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A CAUTIONARY NOTE ON ENERGY MINIMA DERIVED FROM FORCE FIELD CALCULATIONS

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The conditions for true energy minima and partial energy maxima in force field calculations can only be checked when the Newton-Raphson minimization approach is used[1]. A cautionary note must be made as to energy minima obtained by other minimization methods. This can be demonstrated by the following comparisons of published energy minima with those obtained by us using the Newton-Raphson minimization method.

Recently, Ōsawa, Collins, and Schleyer[2] questioned Allinger's *gauche* hydrogen hypothesis[3] because of its force field dependence. Several of their arguments are based upon the comparison of steric energy components of the *anti* and *gauche* conformers of 2,3-dimethylbutane using the Engler force field[4]. We doubt whether the *gauche* conformation presented is a real minimum; if so, it is not the only and lowest one. Data on this compound obtained by us using the Engler force field are given in Table I.

We are convinced that we applied this force field correctly since we can reproduce both geom-

Table I. Data calculated for some conformations of 2,3-dimethylbutane[a].

		minima[b]		transition states[b]	
		anti (A)	*gauche* (G)	G → A	G → G
Point group		C_{2h}	C_2	C_2	C_{2v}
ϕ H-C-C-H[c]		180.00°	70.72° (53.4°)	119.55°	0.00°
Steric energy	stretch	0.574 (0.58)	0.540 (0.55)	0.567	0.908
	bend	1.190 (1.23)	1.501 (1.65)	1.774	2.975
	twist	0.310 (0.27)	0.317 (0.16)	1.885	1.704
	non-bonded	4.238 (4.23)	3.869 (3.93)	4.498	6.408
	total	6.312 (6.32)	6.226 (6.29)	8.724	11.995
Conformational energy[d]		0.497 (0.44)	0.000 (0.00)	2.498	6.180

[a] Energy data in kcal mole^{-1}, conformational energy at 25°; data in parentheses from ref. 2.
[b] The final second derivative matrix gives six eigenvalues equal to zero and in the case of transition states also one value less than zero. [c] Dihedral angle about the central bond.
[d] The conformational energies of the *gauche* conformer and the *gauche* → *anti* transition state have been corrected by RT ln 2. The data are given relative to the *gauche* conformer.

etry and steric energy components of tri-*tert*-butylmethane from the Cartesian coordinates give in ref. 4 exactly. However, we find the minimum 0.056 kcal mole^{-1} lower with differences up to 0.96 kcal mole^{-1} in the steric energy components.

The results given in Table I for the *anti* conformer are almost identical[5] but those for the *gauche* conformations differ significantly. Most striking is the difference between the values of the H-C-C-H dihedral angle about the central bond. Our value is almost equal to the one reported[3] using the Allinger 1973 force field (about 72°). Rotation about the central bond did not reveal any additional minimum. Data on the transition states are given in Table I.

The second example concerns the energy and geometry of *axial tert*-butylcyclohexane. In the minimum there is no mirror plane through the carbon atoms 1 and 4 of the cyclohexane ring and the central atom of the *tert*-butyl group[6]. The "minimum" of ref. 2 is what we find to be the transition state between the two *axial tert*-butylcyclohexane enantiomers. Relevant data are given in Table II.

Table II. Data calculated for some conformations of *tert*-butylcyclohexane[a].

	minima[b]		transition state[b]
	equatorial (E)	*axial* (A)	A → A
Point group	C_1	C_1	C_{1v}
Ø H-C-C-C[c]	171.74°	158.96°	180.00°
Total steric energy	12.661	17.390	18.087
Strain energy	5.421 (5.45)	10.150 (10.87)	10.857
Conformational energy[d]	0.000 (0.00)	4.729 (5.42)	1.118

[a-b] See note a-b of Table I. [c] Dihedral angle about the bond between the cyclohexane ring and the *tert*-butyl group. [d] The conformational energies of the *equatorial* and *axial* conformers have been corrected by RT ln 2. The data of the *axial* conformer are relative to the *equatorial* one, those of the *axial* → *axial* transition state relative to the *axial* conformer.

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