

Fig. 2. View of the crystal structure as seen along the  $b$  axis. Broken lines represent the hydrogen bonds.

Geometrical considerations indicate that two are linear hydrogen bonds whereas the third is a bifurcated hydrogen bond. These hydrogen bonds give rise to double columns of 2-AT molecules running parallel to the  $b$  direction and centered around  $x = 0, z = 0$  and  $x = 0, z = \frac{1}{2}$  respectively (Fig. 2). Each double column consists of two individual columns of 2-AT molecules which are related to each other by a linear array of inversion centers. The chloride ions in each double column are sandwiched between the two individual

columns of 2-AT molecules. Thus, each double column has a central polar region consisting of (partially) positively charged  $\text{NH}$  and  $\text{NH}_2$  groups and negatively charged chloride ions, flanked by non-polar regions made up of  $\text{CH}_2$  groups and  $\text{S}$  atoms. The double columns are packed together in the crystal in such a way that each is surrounded by six other double columns.

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### Structure of *trans*-3-*tert*-Butyl-4-cyano-1-cyclohexenyl Acetate: a Sofa Conformation\*

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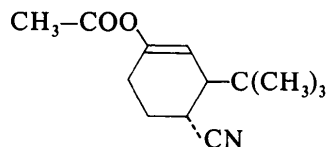
**Abstract.**  $\text{C}_{13}\text{H}_{19}\text{NO}_2$ ,  $M_r = 221.30$ , m.p. 332 K, monoclinic,  $P2_1/c$ ,  $Z = 4$ ,  $a = 8.498$  (4),  $b = 18.094$  (7),  $c = 10.630$  (4) Å,  $\beta = 127.88$  (3)°,  $V = 1290.1$  Å<sup>3</sup>,  $d_m = 1.15$  (2),  $d_x = 1.15$  Mg m<sup>-3</sup>,  $\mu(\text{Cu K}\alpha) = 0.624$

mm<sup>-1</sup>,  $F(000) = 480$ . With X-ray diffraction data collected on a three-circle diffractometer, the crystal structure was solved by direct methods and refined to an  $R$  of 0.053 for 1778 observed reflections. The molecular structure shows a sofa conformation; C(5) is the only C atom out of the mean plane of the other C atoms of the ring.

\* Strained Cyclic Molecules. III.

**Introduction.** The structure determination of the *cis* isomer of the title compound was reported by Viani & Lapasset (1978). For the *cis* isomer, the strong *gauche* interaction between the *tert*-butyl and the vicinal cyano group is partly minimized by the ring conformation itself, which is then intermediate between a half-chair and a sofa (Bucourt, 1974).

For the *trans* isomer studied here



it has been shown by proton magnetic resonance (Lafrance, Aycard & Bodot, 1977) and infrared studies (Monnier, Davidovics, Aycard & Bodot, 1979) that, in solution, there are two conformers quite equal in population. The mean vicinal coupling constants are consistent with the hypothesis of two half-chair conformers, the *tert*-butyl and the cyano group being, respectively, pseudoequatorial and equatorial for the one, and pseudoaxial and axial for the other.

The purpose of the present paper is to give the crystal and molecular structure of the conformer of the title compound existing in the crystal form and to acquire information which is more accurate than that furnished by spectroscopic data.

The compound was prepared and purified by Lafrance (1975).

A major difficulty, during the initial stages of this work, was a tendency for the crystal to deteriorate when exposed to a tropical atmosphere for a few days. This deterioration, which manifested itself by the formation of a white deposit on the surface of the crystal, did not occur when crystals were kept in a sealed container.

The crystal used for all X-ray measurements made at room temperature was a transparent colourless parallelepiped of approximate dimensions  $0.33 \times 0.27 \times 0.21$  mm, cut from a plate. It was enclosed in a Lindemann-glass capillary and mounted along *a*.

Preliminary information about cell dimensions and the symmetry was obtained from oscillation, Weissenberg and precession photographs taken with Ni-filtered Cu *K* $\alpha$  radiation.

A more accurate determination of the cell parameters was made by a least-squares fit of the positions of 12 high-angle reflections centred on an on-line three-circle Enraf-Nonius CAD-3 diffractometer.

The intensities of reflections up to  $\theta = 65^\circ$  were also collected on this instrument using graphite-monochromatized Cu *K* $\alpha$  radiation. 2006 independent reflections were recorded with the  $\theta$ - $2\theta$  scan mode, of which 1778 were considered as observed.

Two reference reflections, checked every 30 measurements, remained constant to within 3.8% of

their initial intensities; no crystal decomposition was detectable.

The intensities were corrected for the Lorentz-polarization factor but an absorption correction was not applied because of the small size of the crystal and the low  $\mu$ .

The data were adjusted to an absolute scale using Wilson's (1942) method giving the preliminary absolute scale ( $K = 0.1962$ ) and overall temperature factor ( $B = 4.64 \text{ \AA}^2$ ).

The structure was solved by the symbolic addition method for a centred group (Karle & Karle, 1966) with the *LSAM* program system (Main, Woolfson & Germain, 1970). Thus the phases of the 300 largest normalized structure factors ( $E > 1.5$ ) were determined, the three origin-defining reflections (132, 346 and 431) were selected and the numerical phase values of three additional reflections were given by the Hauptman & Karle (1959*a,b*) method. Among the sets of phases generated, that having the highest absolute figure of merit was used; this starting set is listed in Table 1.

On the resulting *E* map calculated with the 300 reflections, the 16 strongest peaks defined all the non-hydrogen atoms. The coordinates derived from this

Table 1. *The starting set of phases*

<i>h</i>	<i>k</i>	<i>l</i>	<i>E</i>	Phase ( $^\circ$ )
1	3	$\bar{2}$	2.33	0
3	4	$\bar{6}$	3.47	0
4	3	1	2.73	0
2	10	4	3.32	180
6	8	$\bar{6}$	2.93	0
6	10	$\bar{6}$	3.19	0

Table 2. *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.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
C(1)	5258 (4)	442 (2)	7512 (3)	3.90
C(2)	3731 (4)	407 (2)	5995 (3)	3.80
C(3)	3230 (4)	974 (1)	4769 (3)	3.61
C(4)	4818 (4)	1608 (2)	5523 (3)	4.27
C(5)	6886 (4)	1341 (2)	6972 (4)	4.95
C(6)	6858 (5)	1021 (2)	8257 (4)	4.93
C(7)	1033 (4)	1266 (2)	3865 (3)	4.29
C(8)	561 (5)	1871 (2)	2648 (4)	5.17
C(9)	700 (6)	1568 (2)	5007 (5)	6.69
C(10)	-386 (5)	620 (2)	2906 (4)	5.62
C(11)	4997 (5)	1919 (2)	4358 (4)	5.25
N(12)	5237 (6)	2152 (2)	3489 (4)	7.91
O(13)	5375 (3)	-79 (1)	8561 (2)	4.59
C(14)	6880 (5)	-590 (2)	9238 (3)	4.27
C(15)	6803 (6)	-1089 (2)	10298 (5)	6.21
O(16)	8026 (4)	-615 (1)	8954 (3)	5.50

map yielded  $R = 0.24$  for 1023 reflections with  $R = \sum |KF_o - |F_c|| / \sum |KF_o|$ .

The structure was then refined by the full-matrix least-squares method with the Busing, Martin & Levy (1962) program, first isotropically (four cycles) and then anisotropically (two cycles). At this stage, difference Fourier maps revealed all the H atoms with the exception of H(152) and H(153) which were placed in their theoretical sites with respect to H(151).

The H atoms were included in the last three cycles of refinement but their parameters were not refined; their thermal vibrations were constrained to the mean isotropic thermal parameters of the atoms to which they are bonded.

The final weighted  $R$  was 0.053 with Hughes's (1941) weighting scheme for 1778 independent reflections [ $F_o(\text{min.}) = 0.1$ ].

The scattering factors used for C, N and O were those of Doyle & Turner (1968). For H, the values given by Stewart, Davidson & Simpson (1965) were used.

The final positional parameters are shown in Table 2.\*

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

**Discussion.** The molecular structure with the numbering scheme is illustrated in Fig. 1. The bond lengths and the valence angles for non-hydrogen atoms are shown in Fig. 2. The torsion angles in the form of Newman projections are given in Fig. 3. All the drawing frameworks were made with a plotter using a local program (Lapasset, 1977).

\* 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 35517 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

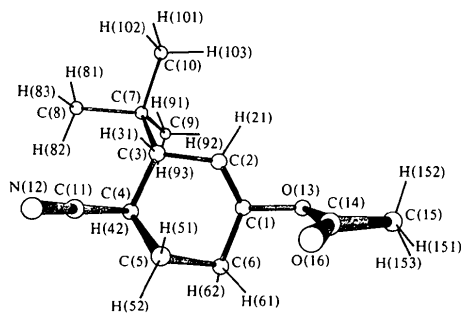


Fig. 1. The molecular structure, with the numbering scheme, viewed in the direction normal to the C(1), C(2), C(6) and O(13) mean plane.

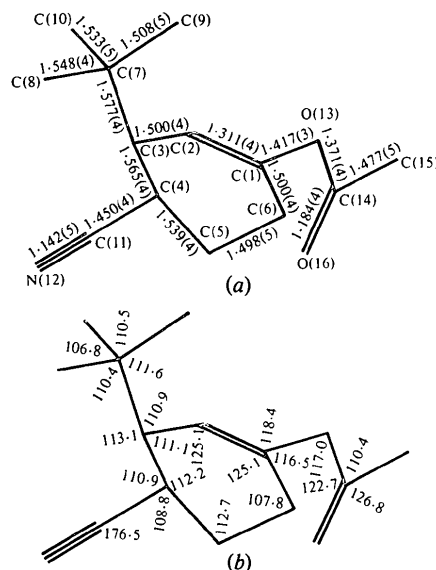


Fig. 2. Projection of the structure along  $b$  showing: (a) the bond lengths (Å) with their standard deviations given in parentheses to the last digit quoted; (b) the valence angles ( $^{\circ}$ ) (standard deviations  $\sim 0.3^{\circ}$ ). H atoms are omitted for clarity. Angles not shown: C(3)–C(7)–C(10)  $107.7^{\circ}$ , C(8)–C(7)–C(9)  $109.7^{\circ}$ .

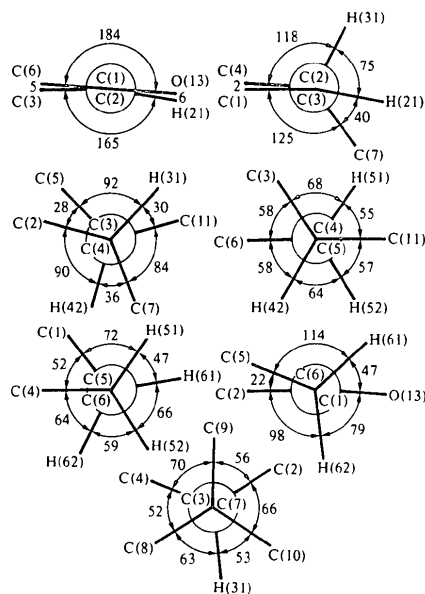


Fig. 3. Selected Newman projections (torsion angles in degrees, standard deviations for angles involving non-hydrogen atoms  $\sim 0.6^{\circ}$ ).

The conformation of the six-membered ring can be described with reference to the least-squares plane through C(1), C(2), C(3), C(4) and C(6). These five atoms are coplanar within  $0.03 \text{ \AA}$ , but C(5), the remaining atom of the ring, deviates by  $0.66(4) \text{ \AA}$ ; this ring geometry agrees with a sofa conformation (Bucourt, 1974).

Table 3. *Endocyclic torsion angles* (°)

Central bond	This work*	Calculated sofa†
C(1)–C(2)	–5.3	–5.7
C(2)–C(3)	2.0	0
C(3)–C(4)	28.2	32
C(4)–C(5)	–57.8	–58
C(5)–C(6)	52.4	51
C(6)–C(1)	–22.3	–20

\* Standard deviations are ~0.6°.

† Bucourt (1974).

From another viewpoint, the near-zero values of the endocyclic torsion angles  $-5.3(6)$  and  $+2.0(6)^\circ$  associated respectively with C(1)–C(2) and C(2)–C(3) as central bonds are in agreement with this conformation. A better confirmation is shown in Table 3 by the excellent agreement between the values of the endocyclic torsion angles of this ring and those of a calculated cyclohexene ring in the sofa conformation (Bucourt, 1974).

The Newman projections about the C(3)–C(4) bond show that the *tert*-butyl and the cyano group are in pseudoequatorial and equatorial positions with a large dihedral angle of  $84.4(6)^\circ$ , which is a good way to minimize the *gauche* interaction between these two substituents.

The dihedral angle between the mean planes through C(6), C(1), C(2), O(13) and C(1), O(13), C(14), C(15), O(16) is  $70.2(6)^\circ$ ; the deviation of any atom from these planes is, respectively, less than 0.02 and 0.007 Å.

The best *anti* relations between vicinal atoms are found with C(11), C(4), C(5), C(6) and C(2), C(3), C(7), C(8) which are respectively coplanar within 0.006 and 0.014 Å.

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

The main structural feature of the title compound is the shape of the cyclohexene ring, which is found in the sofa conformation characterized by a zero value for the endocyclic dihedral angle about the C(2)–C(3) bond, C(5) then being the only C out of the mean plane through the other C atoms of the ring.

This conformation was predicted by Bucourt (1974) from molecular-mechanics calculations. It allows a substantial moving apart of the two vicinal substituents in a *gauche* interaction. Thus, these substituents are in pseudoequatorial and equatorial positions and the dihedral angle between them is  $84.4(6)^\circ$ .

As the driving force of the ring deformation is surely intramolecular, the geometry of the conformer under investigation is certainly not changed on going from the crystal to solution. The endocyclic dihedral angle with C(4)–C(5) as the central bond [ $57.8(6)^\circ$ ] is not too far from the theoretical value ( $63^\circ$ ) for a half-chair conformation (Scharpen, Wollrab & Ames, 1968); this gives one more confidence in the PMR estimate of the conformer populations calculated on the basis of the value of the dihedral angle (Lafrance *et al.*, 1977).

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