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Strained Cyclic Molecules.
II. The Crystal and Molecular Structure of *cis*-1-Acetoxy-3-*tert*-butyl-4-cyanocyclohexene

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cis-1-Acetoxy-3-*tert*-butyl-4-cyanocyclohexene, $C_{13}H_{19}O_2N$, crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The lattice parameters are a = 15·477 (3), b = 7·150 (2), c = 6·027 (2) Å and α = 85·21 (2), β = 95·82 (2), γ = 101·01 (2)°. With X-ray diffraction data collected on a four-circle diffractometer, the crystal structure was solved by direct methods and refined to an R of 0·045 for 2028 observed reflections. The molecular structure shows that the ring conformation is intermediate between a half chair and sofa, with C(5) at a short distance (0·17 Å) from the C(6), C(1), C(2) plane.

Introduction

The prevailing conformation for cyclohexenic compounds is the half-chair (Bucourt, 1974), but strong intramolecular interactions between substituents may be minimized by modification of this conformation. The PMR study of *cis*-1-acetoxy-3-*tert*-butyl-4-cyanocyclohexene-6-6-d_2 (Lafrance, Aycard & Bodot, 1977) was unable to reveal such structural detail but proved the greater stability of the conformer with a pseudo-equatorial *tert*-butyl and an axial cyano group.

The purpose of the present paper is to describe the crystal and molecular structures of this compound, with a view to obtaining more precise information on the deformations associated with the *gauche* interaction between the two vicinal substituents.

Experimental

A summary of the crystal data is given in Table 1. The compound has been prepared and purified by Lafrance (1975).

Table 1. *Crystal and experimental data*

Estimated standard deviations given in parentheses refer to the least significant digit. The cell parameters are the diffractometer-determined values.

Molecular formula: $C_{13}H_{19}O_2N$	a = 15·477 (3) Å
FW 221·30	b = 7·150 (2)
m.p. 52·5 °C	c = 6·027 (2)
Crystal system: triclinic	α = 85·21 (2)°
Space group: $P\bar{1}$	β = 95·82 (2)
Laue class: $\bar{1}$	γ = 101·01 (2)
d_o (by flotation) = 1·12 (2) g cm^{-3}	V = 649·91 Å^3
d_c (with Z = 2) = 1·13	λ(Cu $K\bar{\alpha}$) = 1·54178 Å
Z = 2	μ(Cu $K\bar{\alpha}$) = 6·13 cm^{-1}
	F(000) = 240

A colourless fragment of approximate dimensions 0·35 × 0·25 × 0·20 mm, mounted on a Lindemann-glass capillary along **c**, was used for all the X-ray measurements, which were made at room temperature.

Preliminary unit-cell parameters (a = 15·45, b = 7·16, c = 6·04 Å and α = 85·0, β = 96·1, γ = 101·0°) and space-group information were obtained from oscillation, Weissenberg and precession photographs taken with Ni-filtered Cu $K\alpha$ radiation.

Accurate cell parameters were determined from a least-squares analysis of the positions of 15 reflections measured on an on-line four-circle Syntex $P2_1$ diffractometer.

Intensity data were then collected on this instrument operating in the θ–2θ scan mode and using graphite-monochromatized Cu $K\alpha$ radiation. 2028 independent reflections were obtained within the range of $0 < \theta < 65°$.

Two reference reflections were measured every 30 reflections to monitor gradual variations in the experimental conditions but no systematic deviation from counting statistics (maximum deviation 2·8%) was observed.

The intensities were corrected for the Lorentz–polarization factor. An absorption correction was not deemed necessary on account of the small size of the crystal and the low μ.

Structure determination and refinement

The data were adjusted to an absolute scale with Wilson's (1942) method giving the preliminary absolute scale (K = 0·0408) and overall temperature factor (B = 4·95 Å^2).

The structure was solved by the multisolution procedure of *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974); 16 non-hydrogen atoms were located on an E map based on phases determined by symbolic addition (Karle & Karle, 1966). A structure factor calculation gave an R of 0·24 for all the collected reflections with $R = \Sigma|KF_o - |F_c||/\Sigma\, |KF_o|$.

The positional and isotropic thermal parameters were refined to an R of 0·102 (three cycles) by the full-matrix least-squares method. Allowance was then made for anisotropic thermal vibration. After two cycles of anisotropic refinement, a difference map revealed all the H atoms, which were included in the last two stages of refinement, but whose parameters were not refined. The H thermal vibrations were constrained to the mean isotropic thermal parameters of the atoms to which they are bonded.

The weighted final R value was then 0·045 with Hughes's (1941) weighting scheme for the 2028 independent reflections ($F_o$min. = 0·0). The Busing, Martin & Levy (1962) program was used for refinement calculations. The scattering factors for the heavy atoms were those of Doyle & Turner (1968), for H those of Stewart, Davidson & Simpson (1965).

The final positional and H isotropic thermal parameters are listed in Tables 2 and 3.*

Table 2. *Final fractional coordinates* ($\times 10^4$) *for non-hydrogen atoms*

Standard deviations in parentheses refer to the last digit quoted.

	x	y	z
C(1)	1762 (1)	5463 (2)	2517 (3)
C(2)	2452 (1)	5319 (2)	3929 (3)
C(3)	2707 (1)	6512 (2)	5918 (2)
C(4)	2286 (1)	8313 (2)	5520 (3)
C(5)	1287 (1)	7719 (3)	4851 (4)
C(6)	1116 (1)	6739 (3)	2659 (3)
C(7)	3710 (1)	6786 (3)	6695 (3)
C(8)	3944 (2)	8265 (4)	8455 (4)
C(9)	4296 (1)	7399 (3)	4783 (3)
C(10)	3885 (2)	4855 (4)	7767 (4)
C(11)	2679 (1)	9707 (3)	3804 (4)
N(12)	2941 (2)	10812 (3)	2449 (4)
O(13)	1631 (1)	4438 (1)	567 (2)
C(14)	1069 (1)	2740 (2)	580 (3)
C(15)	1078 (1)	1803 (3)	−1514 (3)
O(16)	652 (1)	2132 (2)	2117 (2)

Table 3. *Fractional coordinates* ($\times 10^4$) *and isotropic thermal parameters for hydrogen atoms*

	x	y	z	B(Å^2)
H(21)	2827	4409	3633	3·93
H(31)	2412	5794	7251	4·25
H(41)	2359	8964	6966	5·11
H(51)	1026	6774	6193	5·98
H(52)	977	8861	4747	5·98
H(61)	495	5964	2476	5·69
H(62)	1190	7718	1283	5·69
H(81)	4523	8223	9128	7·50
H(82)	3863	9600	7808	7·50
H(83)	3514	7902	9752	7·50
H(91)	4916	7505	5317	5·85
H(92)	4190	6387	3621	5·85
H(93)	4208	8634	4024	5·85
H(101)	4531	4960	8233	7·18
H(102)	3553	4513	9209	7·18
H(103)	3753	3823	6608	7·18
H(151)	675	676	−1615	5·61
H(152)	1649	1428	−1544	5·61
H(153)	993	2718	−2874	5·61

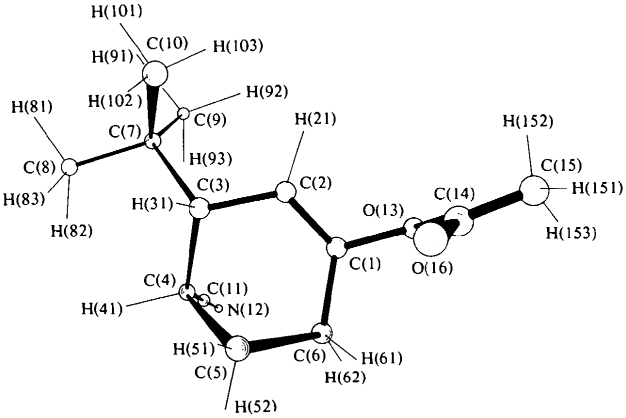

Fig. 1. The molecular structure viewed in the direction normal to the C(1), C(2), C(6) and O(13) mean plane, showing the numbering scheme.

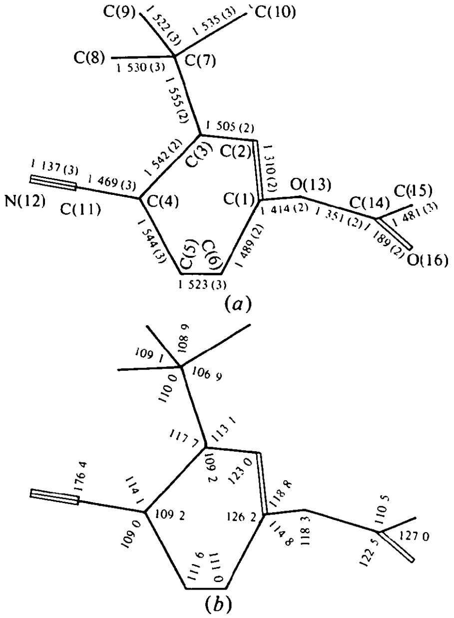

Fig. 2. Projection of the structure along **c** showing: (*a*) the bond lengths (Å) with their standard deviations given in parentheses to last digit quoted; (*b*) the valency angles (°); standard deviations near 0·2°. Hydrogen atoms are omitted for clarity. Angles not shown in the figure: C(3)–C(7)–C(9) 113·0, C(8)–C(7)–C(10) 108·7°.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33085 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Molecular structure

The molecular structure with the atom numbering is shown in Fig. 1. The bond lengths and the valency angles for non-hydrogen atoms are illustrated in Fig. 2. The C–H bond lengths are reported in Table 4. The torsional angles in the form of Newman projections and the molecular packing are given in Figs. 3 and 4 respectively.

Table 4. *The* C–H *bond lengths* (Å)

C(2)–H(21)	0·99	C(9)–H(91)	0·97
C(3)–H(31)	1·02	C(9)–H(92)	1·03
C(4)–H(41)	1·01	C(9)–H(93)	0·99
C(5)–H(51)	1·07	C(10)–H(101)	1·00
C(5)–H(52)	1·02	C(10)–H(102)	1·04
C(6)–H(61)	1·01	C(10)–H(103)	1·04
C(6)–H(62)	1·04	C(15)–H(151)	0·92
C(8)–H(81)	0·95	C(15)–H(152)	0·97
C(8)–H(82)	1·02	C(15)–H(153)	1·02
C(8)–H(83)	1·06		

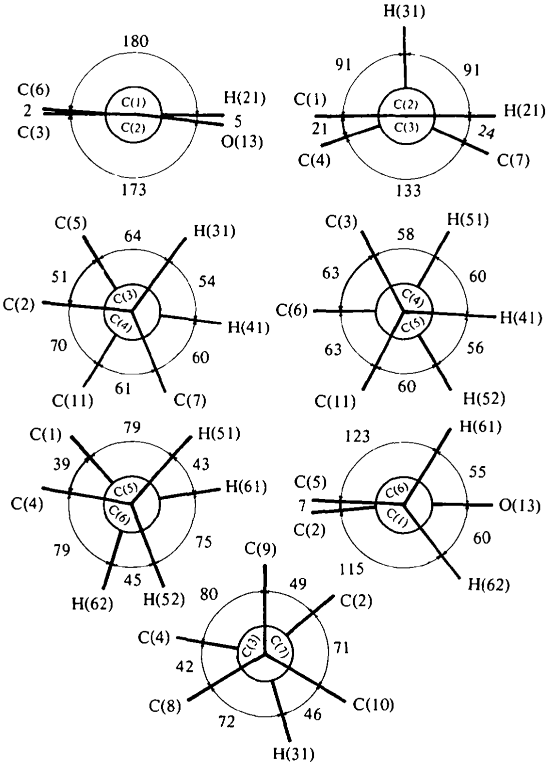

Fig. 3. Selected Newman projections (°).

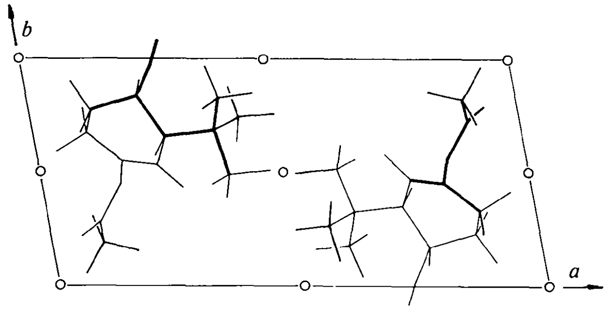

Fig. 4. The molecular packing viewed along c.

The Newman projections about the C(3)–C(4) bond (Fig. 3) confirm the conformational positions of the *tert*-butyl (pseudo-equatorial) and cyano (axial) groups (Lafrance, Aycard & Bodot, 1977). The endocyclic torsion angle of the C(6)–C(1) bond ($\varphi = 7°$) shows that the ring conformation is intermediate between a half-chair ($\varphi = 15°$) and sofa ($\varphi = 0°$) (Bucourt, 1974), which explains why C(5) is close (0·17 Å) to the C(6), C(1), C(2) plane.

The best planes through selected atoms show that C(1), C(2), C(6), O(13) and H(21) are coplanar within 0·03 Å and that C(1), O(13), C(14) and O(16) are coplanar within 0·04 Å. These two planes are quite orthogonal, the torsion angle C(6)–C(1)–O(13)–C(14) being 85° as opposed to zero for vinyl formate (Rao & Curl, 1964). This difference may be related to the molecular packing, but the rotational isomerism of enol acetates is more complex than expected (Davidovics, Monnier & Aycard, 1977).

Conclusion

The modification of the cyclohexene ring towards the sofa conformation is the main structural feature of *cis*-1-acetoxy-3-*tert*-butyl-4-cyanocyclohexene and it must occur in order to relieve the strong *gauche* interaction. The generality of this statement will have to be proved with more experimental data; then it will be possible to present a more detailed discussion. This will be carried out by the group of Laboratoire de Chimie Organique Structurale (Professor H. Bodot), Université de Provence, Marseille, France, which has promoted this research.

The authors are indebted to Professor Bodot for his stimulating and helpful interest and to Dr Aycard and Dr Lafrance for providing the crystalline samples and for valuable discussions. They are very grateful to Professor Renaud and Dr Fourme for their kindness in allowing them to use the Syntex $P2_1$ diffractometer of the Laboratoire de Physico-Chimie Structurale, Université de Paris–Val de Marne, Créteil, France.

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Crystal and Molecular Structures of 2,2′-Methylenebis(4-chloro-3-methyl-6-isopropylphenol)

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The crystal and molecular structures of 2,2′-methylenebis(4-chloro-3-methyl-6-isopropylphenol) have been determined by single-crystal X-ray diffraction studies. Crystals are monoclinic, space group $P2_1/c$ with unit-cell parameters $a = 11{\cdot}977$ (2), $b = 19{\cdot}035$ (3), $c = 9{\cdot}244$ (4) Å, $\beta = 109{\cdot}25°$ and $Z = 4$. The intensities of 3779 reflections were measured on a Nonius CAD-4 automatic diffractometer. The structure was solved by direct methods and refined by least-squares calculations to an R of 0·056. The structure determination establishes the molecular geometry and shows that the value of the C—C—C valency angle (118·6°) at the methylene group is appreciably in excess of tetrahedral. Molecules are held together by weak hydrogen bonds (3·05 Å) forming chains interrelated by van der Waals contacts.

Introduction

This work forms part of a study of phenols with remarkable biological activity; our interest centres on a series of 'bisphenols' with a $C_{Ar}{-}C_{CH_2}{-}C_{Ar_2}$ linkage in a position *ortho* to the hydroxyl group; the present paper describes the crystal structure and molecular configuration of 2,2′-methylenebis(4-chloro-3-methyl-6-isopropylphenol).* The only crystal structure determinations of 'bisphenols' with a $C_{Ar}{-}C_{CH_2}{-}C_{Ar}$ linkage that have been reported are by Whittaker (1953) and Chaudhuri & Hargreaves (1956); in these compounds the methylene group is in the *para* position relative to the OH group.†

Faith (1952) registered a patent for the title substance. Because of its bactericidal property, it also has a French medicinal patent (1967) No. 4620. It is used under the common name 'Bichlothymol' as a pulmonary antiseptic in a medicine called 'hexapneumine'.

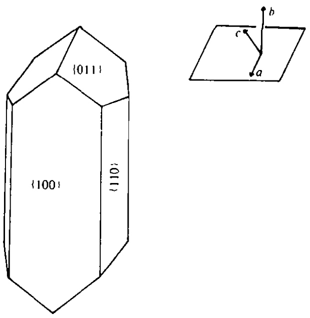

Fig. 1. Crystal morphology.

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