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# CONFORMATIONAL ANALYSIS BY COMBINED AB INITIO AND MOLECULAR MECHANICS PROCEDURES: AB INITIO CALCULATIONS OF SOME DITERTIARYBUTYL-CYCLOHEXANES

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The most successful computational approach to the conformational analysis of medium-sized molecules with 30-40 atoms or more is presently based on molecular mechanics and empirical force fields. Because of their empirical nature, these procedures can at times lead to rather inconclusive results. In the case of cis-1,4-di-t-but-cyclohexane (I), e.g.[1], a chair or a boat were found as the ground state of the molecule (Table 1) depending on whether the force field of JTB [2] or of LW[3] was used in the conformational analysis of the molecule. For a series of similar systems[4] we are presently attempting to use ab initio calculations to produce additional data which might help to clear such contradictions.

For this study of I,standard single determinant molecular orbital theory[5] was used on the STO-3G minimal basis set level. The total energies were calculated for each of the three minimum energy conformations (chair, boat I, and boat II [1]) obtained for I by molecular mechanics using the force fields of JTB and LW. About 12-15 hours of computing time were needed for each conformation on the University of Arkansas IBM 370/158. The results are given in Table 1.

In contrast to the LW molecular mechanics results, boat I emerged as the most stable conformer of I, when both the JTB and the LW optimized coordinates were used as input to the STO-3G calculations. The STO-3G energy differences between boat I and the other minima seem to be greater than indicated by the experiment[1]. This may be a consequence of the well known limitations [6] of the STO-3G procedure. There is good qualitative agreement, however, in that both STO-3G and experiment favor boat I as the ground state compared to the chair and boat II as less stable local energy minima.

Similar calculations were also performed to test the hypothesis[7] that trans-1,2-di-t-but-cyclohexane (II) should have a diaxial-chair or a boat as ground state. The results (Table 1) indicate that both forms should indeed be of importance for samples of II. Because of the men-

Table 1. Cols. MM give the molecular mechanics results obtained by the JTB and LW force fields for I and II (energies in kcal/mole). Cols. STO-3G give the ab initio results (total energies in a.u., relative energies in kcal/mole, dipole moments in debye) which were obtained when the JTB and LW optimized coordinates were used as input to the STO-3G calculations.

| | MM | | STO-3G | | | | DIPOLE | |
|---|---|---|---|---|---|---|---|---|
| | JTB | LW | JTB(total) | JTB(rel) | LW(total) | LW(rel) | JTB | LW |
| cis-1,4-ditertiarybutyl-cyclohexane | | | | | | | | |
| chair | 1.7 | 0.0 | -540.067590 | 3.78 | -540.070347 | 3.76 | 0.11 | 0.12 |
| boat I | 0.0 | 1.9 | -540.073614 | 0.0 | -540.076345 | 0.0 | 0.01 | 0.0 |
| boat II | 1.8 | 3.4 | -540.069395 | 2.65 | -540.074085 | 1.42 | 0.05 | 0.05 |
| trans-1,2-ditertiarybutyl-cyclohexane | | | | | | | | |
| ch(diax) | 0.0 | 0.0 | -540.052997 | 0.0 | | | 0.10 | |
| ch(dieq) | 19.8 | 14.6 | -540.031956 | 13.20 | | | 0.03 | |
| boat | 0.8 | 7.4 | -540.052631 | 0.23 | | | 0.07 | |

tioned limitations of the STO-3G approximation[6], however, clear identification of the ground state of II is not possible. Only the JTB coordinates of II were used in the ab initio calculations because of the length of the computations.

The application of ab initio procedures to medium-sized systems is an exciting aspect of these studies. It is still impossible to use ab initio techniques in an energy optimization scheme relaxing all the parameters of molecules of this size. It seems to be a promising approach, however, to use the ab initio procedures as objective standards in connection with other methods, e.g. to test the conformational conclusions derived from molecular mechanics computations.

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