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

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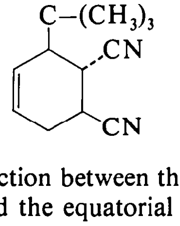
Abstract. $C_{12}H_{16}N_2$, $M_r = 188{\cdot}27$, m.p. 353 K, monoclinic, $P2_1/c$, $Z = 4$, $a = 8{\cdot}150\,(4)$, $b = 7{\cdot}532\,(4)$, $c = 19{\cdot}596\,(6)$ Å, $\beta = 103{\cdot}32\,(4)°$, $V = 1170{\cdot}5$ Å^3, $d_m = 1{\cdot}07\,(2)$, $d_x = 1{\cdot}069$ Mg m^{-3}, μ(Cu $K\bar{\alpha}$) = 0·500 mm^{-1}, $F(000) = 408$. The crystal structure has been determined by direct methods from three-dimensional diffractometer data, and refined to an R of 0·058 for 1524 independent reflections. The molecular structure corresponds to that of a triequatorial conformer; the ring conformation is intermediate between half-chair and sofa, as a result of the influence of the *gauche tert*-butyl–cyano interaction restricted by the dicyano interaction.

Introduction. All the molecules under investigation in this series of papers have a *tert*-butyl substituent vicinal to a cyano or oxycarbonyl group (Viani, Lapasset, Aycard, Lafrance & Bodot, 1978; Viani & Lapasset, 1978, 1981). The strong *gauche* interaction between them provides steric modifications which are different according to their relative positions and their relation to the six-membered ring. The results being uncommon, these molecules are good structural models for studying the strong steric interactions. Other examples are required to prove that these steric interactions mainly govern the conformational behaviour.

Like the molecule studied in the preceding paper (Viani & Lapasset, 1981), the present compound



has a *gauche* interaction between the pseudoequatorial *tert*-butyl group and the equatorial cyano substituent; furthermore, there is another interaction between the two vicinal cyano substituents. The competitive influence of these two diequatorial interactions has been studied byAycard & Bodot (1973).

This paper presents the crystal and molecular structures of this compound, with the purpose of specifying which of these interactions orients the conformation.

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

The colourless crystal used in the structure determination has approximate dimensions 0·30 × 0·20 × 0·15 mm. It was mounted along **b** on a Lindemann-glass capillary and measured at room temperature.

Preliminary cell parameters and space-group information were obtained from oscillation and Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation.

The accurate cell dimensions were obtained by least-squares refinement of the angular settings of 15 middle-intensity reflections recorded on an automated four-circle Enraf–Nonius CAD-4 diffractometer using a centring program.

Three-dimensional X-ray intensity data were collected on the same instrument, operating in the θ–2θ scan mode with Cu $K\alpha$ radiation. 1687 reflections up to $\theta = 65°$ were collected and 1528 were considered as observed. Two standard reflections were monitored every 72 reflections to check for counter or crystal instability. At the end of the data collection, the intensity of the standard reflections had dropped by 12% and the crystal faces had changed from colourless to whitish. This reduction was used to place the data on a uniform scale.

The structure amplitudes were corrected for Lorentz and polarization effects, but no absorption corrections were applied because of the low μ and the small size of the crystal.

The preliminary absolute scale ($K = 0{\cdot}2267$) and overall temperature factor ($B = 4{\cdot}50$ Å^2) were estimated using Wilson's (1942) method.

The structure was solved by the multisolution procedure of *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The solution was based on phases determined for 300 reflections with $E >$

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* Strained Cyclic Molecules. IV.

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

Standard deviations in parentheses refer to the last digit quoted.

	x	y	z	B (Å^2)
C(1)	162 (5)	2555 (6)	64 (3)	5·77
C(2)	569 (5)	3026 (6)	732 (3)	5·48
C(3)	2337 (4)	3152 (5)	1189 (2)	4·13
C(4)	3621 (4)	2459 (4)	781 (2)	3·46
C(5)	3112 (4)	2986 (5)	−3 (2)	4·16
C(6)	1418 (6)	2189 (6)	−361 (2)	5·70
C(7)	2463 (5)	2182 (5)	1908 (2)	4·78
C(8)	4276 (5)	2130 (6)	2338 (2)	5·57
C(9)	1781 (6)	293 (6)	1791 (2)	5·89
C(10)	1418 (8)	3222 (9)	2331 (3)	7·70
C(11)	5338 (4)	3136 (5)	1059 (2)	4·46
N(12)	6662 (4)	3711 (6)	1230 (2)	6·52
C(13)	4432 (5)	2450 (5)	−366 (2)	4·71
N(14)	5450 (5)	2030 (6)	−643 (2)	6·83

1·43. The E map with the best figure of merit revealed the positions of all the non-hydrogen atoms. One cycle of isotropic least-squares refinement gave an R of 0·26 for 1263 reflections. Refinement was continued, initially with isotropic (two cycles), but later with anisotropic thermal parameters (four cycles). All the H atoms were then located on a difference map, except H(91) and H(93) for which calculated positions were adopted and used in the next two stages of refinement, including the H atoms which were assigned the isotropic temperature factors of the C atoms to which they were attached. The four strong reflections (104, 20$\bar{6}$, 022 and 023) severely affected by extinction were then excluded from the last two stages of refinement. The final R for 1524 reflections is 0·058 with Hughes's (1941) weighting scheme [F_0(min.) = 0·1]. The Busing, Martin & Levy (1962) program was used for refinement. The scattering factors for the heavy atoms were those of Doyle & Turner (1968), for H those of Stewart, Davidson & Simpson (1965).

The final positional parameters are listed in Table 1.*

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

Discussion. The shape of the molecule with its numbering scheme is shown in Fig. 1. The final bond distances and bond angles for the non-hydrogen atoms are given in Fig. 2. The torsion angles in the form of Newman projections are illustrated in Fig. 3.

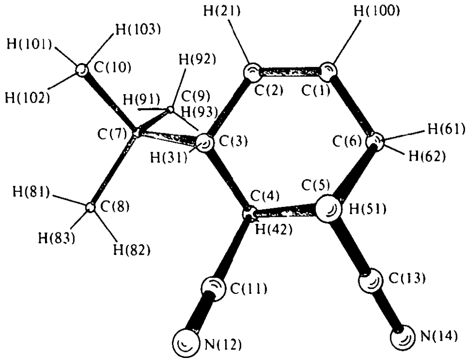

Fig. 1. The molecular structure, with the numbering scheme, viewed in the direction normal to the C(6), C(1), C(2) and C(3) mean plane.

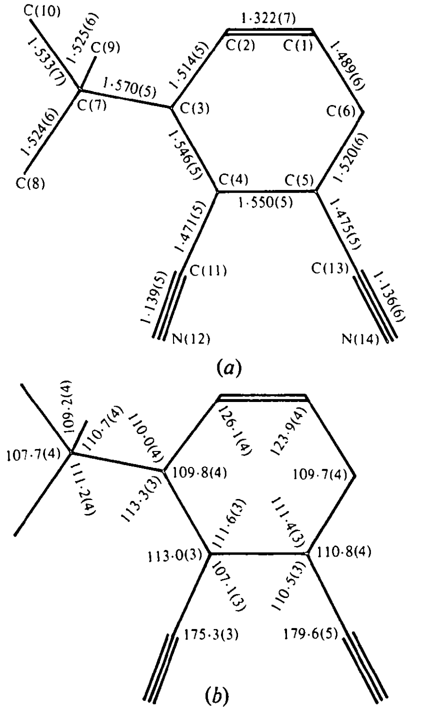

Fig. 2. Projection of the structure along **b** showing: (*a*) the bond lengths (Å); (*b*) the valency angles (°). Standard deviations given in parentheses refer to the last digit quoted. H atoms are omitted for clarity. Angles not shown: C(8)–C(7)–C(9) 109·4 (4), C(3)–C(7)–C(10) 108·6 (4)°.

The best planes through selected atoms show that C(1), C(2), C(3) and C(6) are coplanar within 0·02 Å; C(6) is 0·26 (1) Å from C(3), C(7), and C(9). The best *anti* relationship between vicinal atoms is found with C(2), C(3), C(7) and C(8) which are coplanar within 0·04 Å. Table 2 gives the values of the endocyclic torsion angles together with those of half-chair cyclohexene (Scharpen, Wollrab & Ames, 1968) and those of the calculated sofa conformation (Bucourt, 1974).

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* 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 35519 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

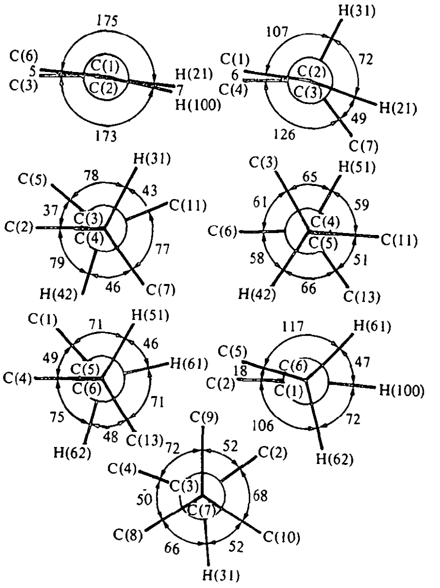

Fig. 3. Selected Newman projections (torsion angles in degrees, standard deviations for angles involving non-hydrogen atoms are ~0·6°).

The endocyclic torsion angle φ_{2-3} around the C(2)–C(3) bond being −5·8 (5)° (Table 2), the ring conformation may be considered as more sofa than half-chair.

The evolution to sofa decreases the *gauche tert*-butyl–cyano interaction, the dihedral angle C(7)–C(3)–C(4)–C(11) being 77·4 (4)°; moreover, the torsion angle C(1)–C(2)–C(3)–C(7) is 131·7 (5)°, showing that the *tert*-butyl group is between a pseudoequatorial and an isoclinal position (Bellucci, Berti, Colapietro, Spagna & Zambonelli, 1976), *i.e.* 140 and 120° respectively; likewise, the cyano group is more isoclinal, $\Delta\varphi = \varphi_{3-4} - \varphi_{4-5} = 98{\cdot}7\ (8)°$, instead of 109° for a pure equatorial position (Scharpen *et al.*, 1968). The *gauche tert*-butyl–cyano interaction is also minimized by the fact that C(3)–C(4) is 0·026 Å longer than the corresponding C(5)–C(6) bond (Fig. 2).

Like *trans*-3-*tert*-butyl-4-cyano-1-cyclohexenyl acetate (Viani & Lapasset, 1981), a quite pure sofa cyclohexene [$\varphi_{2-3} = 2{\cdot}0\ (6)°$], the conformation of the present molecule is also governed by the strong steric repulsion between the *tert*-butyl and the cyano groups, the influence of which is smoothly limited by the *gauche* dicyano interaction.

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

The ring conformations of *r*-3-*tert*-butyl-*t*-4,*c*-5-cyclohexenedicarbonitrile and *trans*-3-*tert*-butyl-4-cyano-1-cyclohexenyl acetate being so similar, we have more evidence that the *gauche tert*-butyl–cyano diequatorial interaction is the main driving force of the conformational adaptation. More detailed comparisons will be considered soon.

Table 2. *Endocyclic torsion angles* (°)

Central bond	This work*	Experimental half-chair†	Calculated sofa‡
C(1)–C(2)	−4·5	0	−5·7
C(2)–C(3)	−5·8	−16	0
C(3)–C(4)	37·2	46	32
C(4)–C(5)	−61·5	−63	−58
C(5)–C(6)	49·3	46	51
C(6)–C(1)	−17·9	−16	−20

* Standard deviations are ~0·6°.
† Scharpen, Wollrab & Ames (1968).
‡ Bucourt (1974).

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