# Stereoisomers of Hydrogenated Triptycene: a Joint Crystallographic and Conformation Study of a Set of Strained Hydrocarbon Molecules

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A joint *X*-ray single-crystal and conformational (molecular mechanics) study has been carried out on several hydrogenated triptycene stereoisomers. The calculated and observed geometries compare quite satisfactorily. In particular the lowest-energy conformation of the cyclohexane rings *cis*-attached to the bicyclo-octane cage always coincides with the unusual boat-conformation. The free energy of the most stable perhydrotriptycene stereoisomers in the gaseous state, calculated neglecting vibrational entropy contribution, is also in good agreement with the equilibrium concentrations reached in solution after one month at 172 °C, in the presence of Pd/C catalyst.

IN a recent study of the hydrogenation of triptycene (1) several pentacyclic hydrocarbons were isolated, their central nucleus corresponding to bicyclo[2.2.2]octane.[1,2] Their molecular structure was determined through mass spectrometry, $^1$H and $^{13}$C n.m.r. spectroscopy, thermodynamic and kinetic criteria, and in some significant cases through *X*-ray single-crystal analysis.[3-6] With these methods six fully hydrogenated stereoisomers were characterized, as well as two compounds with an aromatic ring and one with two aromatic rings. In the present paper we discuss some particular conformational aspects relating to this series of compounds.

TABLE 1

Summary of potential and free-energy calculations for the different stereoisomers

(*a*) Torsional barrier height 3.0 kcal mol$^{-1}$

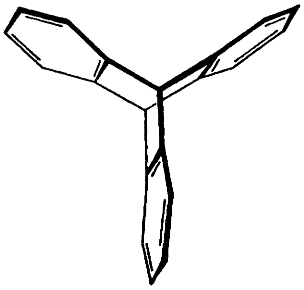
| Stereoisomer | $n$ | $\sigma$ | $E_{\text{conformer}}$ | $G$ | $G - G_{ttt}$ | % Calc. | % Exp. |
|---|---|---|---|---|---|---|---|
| *ttt* | 2 | 6 | 0 | 0.971 | 0 | 64.3 | 61.2 |
| *ttc* | 2 | 1 | $E(ttc)$ 2.77<br>$E(ttc_c)$ 3.86 | 1.931 | 0.960 | 20.6 | 27.0 |
| *tcc* | 2 | 1 | $E(tcc)$ 3.79<br>$E(tc_cc)$ 5.14<br>$E(tcc_c)$ 5.40 | 2.893 | 1.922 | 6.6 | 7.3 |
| *ccc* | 1 | 3 | 2.56 | 2.918 | 1.947 | 6.4 | 3.4 |
| *tc'c* | 2 | 2 | $E(tc'c)$ 4.73<br>$E(tc'c_c)$ 6.36 | 4.600 | 3.629 | 0.8 | 1.1 |
| *cc'c* | 1 | 1 | 9.65 | 9.65 | 8.679 | $2 \times 10^{-5}$ | $<0.1$ |

(*b*) Torsional barrier height 2.5 kcal mol$^{-1}$

| Stereoisomer | $n$ | $\sigma$ | $E_{\text{conformer}}$ | $G$ | $G - G_{ttt}$ | % Calc. | % Exp. |
|---|---|---|---|---|---|---|---|
| *ttt* | 2 | 6 | 0 | 0.971 | 0 | 39.3 | 61.2 |
| *ttc* | 2 | 1 | $E(ttc)$ 2 14<br>$E(ttc_c)$ 3.45 | 1.346 | 0.375 | 25.7 | 27.0 |
| *tcc* | 2 | 1 | $E(tcc)$ 2.58<br>$E(tc_cc)$ 4.10<br>$E(tcc_c)$ 4.31 | 1.721 | 0.750 | 16.8 | 7.3 |
| *ccc* | 1 | 3 | 0.82 | 1.791 | 0.820 | 15.5 | 3.4 |
| *tc'c* | 2 | 2 | $E(tc'c)$ 3.49<br>$E(tc'c_c)$ 5.24 | 3.376 | 2.404 | 2.6 | 1.1 |
| *cc'c* | 1 | 1 | 7.86 | 7.86 | 6.89 | $2 \times 10^{-4}$ | 0.1 |

Column headings are defined as follows: $n$ no. of enantiomers; $\sigma$ symmetry number (proper rotations are considered only); $E_{\text{conformer}}$ is conformational potential energy (kcal mol$^{-1}$) relative to the *ttt* stereoisomer, different values relative to the same stereoisomer refer to different conformers when their energy is not $>2.0$ kcal mol$^{-1}$ above the minimum (*c* indicates a *cis*-attached cyclohexane ring in boat conformation, $c_c$ indicates the same ring in a chair conformation); $G$ is conformational free energy (kcal mol$^{-1}$) calculated as $G = -RT \ln[n \, \Sigma \, \sigma_j^{-1} \exp(-E_j/RT)]$, where the $j$ index runs over all conformers which are accessible to the given stereoisomer. Note: calculations refer to the gas phase, experimental data in solution at same temperature ($T$ 445 K).

Interest in this problem arises from structural and thermodynamic considerations. Inspection of the molecular structures reveals a high degree of internal stress. The spontaneous tendency of the cyclohexane rings towards staggered chair conformations is counteracted by the presence of the bicyclo-octane system allowing only limited deformations from eclipsed torsional angles. From the thermodynamic viewpoint we stress some interesting experimental aspects. Under equilibrium conditions (which may be reached after more than one month at 172 °C in the presence of Pd/C) five saturated compounds were present having $>1\%$ concentration (see Table 1, where *t* and *c* stand for *trans* and *cis* respectively and apex means that the cyclohexane ring is oriented anticlockwise). The *ttt* and *ccc* stereoisomers, whose structure was determined by *X*-ray analysis, contain cyclohexane rings with a chair and a boat conformation respectively. Nevertheless, their formation free-energy only differs by 2.55 kcal mol$^{-1}$ at 172 °C.[2] The *ttc* and *tcc* compounds have an intermediate stability. As a consequence of these facts we have been prompted to undertake a conformational study of the most stable stereoisomers of perhydrotriptycene, with the usual methods of molecular mechanics. We wished both to compare the lowest-energy conformations with those observed in the crystal state and to justify the differences between their formation free-energies, to an extent compatible with the inherent accuracy of the calculations. To provide additional comparison between observed and calculated data we also extended our conformational analysis to one of the partially hydrogenated derivatives of triptycene,[2,4] A*c*′*c* (A = aromatic)



**(1)**

formed during the kinetic process leading to equilibrium, the *X*-ray structure of which was also obtained by us.

*Conformational Analysis of Hydrogenated Stereoisomers of Triptycene.*—(a) *Energy parameters.* The conformational energy of a molecule in the gaseous state may be expressed as

$$E = \sum_i \tfrac{1}{2}K_{l_i}(l_i - l_i^{\circ})^2 + \sum_j \tfrac{1}{2}K_{\theta j}(\theta_j - \theta^{\circ}_j)^2 + \frac{1}{18}V^{\circ}\sum_k (1 + \cos 3\phi_k) + \sum_{p<q}\sum (A_{pq}\exp(-B_{pq}r_{pq}) - C_{pq}/r_{pq}^{6}) \quad (1)$$

where $l_i$, $\theta_j$, and $\phi_k$ stand for the general bond length, bond angle, and torsion angle, respectively, and $A_{pq}$, $B_{pq}$, and $C_{pq}$ are Buckingam parameters characteristic of the ($p$, $q$) atom pair, separated by a distance $r_{pq}$. In view of some rather severe distortions from the ideal tetrahedral geometry which we found, the torsional energy pertaining to each C–C bond in equation (1) has been approximately decomposed into the sum of nine terms corresponding to the different X–C–C–Y sequences, $V^{\circ}$ being the inherent potential-energy barrier between staggered conformations for tetrahedral carbon atoms. All the parameters involved in equation (1) are listed in Table 2. They are all identical to those utilized by Boyd in several molecular mechanics calculations,[7] with the exception of the parameter $V^{\circ}$ which was set at 3.00 instead of 2.10 kcal mol$^{-1}$; this parameter was recently changed to 2.50 kcal mol$^{-1}$ by the same author.[8] Our basic reason for preferring 3.00 to 2.50 kcal mol$^{-1}$ was that we then obtained much better agreement between observed and calculated energy values (see Table 1). However, we were also encouraged by the following: (*a*) although the former value gives a barrier height for ethane somewhat larger than that found experimentally (3.30 *vs.* 3.0 kcal mol$^{-1}$ from microwave spectroscopy [9]),

TABLE 2

Potential function constants

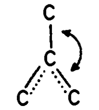
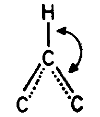
(*a*) Bond stretching

$V_{str} = 0.5K_l\,(l - l^{\circ})^2$

| | | $K_l$/kcal Å$^{-2}$ mol$^{-1}$ | $l^{\circ}$/Å |
|---|---|---|---|
| C–H | | 655 | 1.09 |
| C–H | (pendant to aromatic) | 727 | 1.09 |
| C–C | | 634 | 1.53 |
| C–C | (pendant to aromatic) | 655 | 1.50 |
| C⋯C | (aromatic) | 1 102 | 1.39 |

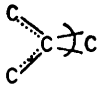
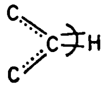
(*b*) Bond-angle bending

$V_{bend} = 0.5K_{\theta}\,(\theta - \theta^{\circ})^2$

| | | $K_{\theta}$(kcal K$^{-2}$ mol$^{-1}$ | $\theta^{\circ}$/° |
|---|---|---|---|
| C–C–C | | 0.0351 | 111.0 |
| C–C–H | | 0.0267 | 109.5 |
| H–C–H | | 0.0223 | 107.9 |
| C⋯C⋯C | (aromatic) | 0.0439 | 120.0 |
|  | (pendant to aromatic) | 0.0307 | 120.0 |
|  | (pendant to aromatic) | 0.0219 | 120.0 |

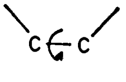
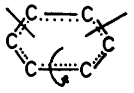
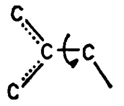
(*c*) Out-of-plane bending

$V = 0.5K_{\delta}\,(\delta - \delta^{\circ})^2$

| | | $K_{\delta}$/kcal K$^{-2}$ mol$^{-1}$ | $\delta^{\circ}$/° |
|---|---|---|---|
|  | (pendant to aromatic) | 0.0351 | 0.0 |
|  | (pendant to aromatic) | 0.0127 | 0.0 |

(*d*) Bond torsion

$V_{tor} = 0.5V^{\circ}\,(b + \cos 3\phi)$

| | | $V^{\circ}$/kcal mol$^{-1}$ | $b$ |
|---|---|---|---|
|  | | 3.0 | 1.0 * |
|  | Out-of-plane aromatic twisting | −11.5 | −1.0 |
|  | C–C twisting (pendant to aromatic) | 0.144 | 1.0 |

* See text.

the latter leads to a slightly defective result (2.80 kcal mol$^{-1}$); (*b*) the effect of changing from 2.50 to 3.00 kcal mol$^{-1}$ is relatively unimportant except in the relatively rare cases when strong departures from staggered conformations are present, as with our molecules; and (*c*) there seems to be relatively little correlation between this and all the other energy parameters. The last proposition is in agreement with the results of our minimum-energy calculations on two of the investigated molecules (the *ttt* and *ccc* stereoisomers, see later), which gave very similar geometrical parameters in spite of different strain-energy values, no matter which of the two values was adopted. However, we should stress that the good agreement with experimental data obtained by taking $V^\circ$ 3.0 kcal mol$^{-1}$ may also be related to some fortuitous cancellation of errors, in view of the inherent uncertainty of the method. For the sake of completeness, we also report in Table 1 the energy results for the perhydrotriptycene stereoisomers obtained with $V^\circ$ 2.5 kcal mol$^{-1}$.

The program for the optimization of strain energy was used in the MOLBD 3 version described in ref. 10 by Boyd, while the trial structures necessary for the first iteration were generated by the program MOLGEN starting from an approximate geometry of the molecules. Iterations were carried out until corrections $\Delta x_i$ to Cartesian co-ordinates of the atoms had a root-mean-square value <0.003 Å.

*Results of geometrical calculations and comparison with X-ray structural data.* We applied Boyd's method of conformational energy optimization [10] to several stereoisomers of perhydrogenated derivatives of triptycene. The key to the names of compounds is given in Figure 1 which shows *ttt*, *ttc*, *tcc*, *ccc*, and *tc'c*, representing the most thermodynamically stable stereoisomers in decreasing order. In addition, we also investigated the molecule *cc'c* (Figure 1), which was isolated in an intermediate step of the hydrogenation process in spite of its relatively low stability,[2] as well as the partially hydrogenated compound A*c'c*.[2] In the following our analysis is confined to the most significant results; for a more detailed description of the *X*-ray structures of the compounds see *ttt* and *ccc* ref. 6, *tcc* ref. 5, *cc'c* ref. 3, and A*c'c* ref. 4. Although some overall features of *ccc* are discussed, no reference to its geometrical parameters is made, in view of the low accuracy of the *X*-ray results, which were strongly affected by large atomic motion. Furthermore, reference to the observed geometry of *ttt* is limited to the bond angles within the bicyclo-octane cage, since the other parameters are severely affected by thermal motion within the crystal. Finally, as far as the *X*-ray results for *cc'c* are concerned, our attention is restricted to those pertaining to the molecule not affected by structural disorder, neglecting the other one contained within the asymmetric unit. Unless otherwise stated, the observed and calculated values of a given geometrical parameter are reported as the average of the corresponding data derived from the crystal structures of *ttt*, *tcc*, *cc'c*, and A*c'c*; for both the observed and the calculated results, the associated root-mean-square error deviations were obtained either from the scattering of their separate values or from the average error standard deviation of each, depending on which value is the larger.

We have confined our analysis to bond angles and internal rotation angles, since the calculated C–C bond lengths never deviate by more than ±0.015 Å from their mean of 1.547 Å, in substantial agreement with observation.

TABLE 3

Comparison between some observed and calculated bond angles and torsion angles (°)*

| Angle | Cpd. | Obs. | Calc. | No. non-equiv. obsns. |
|---|---|---|---|---|
| $\alpha_1$ | *ttt* | 106.9(3) | 106.8(2) | 2 |
| | *ttc* | | 106.8(2) | |
| $\alpha_2$ | *cc'c*, *tcc* | 108.9(4) | 108.4(3) | 4 |
| | *ccc* | | 109.2(4) | |
| $\alpha_3$ | *tcc* | 105.1(3) | 103.5(1) | 1 |
| | *ttc* | | 103.3(2) | |
| $\alpha_4$ | *tcc* | 108.9(3) | 109.6(1) | 1 |
| | *ttc* | | 109.0(2) | |
| $\alpha_5$ | *tcc* | 108.8(3) | 106.9(1) | 1 |
| | *ttc* | | 106.7(2) | |
| | *tc'c* | | 106.4(1) | |
| $\alpha_6$ | *tcc* | 113.1(3) | 113.0(1) | 1 |
| | *ttc* | | 112.6(3) | |
| | *tc'c* | | 113.1(1) | |
| $\alpha_7$ | *cc'c* | 104.1(9) | 105.0(1) | 2 |
| | A*c'c* | 108.2(5) | 108.8(10) | 2 |
| | *tc'c* | | 105.4(1) | |
| $\alpha_8$ | *cc'c* | 116.3(3) | 114.1(1) | 2 |
| $\beta_t$ | *ttt*, *tcc* | 109.4(18) | 108.5(2) | 4 |
| | *ttc* | | 108.8(2) | |
| | *tc'c* | | 108.5(1) | |
| $\beta_c$ | *cc'c*, *tcc*, A*c'c* | 108.7(9) | 109.7(3) | 14 |
| | *ttc*, *ccc*, *tc'c* | | 109.7(5) | |
| $\phi_t$ | *tcc* | 25.7(5) | 27.1(3) | 1 |
| | *ttc* | | 28.7(3) | |
| | *ttt* | | 30.2(1) | |
| | *tc'c* | | 27.9(1) | |
| $\phi_c$ | *tcc* | 17.2(15) | 13.7(3) | 2 |
| | *cc'c* | 12.3(6) | 0.0(1) | 3 |
| | *ccc* | | 8.0(1) | |
| | *ttc* | | 16.1(1) | |
| | *tc'c* | | 12.8(1) | |

* For numbering see Figure 2. Subscripts *t* and *c*, attached to the β and $\phi$ angles, refer respectively to *trans*- and *cis*-substituted cyclohexane rings. The agreement index $s = \{(n-1)^{-1}\Sigma_i[q_i(\text{obs.}) - q_i(\text{calc.})]^2\}^{1/2}$ for bond angles is 1.4°

In the bicyclo-octane group BCO in Figure 2, Table 3 shows that the β angles are little affected by the type of co-ordination of the adjacent cyclohexane ring (*i.e.* where *t* or *c*), while each α angle is strongly influenced by both its adjacent rings. In particular, in the fully hydrogenated stereoisomers the largest and the smallest values are observed when two adjacent *cis* rings are directed towards each other ($\alpha_8$ 116.3 ± 0.3°) and away from each other ($\alpha_7$ 104.1 ± 0.9°); in the partially hydrogenated compound A*cc*, Table 3 shows that $\alpha_7$ increases to 108.2 ± 0.5°, probably because the substitution of an aromatic ring for the bulkier cyclohexane group tends to relax the intramolecular strain, decreasing the push of the two remaining cyclohexane rings one against the other. As an overall measure of the discrepancy between calculated and observed bond angles, the agreement index calculated according to ref. 11 is 1.4° (see heading of Table 3). No such index was calculated for the $\phi$ angles, in view of the shallow energy minima that may correspond to them (see later). No significant deviation from planarity was found for the aromatic ring, in agreement with observation. The value of the rotation angle $\phi$ (see Figure 2), defined along the bicyclo-octane frame, was appreciably larger when the related C–C bond belonged to a *trans*- (*ca.* 26°) rather than to a *cis*-ring (*ca.* 15°, see Table 3). The root-mean-square value found for this angle in bicyclo-octane from electron diffraction studies is 12.0 ± 1.5°, comparing fairly well with the values observed for $\phi_c$. The larger value of $\phi_t$ is clearly related to the strain involved with the ring closure of *trans*-substituted cyclohexane rings, compared to the *cis*-case. To illustrate this point Figure 3 shows the conformational energy plots for *ccc* and *ttt vs.* $\phi$, as minimized over all the geometrical parameters except the $\phi$ angle. The plot is symmetrical

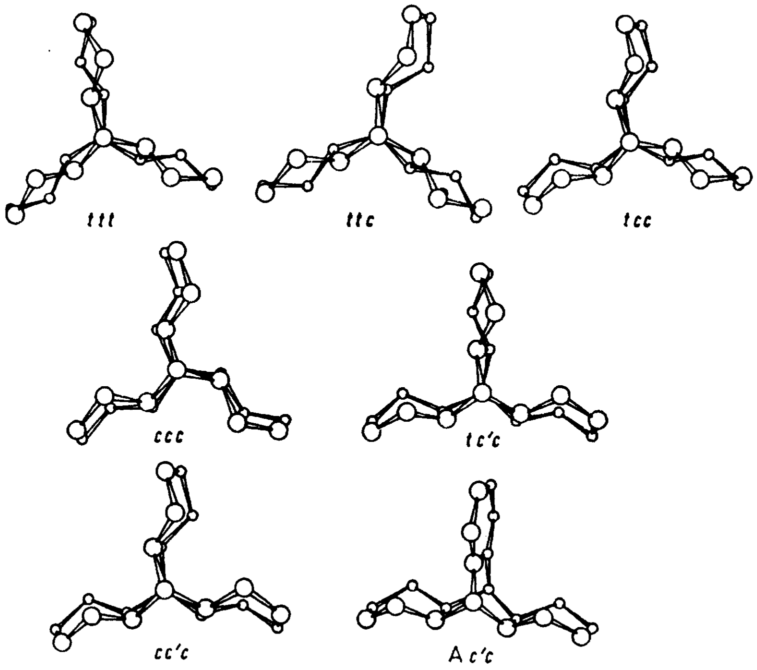


FIGURE 1 The molecules investigated in this paper: stereoisomers of perhydrotriptycene and the partially hydrogenated A*c'c*

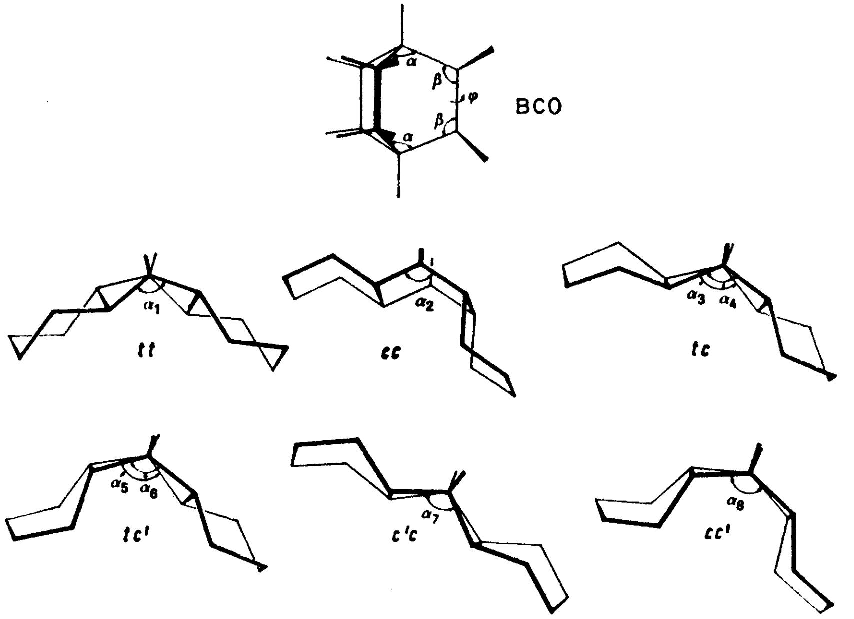


FIGURE 2 Bond and torsional angles selected for comparison between observed and calculated geometries

around 0° in *ccc*, as expected according to molecular symmetry, and approximately symmetrical around 30° in *ttt*. The curve is much broader in the former than in the latter case. Analogous plots for *cc'c* and *tcc* are technically more difficult to evaluate because of the lower symmetry of these molecules. However, it may be reasonably assumed that the results reported in Figure 3 may be extrapolated to them at least qualitatively, although the simultaneous presence of *trans* and *cis* rings should tend to narrow $E_c$ while broadening $E_t$, with some simultaneous shift of the energy minima. As for the *cc'c* stereoisomers, the lowest energy $\phi$ value is evaluated as 0° (*cf.* the corresponding value of *ca.* ±8° for *ccc*, see Figure 3). Although the disagreement with the experimental value (12.3°) is quite large, the energy difference between $\phi$ 0 and 12.3° probably does not exceed 0.2 kcal mol$^{-1}$, as a qualitative comparison with Figure 3 seems to suggest, considering the structural analogy between the *cc'c* and *ccc* stereoisomers.

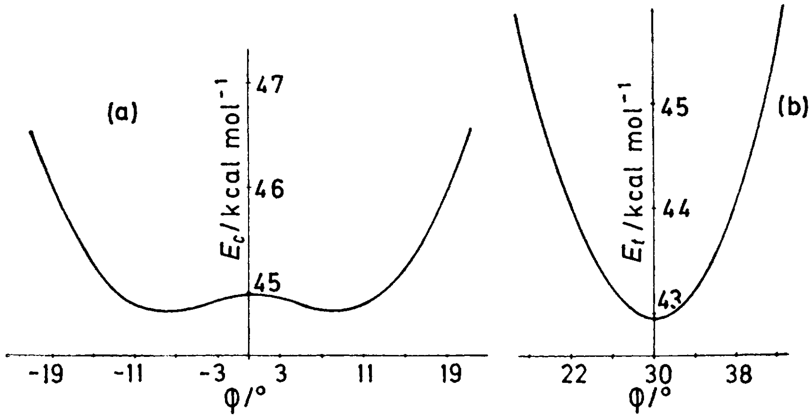


FIGURE 3 Conformational energy plots for (a), *ccc* ($E_c$) and (b), *ttt* ($E_t$) *vs.* $\phi$ (see Figure 2)

TABLE 4

Comparison between observed and calculated values of the ν angles *

| Angle | Cpd. | Obs. | Calc. | No. non-equiv. obns. |
|---|---|---|---|---|
| (*a*) *cis*-Substituted cyclohexane rings (boat conformation) | | | | |
| $\nu_1$ | *cc'c, tcc, Ac'c* | 112.1(7) | 112.4(2) | 14 |
| | *ttc, ccc, tc'c* | | 112.3(3) | |
| $\nu_2$ | *cc'c, tcc, Ac'c* | 109.9(14) | 111.0(5) | 14 |
| | *ttc, ccc, tc'c* | | 111.0(5) | |
| $\nu_3$ | *cc'c, tcc, Ac'c* | 112.3(9) | 112.6(2) | 14 |
| | *ttc, ccc, tc'c* | | 112.6(4) | |
| $\nu_4$ | *cc'c, tcc* | 115.7(13) | 115.6(14) | 10 |
| | *Ac'c* | 112.6(4) | 110.9(8) | 4 |
| | *ttc, ccc, tc'c* | | 114.5(6) | |
| (*b*) *trans*-Substituted cyclohexane rings (chair conformation) | | | | |
| $\nu_1$ | *tcc* | 108.8(3) | 109.1(9) | 2 |
| | *ttt, ttc, tc'c* | | 109.0(5) | |
| $\nu_2$ | *tcc* | 108.8(5) | 107.9(3) | 2 |
| | *ttt, ttc, tc'c* | | 108.0(2) | |
| $\nu_3$ | *tcc* | 113.4(2) | 113.3(1) | 2 |
| | *ttt, ttc, tc'c* | | 113.2(1) | |
| $\nu_4$ | *tcc* | 121.4(14) | 119.9(12) | 2 |
| | *ttt, ttc, tc'c* | | 119.3(7) | |

* For numbering scheme see Figure 4: The agreement index $s = [(n-1)^{-1}\Sigma_i(q_i^{\text{obs.}} - q_i^{\text{calc}})^2]^{1/2}$ is 1.3°.

Table 4 compares observed and calculated bond angles in the cyclohexane rings (Figure 4). The agreement is nearly always within the mean-square error (*s* 1.3°,[11] see Table footnote). As could be predicted, the largest values correspond to $\nu_4$ particularly when the ring is *trans*-substituted, in which case a larger strain in the bond angles is involved (see also Table 5, which compares, *e.g.* the bending energies of *ttt* and *ccc*).

*Relative Thermodynamic Stability of the Perhydrotriptycene Stereoisomers.* We used the results of our conformational calculations on the perhydrotriptycene stereoisomers to derive an approximate estimate of their relative free-energy, to be compared with the values from catalytic equilibration experiments at 172 °C.[2] We took into account the possible existence of different conformers of a given molecule, evaluating their conformational energy, unless it was too high to have any appreciable effect. For each stereoisomer, the approximate value of the free-energy was obtained from the partition function evaluated over the energy minima of the separate conformers, with complete neglect of both the energy and the entropy associated with molecular vibrations. The reason for making such an approximation was that the vibrational partition function of molecules containing so many degrees of freedom is critically dependent on the choice of the energy parameters, which are subjected to considerable uncertainty in their turn (neglecting the vibrational effects amounts to assuming that they are approximately equal for all stereoisomers). The entropy contribution associated with molecular symmetry as well as with the possible existence of optical antipodes was also taken into account.

Our analysis included all the stereoisomers reported in Figure 1, and was also extended to *tcc'* (differing from *tc'c* in that the two *cis*-substituted rings are oriented against each other) and *tt't* (Figure 5). While in this last case the minimum conformational energy is $>15$ kcal mol$^{-1}$ above that of *ttt* (the most stable isomer), thereby making the probability of its existence vanishingly small, the free energy of *tcc'* turns out to be very close (*i.e.* within 0.2 kcal mol$^{-1}$) to that of *cc'c*. We recall that, although both these molecules are not sufficiently stable to appear in the equilibrium mixture, *cc'c* has been isolated in the presence of Ru/C catalyst.[2] The existence of a large intramolecular strain associated with the simultaneous presence of oppositely connected *trans*-substituted rings (*i.e. t* and *t'*) is apparent from Figure 5; this conclusion may be safely extended to *tt'c*.

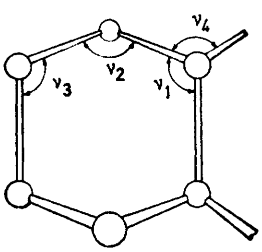


FIGURE 4 Key to bond angles of cyclohexane rings listed in Table 4

Low-energy conformers other than the most stable one were found in all the molecules investigated with the exception of *ttt*; most of them are associated with the boat and chair conformations of the *cis*-substituted cyclohexane rings, and, in the case of *ccc* and *cc'c* only, with the existence of two symmetrically equivalent energy minima (see Figure 3). It is remarkable that the most stable conformations of the cyclohexane rings are invariably boat and deformed chair, depending on whether they are *cis*- or *trans*-substituted, in full agreement with the *X*-ray data. It is apparent that this is related to the constraint imposed by the central bicyclooctane nucleus, which tends to keep its $\phi$ angle (see Figure 2) close to 0 °C, thus strongly favouring the aforementioned geometries. However, while the chair–boat rearrangement requires $>4$ kcal mol$^{-1}$ for the *trans*-substituted ring, the *cis*-substituted ring may undergo the reverse boat–chair rearrangement with an energy difference of between 1.1 and 2.1 kcal mol$^{-1}$ (see *e.g.* Figure 6).

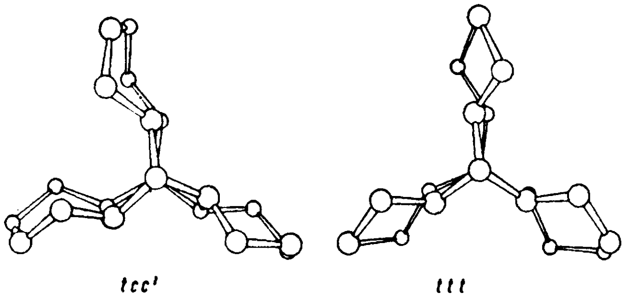


FIGURE 5 A view of *tcc'* and *tt't* showing highly strained conformations (steric interference between adjacent *cis*-cyclohexane rings in *tcc'*, large deformations of ring geometry in *tt't*)

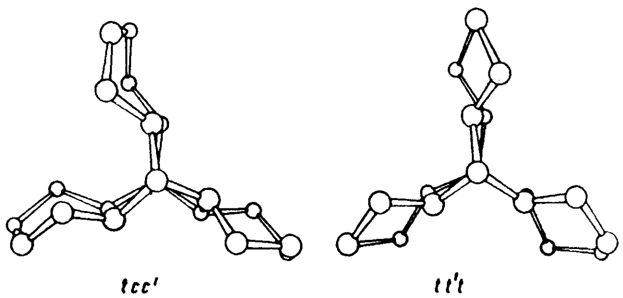


FIGURE 6 An example of a *cis*-attached cyclohexane ring with a deformed *chair* conformation (on the right)

Although the overall conformational energies of the four most stable steoisomers are within a comparatively narrow range (see Table 1), the relative contributions of the bond angle and of the rotational strain energies [*i.e.* the second and the third summation in equation (1)] may differ considerably. Table 5 shows the different contributions to the overall energy for the most important stereoisomers. While the most important contributors to the bond angle and to the torsional strain may be directly deduced from Tables 3 and 4, the relevant terms making up the non-bonded repulsive energy are derived from the C · · · C interactions between atoms separated by three bonds (if separated by two

TABLE 5

Different contributors to the conformational energy (kcal mol$^{-1}$) for the most stable conformers of the most important stereoisomers

| Stereoisomer | Bond-stretching | Bond-angle bending | Torsional | Non-bonded interaction | Total |
|---|---|---|---|---|---|
| *ttt* | 2.31 | 14.28 | 8.17 | 18.72 | 43.48 |
| *ttc* | 2.45 | 12.75 | 12.01 | 19.04 | 46.25 |
| *tcc* | 2.58 | 9.48 | 15.56 | 19.65 | 47.27 |
| *ccc* | 2.49 | 4.32 | 18.78 | 20.45 | 46.04 |

bonds the corresponding repulsive energy is assumed to be due to the bond-angle strain), and the H · · · H interactions involving at least one hydrogen belonging to a carbon atom of the bicyclo-octane nucleus. Within the limits of the assumption of additivity inherent with the methods of molecular mechanics, we conclude that while the bond-length strain-energy is essentially constant and the non-bonded interactions contribution ranges to within 1.7 kcal mol$^{-1}$ only, the rotational and bond-angle energies differ by as much as 10 kcal mol$^{-1}$ between the two extremes represented by *ttt* and *ccc*, tending to compensate each other.

Computer output containing the detailed numerical results for *ttt*, *tcc*, *ccc*, and *tc'c* has been deposited as Supplementary Publication No. SUP 22646 (37 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, Index issue, 1979.

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