EMPIRICAL FORCE FIELD CALCULATIONS OF SOME t- BUTYL
SUBSTITUTED CYCLOHEXANE COMPOUNDS

B. van de Graaf and B. M. Wepster

Laboratory of Organic Chemistry, Delft University of Technology

Julianalaan 136, Delft, The Netherlands

Recently, we discussed the conformations in solution of cis- and trans- 1,2-di-t- butyl-cyclohexane.[1] For the cis compound a chair conformation explained the experimental data. For the trans compound the preliminary conclusion was reached that it exists as a conformational mixture, a twist conformation and a diaxial chair conformation being the major components.

In order to obtain additional information about the conformations of trans-1,2-di-t-butyl-cyclohexane empirical force field calculations were carried out using a force field of Allinger et al.[2] and a modified version of the minimalisation procedure described by Boyd.[3] For a proper evaluation of the results we included in our calculations t-butylcyclohexane and cis- and, trans-1,4-di-t-butylcyclohexane. Minimum values obtained for the steric energies and the heats of formation derived[2] from them are given in table I.

The steric energy values calculated for the various conformations of cis-1,4-di-t-butyl-cyclohexane suggest that this compound in solution and in the gas phase exists as a conformational mixture, the twist 1 conformation being the major component. This agrees well with the available experimental evidence.[4-6] Also, the difference (3.3 kcal mol^{-1}) between the heats of formation calculated for cis- and trans-1,4-di-t-butylcyclohexane is certainly of the right order of magnitude when compared with the experimental value of 4.7 kcal mol^{-1} (liquid state).[4] In view of this we feel justified to conclude that the results of the calculations for trans-1,2-di-t-butylcyclohexane substantiate our preliminary conclusion cited above.

Furthermore, our results show that an evaluation[7] of the A-value of the t-butyl group from experimental data for di-t-butylcyclohexanes may be too naive. The same applies for the energy difference between the chair and twist conformations of cyclohexane since the force field gives this difference as 4.8 kcal mol^{-1}. The steric energies calculated for t-butylcyclohexane give the A-value of the t-butyl group as 4.8 kcal mol^{-1}. We consider this to be the best value available at the moment.

Several features in the calculated geometries reflect how the compounds avoid extreme non-bonded interactions: e.g. in both chair conformations of trans-1,2-di-t-butylcyclohexane the cyclohexane ring is considerably flattened. A detailed discussion of the calculated geometries

Table I.   Steric energies and heats of formation calculated for some $\underline{t}$-butyl substituted
cyclohexane compounds.[a]

Cyclohexane derivative	Conformation	Steric energy	ΔH_f (gas, 25°)
1 - $\underline{t}$ Bu	chair e	6.01	-53.96
1 - $\underline{t}$ Bu	chair a	10.82	
$\underline{\text{trans}}$-1,4-di-$\underline{t}$ Bu	chair e, e 1[b]	5.95	-78.14
$\underline{\text{trans}}$-1,4-di-$\underline{t}$ Bu	chair e, e 2[b]	6.02	
$\underline{\text{cis}}$ - 1,4-di-$\underline{t}$ Bu	twist 1[c]	8.95	-74.87
$\underline{\text{cis}}$ - 1,4-di-$\underline{t}$ Bu	twist 2[c]	10.07	
$\underline{\text{cis}}$ - 1,4-di-$\underline{t}$ Bu	chair 1[b]	10.38	
$\underline{\text{cis}}$ - 1,4-di-$\underline{t}$ Bu	chair 2[b]	10.73	
$\underline{\text{trans}}$ - 1,2-di-$\underline{t}$ Bu	twist	15.17	-68.90
$\underline{\text{trans}}$ - 1,2-di-$\underline{t}$ Bu	chair, a, a	15.28	
$\underline{\text{trans}}$ - 1,2-di-$\underline{t}$ Bu	chair e, e[d]	25.25	

a. Steric energies and heats of formation in kcal mol^{-1}. For each compound the heat of for-
mation is only given for the conformation with lowest energy. Contributions of other confor-
mations coexisting at 25° have been taken in account assuming ΔS (twist-chair)=0. b. See
text. c. Twist 1 both $\underline{t}$-butyl groups pseudo equatorial, twist 2 both $\underline{t}$-butyl groups isoclinal.
d. For this conformation several energy minima were found, the lowest value calculated for
the steric energy is given in the table.

will be given in a subsequent paper. However, we wish to point out that the force field predicts
both for an equatorial and for an axial $\underline{t}$-butyl group that its position with respect to the cyclo-
hexane ring differs (15 and 22 degrees respectively) from perfect staggered. This explains why
two minima were found for the chair conformations of $\underline{\text{cis}}$- and $\underline{\text{trans}}$-1,4-di-$\underline{t}$-butylcyclohexane.
The result for the equatorial $\underline{t}$-butyl group agrees with earlier force field calculations[8] and ex-
perimental evidence.[9]

<div align="center">REFERENCES</div>

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