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# TETRA-TERT-BUTYLTETRAHEDRANE HAS T SYMMETRY[‡]

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Summary. Calculations using a variety of force fields indicate that tetra-tert butyltetrahedrane has ground state T symmetry and is therefore chiral.

We recently showed that molecules of the type t-$Bu_4M$ (M = group IVA element) exhibit T symmetry in the ground state[1] In connection with these studies, our interest was aroused by the recently reported synthesis of tetra-tert-butyltetrahedrane (TTT).[2] If the four-carbon framework of tetrahedrane were to be considered a super-atom of type M, one might then expect that TTT would also exhibit ground state T symmetry Indeed, empirical force field (EFF) calculations support this expectation.

The results of calculations on TTT using four force fields[3] are presented in Table I. In these calculations,[4] the tetrahedrane frame was assumed to have local $T_d$ symmetry, all six C-C bond lengths were held fixed at 1.482 Å[5] and all four C-$C_q$ bonds[6] were fixed along the $C_3$ axes[7] While the assumption of skeletal $T_d$ symmetry does not affect structures with $T_d$ and T symmetry, it does constitute a constraint on structures with any other symmetry (e g., $S_4$, see below)

In all cases the ground state is predicted to have T symmetry, with all four tert-butyl groups twisted by ca 14° and all twelve methyl groups by ca 2-6°, all in the same direction from a staggered $T_d$ conformation. That is,

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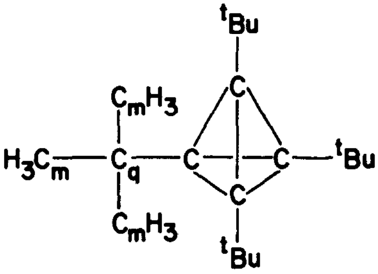
[‡] Dedicated to Professor A Dreiding on the occasion of his 60th birthday

Table I. Calculated Structures of Tetra-tert-butyltetrahedrane (TTT)



| Force Field[a] | Symmetry | Rel. Energy (kcal/mol) | r(C-$C_q$) (Å) | θ($C_m$-$C_q$-$C_m$) (deg) | φ(C-C-$C_q$-$C_m$) (deg) |
|---|---|---|---|---|---|
| Allinger 1971 | $T$ | 0 | 1.555 | 111.1 | 46.4 |
| | $S_4$ | 3.62 | 1.560 | 110.5 | 47.9 |
| | $T_d$[b] | (5.32) | 1.562 | 109.8 | 60[b] |
| Allinger 1971 (no stretch-bend) | $T$ | 0 | 1.519 | 110.7 | 45.8 |
| | $S_4$ | 3.87 | 1.524 | 110.1 | 47.6 |
| | $T_d$[b] | (5.95) | 1.526 | 109.3 | 60[b] |
| EAS | $T$ | 0 | 1.532 | 109.5 | 46.1 |
| | $T_d$[b] | (5.02) | 1.539 | 108.6 | 60[b] |
| Allinger 1977 | $T$ | 0 | 1.487 | 109.7 | 45.4 |
| | $T_d$[b] | (4.03) | 1.495 | 108.7 | 60[b] |
| MUB-2 | $T$ | 0 | 1.452 | 109.1 | 47.6 |
| | $T_d$[b] | (1.71) | 1.454 | 108.8 | 60[b] |

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[a] See reference 3.

[b] Four dihedral angles (φ(C-C-$C_q$-$C_m$)) were frozen at 60°. This constraint enforces approximate $T_d$ symmetry. This conformation does not correspond to a local energy minimum.

TTT is chiral[8] However, enantiomerization is expected to be facile since the structure with $T_d$ symmetry, a possible achiral transition state, lies only ca 2-5 kcal/mol above the ground state Another possible enantiomerization pathway proceeds through a form with $S_4$ symmetry As in the other t-Bu$_4$M compounds,[1] a local minimum with $S_4$ symmetry was found using the Allinger 1971 force field[9]

In our previous study[1] it had been found that, using the Allinger 1971 force field, plots of $\Theta$ ($C_m$-$C_q$-$C_m$) and of $\Delta E$ (the difference in energy between the $S_4$ and $T$ forms) vs. $r^o$ (the "preferred" M-$C_q$ bond length[1]) were linear over the range of values studied. If one includes TTT in this plot by considering the $C_4$ skeleton to be a super-atom with $r^o$ = 2.42 Å,[10] the points for TTT ($\Delta E$ = 3.62 kcal/mol, $\Theta$ = 111.1°, see Table I) lie very close to the same lines.[11]

We add a note of caution. The lack of parameters for the tetrahedrane frame precludes full relaxation. Since our assumption of $T_d$ frame symmetry constitutes a constraint on the $S_4$ (but not on the $T$) conformation, $\Delta E(S_4-T)$ is somewhat overestimated. In addition, due to the large C-C-$C_q$ bond angles,[7] the C-$C_q$ bond distance is somewhat suspect[12] Nevertheless, as in the other t-Bu$_4$M compounds,[1] the main conformational features are governed by nonbonded interactions between the tert-butyl groups, and the conclusion that TTT is chiral is therefore tenable.[14]

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## References and Notes

1 L. D. Iroff and K Mislow, *J. Am Chem. Soc.*, *100*, 2121 (1978).

2 G Maier, S Pfriem, U Schäfer, and R Matusch, *Angew Chem. Internat. Ed* , *17*, 520 (1978). We thank Professor Maier for sending us a preprint of his paper prior to publication.

3 (a) Allinger 1971 N L Allinger, M. T. Tribble, M A. Miller, and D H Wertz, *J. Am. Chem. Soc* , *93*, 1637 (1971), (b) EAS E M Engler, J D Andose, and P v.R Schleyer, *ibid* , *95*, 8005 (1973), (c) Allinger 1977 N L Allinger, *ibid* , *99*, 8127 (1977), (d) MUB-2 S Fitzwater and L S. Bartell, *ibid* , *98*, 5107 (1976), see also footnote 4 in L S Bartell, *ibid.*, *99*, 3279 (1977).

4. The program used (BIGSTRN) is available from QCPE, Department of

Chemistry, Indiana University, Bloomington, Indiana 47401 (J. D. Andose, et al., QCPE, 10, 348 (1978)). All structures were relaxed using a modified version of the pattern search technique, with an energy criterion of 0.005 kcal/mol over one iteration. Torsional angles were held fixed at a given value by imposing a large quadratic potential.

5. This is the bond length calculated for tetrahedrane by *ab initio* methods. J. M. Schulman and T. J. Venanzi, J. Am. Chem. Soc., 96, 4739 (1974).
6. For definitions of C, $C_q$, and $C_m$, see the picture at the top of Table I.
7. This second assumption is necessary since the large C-C-$C_q$ bond angle (ca. 144.7°) is well outside the parametrization of any force field.
8. Concerning the chirality of the parent compound, tetrahedrane, the reader's attention is directed to the remarkable report by our esteemed colleague, Professor A. Troischose, Zürich (Nachr. Chem. Techn., 18, 127 (1970)).
9. An $S_4$ minimum was not located using the other force fields.
10. That is, the distance from the center of the tetrahedrane to C (0.91 Å) plus the "preferred" C-$C_q$ bond length (1.512 Å).
11. See Figure 2 in reference 1.
12. Using MUB-2, diminished 1-3 (Urey-Bradley) nonbonded interactions lead to an unusually short C-$C_q$ bond (1.452 Å). On the other hand, the stretch-bend term in the Allinger 1971 force field leads to lengthened bonds (1.555 Å). However, such a term is unrealistic. In fact, an opening of the C-C-$C_q$ angle should lead to increased s character in the orbital on C which is used to form the C-$C_q$ bond. Therefore this bond should be shorter than "normal". This effect, which has been discussed previously,[13] is not accounted for in this force field. Omitting this term for the C-C-$C_q$ angles does indeed lead to a much shortened bond (see Table I).
13. M.H.P. Ardebili, D. A. Dougherty, K. Mislow, L. H. Schwartz, and J. G. White, J. Am. Chem. Soc., 100, 7994 (1978).
14. Twisting of tert-butyl groups in substituted cyclohexanes has previously been noted, cf., e.g., C. Altona and M. Sundaralingam, Tetrahedron, 26, 925 (1970), D. H. Faber and C. Altona, J. Chem. Soc., Chem. Comm., 1210 (1971), H. van Koningsveld, Acta Crystallogr., B28, 1189 (1972), B. van de Graaf and B. M. Wepster, Tetrahedron Lett., 2943 (1975).

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