Fig. 3. Contacts intermoléculaires. Les distances sont données en Å.

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The Crystal Structure of 1-Phenyl-4-t-butylcyclohexane-1-carboxylic Acid

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The structure of 1-phenyl-4-t-butylcyclohexane-1-carboxylic acid, $C_{17}H_{24}O_2$, has been determined from X-ray data collected photographically. The crystals are monoclinic, space group $P2_1/c$, with $a = 15.956$ (5), $b = 6.314$ (6), $c = 16.558$ (6) Å, $\beta = 116.85$ (6)° and $Z = 4$. The structure has been solved by direct methods and refined to a final R value of 0.085 for 2157 observed reflexions. The phenyl group in the equatorial position is tilted by 13° from the C(2)–C(3)–C(5)–C(6) plane of the cyclohexane ring. The carboxyl group is nearly parallel to the C(2)–C(6) direction. The equatorial t-butyl group is twisted 6.3° from the staggered position.

Introduction

This paper is part of a general study on the non-additivity of conformational free energy, $-\Delta G$, for *gem*-substituted cyclohexanic rings (Sicsic & Welvart, 1966, 1967; Malissart, Sicsic, Welvart, Chiaroni, Riche & Pascard-Billy, 1973).

The X-ray structure of 1-phenyl-4-t-butylcyclohexane-1-carboxylic acid was undertaken to deter- mine the stablest conformation of rotation for the equatorial phenyl group.

Experimental

Crystal data

$C_{17}H_{24}O_2$	M.W. 260·4
Monoclinic, $P2_1/c$	
$a = 15.956$ (5) Å	$V = 1488.6$ Å^3

$b=$ 6·314 (6) $\lambda=$ 1·5418 Å (Cu $K\bar{\alpha}$)

$c=$ 16·558 (6) $D_m=$ 1·15 g cm^{-3}

$\beta=116\cdot85$ (6)° $D_c=$ 1·162

                       $Z=$ 4

Number of independent reflexions:
  observed: 2582
  non-zero: 2157.

The lattice constants were determined from oscillation and Weissenberg photographs, calibrated with superposed Al lines. Intensity data were collected on multiple-film equi-inclination Weissenberg photographs with the same prismatic crystal. The intensities, measured by a Huet manual microdensitometer were corrected for Lorentz–polarization effects and for spot size.

Structure determination

The structure was solved by direct methods, with the phase function (Riche, 1970, 1973) applied to the symbolic addition method (Karle & Karle, 1966) to determine the numerical values of the symbols. A detailed description of the procedure for centrosymmetric space groups has been given by Cesario & Pascard-Billy (1973).

The starting set was introduced into the program *DEVIN* (Riche, 1972). Nine symbols were chosen and, from the $2^9 = 512$ possible solutions, two were selected after two cycles of weighted symbolic addition and the interpretation of the phase function. The E map, computed from the first phase combination, revealed the whole structure.

Refinement was carried out by full-matrix least-squares calculations. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

After the last cycle of refinement with anisotropic thermal parameters for the heavy atoms, the R value was 0·085. The hydrogen atoms were located on a difference map and were given the isotropic thermal factor of the bonded carbon atom. The different parameters of the hydrogen atoms were not refined.*

Table 2. *Positional parameters* ($\times 10^3$)
and B values for the hydrogen atoms

	x	y	z	B (Å^2)
H(21)	162	524	218	2·45
H(22)	243	714	293	2·45
H(31)	116	631	332	2·43
H(32)	230	557	419	2·43
H(4)	90	262	282	1·95
H(51)	195	−15	364	2·24
H(52)	276	177	438	2·24
H(61)	209	135	236	2·07
H(62)	323	65	324	2·07
H(9)	277	741	185	3·37
H(10)	339	771	77	4·59
H(11)	438	488	59	3·66
H(12)	470	168	151	4·07
H(13)	406	128	264	3·34
H(151)	28	−16	349	4·02
H(152)	16	−16	446	4·02
H(153)	107	−47	448	4·02
H(161)	130	328	560	3·72
H(162)	175	493	508	3·72
H(163)	214	224	535	3·72
H(171)	−31	391	319	3·51
H(172)	−26	397	416	3·51
H(173)	0	531	373	3·51
H(18)	437	657	465	3·10

Table 1. *Final atomic coordinates and anisotropic thermal parameters* ($\times 10^4$) *for the non-hydrogen atoms*
(*standard deviations in parentheses*)

The anisotropic thermal factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. B is the isotropic thermal factor before anisotropic refinement.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B (Å)^2
C(1)	2981 (2)	3999 (4)	3025 (2)	23 (1)	91 (8)	27 (1)	−4 (2)	12 (1)	−8 (2)	1·86 (9)
C(2)	2169 (2)	5534 (4)	2855 (2)	25 (1)	95 (8)	35 (1)	5 (2)	15 (1)	6 (2)	2·45 (10)
C(3)	1757 (2)	5232 (5)	3516 (2)	29 (1)	111 (9)	39 (1)	2 (2)	19 (1)	−7 (2)	2·43 (10)
C(4)	1402 (2)	2979 (4)	3506 (2)	24 (1)	88 (8)	29 (1)	0·3 (2)	15 (1)	−5 (2)	1·95 (9)
C(5)	2219 (2)	1451 (4)	3703 (2)	31 (1)	69 (8)	38 (1)	7 (2)	20 (1)	1 (2)	2·24 (9)
C(6)	2636 (2)	1722 (4)	3038 (2)	29 (1)	89 (8)	34 (1)	−7 (2)	17 (1)	−14 (2)	2·07 (9)
C(7)	3845 (2)	4444 (4)	3931 (2)	25 (1)	61 (9)	30 (1)	−4 (2)	15 (1)	−5 (2)	1·74 (9)
C(8)	3352 (2)	4247 (4)	2316 (2)	24 (1)	137 (8)	27 (1)	−12 (2)	11 (1)	−9 (2)	2·24 (9)
C(9)	3177 (3)	6078 (5)	1786 (2)	59 (2)	172 (10)	41 (1)	−9 (3)	30 (1)	4 (3)	3·37 (12)
C(10)	3546 (3)	6281 (6)	1174 (3)	79 (2)	217 (12)	51 (2)	−36 (4)	40 (2)	4 (3)	4·59 (15)
C(11)	4091 (2)	4699 (6)	1073 (2)	48 (2)	307 (13)	46 (2)	−39 (4)	32 (1)	−22 (3)	3·66 (13)
C(12)	4273 (2)	2905 (6)	1597 (3)	43 (2)	323 (13)	52 (2)	4 (4)	32 (1)	−17 (4)	4·07 (14)
C(13)	3907 (2)	2671 (6)	2214 (2)	38 (1)	227 (11)	46 (2)	23 (3)	26 (1)	11 (3)	3·34 (12)
C(14)	909 (2)	2654 (5)	4124 (2)	31 (1)	128 (9)	36 (1)	−16 (3)	21 (1)	−3 (2)	2·51 (10)
C(15)	623 (3)	343 (6)	4101 (3)	62 (2)	179 (12)	65 (2)	7 (2)	47 (2)	5 (3)	4·02 (14)
C(16)	1546 (2)	3311 (5)	5109 (2)	49 (2)	310 (13)	37 (1)	15 (4)	23 (1)	−12 (3)	3·72 (13)
C(17)	7 (2)	3991 (6)	3767 (2)	37 (2)	223 (11)	56 (2)	15 (3)	30 (1)	6 (3)	3·51 (12)
O(1)	4391 (1)	3029 (3)	4358 (1)	33 (1)	134 (6)	38 (1)	3 (2)	5 (1)	−1 (2)	2·91 (8)
O(2)	3982 (1)	6422 (3)	4172 (1)	35 (1)	126 (7)	42 (1)	−11 (2)	6 (1)	−23 (2)	3·10 (9)

Tables 1 and 2 contain the atomic coordinates and thermal parameters.

Results

Bond lengths and angles are shown in Fig. 1(a) and (b). The standard deviations are: C–C bonds, 0·005 Å; C–O bonds, 0·003 Å; C–C–C angles, 0·3°.

The Newman projection along C(8)–C(1) (Fig. 2) shows the phenyl ring tilted by 13° with respect to the normal to the C(7)–C(1)–C(8) plane.

A perspective view of the molecule can be seen in the packing diagram, Fig. 3.

The short distances between the hydrogen atoms of the benzene and cyclohexane rings are indicated in Fig. 1(a).

The carboxyl group is perpendicular to the C(8)–C(1)–C(7) plane, as can be seen in Fig. 2. The carbonyl atom C(1) is twisted away from the C(6) eclipsed position by 31·1°, in contrast to the 6·4° deviation observed by Koningsveld (1972) in cis-4-t-butylcyclohexane-1-carboxylic acid.

The t-butyl group, in the equatorial position, occupies a slightly deviated staggered position, with respect to the three atoms bonded to C(4). The mean deviation appearing on the Newman projection of Fig. 2 is 6·3°. This low value can be compared with the observed values of 3° (Parthasarathy, Ohrt, Kagan & Fiaud, 1972), 9° and 11° (Faber & Altona, 1971), and the theoretical value of 17° (Altona & Sundaralingam, 1970).

The values of 112° for the C(4)–C(14)–C(16) angle, and 114° for the C(3)–C(4)–C(14) and C(5)–C(4)–C(14) angles show the slight distortion caused by the presence of a bulky substituent.

Table 3 contains the shortest intramolecular H–H distances.

Table 3. *Shortest intramolecular distances*

H(9)····H(22)	2·10 Å		H(52)···H(163)	2·25 Å
H(13)···H(62)	2·02		H(31)···H(173)	2·33
H(32)···H(162)	2·07			

Cyclohexane ring

The torsional angles listed in Table 4 and the equivalent distances (0·67 and −0·69 Å) of C(1) and C(4) to the mean plane through the atoms C(2), C(3), C(5) and C(6)* show that the cyclohexane ring is in a regular chair conformation.

The intracyclic angles [see Fig. 1(b)] are in agreement with the theoretical values given by Bucourt & Hainaut (1964).

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* Equation of this plane in an orthogonal system: $-0·6054X -0·2387Y -0·7593Z +4·8391 = 0$. Deviations (Å) of atoms from the plane: C(1), 0·667; C(2), 0·001; C(3), −0·001; C(4), −0·690; C(5), 0·001; C(6), −0·001.

Table 4. *Torsional angles* (°) *in the cyclohexane ring*

|	
C(1)–C(2)–C(3)–C(4)	−57·3
C(2)–C(3)–C(4)–C(5)	56·1
C(3)–C(4)–C(5)–C(6)	−56·0
C(4)–C(5)–C(6)–C(1)	57·2
C(5)–C(6)–C(1)–C(2)	−53·4
C(6)–C(1)–C(2)–C(3)	53·4
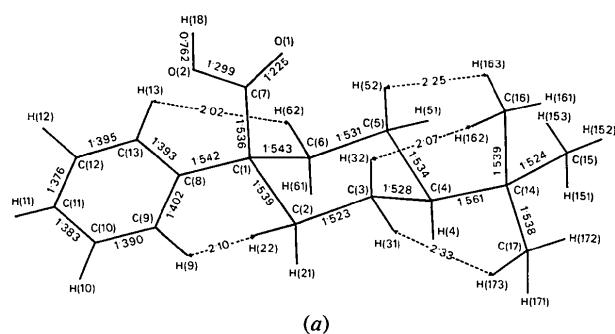
(a)
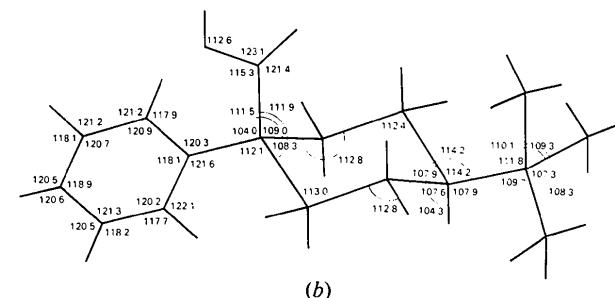
(b)

Fig. 1. (a) Labelling of the atoms and bond lengths (Å). (b) Valency angles (°).
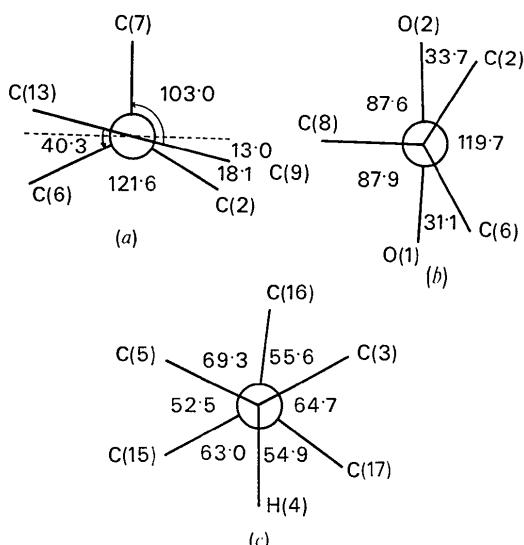
Fig. 2. Newman projections down the principal bonds. (a) C(8)–C(1). (b) C(1)–C(7). (c) C(4)–C(14).
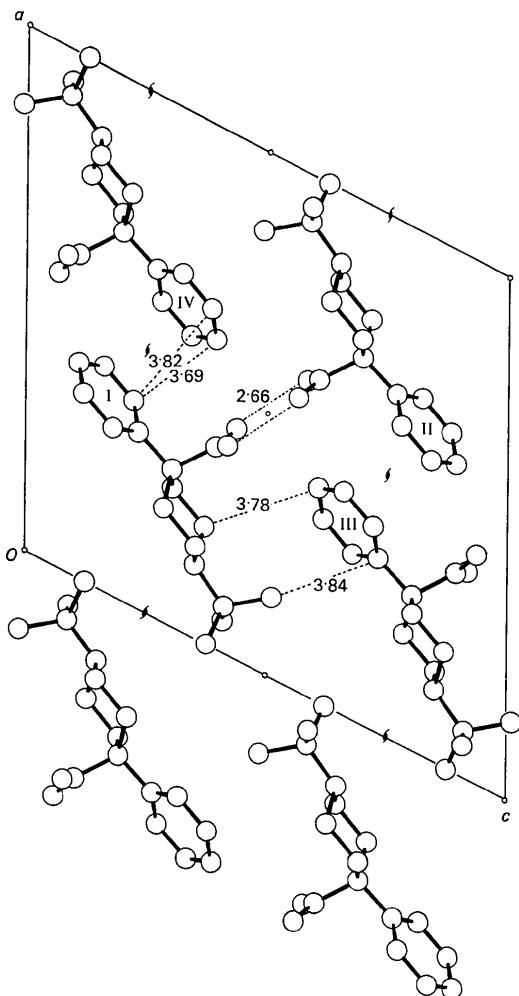
Fig. 3. Molecular packing projected down the *b* axis. Molecule I (x,y,z); molecule II $(1-x,1-y,1-z)$; molecule III $(x,\frac{1}{2}-y,\frac{1}{2}+z)$; molecule IV $(1-x,\frac{1}{2}+y,\frac{1}{2}-z)$.

Packing

The packing (Fig. 3) shows an interesting arrangement of the molecules. The carboxyl groups face each other across a centre of symmetry, the short O···O distances (2·66 Å) implying strong hydrogen bonding. The two molecules form a dimer, with the two carboxyl groups nearly coplanar (they lie in parallel planes

0·25 Å apart). The mean plane through both carboxyl groups is perpendicular to the stretching direction of the molecule.

The calculations were performed on the IBM 370-165 computer at CIRCE, Orsay, France, with the following programs: a local version of *ORFLS* (Busing, Martin & Levy, 1962) for the refinement; the NRC programs (Ahmed, Hall, Pippy & Huber, 1966) for the distances, angles, mean-planes calculations; *ORTEP* (Johnson, 1965) for Fig. 3.

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