Crystal and Molecular Structure of *cis*-2,*trans*-3-Dibromo-*cis*-4-t-butylcyclohexyl *p*-Nitrobenzoate: a Case of Non-chair Conformation of a Saturated Monocyclic Cyclohexane Derivative

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The complete crystal structure of the title compound (I) was determined by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 7.697(5)$, $b = 12.506(7)$, $c = 19.520(9)$ Å, $\beta = 99.43(4)°$. The structure was solved by Patterson and Fourier methods from diffractometer data and refined by least-squares techniques to *R* 0.078 for 1 356 observed reflections. The molecule exists in a twist conformation, with the staggered t-butyl group and the ester group in pseudo-equatorial positions and the bromines in a pseudo-axial and an isoclinal position. This conformation is that in which interactions between substituents are minimized, and is slightly biased towards a boat form. This is the first reported structure of a saturated monocyclic cyclohexane derivative in a non-chair conformation, and confirms the strong repulsive interaction between t-butyl and a *trans*-2-substituent on cyclohexane, which had been deduced from spectroscopic and thermodynamic data. In solution at room temperature the title compound exists, according to its ^{1}H n.m.r. spectrum, as an equilibrium probably also involving a chair conformation.

EXCEPTIONS to the normal preference of six-membered rings for chair conformations, although not very frequent, have been repeatedly reported, and recently reviewed.[1] Competition by flexible twist-boat forms can be caused by geometrical constraints due to chemical bonding involving bridging or ring fusions which induce prohibitive strains in the chair conformations, or by the presence of sp^2 hybridized ring carbons which in some cases appear to confer an intrinsic preference for flexible conformations. Cases of this type are clearly and precisely defined by diffractometric structural evidence.[1]

For a third type of molecule, in which the preference for twist conformations is caused by the possibility of easing unusually high repulsive strain existing between substituents in the chair form, the available evidence is much less direct, being based mainly on sometimes controversial interpretations of i.r. and ^{1}H n.m.r. data.[1] No structural data have so far been reported for any

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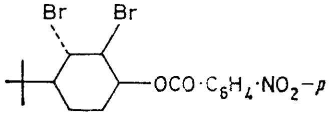
[1] G. M. Kellie and F. G. Riddell, *Topics in Stereochem.*, 1974, **8**, 225.

saturated monocyclic cyclohexane existing in a non-chair conformation in the crystal. We therefore thought it worthwhile to carry out an *X*-ray diffraction study of a compound for which spectroscopic and kinetic evidence indicated a possible preference for a twist conformation, in order to obtain structural parameters to be compared with those deduced theoretically.[2-4]

A good candidate for this study appeared to be a compound presenting the *r*-1,*t*-2-dibromo-*c*-3-t-butylcyclohexane part structure, which on the basis of previous work, involving equilibration of dihalides by ' 1,2-interchange,' had revealed a particularly strong repulsive interaction between the t-butyl and 2-bromo-substituents.[5-7] The ^{1}H n.m.r. spectra of compounds of this type also indicate that they certainly do not exist in solution as pure chair conformers.[8] The introduction of a fourth substituent in position 4 and *cis* to t-butyl group was expected to further shift the equilibrium in favour of twist conformations, because of its axial nature in the chair form. The ester (I)[9] was therefore chosen for structural analysis.



(I)

EXPERIMENTAL

Compound (I) was prepared as previously described,[9] and crystallized slowly from ethanol. Its ^{1}H n.m.r. spectrum was determined with a JEOL PS 100 spectrometer in CCl$_4$ and coupling constants calculated by the use of a LAOCOON 3 iterative program.

Crystal Data.—$C_{17}H_{21}Br_2NO_4$, $M = 463.17$. Monoclinic, $a = 7.697(5)$, $b = 12.506(7)$, $c = 19.520(9)$ Å, $\beta = 99.43(4)$°, $U = 1\,853.64$ Å^3, $D_m = 1.66(1)$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.660$ g cm^{-3}, $F(000) = 926.32$. Space group $P2_1/c$, from systematic absences: $0k0$ for k odd, $h0l$ for l odd. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 46.54 cm^{-1}.

Unit-cell parameters and their estimated standard deviations were determined from a least-squares refinement of the setting angles of 14 *X*-ray reflections which had been centred on a Siemens AED automatic diffractometer by use of Mo-K_α radiation.

Data Collection.—A crystal with dimensions 0.05 × 0.22 × 0.35 mm was mounted on a Siemens AED single-crystal diffractometer, equipped with scintillation counter and pulse-height analyser, on-line to a Siemens 302 P computer controlled by locally developed software.[10]

The *a* axis (along the 0.35 mm dimension of the crystal) was coincident with the polar ϕ axis of the goniostat. Intensities were recorded by use of zirconium-filtered Mo-K_α radiation, and the ω-scan technique. Each reflection was scanned once: the scan rate and absorbers for the incident beam were automatically chosen, according to the peak intensity, so as to have measured peak counting with almost the same standard deviation, avoiding errors for counting loss.

A symmetrical scan range of 0.60° from the computed Mo-K_α peak was used. At each end of the scan stationary-crystal–stationary-counter background counts were taken for half the scan time. Since there were few reflections of significant intensity for values of $\theta > 22°$, only the 2 368 independent reflections within $\theta < 22°$ were gathered. The intensities of three standard reflections, chosen in different regions of the reciprocal space and measured every 100 reflections, remained essentially constant throughout.

From the collected data the values of F_o^2 and $\sigma(F_o^2)$ were obtained by a procedure described previously.[11] A value of 0.06 was chosen for the constant p, which is used in the formula for calculating $\sigma(F_o^2)$, according to the variance of the standard reflections. Of the 2 368 observations, 1 012 had $F_o^2 < 3\sigma(F_o^2)$ and were discarded. The shape anisotropy of the crystal, which has a high absorption coefficient, caused up to a 60% variation in intensity, as measured at χ 90°, over the ϕ range used in the collection of data. In order to correct for the shape anisotropy the variation in intensity of the conveniently positioned reflection $(6,0,-2)$ was measured as a function of ϕ. For this correction the method described in refs. 12 and 13 was used, with a procedure similar to that described previously.[14] No extinction correction was applied.

Solution and Refinement of the Structure.—The structure was solved by the usual combination of Patterson and Fourier methods. Isotropic least-squares refinement lowered R from 0.253 to 0.138. Refinement was continued allowing all atoms to vibrate anisotropically and convergence was reached at R 0.085. At this stage in no region of the difference Fourier synthesis did the electron density exceed $\pm 3\sigma(\rho)$ [$\sigma(\rho) = 0.23$ eÅ^{-3}]. Hydrogen atoms were positioned geometrically and included in the structure-factor calculation being readjusted after each least-squares cycle. The final R index is 0.078 (R' 0.104).

Refinement was carried out with a two-block approximation of the normal-equations matrix, using one block for the positional co-ordinates and one block for the temperature factors and the scale factor. The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$; the weighting scheme used was $w = (a + F_o + bF_o^2)^{-1}$ with $a = 2F_{\text{min.}}$ and $b = 2/F_{\text{max.}}$.[15]

Table 1 gives final positional parameters for the non-hydrogen atoms. The idealized positions of the hydrogen atoms are given in Table 2. Observed and calculated structure factors and anisotropic thermal parameters are

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[2] R. Bucourt, ref. 1, p. 173.

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[8] P. L. Barili, G. Bellucci, G. Ingrosso, F. Marioni, and I. Morelli, *Tetrahedron*, 1972, **28**, 4583.

[9] P. L. Barili, G. Bellucci, G. Berti, M. Golfarini, F. Marioni, and V. Scartoni, *Gazzetta*, 1974, **104**, 107.

[10] M. Colapietro, to be published.

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[13] A. C. T. North, D. C. Phillips, and F. Scott Matthews, *Acta Cryst.*, 1968, **A24**, 351.

[14] R. Spagna and L. Zambonelli, *J. Chem. Soc.* (*A*), 1971, 2544.

[15] D. W. J. Cruickshank, in ' Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon, Oxford, 1965, p. 114.

listed in Supplementary Publication No. SUP 21698 (8 pp., 1 microfiche).* Atomic scattering factors were taken from ref. 16 for bromine, oxygen, nitrogen, and carbon and from ref. 17 for hydrogen. The effects of anomalous dispersion were included in the structure factors, the values $\Delta f'$ and $\Delta f''$ for bromine being taken from ref. 18. Calculations were carried out on a UNIVAC 1108 computer at Rome University, with the system of local programmes.

TABLE 1

Positional (× 10^4) parameters for non-hydrogen atoms

	x	*y*	*z*
Br(1)	4 281(3)	3 587(2)	7 145(1)
Br(2)	−1 320(2)	4 240(1)	6 082(1)
O(1)	3 983(13)	3 462(8)	5 490(5)
O(2)	1 624(14)	2 588(10)	4 937(7)
O(3)	9 466(19)	30(11)	4 159(8)
O(4)	7 204(21)	−961(11)	3 720(7)
N	7 900(20)	−180(10)	4 017(7)
C(1)	2 851(18)	4 249(12)	5 747(7)
C(2)	2 282(20)	3 823(13)	6 399(7)
C(3)	999(19)	4 631(12)	6 630(7)
C(4)	1 371(18)	5 806(13)	6 523(8)
C(5)	3 297(20)	5 960(12)	6 451(9)
C(6)	3 929(17)	5 339(11)	5 771(9)
C(7)	3 180(19)	2 656(11)	5 079(8)
C(8)	4 473(18)	1 912(12)	4 815(7)
C(9)	6 270(19)	1 988(12)	5 054(8)
C(10)	7 383(19)	1 308(11)	4 789(7)
C(11)	6 668(20)	571(10)	4 311(6)
C(12)	4 895(22)	499(14)	4 062(8)
C(13)	3 744(19)	1 213(11)	4 320(7)
C(14)	773(22)	6 514(12)	7 092(8)
C(15)	−1 152(29)	6 436(17)	7 110(11)
C(16)	1 749(29)	6 314(14)	7 814(8)
C(17)	1 007(32)	7 722(16)	6 889(10)

TABLE 2

Idealized co-ordinates (× 10^3) for hydrogen atoms
(*B* all 3.0 Å^2)

	x	*y*	*z*
H(1) [C(1)]	176	435	540
H(2) [C(2)]	169	312	630
H(3) [C(3)]	100	452	714
H(4) [C(4)]	60	607	609
H(5) [C(5)]	404	568	688
H(6) [C(5)]	351	674	640
H(7) [C(6)]	523	521	585
H(8) [C(6)]	359	576	533
H(9) [C(9)]	674	253	541
H(10) [C(10)]	869	135	494
H(11) [C(12)]	443	−5	371
H(12) [C(13)]	245	120	415
H(13) [C(15)]	−146	691	749
H(14) [C(15)]	−146	568	720
H(15) [C(15)]	−183	667	665
H(16) [C(16)]	129	680	815
H(17) [C(16)]	303	645	783
H(18) [C(16)]	158	555	795
H(19) [C(17)]	63	820	725
H(20) [C(17)]	227	786	686
H(21) [C(17)]	27	787	643

DISCUSSION

The structure is shown in Figure 1, together with the atom numbering system used. The compound, which has four chiral carbon atoms, is present in the crystal in the racemic form, the C(1)(*R*)–C(2)(*R*)–C(3)(*R*)–C(4)(*R*) and C(1)(*S*)–C(2)(*S*)–C(3)(*S*)–C(4)(*S*) configurations[19] being related by the glide plane: co-ordinates and torsion angle signs[20] given in the Tables refer to the molecule with configuration C(1)(*R*)–C(2)(*R*)–C(3)(*R*)–C(4)(*R*). Bond lengths and angles corresponding to the final co-ordinates are listed in Table 3. There are no close intermolecular contacts; a diagram illustrating the packing of the molecules is given in Figure 2. The values of some of the bond lengths and angles are rather different from the average normal values. These discrepancies could be due in part to the fact that the accuracy of the structure is not very high. The data, in fact, cannot be considered very satisfactory because of the strong absorption and the irregular shape of the

TABLE 3

Intramolecular bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances			
C(1)–C(2)	1.510(21)	C(8)–C(9)	1.389(19)
C(2)–C(3)	1.531(22)	C(9)–C(10)	1.367(22)
C(3)–C(4)	1.518(22)	C(10)–C(11)	1.361(18)
C(4)–C(5)	1.524(21)	C(11)–C(12)	1.374(22)
C(5)–C(6)	1.676(24)	C(12)–C(13)	1.408(23)
C(6)–C(1)	1.593(19)	C(13)–C(8)	1.355(19)
C(1)–O(1)	1.457(18)	C(11)–N	1.513(21)
C(2)–Br(1)	1.959(14)	N–O(3)	1.221(21)
C(3)–Br(2)	1.986(14)	N–O(4)	1.214(19)
C(4)–C(14)	1.548(23)	C(14)–C(15)	1.491(28)
O(1)–C(7)	1.370(17)	C(14)–C(16)	1.507(22)
C(7)–O(2)	1.187(18)	C(14)–C(17)	1.579(25)
C(7)–C(8)	1.513(21)		
(*b*) Angles			
C(6)–C(1)–C(2)	119.9(12)	C(7)–C(8)–C(13)	114.9(12)
C(1)–C(2)–C(3)	107.8(12)	C(13)–C(8)–C(9)	123.8(14)
C(2)–C(3)–C(4)	117.0(13)	C(8)–C(9)–C(10)	118.8(13)
C(3)–C(4)–C(5)	110.0(12)	C(9)–C(10)–C(11)	118.2(13)
C(4)–C(5)–C(6)	115.3(12)	C(10)–C(11)–C(12)	123.6(14)
C(5)–C(6)–C(1)	101.7(11)	C(11)–C(12)–C(13)	118.6(14)
C(2)–C(1)–O(1)	109.0(11)	C(12)–C(13)–C(8)	116.9(13)
C(6)–C(1)–O(1)	104.5(11)	C(10)–C(11)–N	118.2(13)
C(1)–C(2)–Br(1)	112.2(10)	C(12)–C(11)–N	118.2(12)
C(3)–C(2)–Br(1)	110.3(9)	C(11)–N–O(3)	115.9(13)
C(2)–C(3)–Br(2)	104.2(9)	C(11)–N–O(4)	115.2(15)
C(4)–C(3)–Br(2)	109.7(9)	O(3)–N–O(4)	128.6(16)
C(3)–C(4)–C(14)	111.8(13)	C(4)–C(14)–C(15)	113.1(13)
C(5)–C(4)–C(14)	113.7(12)	C(4)–C(14)–C(16)	114.5(14)
C(1)–O(1)–C(7)	117.4(11)	C(4)–C(14)–C(17)	108.0(14)
O(1)–C(7)–O(2)	122.0(14)	C(15)–C(14)–C(16)	108.2(16)
O(1)–C(7)–C(8)	113.1(12)	C(15)–C(14)–C(17)	102.9(15)
O(2)–C(7)–C(8)	124.8(14)	C(16)–C(14)–C(17)	109.5(14)
C(7)–C(8)–C(9)	121.2(13)		

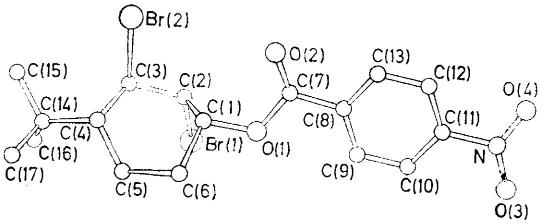

FIGURE 1 A perspective view of the molecule of *cis*-2,*trans*-3-dibromo-*cis*-4-t-butylcyclohexyl *p*-nitrobenzoate (I)

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[16] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[17] H. P. Hanson, F. Herman, J. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[18] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[19] R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, 1956, **12**, 81.

crystal. Several crystallizations did not provide better crystals and the correction for the shape anisotropy, although applied, does not perhaps give very good results in cases like this of strong shape anisotropy. The twist-boat conformation of the cyclohexane ring appears however very clear and well beyond any doubt, as shown by the values of the ring torsion angles (first six entries in Table 4) and by Figure 3.

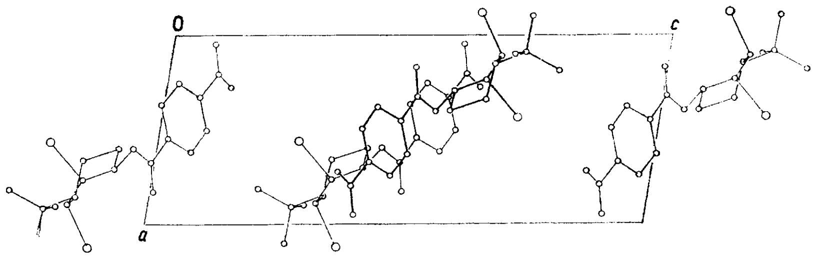

FIGURE 2 Projection of the structure of (I) on the crystallographic *ac* plane. The co-ordinates of Table 1 refer to the lower molecule at the centre of the Figure

Examination of models of compound (I) suggests that the chair destabilizing effects should be due mainly to steric repulsion between t-butyl and Br(2), to steric and dipole–dipole repulsion involving the two bromine atoms and to the axial nature of the ester grouping. This will decrease considerably the *ca.* 6 kcal mol^{-1} energy difference between chair and flexible conformations, if a twist form is available in which some or all the above unfavourable interactions are substantially decreased. A tetrasubstituted flexible cyclohexane can assume in its pseudorotational cycle six pure boat and six pure twist forms which are all different. Table 5 surveys these 12 limiting forms and shows the positions occupied by the substituents in each of them, the cyclohexane torsion angles (a—f) and those involving the substituents (A—C). Since general nomenclature rules for all the positions of substituents on non-chair cyclohexanes do not seem to have been suggested, we adopted the symbols indicated in Figure 4, the subscript τ and β referring respectively to twist and boat forms. For the ring dihedral angles we used the values recently suggested by Bucourt.[2]

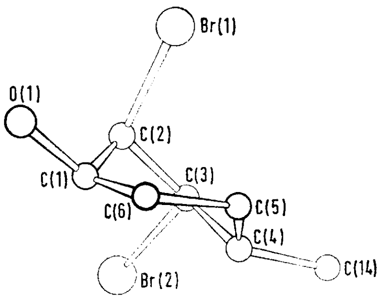

FIGURE 3 A view of the cyclohexane ring of the molecule, with the atoms directly bound to it, and showing the actual conformation

TABLE 4

Relevant torsion angles,* with estimated standard deviations in parentheses

Internal cyclohexane ring	
C(6)–C(1)–C(2)–C(3)	63.5(15)
C(1)–C(2)–C(3)–C(4)	−36.5(15)
C(2)–C(3)–C(4)–C(5)	−20.6(17)
C(3)–C(4)–C(5)–C(6)	61.8(16)
C(4)–C(5)–C(6)–C(1)	−37.6(15)
C(5)–C(6)–C(1)–C(2)	−25.4(15)
External cyclohexane ring	
C(6)–C(1)–C(2)–Br(1)	−58.1(15)
O(1)–C(1)–C(2)–Br(1)	62.1(12)
O(1)–C(1)–C(2)–C(3)	−176.3(10)
C(1)–C(2)–C(3)–Br(2)	84.8(11)
Br(1)–C(2)–C(3)–C(4)	86.4(13)
Br(1)–C(2)–C(3)–Br(2)	−152.3(7)
C(2)–C(3)–C(4)–C(14)	−148.0(12)
Br(2)–C(3)–C(4)–C(5)	−139.0(11)
Br(2)–C(3)–C(4)–C(14)	93.6(12)
C(14)–C(4)–C(5)–C(6)	−171.9(12)
C(5)–C(6)–C(1)–O(1)	−147.8(9)
Relative to the Bu^t group	
C(3)–C(4)–C(14)–C(15)	−60.3(17)
C(3)–C(4)–C(14)–C(16)	64.3(17)
C(3)–C(4)–C(14)–C(17)	−173.5(13)
C(5)–C(4)–C(14)–C(15)	174.3(14)
C(5)–C(4)–C(14)–C(16)	−61.1(19)
C(5)–C(4)–C(14)–C(17)	61.1(17)

* The convention of Klyne and Prelog [20] is adopted.

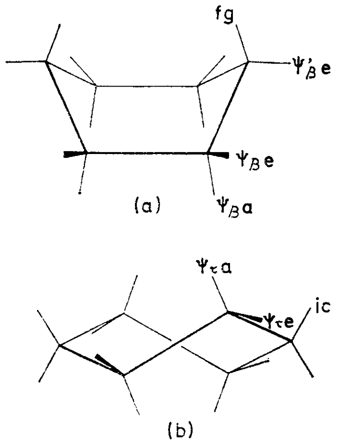

FIGURE 4 Schematic drawings of (a) pure boat and (b) twist forms. A boat form has four distinct positions: two flagpole (fg) and two pseudo-equatorial (ψ'_βe) at the ' ends ' of the boat, four pseudo-axial (ψ_βa) and four pseudo-equatorial (ψ'_βe) at the ' sides ' of the boat. A twist form has three distinct positions: four isoclinal (ic), four pseudo-axial (ψ_τa) and four pseudo-equatorial (ψ_τe)

Of the conformations given in Table 5, the odd-numbered ones, corresponding to boat forms, certainly do not correspond to energy minima, and also the twist

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[20] W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

forms (2) and (12) can be ruled out *a priori* because they have among other unfavourable conformational features the t-butyl group in the very hindered pseudoaxial position. In conformer (4) the bromine–bromine interaction is at a maximum; in (6) the Br(2) • • • t-butyl distance is at a minimum, and the dihedral angle A is only 31°, as in (10), where there is also a very short distance between Br(1) and t-butyl. Form (8) would therefore appear to be the minimum-energy conformation, and, as can be seen from entry (8a) in Table 5, giving the experimentally found torsion angles of compound (I), there is a rather satisfactory agreement between theoretical and experimental data. The agreement is even better if one considers that the actual conformation of (I) is not the pure twist form (8), but rather one which is slightly shifted towards the boat form (9), a situation in which there is an advantage since it involves an increase in the Br • • • Br and t-butyl • • • Br(2) distances, which cannot, however, proceed too far since it also involves the moving of Br(1) towards a 'flagpole' position. The deviation of the experimental torsion angles are all in the right direction to support these assumptions. The main factor in favour of the experimentally found conformation appears to be the easing of the Bu^t • • • Br(2) interaction. The distance between Br(2) and the nearest methyl carbon, which is *ca.* 2.5 Å, as measured on a Dreiding model of the chair conformation, is found experimentally to be increased to 3.4 Å.

TABLE 5

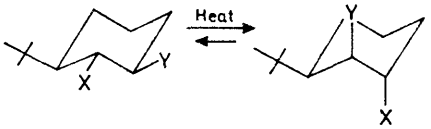
Positions of substituents and theoretical torsion angles * in the pure boat and twist forms of (I)

	Ester	Br(1)	Br(2)	Bu^t	a	b	c	d	e	f	A	B	C
(1)	fg	ψ_βe	ψ_βa	fg	−54	0	54	−54	0	54	−54	−120	174
(2)	ψ_τa	ψ_τe	ic	ψ_τa	−65	31	31	−65	31	31	−65	−89	151
(3)	ψ_βa	ψ'_βe	ψ_βe	ψ_βa	−54	54	0	−54	54	0	−54	−66	120
(4)	ic	ψ_τe	ψ_τe	ic	−31	65	−31	−31	65	−31	−31	−55	89
(5)	ψ_βe	ψ_βe	ψ'_βe	ψ_βe	0	54	−54	0	54	−54	0	−66	66
(6)	ψ_τe	ic	ψ_τe	ψ_τe	31	31	−65	31	31	−65	31	−89	55
(7)	ψ'_βe	ψ_βa	ψ_βe	ψ'_βe	54	0	−54	54	0	−54	54	−120	66
(8)	ψ_τe	ψ_τa	ic	ψ_τe	65	−31	−31	65	−31	−31	65	−151	89
(8a) †					63.5	−36.5	−20.6	61.8	−37.6	−25.4	62.1	−152.3	93.6
(9)	ψ_βe	fg	ψ_βa	ψ_βe	54	−54	0	54	−54	0	54	−174	120
(10)	ic	ψ_τa	ψ_τa	ic	31	−65	31	31	−65	31	31	175	151
(11)	ψ_βa	ψ_βa	fg	ψ_βa	0	−54	54	0	−54	54	0	−174	174
(12)	ψ_τa	ic	ψ_τa	ψ_τa	−31	−31	65	−31	−31	65	−31	−151	−175

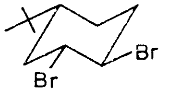
* a—f correspond to the ring torsion angles, starting from the 1–2 bond, A—C to the torsion angles O(1)–C(1)–C(2)–Br(1), Br(1)–C(2)–C(3)–Br(2), and Br(2)–C(3)–C(4)–C(14). † Values found experimentally for (I)

The *p*-nitrobenzoyloxy-group is approximately planar and its orientation with respect to the cyclohexane ring determines values for the torsion angles C(2)–C(1)–O(1)–C(7) and C(6)–C(1)–O(1)–C(7) of 84.5(14) and −146.2(12)° respectively. The t-butyl group is in an almost exactly staggered orientation with respect to the cyclohexane ring as shown by the last entries in Table 4. This is somewhat surprising, since one would have expected compound (I) to be a particularly favourable case for observing the twisting of the t-butyl group from the staggered conformation, foreseen on the basis of calculations,[21] and actually found in one case.[22] The structure determination on compound (I) thus confirms unequivocally the strong repulsive interaction between a t-butyl and a second substituent in a *trans*-1,2 relationship on a cyclohexane chair, which had been deduced from equilibration experiments on hydroxy [23] and cyano derivatives,[24] showing a preference (as high as 1.5 kcal mol^{-1} for 2-t-butylcyclohexane-1-carbonitrile [24]) for the *cis*-isomer with an axial substituent. No satisfactory explanation has so far been given for this preference, which appears surprising, since in an undistorted chair conformation with a staggered equatorial t-butyl the distances between one of the methyl groups and the second substituent are exactly the same in the *trans* and in the *cis* isomer. The tentative explanation of a ring distortion around the t-butyl group [25] is not confirmed by the available structural data.[22,26]

The increase in the destabilization of the chair conformation produced by a third substituent in position *cis*-3 to the t-butyl group is clearly evidenced by the thermal equilibrations of compounds (II; a—e),[5-7] which are converted into (III; a—e) for >90% [more than 99.5%, corresponding to a ΔG_{374} of >3.9 kcal mol^{-1} in the case of the equilibrium (IIa)–(IIIa)], and points to a strong contribution of the dipole–dipole repulsion term.



(II) (III)



(IV)

	X	Y
a;	Br,	Br
b;	Cl,	Br
c;	Br,	Cl
d;	Br,	OH
e;	Br,	OAc

The coupling constants between the protons α to the

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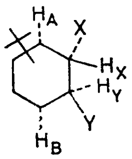
substituents in (II; a—e) when compared to those of compound (IV), which is taken as a reference for a normal chair conformation, clearly indicate (Table 6) that these compounds are not in a rigid chair conformation. The easily measured value of the coupling constants between the protons geminal to X and Y can be taken as an indication of the extent of contribution of non-chair forms to the conformational equilibrium of this type of compound. This value is particularly low, as expected, for compound (I). However, if the conformation of (I) in solution were the same as that found in the crystal, this coupling constant should be of 0 Hz, since the dihedral angle H(2)–C(2)–C(3)–H(3) is very near to 90°. The experimental value of 5.9 Hz therefore implies an equilibrium of different conformers. It is highly unlikely that (I) can go through the entire pseudorotational cycle at room temperature, since forms (1)—(3) and (11) and (12) are certainly of very high energy. The range of attainable flexible forms should therefore be limited at most to those (4)—(10). It would be unwise to try to deduce from the limited available ^{1}H n.m.r. data the relative weight of each conformer at equilibrium, but a rough preliminary evaluation points to a contribution of the chair conformer, which should not differ too much in energy from the most favourable flexible ones. A variable-temperature ^{1}H n.m.r. study on (I) and some of its analogues will give more information on this point.

TABLE 6

Coupling constants (Hz) for CCl_4 solution



Compound	$J(H_XH_Y)$	$J(H_AH_X)$	$J(H_BH_Y)$
(IIa) *	7.5	7.9	4.3
(IIb) †	9.2	9.3	
(IIc) †	7.7	8.1	
(IId) *	9.2	9.9	
(I)	5.9	6.1	4.2
(IV) *	10.4	12.1	4.4

* Ref. 8. † Unpublished data.

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