The Eclipsed Non-alternating Ground-state Conformation for 1,1,2-Tri-t-butylethane. Molecular Mechanics Calculations and NMR Spectrum

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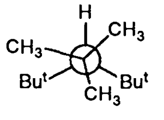
Staggered conformations of the title compound are calculated by Allinger's MM282 molecular mechanics program to be less stable than a conformation in which t-butyl groups and ethane hydrogens are near to eclipsed with dihedral angles of +5.4°, +23.5° and −3.2°. The Newman projection is non-alternating with the H–C–H projection within the t-butyl-C-t-butyl projection. The vicinal NMR proton–proton coupling constant reflects this eclipsing. Evidence is adduced for other molecules with near-to-eclipsed ground states.

Conformations far from standard staggered ones are found in relatively simple hydrocarbons when carbon–carbon bonds have several tertiary alkyl groups at either end. In tri-t-butylmethane,[1] and similar compounds,[2] the staggered conformation **2** of each t-butyl group is a transition state between two skewed conformations, like **1** and **3**, and there is a high barrier to interconversion of these conformations, by way of **2**. Isopropyl-di-t-butylmethane exists[3] in a conformation like **4**, showing rotation away from staggered to reduce methyl–t-butyl interactions until the H–C–C–H dihedral angle is near to 90°.

In these conformations the Newman projection is alternating as in ethane itself, *i.e.* looking at *e.g.* **4**, as one progresses clockwise, successive groups are alternately attached to the front and back atoms of the bond whose Newman projection is being studied. Mislow and co-workers[4] have called attention to the possible significance of conformations with non-alternating Newman projections. These are likely to occur near the rotational transition state for even simply substituted ethanes, if only because thereby three pairs of substituents need not be exactly eclipsed simultaneously. Osawa and co-workers,[5] using other molecular mechanics calculations, have supported this idea. Mislow also suggested the possibility of a ground-state conformation being non-alternating. His calculations[4] for 1,1,2,2-tetra-t-butylethane, known from NMR studies[6,7] to be much distorted from staggered, suggested just such a conformation, shown diagrammatically as **5** interconverting with its rotational isomer **6**. Osawa's calculations[5] disagreed with this, predicting the distorted, but still alternating, structure **7**. Recently the structure of two analogous 1,2-di-t-butyl-1,2-diadamantylethanes has been determined by X-ray diffraction[8] and shown to be alternating, if greatly distorted, as in **8** with two sets of eclipsing interactions. The more likely structure for tetra-t-butylethane is therefore like **7**, in which the asterisked groups can move apart by rotation without increasing eclipsing elsewhere. In the non-alternating conformation **5**, rotation apart of the signalled groups increases eclipsing.



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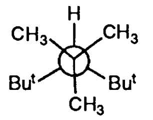

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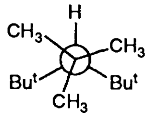

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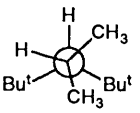

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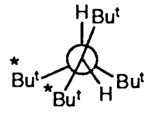

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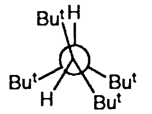

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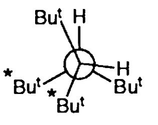

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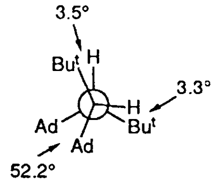

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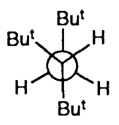

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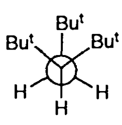

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This last point directs attention to the title compound, 1,1,2-tri-t-butylethane (**9**), with, crucially, one t-butyl group fewer. Compound **9** has two staggered, alternating conformations represented diagrammatically as *gauche* **10**, which has an enantiomer, and *anti*, **11**. The compound is known,[9] and in its ${}^1H$ NMR spectrum has a coupling of 3.6 Hz between the methylene and methine protons.[9b] This agrees particularly poorly with the *gauche* conformation **10**, where a coupling of *ca.* 7.1 Hz, the value found in a simpler $R_2CH–CH_2R'$ molecule, 2,4-dimethylpentane, and reflecting an average of 60° and 180° dihedral angles, might be expected. The *anti* conformation **11**, with two 60° dihedral angles, might give rise to such a coupling constant, but looks unpropitiously crowded. The examples quoted in the introduction suggest that the idealised *gauche* conformations could become more stable by rotation about the central bond to move the vicinal t-butyl groups apart, so molecular mechanics calculations, using Allinger's MM282 program,[10,*] have been used to investigate the rotational potential about the ethane bond.

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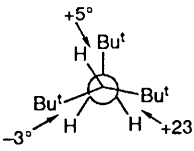
[*] Referees have asked for comments on the reliability of such a program and its minimisation procedure. Optimisation was terminated when $\Delta E = 0.003\,52$ (= $0.000\,08N$) kcal mol^{-1}. The global minimum was reached by minimisation from several points on the profile while other minimisations led to the discovery of the incoherently skewed minimum **14**. The program derives its parameters from experimental heats of formation of hydrocarbons, including highly branched ones, and these and its minimisation procedures have been widely used (U. Burkert and N. L. Allinger, *Molecular Mechanics*, ACS Monograph 177, 1982, ch. 4) for distorted saturated hydrocarbons with no indication of false metastable minima.

Table 1 Calculated structures of stable conformational minima for **9**

Conformation and description	**12** Non-alternating eclipsed[a–c]	**10** Alternating[a] *gauche*	**11** Alternating[a] *anti*	**14** Non-alternating eclipsed,[a] incoherent skewing
Energies/kcal mol^{-1}				
Relative steric energy	0.00	4.29	7.15	1.17
Compression	4.94	5.06	4.95	4.57
Bending	9.56	11.23	15.48	9.78
Stretch-bend	1.11	1.11	1.29	1.04
Van der Waals, 1,4	9.08	9.87	10.78	9.78
Van der Waals, other	1.59	2.37	1.03	0.95
Torsional	7.10	8.03	7.01	8.43
Total steric energy	33.38	37.67	40.53	34.55
Dihedral angles/°[d,e]				
C(2)–C(3)–C(4)–H	+5.4 (+58.6)	+23.5 (+101.8)	+176.9 (+24.7)	−6.4 (+14.2)
H–C(3)–C(4)–C(5)	+23.5 (+38.1)	+43.9 (+87.6)	−54.3 (+44.2)	+3.0 (+65.2)
H–C(3)–C(4)–C(10)	−3.2 (+57.0)	+11.7 (+65.7)	+45.6 (+105.9)	−28.8 (+79.4)
Bond lengths/Å[e]				
C(3)–C(4)	1.563	1.566	1.569	1.563
C(3)–C(2)	1.560	1.557	1.560	1.563
C(4)–C(5)	1.587	1.586	1.577	1.577
C(4)–C(10)	1.586	1.583	1.585	1.581
Bond angles/°[e]				
C(2)–C(3)–C(4)	121.9	123.3	127.4	122.6
C(3)–C(4)–C(5)	111.0	110.5	116.4	113.2
C(3)–C(4)–C(10)	113.7	113.1	116.711	111.0
C(5)–C(4)–C(10)	118.5	120.4	121.6	120.2

[a] There exists an enantiomeric version of this conformation with dihedral angles of opposite sign. [b] The enantiomeric conformation is **13**. [c] ΔH_f = −76.05 kcal mol^{-1}. [d] Each geminal t-butyl group has two such values, so only the arithmetically smaller one is given. The angles in brackets are CH_3–C–C–C dihedrals for each t-butyl group. The smallest positive such value is quoted in each case. [e] The structure is labelled $(CH_3)_3C(2)–C(3)H_2–C(4)H[–C(5)(CH_3)_3][–C(10)(CH_3)_3]$.



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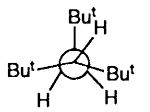

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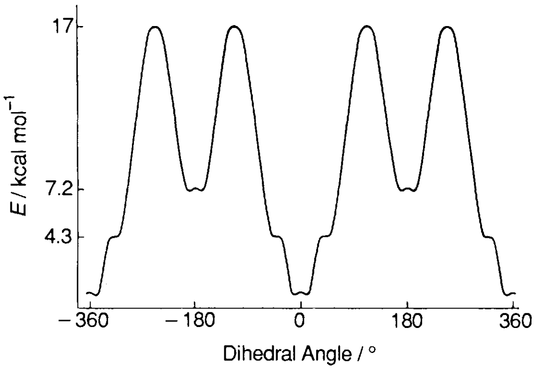

Fig. 1 Calculated steric energy relative to the ground state as the dihedral angle (lone t-butyl)–C–C–(lone H) varies

Results

Table summarises the results of molecular mechanics calculations and shows that, while distorted *gauche* and *anti* minima do exist, there is a considerably more stable conformation **12**, which equilibrates with its enantiomer **13**. In these ground state conformations dihedral angles along the central ethane bond are near-to-eclipsed, and substituents are non-alternating in the Newman projection.

It is an important feature of a conformation like **13**, which is related to the perfectly staggered conformation **10** by anticlockwise rotation of the front group, that there be concomitant rotation about all other carbon–carbon bonds in the molecule, in the same anticlockwise sense (coherent skewing), for long range interactions are thereby reduced.[1] There exists a conformation **14**, not shown but like **13** except that the lone t-butyl group is skewed in the opposite sense. Conformation **14** is, as expected, less stable than **12** but, in the course of exploring the rotational potential of **9**, minimisation from several high energy conformations leads to **14** rather than **13**. This points to the value of confirming the coherence of skew in a structure before designating it as the local minimum.

All conformations show abnormally long C–C bonds, and large C–C–C bond-angles. The relative instability of the *gauche* and *anti* conformations appears, from the energy terms in Table 1, to be due mostly to bond-angle strain, and to repulsive van der Waals interactions. The conformation **12**, although eclipsed, does not have abnormally high torsional interactions compared with **10** and **11**. The values in parentheses in Table 1 show that eclipsed t-butyl groups have much more normal internal dihedral angles than other t-butyl groups, so overall the torsional term is, if anything, better for the eclipsed conformation.

The option of the molecular mechanics program[10] to drive the H–C–C–t-butyl angle X was used to calculate a rotational potential energy diagram. Fig. 1 shows a version of this, made symmetrical to correct for difficulties in moving from the *gauche* to the *anti* conformation by driving a single dihedral angle. The

Table 2 Calculated coupling constants ($^3J_{CH_2CH}$/Hz) for various conformations of Bu$^t_2$CHCH$_2$R, for **9** (R = Bu^t) and **15** (R = Me)

			Calculated coupling constant[a]/Hz					
Compound and conformation	H–C–C–H dihedral angle/°		Garbisch	Karplus	Altona	Pachler	Mean	Obs.[b]
9 eclipsed, **12**	115	135	4.43	4.65	5.02	6.99	5.22	
9 *anti*, **11**	49	57	4.61	3.60	4.33	4.85	4.35	3.6
9 *gauche*, **10**	96	158	4.82	4.64	5.17	6.42	5.26	
15 eclipsed	114	142	5.30	5.14	5.80	7.13	5.84	3.7

[a] See text. [b] See refs. 9 and 26.

double-minimum of the eclipsed ground-state conformation has a barrier of 0.14 kcal mol^{-1} to interconversion of **12** and **13** through the exactly eclipsed $X = 0°$ conformation. There is a similar double minimum about $X = 180°$ in the *anti* conformation **11**. The *gauche* conformation **10** is a very shallow minimum separated by a barrier of 0.05 kcal mol^{-1} from the global minimum.

The H–C–C–H dihedral angles Z in the lone stable conformation of **9** can be linked to the three bond CH$_2$ to CH coupling constant J by a Karplus[11] relationship of the form $J = a\cos^2 Z + b\cos Z + c$. Various authors[11,14] have suggested values of the constants a, b and c and we have used these versions in the past[15] to investigate distorted saturated acyclic hydrocarbons. Modifications[16] of such formulae to accommodate electronegative substituents are unlikely to be relevant here.

Table 2 lists the calculated values of the CH$_2$–CH coupling constant from the various equations, and the dihedral angles calculated for the conformations, non-alternating eclipsed **12**, *gauche* **10** and *anti* **11**. The experimentally observed value of J is 3.6 Hz,[8h] while all conformations predicted by molecular mechanics are calculated to have coupling constants greater than that observed, the minimum energy eclipsed conformation **12** having a calculated value of 5.22 Hz.

Discussion

The discrepancy between calculated and experimental coupling constant values for all conformations fits with our previous experience,[3,17] also for strained saturated acyclic hydrocarbons in unusual conformations; very generally, as here, the observed coupling constant is *ca.* 2 Hz less than the mean of the values predicted by the various relationships. These versions of the Karplus relationship often take reference values for coupling constants, at dihedral angles far removed from staggered, from strained polycyclic compounds. It seems that these relationships do not apply satisfactorily to such uncommon dihedral angles in acyclic molecules with strain of a different kind.

It might be argued that the molecular mechanics calculations are wrong simply because they predict a near-to-eclipsed conformation, even though they have been successful for other far from staggered structures.[1b,2b,3,5,8] However, in the parameterisation, experimental rotational barriers, *i.e.* eclipsed structures, as well as staggered ground states, are used, *i.e.*, parameterisation tries to avoid the weakness that we have just indicated for calculated coupling constants.

The potential energy diagram in Fig. 1 predicts that, during 360° of rotation, only one conformation is populated, and that **9** has a one-fold barrier to rotation, if one sets aside the low energy libration through the perfectly eclipsed conformation. At room temperature *ca.* one molecule in a thousand exists in a non-coherent eclipsed conformation. Using the calculations of the rotational transition state, the average lifetime for a molecule in the coherent eclipsed conformation before undergoing a 360° rotation is 0.3 s, if there is no entropy of activation.

The two striking features calculated for the preferred conformation **12** are that it is non-alternating and eclipsed, although in the minimum energy position dihedral angles are not exactly 0°. That the three large substituents each eclipse hydrogen atoms is much less significant than their being as far away from each other as possible, so two t-butyl groups at one end of the bond and one at the other, quite naturally take up the eclipsed conformation.

A sure way to reduce more important interactions in such a crowded molecule is for H–C–H bond-angles to close down below the tetrahedral value, and t-butyl–C–t-butyl bond angles to open up, so a non-alternating projection is a natural consequence of the eclipsing in **12**. The tetra substituted ethane **7** is not quite non-alternating because it is rather far removed from perfect eclipsing.

For a perfectly eclipsed bond the sum of the three smallest dihedral angle arithmetic values is 0°, while for perfect staggering it is 180°. For the ground-state conformation of **9**, this 'eclipsing sum' is 32.1°. There are a few other examples from the literature of acyclic carbon–carbon bonds which are near-to-eclipsed. Mislow and co-workers[4] have calculated that the racemic configuration of 1,2-di-t-butyl-1,2-di(2,6-dimethylphenyl)ethane has a non-alternating conformation with an eclipsing sum of 49.7°. In 1,2-diphenylethane substituted with t-butyl groups in the 2,4- and 6-position of each phenyl ring, the eclipsing sum is calculated to be 62.8°, and the X-ray diffraction determination of the structure suggests that it may be somewhat less.[18] It has already been reported[19] that the most stable conformation of a molecule as simple as 3-t-butylpentane is calculated to be alternating, but near-to-eclipsed, with an eclipsing sum of only 53°. As might be expected, calculations of some crowded compounds, both cyclic[20] and acyclic,[21,22] have produced near-eclipsed and non-alternating conformations as the second most stable conformation.

An experimental indication of the energy associated with a t-butyl group eclipsing a hydrogen is provided by the methyl group rotational barrier in 2,2-dimethylbutane[23] which is smaller than 4.9 kcal mol^{-1}, the measured t-butyl group rotational barrier, and so, at most, 2 kcal mol^{-1} greater than that in ethane.[24] While it is tendentious to rely on additivity, the 6 kcal mol^{-1} that three such eclipsing interactions might imply for conformation **12** of tri-t-butylethane, are undoubtedly much less than the many parallel 1,3-interactions present in a perfectly staggered ground state for that molecule. To that extent, the suggestion that the relief of such ground state interactions takes the molecule as far as the eclipsed ground state of **12** and **13** is not unreasonable.

Following from all these observations, it may be that in any molecule RCH$_2$CHAB, if A and B sufficiently restrict the available space, the substituent R will be most stable in a rotational position near to eclipsing the undemanding proton. Any 2,2-di-t-butylethyl derivative $(Bu^t)_2CHCH_2X$ falls into this class, and the example when X = methyl shows how this applies. Calculations have been reported[25] for $(Bu^t)_2$-$CHCH_2CH_3$, 1,1-di-t-butylpropane (**15**), giving a ground-state conformation with dihedral angles of 7.4°, 14.7° and 31.8°. This conformation is markedly eclipsed (eclipsing sum 53.9°), but less so than **9**, so it is not unexpected that it is alternating. The CH–CH_2 coupling constant in this molecule is 3.7 Hz,[26] very similar to that observed in **9**, and the H–C–C–H dihedral angles are calculated to be 114.4° and 142.1°. The instability of the perfectly staggered conformation of RCH_2CHAB is due to parallel 1,3-interactions, so for most marked eclipsing, a fair degree of branching in R, A and B is desirable.

Further, rather different RCH_2CHAB molecules showing near-to-eclipsed conformations may emerge. If A and B are only moderately space-demanding, but are inflexible, a sizeable group R may prefer to eclipse a hydrogen atom as a means of distancing itself from A and B. Such inflexibility may arise if A and B are incorporated in a ring system, and the equatorial conformation of 1,8-dimethyl-9,10-dihydroanthracene with a 9-ethyl-, or 9-neopentyl- substituent or the all-equatorial conformation of 1-ethyl- or 1-neopentyl-2,6-dimethylcyclohexane are possible examples. An averaged vicinal coupling constant of about 3.6 Hz may serve as one criterion of eclipsing. The same rigidity of the ring, however, may make a non-alternating conformation unlikely.

Acknowledgements

Useful discussions with Professor L. Lunazzi, with the help of a NATO collaboration grant, are gratefully recognised.

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Paper 0/03840G
Received 21*st August* 1990
Accepted 25*th October* 1990