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Intramolecular Interactions. 33.[1] Conformational and Geometrical Adaptations to Strong Gauche Interactions: Analysis of the X-ray Crystallographic Data of Six Congested 3-*tert*-Butylcyclohexene Derivatives

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The congestion comes from the repulsive nonbonded interactions between the 3-*tert*-butyl substituent and a 4-cyano or a 4-carboxy group. Five of the six molecules on investigation exhibit a conformational trend toward sofa conformations, the ring dihedral angle evolution being $\phi_{23} \rightarrow 0°$ with trans substituents and $\phi_{61} \rightarrow 0°$ with cis ones. A 5° twisting of the double bond is observed in the trans series. The main increases of exocyclic valence bond angles are those of C(4)–C(3)–C(7) (max 117.7°), of C(3)–C(7)–C(9) (max 113.7°), and of C(3)–C(4)–C(11) (max 114.7°), the deviations from "normal values" being larger in the cis series; C(7) is the *tert*-butyl central carbon atom, C(9) is the methyl carbon anti to the hydrogen bonded to C(3), and C(11) is the cyano or the carboxyl carbon atom. The *tert*-butyl group rotates in the direction which brings C(9) and C(2) closer, the larger deviations (near to 17°) being observed in the cis series. A lot of short nonbonded distances are observed, only small discrepancies are observed within each series, and the shortest distances are those involving some *tert*-butyl atoms and C(11), H(4), C(2), and H(2).

For organic molecules involving strong steric strains, there are still some challenges to an exhaustive understanding and to the forecast of structure and reactivity data. As an example, for some substituted ethanes with one, two, or four *tert*-butyl groups,[3] the more stable conformer is that one which looks like the more congested. To forecast energy differences, the molecular mechanic calculations are now very successful even in highly distorted frameworks as shown recently in a *peri*-di-*tert*-butylnaphthalene,[4a] but disagreements come from some highly strained molecules such as *cis*- and *trans*-di-*tert*-butylethylenes, the differences between the calculated and experimental heats of formation being respectively[4b] 4.0 and 2.7 kcal mol^{-1}.

Improvements in this field require a large set of precise experimental data, mainly about the geometries of such molecules. The electron diffraction technique may seem the best because it gives information about isolated molecules; it may, however, lead to some uncertainties on highly strained molecules such as tri-*tert*-butylmethane[5] or di-*tert*-butylcyclohexanes.[6] Therefore, X-ray crystallographic studies are still competitive, expecting that the molecular packing is unable to modify the geometries of the molecules where the intramolecular forces are strong enough; moreover, the investigation of a series of molecules provides the usual means to avoid an exceptional situation.

With six-membered ring molecules having a *tert*-butyl group and a vicinal substituent, the gauche interaction provides sufficient steric strain to produce unique conformational data[7] and novel reaction stereoselectivities.[8] Thus, we have shown that *cis*-2-*tert*-butylcyanocyclohexane is more stable than its trans isomer[8d] by 1.5 kcal mol^{-1}; large conformational heterogeneities have been detected for *trans*-3-*tert*-butyl-4-X-cyclohexenes[7g,l,m] and cyclohexanones.[7h,n]

With the comparison of the molecular structures of a series of cyclohexenes (Figure 1), having as a common feature a 3-*tert*-butyl group and a 4-cyano (or a 4-carboxy) substituent in a trans (**1** to **3**) or cis (**4** to **6**) relationship, we expect to bring out in the present paper some general trends of the conformational and the geometrical modifications which explain how the strong gauche interactions are minimized. The crystal structures of these compounds will be published later.[9]

Ring Conformations

The best way to describe these conformations is to use the endocyclic torsion angles;[10] in Table I, we have grouped our experimental data together with those of the half-chair cyclohexene[11] and of the calculated sofa conformation.[10] If the twisting of the double bond of cyclohexene itself is taken into account in the molecular mechanic calculations, the energy of this sofa conformation is expected to be only 0.8 kcal mol^{-1} higher than for the half-chair.[10]

The torsion angles ϕ_{23} (central bond C(2)–C(3)) of compounds **1** to **3** are clearly smaller than the half-chair's (absolute values). **1** has a pure sofa conformation, C(1), C(2), C(3), C(4), and C(6) being coplanar within 0.03 Å; there is also a fair agreement between experimental and calculated values for the other torsion angles. For **2** and **3**, the conformation is intermediate between the two extreme limits. The evolution

Table I. Endocyclic Torsion Angles Φ_{ij} (deg) of 3-*tert*-Butylcyclohexene Derivatives

							C_6H_{10}		
central bond	1[d]	2[e]	3[f]	4[g]	5[h]	6[i]		b′	b″
C(1)–C(2)	−5.3	−4.5	−5.0	−2.0	−0.2	0.0	0	−5.7	−5.7
C(2)–C(3)	+2.0	−5.8	−7.4	−21.1	−17.9	−21.9	−16	0	−20
C(3)–C(4)	+28.2	+37.2	+38.7	+51.5	+46.6	+49.8	+46	+32	+51
C(4)–C(5)	−57.8	−61.5	−60.9	−62.8	−60.6	−61.9	−63	−58	−58
C(5)–C(6)	+52.4	+49.3	+47.1	+38.9	+41.6	+40.1	+46	+51	+32
C(6)–C(1)	−22.3	−17.9	−15.5	−7.0	−12.1	−8.4	−16	−20	0
θ[c]	28.6	30.4	30.2	30.5	28.7	29.6	30		

[a] Experimental half-chair cyclohexene geometry from the microwave study[11b] (Figure 2). [b] Calculated values for the sofa conformation[10] (Figure 2). All the carbon atoms are coplanar except C(5) (b′) or C(4) (b″). [c] Dihedral angle measuring "the deviation from ring planarity" (g).[11b,19] [d] Registry no. 68796-74-7. [e] Registry no. 68796-75-8. [f] Registry no. 31752-75-7. [g] Registry no. 68796-76-9. [h] Registry no. 68852-28-8. [i] Registry no. 68796-77-0.

Table II. Dihedral Angle Φ_{1237} (deg) as a Measure of the Inclination of C_3–C_7 Bond with Respect to the Double Bond Plane

isoclinal	1	2	3	"pure" e′[a]	4	5	6
≃−120	−125	−132	−135	≃−140	−154	−150	−155

[a] From the cyclohexene experimental geometry (half-chair).[11b]

Table III. Dihedral Angle Difference ($\Phi_{34} - \Phi_{45}$) (deg) as a Measure[10] of the Puckering of the Ring in the C(4) Region

X_1 equatorial			half-chair[a]	X_1 axial		
1	2	3	C_6H_{10}	5	6	4
86.0	98.7	99.6	109	107.2	111.7	114.3

← X_1 more isoclinal

X_1 more axial →

[a] From the cyclohexene experimental geometry.[11b]

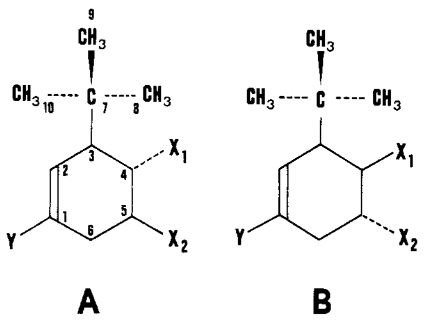

Figure 1. Formula of the six 3-*tert*-butylcyclohexene derivatives, H(*ni*) is bonded to C(*n*), the ring hydrogens being below (*i* = 1) or above (*i* = 2) the plane; C(11) is the X_1 carbon atom bonded to C(4).

X_1	X_2	Y	A	B
CN	H	OAc	1	4
CN	CN	H	2	5
CO_2H	H	H	3	
CO_2CH_3	H	OAc		6

from the half-chair to the sofa conformation decreases the ϕ_{34} torsion angle, which allows the increase of the exocyclic dihedral angle associated with the trans ee′ substituents; thus, the dihedral angles C(7)-C(3)-C(4)-C(11) are 84° (1), 77° (2), and 76° (3). Therefore, the evolution toward the sofa conformation provides a means to minimize the gauche interaction between X_1 and the *tert*-butyl group; the latter goes from a pseudoequatorial to an isoclinal position (Table II); a similar trend is observed for X_1 (Table III).

Table IV. Exocyclic Valence Bond Angles (deg)[a]

	1	2	3	4	5	6
C(2)–C(3)–C(7)	110.9	111.0	111.0	113.1	113.9	113.6
C(4)–C(3)–C(7)	113.1	113.3	115.5	117.7	115.7	117.2
C(3)–C(7)–C(8)	110.4	111.2	111.0	110.0	110.2	110.3
C(3)–C(7)–C(9)	111.6	110.7	111.4	113.0	112.1	113.7
C(3)–C(7)–C(10)	107.7	108.6	108.6	106.9	107.1	106.9
C(3)–C(4)–C(11)	110.9	113.0	113.0	114.1	114.7	114.1
C(5)–C(4)–C(11)	108.8	107.1	105.8	109.0	106.5	111.0

[a] C(11) is the first atom of X_1.

Table V. Exocyclic Dihedral Angles (deg)

	1	2	3	4	5	6
C(2)–C(3)–C(7)–C(9)	+55.7	+52.0	+54.3	+48.6	+46.2	+52.4
C(2)–C(3)–C(7)–C(10)	−65.8	−67.8	−66.7	−71.3	−73.1	−67.1
C(4)–C(3)–C(7)–C(8)	+52.3	+49.9	+52.0	+41.9	+39.1	+47.9
C(4)–C(3)–C(7)–C(9)	−70.0	−72.0	−69.8	−80.3	−82.9	−76.5
$\Delta\phi$[a]	−6.4	−8.7	−7.4	−14.5	−16.9	−9.5
C(7)–C(3)–C(4)–C(11)	−84.4	−77.4	−76.3	+59.9	+57.3	+57.3
C(8)–C(7)–C(4)–C(11)[b]	−25.7	−21.4	−19.0			
C(9)–C(7)–C(4)–C(11)[b]				−17.1	−22.1	−15.6

[a] $\Delta\phi$ being the mean deviation to the staggered conformation of the *tert*-butyl group. [b] Uncommon dihedral angle showing the deviation from a pure 1,3-syn situation for the methyl and X_1 groups.

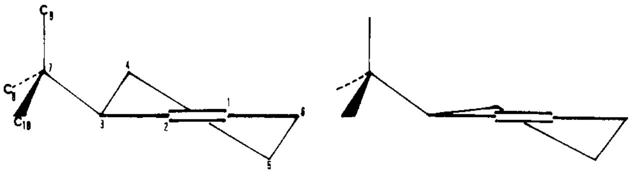

Figure 2. 3-*tert*-Butylcyclohexene in the half-chair and sofa (b′) conformations.

In the three other molecules of our series (4 to 6), the X_1 substituent is cis relative to the *tert*-butyl group. The endocyclic torsion angles of 5 are within 5° of that found in the half-chair cyclohexene (Table I); the 4 and 6 conformations are intermediate between the half-chair and the sofa confor-

Table VI. Intramolecular Short Contacts[a] (Å) between Nonbonded Atoms[c,d]

	1	2	3	4	5	6	d_0[b]
C(2) C(9)	2.97	2.93	2.94	2.97	2.97	3.02	3.22
C(2) H(92)	$\underline{2.59}$	$\underline{2.61}$	2.73	$\underline{2.67}$	$\underline{2.63}$	2.72	2.99
C(2) C(10)	3.01	3.05	3.02	3.08	3.12	3.05	3.22
C(2) H(103)	2.76	$\underline{2.65}$	2.71	2.77	2.83	2.72	2.99
C(4) C(8)	3.01	2.98	3.02	2.97	2.91	3.03	3.13
C(4) H(82)	2.70	2.76	2.77	2.72	2.69	2.66	2.90
C(4) H(93)	2.85	2.79					2.90
C(11) C(8)	3.02	2.93	2.97				3.22
C(11) H(82)	$\underline{2.60}$	$\underline{2.55}$	$\underline{2.54}$	2.88	2.75	2.92	2.99
C(11) H(83)	2.87	2.78	2.85				2.99
C(11) C(9)					3.21	3.18	3.22
C(11) H(93)				2.61	2.54	2.53	2.99
H(21) H(92)	2.53	2.55	2.56	$\underline{2.30}$	$\underline{2.34}$	$\underline{2.30}$	2.68
H(21) C(10)	2.69	2.75	2.75	2.85	2.83	2.73	2.90
H(21) H(103)	$\underline{2.15}$	$\underline{2.08}$	$\underline{2.15}$	$\underline{2.24}$	$\underline{2.26}$	$\underline{2.14}$	2.68
H(4*i*) C(8)[e]				2.65	2.63	2.68	2.90
H(4*i*) H(82)	$\underline{2.42}$	2.63	2.80	$\underline{2.30}$	$\underline{2.35}$	$\underline{2.23}$	2.68
H(4*i*) C(9)	2.73	2.80	2.84				2.90
H(4*i*) H(93)	$\underline{2.11}$	$\underline{2.07}$	$\underline{2.30}$				2.68

[a] Distances shorter than the d_0 values transcribed in the last column. [b] Distances corresponding to a zero value for the nonbonded energy.[4] [c] Values underlined correspond to very short distances ($<0.9d_0$). [d] *tert*-butyl hydrogens $H(nj)$ ($1 \leqslant j \leqslant 3$) are bonded to C($n$); H(92) and H(103), and H(102) and H(83), H(82) and H(93) are respectively anti to C(8), C(9), C(10). [e] i = 1 or 2 (see Figure 1).

mation having $\phi_{61} = 0°$ (Table I, column b″). This last adaptation obviously releases the gauche interaction by a moderate increase ($\simeq 4°$) of ϕ_{34} which allows the *tert*-butyl to become "more equatorial" (Table II) and the X_1 substituent to become "more axial" (Table III). Moreover, the evolution toward the sofa conformation releases the nonbonded interaction between X_1 and the pseudoaxial H(62).[12] The fact that **5** does not adopt an intermediate conformation may be ascribed to the presence of the axial X_2 (CN) substituent which would develop a stronger nonbonded interaction with H(31).[13]

Another striking difference between the two groups of molecules is the twisting of the double bond which is only important in the first group; the sign and the range of this twisting have been rightly predicted by the molecular mechanics calculations.[10]

At last, it must be pointed out that the ϕ_{45} torsion angle does not change too much in the whole series; this gives an a posteriori checking of the hypothesis used in the NMR studies of some of these molecules.[7g,7l]

Geometrical Modifications

For each kind of bond length, the values are very similar (within 0.04 Å) in the whole series; one should only notice that, except for **5**, C(3)–C(4) is about 0.04 Å longer than the corresponding unsubstituted C(5)–C(6) bond; this increase may be a contribution to the removal of X_1 and *tert*-butyl substituents[7n] as in compounds involving 1,3-syn diaxial interactions.[14]

The endocyclic valence angles show moderate fluctuations in the series; the small pinching of C(2)–C(3)–C(4) ($\simeq$109.7°) is most always associated with the presence of a *tert*-butyl group on a six-membered ring.[15]

Among the exocyclic valence angles (Table IV), C(2)–C(3)–C(7) and C(4)–C(3)–C(7) exhibit the largest variations; they have to be compared to 113.8° which is the mean value in *tert*-butylcyclohexane compounds.[16] As the increase of these valence angles may be associated with large steric strains, the molecules with cis X_1 and *tert*-butyl groups (**4** to **6**) are obviously more congested than their trans isomers (**1** to **3**). For **4**, **5**, and **6**, a related geometrical modification is the increase ($\simeq$+3°) of C(3)–C(7)–C(9) relative to the normal value ($\simeq$109.5°). The increased distances of X_1 and *tert*-butyl substituents are also illustrated by the inequality C(3)–C(4)–C(11) > C(5)–C(4)–C(11) observed in the whole series.

From the *tert*-butyl torsion angles (Table V), it is clear that, in the six molecules, this group rotates in the direction which brings closer C(9) and C(2). The deviations from the staggered conformation are important, from 6 to 17° ($\Delta\phi$ in Table V). In the cyclohexane series, three similar deviations have been observed,[7e,k,17] but the rotation of the *tert*-butyl is inverse when this group is trans relative to the vicinal X_1 substituent;[7k,18] this fact is related to the difference between the dihedral angles C(7)–C(3)–C(4)–C(11) in the cyclohexene ($|\phi| \simeq 80°$) and in the cyclohexane series ($|\phi| \simeq 60°$).

The interactions between the *tert*-butyl and the X_1 groups may be viewed as a 1,3-syn interaction between X_1 and one of the methyl groups C(8) or C(9); the last two lines of Table V show the deviation from parallelism between C–CH_3 and C–X_1.

Nonbonded Interactions

Nonbonded interactions are the driving forces of the geometrical modifications which must give the best compromise about the different nonbonded distances. In congested molecules, it is normal to find out a certain number of "short distances" which are associated with repulsive nonbonded energies. In Table VI, these short distances have been selected on the basis of Allinger's parametrizations;[4,20] some of them must be considered as "very short distances" and they are shown underlined in order to point out the strongest nonbonded interactions.

The distances of Table VI seem not to be sensitive to the structural changes inside each series (**1** to **3** and **4** to **6**) given the inaccuracies on the hydrogen positions;[21] thus, for the second one, the largest discrepancies are equal to 0.12 Å (except C(11)–H(82) = 0.17 Å). Larger differences are observed for the series **1** to **3**; they may be imputed to larger conformational variations in this series.

If we exclude the expected strong nonbonded interactions between C(11) and H(42) and some atoms of the *tert*-butyl group, the striking result of Table V is the importance of the interactions involving C(2) and H(21), and the fact that they are somewhat stronger with the C(9) methyl group than with the C(10) one, owing to the rotation of the *tert*-butyl group.

Conclusion

In our molecules, the congestion is revealed by different structural features selected on the basis of geometrical parameters which clearly have abnormal values. In each series, the observation of similar trends gives some assurance about the generality of the conclusions, and it shows that the intermolecular interactions do not disturb significantly any molecules under investigation.[22]

This new knowledge about the energy minimization ways could be useful to check the different molecular mechanic calculations, and our molecules may be used as new tools for reactivity investigations.

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(12) C(11)–H(62) distances are respectively 2.84 (**4**), 2.75 (**5**), and 3.04 Å (**6**).

(13) This interaction is already strong, the distance between H(31) and the carbon of X_2 being 2.67 Å.

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(16) This value is associated[15] with the flattening of the pyramid with C(2), C(4), and C(7) as a base and C(3) as a top; this flattening decreases the steric interaction between the methyl C(9) and the ring.

(17) Without a vicinal substituent, the *tert*-butyl group rotates about 2°.[15]

(18) In the *trans*-2-*tert*-butylcyclohexane carboxylic acid: M. Cossu, R. Viani, and J. Lapasset, to be published.

(19) The two planes involve the line joining the middles of C(1)–C(2) and of C(4)–C(5) and these two bonds.

(20) A reviewer disagrees with our choice of this parametrization and of the large van der Waal's radii for hydrogen ($\simeq$ 1.4 Å). Our confidence has been established on Allinger's arguments[4] (its criticism of the method to establish the van der Waal's radii) and on Mirsky's calculations: *Acta Crystallogr., Sect. A*, **32**, 199 (1976). In this last paper, the best molecular packings of different hydrocarbons have been calculated with a 1.4 Å hydrogen radii.

(21) The uncertainties on the C$\cdots$C distances are about 0.01 Å. All the hydrogens are located by Fourier differences,[7o,9] but they are not included in the least-squares refinements. The experimental uncertainties on the hydrogen positions and the underestimates (10 to 20%) of CH bond lengths have been largely analyzed: see J. M. Williams, D. J. Duchamp, and R. H. Bohn, "Critical Evaluation of Chemical and Physical Structural Information", Discussion, National Academy of Sciences, Washington, 1974, pp 219–224. In spite of these limitations, we have reported the C$\cdots$H and H$\cdots$H intramolecular distances of Table VI; the exceptional agreements between the values in the series **4** to **6** cannot be fortuitous and it suggests that these distances are meaningful as relative values at least. Neutron diffraction experiments would be required to obtain more accurate data.

(22) As suggested by a reviewer, the influence of "crystal forces" on molecular conformation could be analyzed with the recent methodology of J. Bernstein and A. T. Hagler, *J. Am. Chem. Soc.*, **100**, 673, 6349 (1978). Conformational polymorphism is mainly observed with molecules exhibiting internal rotations of aryl groups. In other series, important deviations to standard structures are induced by the molecular packing when intermolecular interactions occur between nucleophile and electrophile centers as we recently observed in *trans*-4,5-dicyanocyclohexene and in *trans*-3,4-dicyano-1,6-dimethyl-7-oxabicyclo[4.1.0]heptane (to be published). These exceptional situations could be easily detected by observations of abnormal bond lengths and angles. For the series **1** to **6**, such deviations are not observed and we can reasonably state that our X-ray cristallographic data give true pictures of the ground state conformations of these molecules.