structure has been determined by direct methods from three-dimensional diffractometer data (Cu $K\alpha$ radiation) and refined to an R of 0.054 for 1320 independent reflections. The molecular structure shows that the ring adopts a half-chair conformation without evolution towards the sofa since the axial 5-cyano group interacts with the H atom bonded to C(3).

Introduction. The crystal of the title compound



may be compared in terms of strong *gauche* interactions with that of *cis*-3-*tert*-butyl-4-cyano-1-cyclohexenyl acetate which was described in a preceding paper (Viani & Lapasset, 1978).

Indeed, in that case, the *gauche* interaction between the equatorial *tert*-butyl and axial cyano groups induces a ring modification towards the sofa conformation characterized by a zero torsion angle around the C(6)–C(1) bond (Bucourt, 1974).

For this crystal, the main difference being a second cyano group attached at C(5), it would be of great interest to obtain precise information on the deformations associated with this last substituent. This paper presents the results of the structure determination of this compound.

The 3-*tert*-butyl-4,5-cyclohexenedicarbonitrile diastereoisomers have been synthesized by the Diels–Alder reaction between 5,5-dimethyl-1,3-hexadiene and fumaronitrile carried out at 403 K. The two isomers with *trans* cyano groups were separated by vapour-phase chromatography, and recrystallized from chloroform (Gedoux, 1978).

A colourless parallelepiped crystal $0.26 \times 0.24 \times 0.12$ mm was selected, mounted on a Lindemann-glass capillary along **b**, and used for all the X-ray investigations (made at room temperature).

Preliminary unit-cell dimensions were determined from X-ray oscillation and Weissenberg photographs with Ni-filtered Cu $K\alpha$ radiation in agreement with the diffractometer values obtained subsequently.

Systematic absences were observed in hkl for $h + k$ odd and $h0l$ for l odd, indicating possible space groups Cc or $C2/c$. The choice of the centrosymmetric space group $C2/c$ was confirmed by the structural analysis.

Lattice parameters and diffracted intensities were measured on an automatic three-circle Enraf–Nonius CAD-3 diffractometer operating in the θ – 2θ scan mode and using graphite-monochromatized Cu $K\alpha$ radiation.

Accurate cell parameters were determined by a least-squares analysis from 12 middle-intensity reflections using a centring program.

1413 independent reflections up to $\theta = 65^\circ$ were measured and 1320 considered as observed. Deviations in the intensity of a standard reflection, monitored after each group of 40 measurements, were less than 7% and showed no systematic decay.

A Lorentz–polarization correction was applied to the intensity-data set. No absorption corrections were made as test calculations showed them to be unnecessary ($\mu = 0.520$ mm⁻¹).

The preliminary processing step was the determination of the absolute scale ($K = 1.357$) and overall temperature factor ($B = 3.024$ Å²) using Wilson's (1942) method.

The crystal structure was solved by the multi-solution procedure of *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) based on 300 reflections with $E > 1.34$. The E map based on phases corresponding to the best figure of merit yielded all the non-hydrogen atoms. A structure factor calculation gave an R of 0.17 for 1241 reflections with $R = \frac{\sum |KF_o|}{\sum |KF_c|}$.

The structure was refined by full-matrix least squares with *ORFLS* (Busing, Martin & Levy, 1962). After isotropic (two cycles) and anisotropic refinement (two cycles) the R value was 0.083.

* Strained Cyclic Molecules. V.

Table 1. Final fractional coordinates ($\times 10^4$) and isotropic thermal parameters for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
C(1)	4285 (1)	6903 (4)	2988 (2)	3.65
C(2)	4295 (1)	5504 (5)	3576 (1)	3.31
C(3)	3938 (1)	3402 (4)	3601 (1)	2.67
C(4)	3414 (1)	3443 (4)	2989 (1)	2.91
C(5)	3660 (1)	4283 (5)	2183 (1)	3.35
C(6)	3916 (1)	6605 (5)	2254 (2)	4.05
C(7)	3749 (1)	2678 (4)	4452 (1)	3.26
C(8)	3286 (2)	838 (5)	4412 (2)	5.21
C(9)	3476 (1)	4577 (6)	4930 (2)	4.83
C(10)	4332 (1)	1876 (6)	4862 (2)	5.59
C(11)	2888 (1)	4845 (5)	3195 (2)	4.14
N(12)	2468 (1)	5897 (6)	3318 (2)	6.67
C(13)	4132 (1)	2746 (5)	1900 (1)	3.61
N(14)	4492 (1)	1563 (5)	1676 (1)	5.20

A difference synthesis then revealed all the H atoms which were introduced in the refinement procedure but not refined; their thermal factors were kept isotropic at the values of the atoms to which they were bonded.

Four subsequent cycles reduced *R* to a final value of 0.054 for 1320 reflections with Hughes's (1941) weighting scheme [$F_o(\text{min.}) = 0.1$].

The scattering factors were those of Doyle & Turner (1968) for heavy atoms, and those of Stewart, Davidson & Simpson (1965) for H atoms. The final positional and isotropic thermal parameters are listed in Table 1.*

All calculations were carried out on the 370/145 IBM computer of the Office Central de Mécanographie, Abidjan.

Discussion. A perspective view of the molecule is shown in Fig. 1, with the numbering of the atoms.

* Lists of structure factors, anisotropic thermal parameters, atomic coordinates of unrefined H atoms and interatomic distances involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35518 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

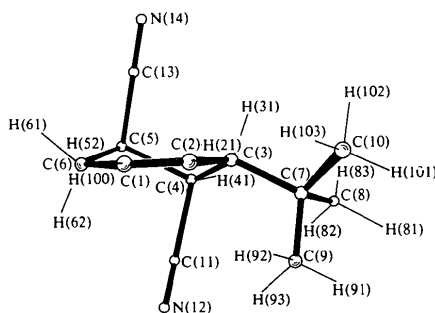


Fig. 1. The molecular structure, with the numbering scheme, projected along the *C*₂ pseudosymmetry axis through the centres of the C(1)–C(2) and C(4)–C(5) bonds.

Interatomic distances and bond angles for non-hydrogen atoms are given in Fig. 2. The torsion angles in the form of Newman projections are illustrated in Fig. 3.

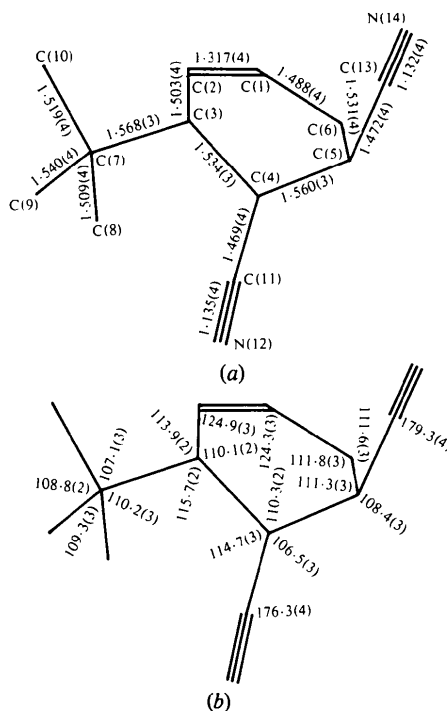


Fig. 2. Projection of the structure along *b* showing: (a) the bond lengths (Å); (b) the valency angles (°). Standard deviations given in parentheses refer to the last digit quoted. H atoms are omitted for clarity. Angles not shown: C(3)–C(7)–C(9) 112.1 (3), C(8)–C(7)–C(10) 109.1 (3)°.

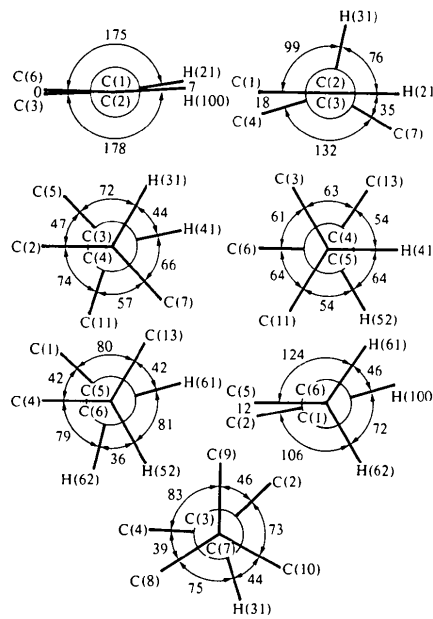


Fig. 3. Selected Newman projections (torsion angles are in degrees, standard deviations for angles involving non-hydrogen atoms are $\sim 0.6^\circ$).

Table 2. *Endocyclic torsion angles* (°)

Central bond	This work*	Experimental half-chair†	Calculated sofa‡
C(1)–C(2)	–0.2	0	–5.7
C(2)–C(3)	–17.9	–16	0
C(3)–C(4)	46.6	46	32
C(4)–C(5)	–60.6	–63	–58
C(5)–C(6)	41.6	46	51
C(6)–C(1)	–12.1	–16	–20

* Standard deviations are ~0.6°.

† Scharpen, Wollrab & Ames (1968).

‡ Bucourt (1974).

The best plane through selected atoms shows that C(6), C(1), C(2), C(3) are coplanar within 0.001 Å, C(4) and C(5) deviating by –0.45 (1) and 0.30 (1) Å respectively. This plane is nearly perpendicular to the planes through atoms C(5), C(4), C(11) [88.8 (4)°] and C(4), C(5), C(13) [84.5 (4)°]; the dihedral angle between these planes is –172.4 (5)°. This shows that the two cyano groups are in axial positions, in agreement with theory.

The endocyclic torsion angles reported in Table 2 show that the molecule is more half-chair (Scharpen, Wollrab & Ames, 1968) than sofa (Bucourt, 1974). However, the *gauche* interaction between the *tert*-butyl and the 4-cyano substituents in the *cis* relationship provides a stereochemical evolution from half-chair to sofa (Viani & Lapasset, 1978).

Thus, the fact that our molecule does not adopt an intermediate conformation may be ascribed to the 1,3-*syn*-diagonal interaction between the second cyano group and H(31); these develop a strong non-bonded interaction, the H...C distance being 2.67 Å, which is shorter than the sum (3.35 Å) of the van der Waals radii (Allinger, 1976).

All intermolecular distances between atoms are greater than the sum of the van der Waals radii.

The ring conformation of the title compound is half-chair because of the cyano group on C(5) which prevents the *gauche* interaction between the *tert*-butyl and the cyano group from producing a sofa, the main interaction being a 1,3-*syn*-diagonal one between the cyano group and the pseudoaxial H(31).

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7,8-Dihydro-2,5-diphenylimidazo[1,2-*f*]-1,3,4,6-thiatriazepine

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Abstract. C₁₇H₁₄N₄S, orthorhombic, *Pca*2₁, *a* = 16.62 (2), *b* = 8.17 (2), *c* = 11.15 (2) Å, *Z* = 4, *D_m* = 1.305, *D_x* = 1.340 Mg m^{–3}. The structure, which was solved by the application of direct methods to dif-

ference Fourier coefficients, was refined to *R* = 0.090. Crystal Structure Search Retrieval (CSSR) was used to compare the ring conformations with those of related molecules. The seven-membered ring exists in the usual