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An axial *tert*-butyl group in strained cyclohexene: X-ray analysis and theoretical calculations of 2-(2-*tert*-butylcyclohex-3-enyl)propan-2-ol

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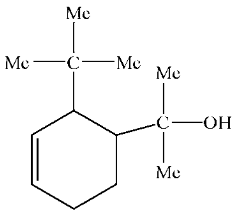
The structure of the title compound, $C_{13}H_{24}O$, (I), shows a sofa conformation of the ring with two pseudo-axial substituents. The dihedral angle between these substituents is 131.56 (12)°. Calculations using the B3LYP/6-31G* level of theory show two minima, one corresponding to the crystal structure and the other to a boat conformation of the ring with two equatorial substituents. The energy of this latter conformation is 17.4 kcal mol^{-1} higher than that of (I). The molecule forms an infinite co-operative hydrogen-bonded chain running in the *b* direction.

Comment

Strained molecules have been known for about a century, but interest in these species is still relevant today. For six-membered ring molecules having strong interactions between a *tert*-butyl group and a vicinal substituent, the *gauche* interaction provides sufficient steric strain to produce unique conformational (Aycard & Bodot, 1975; Stolow, Groom & Lewis, 1969; Stolow, Gallo & Marini, 1969; Viani & Lapasset, 1981) and particular reaction stereoselectivities (Aycard & Bodot, 1973; Pizzala *et al.*, 1978; Bouteiller-Prati *et al.*, 1981). Thus, we have shown that *cis*-2-*tert*-butylcyanocyclohexane is more stable than its *trans* isomer by 1.5 kcal mol^{-1} (Aycard & Bodot, 1973) (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). For cyclohexanones (Lafrance *et al.*, 1976; Viani *et al.*, 1978) and *trans*-3-*tert*-butyl-4-*X*-cyclohexenes in solution, large conformational heterogeneities have been detected and the existence of a pseudo-axial *tert*-butyl has been postulated (Aycard & Bodot, 1975; Lafrance *et al.*, 1977; Bouteiller-Prati *et al.*, 1976). X-ray analysis of a series of congested 3-*tert*-butyl-4-*X*-cyclohexene derivatives (*X* = CN or CO_2CH_3) has shown that *trans* stereoisomers exhibit a sofa conformation which is expected to be only 0.8 kcal mol^{-1} higher than for the half-chair conformation (Bucourt, 1974) with a pseudo-equatorial *tert*-butyl group (Viani *et al.*, 1978; Viani & Lapasset, 1981; Cossu *et al.*, 1981). For the *cis* isomer, we have observed a half-chair conformation with a pseudo-equatorial *tert*-butyl group (Viani *et al.*, 1981, 1985; Viani & Lapasset, 1981). We have never obtained a conformation with a pseudo-axial *tert*-butyl group.



(I)

In solution, the title compound, (I), which is similar to a 3,4-di-*tert*-butyl derivative, presents in its ^{1}H NMR spectrum a very small *trans* $^3J_{HH}$ coupling constant value of 5.8 Hz between H atoms bonded to the C atoms at psitions 4 and 5 (Bouteiller-Prati *et al.*, 1976). This low value is indicative of a conformational heterogeneity with a majority of a pseudo-axial *tert*-butyl conformer (>60%). To obtain structural data on this possible species, we carried out B3LYP calculations (*GAUSSIAN03*; Frisch *et al.*, 2004) and X-ray analysis on a crystal obtained from the NMR solution of *trans*-3,6,6-trideuterio-3-*tert*-butyl 4-dimethylcarbinol cyclohexene. The best way to describe the ring conformation is to use the endocyclic torsion angles Φ_{ij} (central bond *ij*). The values obtained from our X-ray data are reported in Table 3, and are compared with the classic half-chair and sofa values (Bucourt, 1974) and with those obtained from B3LYP calculations for the two expected possible conformers, *viz*. (I) and (I′).

We can see that the absolute value of the torsion angle Φ_{23} [−6.6 (2)°] is smaller than the half-chair value. In fact, the ring has a quasi-pure sofa conformation with a minor twisting of the double bond [−2.8 (3)°], as observed in other *trans* stereoisomers of 3-*tert*-butyl-4-*X*-cyclohexene derivatives

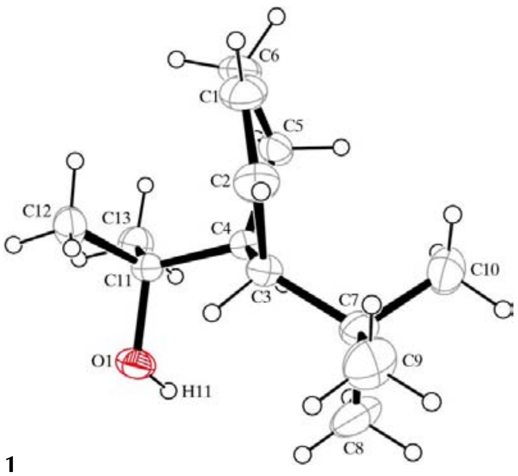


Figure 1
A view of the title molecule, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitary radii.

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(Viani *et al.*, 1978, 1981). Atoms C1–C4/C6 are coplanar to within 0.06 Å. There is also good agreement between the experimental and calculated values for all the torsion angles ($\Delta\Phi_{\max} \simeq 2°$). The value of the C1—C2—C3—C7 torsion angle is a measure of the inclination of the C3—C7 bond with respect to the double-bond plane. The value obtained for (I) [−125.36 (19)°] is similar to that determined for *trans*-1-acetoxy-3-*tert*-butyl-4-cyanocyclohexene [−125.1 (3)°; Viani *et al.*, 1978] and is indicative of a quasi-axial position of the *tert*-butyl substituent. The dihedral difference ($\Phi_{34} - \Phi_{45}$) is a measure of the puckering of the ring in the C4 region (Viani *et al.*, 1981).

A low value with respect to the half-chair value (109°) is indicative of an axial position and a large value of an equatorial position (Chiang & Bauer, 1969; Scharpen *et al.*, 1968). The value obtained for (I) (87°) shows that the dimethylcarbinol group adopts an isoclinal position with respect to the *tert*-butyl group. The C7—C3—C4—C11 torsion angle between the two substituents is 131.56 (12)° (130° theoretically), larger than the values obtained in other strained 3,4-cyclohexenes [84.4 (3), 77.4 (3) and 76.4 (3)°; Viani *et al.*, 1979]. This value is indicative of an increasing axiality of the two substituents, as shown in Fig. 1, and allows the minimization of the *gauche* interaction between the two large substituents.

The bond lengths and endocyclic valence angle values show moderate fluctuations ($\Delta l \simeq 0.03$ Å and $\Delta\theta \simeq 4°$) compared with those obtained for similar compounds (Viani *et al.*, 1978; Viani & Lapasset, 1981) and are similar to the values obtained from theoretical calculations. The exocyclic valence angles around the *tert*-butyl group are very close to the mean value observed in 3-*tert*-butylcyclohexene (110.7°) and *tert*-butylcyclohexane (113°) compounds (Viani *et al.*, 1978, 1981; Viani & Lapasset, 1981; Lectard *et al.*, 1976).

Nonbonded interactions are the driving force of the geometric modifications which must give the best compromise between the different nonbonded distances. Short distances are associated with repulsive nonbonded energies. The short distances here have been selected on the basis of Allinger parametrizations; some of them must be considered as very short distances and are at the origin of the strongest nonbonded interactions (Handal *et al.*, 1977; Allinger, 1976). Some of them are caused by the C9 methyl group of the *tert*-butyl interacting with the ring atoms C2 and C4 and with the H atom bonded to C2.

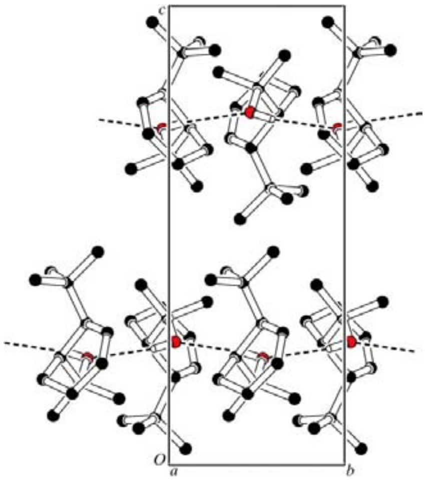

Figure 2
A motif of the O—H···O hydrogen bonds forming chains in the title structure.

Analysis of the packing shows an O—H···O hydrogen bond that links the molecules into infinite chains running in the *b*-axis direction (Fig. 2 and Table 2). These intermolecular bonds stabilize the position of the hydroxyl H atom in a *gauche* position. The C4—C11—O1—H11 torsion angle is −65.2 (18)°. In the optimized structure of this conformer, similar to the gas phase, the C4—C11—O1—H11 torsion angle is 180°.

The theoretical calculations for (I) give very good accuracy between the calculated geometric parameters and those obtained from the X-ray crystal data. For this, starting from a sofa conformation, we have modelled the structure for a diequatorial conformer. We obtained another energy minimum for the structure of (I′). This structure is 17.4 kcal mol^{-1} less stable than (I). If the bond lengths and valence bond angles are similar for the two conformers (Tables 4 and 5), the values of the endocyclic torsion angles (Table 3) are very different and indicate a twist-boat conformation. In solution, this compound can be neglected.

Experimental

The synthesis of the title compound has been described previously by Bouteiller-Prati *et al.* (1981). The compound was obtained as white needles by crystallization from a solution in chloroform. The computational method to establish the molecular structure and the relative energy of the two conformations was that of *ab initio* calculations carried out using *GAUSSIAN03* (Frisch *et al.*, 2004). The different systems were optimized at the B3LYP/6-31G* level of theory (Parr & Yang, 1989).

Crystal data

$C_{13}H_{24}O$
$M_r = 196.33$
Monoclinic, $P2_1/c$
$a = 13.0192$ (4) Å
$b = 6.0581$ (2) Å
$c = 16.3514$ (4) Å
$\beta = 103.915$ (2)°
$V = 1251.81$ (7) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.06$ mm^{-1}
$T = 294$ K
0.30 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
15244 measured reflections
3625 independent reflections
2533 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.105$
$S = 0.91$
2533 reflections
130 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Weighting was based on a Chebychev polynomial (Watkin, 1994; Prince, 1982). All H atoms were discernible in a difference Fourier map. The C—H distances were constrained to 0.95 and 0.98 Å for aryl and methyl H atoms, respectively, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). The positional parameters of O-bound atom H11 were refined freely and the $U_{\rm iso}$(H) value was set at $1.5U_{\rm eq}$(O).

Table 1
Selected geometric parameters (Å, °).

C1−C2	1.319 (2)		
C1−C2−C3	126.23 (15)	C5−C6−C1	110.99 (13)
C4−C5−C6	115.16 (13)	C6−C1−C2	123.94 (15)
C1−C2−C3−C4	−6.6 (2)	C3−C4−C5−C6	−53.09 (16)
C1−C2−C3−C7	125.36 (19)	C4−C5−C6−C1	42.94 (19)
C2−C3−C4−C5	32.81 (16)	C6−C1−C2−C3	−2.8 (3)
C2−C1−C6−C5	−15.2 (2)	C7−C3−C4−C11	131.56 (12)

Table 2
Hydrogen-bond geometry (Å, °).

D−H···*A*	*D*−H	H···*A*	*D*···*A*	*D*−H···*A*
O1−H11···O1^{i}	0.82 (2)	2.42 (2)	3.2320 (17)	170 (2)
C3−H3···O1	0.98	2.47	2.9499 (18)	110

Symmetry code: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

Table 3
Comparison of endocyclic torsion angles (°).

Data for (I*a*) are from experiment, data for (I*b*) and (I′*b*) are from calculations, data for (II) are for a cyclohexene half-chair conformation and data for (III) are for a cyclohexene sofa conformation (Bucourt, 1974; Viani *et al.*, 1978).

Bond	Φ_{ij}	(I*a*)	(I*b*)	(I′*b*)	(II)	(III)
C1−C2	Φ_{12}	−2.8 (3)	−2	6.2	0	−5.7
C2−C3	Φ_{23}	−6.6 (2)	−7	−31	−16	0
C3−C4	Φ_{34}	32.81 (16)	32	10.8	46	32
C4−C5	Φ_{45}	−53.09 (16)	−51	30	−63	−58
C5−C6	Φ_{45}	42.94 (19)	41	−53.3	46	51
C6−C1	Φ_{61}	−15.2 (2)	−14	36.2	−16	−20

Table 4
Experimental and calculated exocyclic valence bond angles (°).

	Experimental value for (I)	Calculated value for (I)	Average value†	Calculated value for (I′)
C2−C3−C7	112.21 (12)	112.9	111	109.9
C3−C7−C8	110.37 (12)	109.9	111	111.6
C3−C7−C9	109.72 (14)	109.6	111	112.3
C3−C7−C10	112.08 (12)	112.3	108	108.9
C3−C4−C11	112.17 (11)	112.2	112	112.5
C4−C3−C7	115.88 (12)	114.7	114	114.6
C4−C11−C13	111.81 (12)	111.5		111.6
C4−C11−C12	115.25 (12)	115.3		112.3
C4−C11−O1	107.409 (10)	103.2		105.4
C5−C4−C11	115.09 (11)	115.5	107	108.8

† Average values were obtained from three strained *trans*-3-*tert*-butyl-4-*X*-cyclohexenes (Viani *et al.*, 1978).

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *CRYSTALS*.

Table 5
Experimental and calculated endocyclic valence bond angles (°).

	Experimental value for (I)	Calculated value for (I)	Calculated value for (I′)
C1−C2−C3	126.30 (15)	126.1	123.9
C2−C3−C4	111.64 (11)	112.2	112.9
C3−C4−C5	111.96 (11)	112.3	114.0
C4−C5−C6	115.16 (13)	115.5	115.3
C5−C6−C1	110.99 (13)	111.5	108.9
C6−C1−C2	123.94 (15)	123.6	120.4

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3183). Services for accessing these data are described at the back of the journal.

References

Allinger, N. L. (1976). *Adv. Phys. Org. Chem.* **13**, 1–82.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Aycard, J.-P. & Bodot, H. (1973). *Can. J. Chem.* **51**, 741–747.
Aycard, J.-P. & Bodot, H. (1975). *Org. Magn. Reson.* **7**, 226–236.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Bouteiller-Prati, J., Bouteiller, J.-C. & Aycard, J.-P. (1976). *C. R. Acad. Sci. Ser. C*, **223**, 617–619.
Bouteiller-Prati, J., Bouteiller, J.-C. & Aycard, J.-P. (1981). *Can. J. Chem.* **59**, 859–864.
Bucourt, R. (1974). *Top. Stereochem.* **8**, 159–224.
Chiang, J. F. & Bauer, S. H. (1969). *J. Am. Chem. Soc.* **91**, 1898–1901.
Cossu, M., Viani, R. & Lapasset, J. (1981). *Acta Cryst.* B**37**, 481–483.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Frisch, M. J. *et al.* (2004). *GAUSSIAN03*. Revision C.02. Gaussian Inc., Wallingford, Connecticut, USA.
Handal, J., White, J. G., Franck, R. W., Yuh, Y. H. & Allinger, N. L. (1977). *J. Am. Chem. Soc.* **99**, 3345–3349.
Lafrance, R., Aycard, J.-P., Berger, J. & Bodot, H. (1976). *Org. Magn. Reson.* **8**, 95–101.
Lafrance, R., Aycard, J.-P. & Bodot, H. (1977). *Org. Magn. Reson.* **9**, 253–259.
Lectard, A., Lichanot, A., Metras, F., Gaultier, J. & Hauw, C. (1976). *J. Mol. Struct.* **34**, 113–122.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Parr, R. G. & Yang, W. (1989). *Density-Functional Theory of Atoms and Molecules*. New York: Oxford University Press.
Pizzala, L., Aycard, J.-P. & Bodot, H. (1978). *J. Org. Chem.* **43**, 1013–1015.
Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
Scharpen, L. H., Wollrab, J. E. & Ames, D. P. (1968). *J. Chem. Phys.* **49**, 2368–2372.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stolow, R. D., Gallo, A. A. & Marini, J. L. (1969). *Tetrahedron Lett.* **10**, 4655–4658.
Stolow, R. D., Groom, T. D. & Lewis, I. (1969). *Tetrahedron Lett.* **10**, 913–916.
Viani, R., Cossu, M. & Lapasset, J. (1981). *Acta Cryst.* B**37**, 484–486.
Viani, R. & Lapasset, J. (1981). *Acta Cryst.* B**37**, 477–480.
Viani, R., Lapasset, J. & Aycard, J.-P. (1985). *Acta Cryst.* C**41**, 791–793.
Viani, R., Lapasset, J., Aycard, J.-P. & Bodot, H. (1979). *J. Org. Chem.* **44**, 899–902.
Viani, R., Lapasset, J., Aycard, J.-P., Lafrance, R. & Bodot, H. (1978). *Acta Cryst.* B**34**, 1190–1194.
Watkin, D. (1994). *Acta Cryst.* A**50**, 411–437.