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CONFORMATIONS AND INTERNAL ROTATION OF TRI-ISOPROPYLMETHANE. DYNAMIC NMR AND MOLECULAR MECHANICS STUDIES

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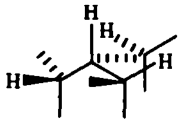
Abstract—The isopropyl group hydrogens of tri-isopropylmethane, 2,4-dimethyl-3-(1-methylethyl)-pentane spend about 75% of time *gauche* to the unique methine hydrogen and about 25% *anti*, as shown by the NMR coupling constant. The temperature dependence of the NMR spectrum shows that interconversion of stable conformations or sets of conformations requires overcoming a barrier of 6.6 kcal/mol. Molecular mechanics calculations suggest that conformations with all three isopropyl hydrogens *gauche*, in the same sense or those with two *gauche* in the same sense and one *anti* are the most stable, although dihedral angles in these conformations are quite different from 60°. The calculations predict a barrier rather lower than that observed, but give a description of the complicated series of partial rotations that allow interconversion of enantiomeric stable conformations.

The isopropyl group has intriguing steric properties for, observed laterally, in the direction of the Me groups, it appears as large as a t-Bu group, yet a view from exactly the opposite side suggests that it is no larger than an Me group. As long as rotation of the group is relatively easy, the isopropyl substituent will be able to profit from this steric anisotropy to reduce interactions where otherwise congestion might seem to be great.

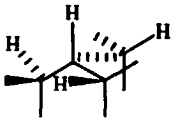
Tri-isopropylmethane, 2,4-dimethyl-3(1-methylethyl)-pentane 1 appears to have a considerable range of reasonably stable conformations available to it, for each isopropyl group may adopt one of three more or less staggered rotational states with respect to the central C atom. We report how NMR studies allow an experimental determination of the conformations favoured, and of the barrier to conformational interconversion, while molecular mechanics calculations indicate the detailed structure and energy of all conformations whether populated or not, and the likely rotational pathway.

The overall conformational possibilities are easy to envisage and to represent, but it is worth discussing the question of representation explicitly at the outset. We will represent staggered conformations with dihedral angles of 60° for the most part, but acknowledge that the likely minimum energy conformation may have dihedral angles somewhat different from 60° since small rotations may dramatically reduce interactions. This point is illuminated by the calculations and will be treated in the discussion.

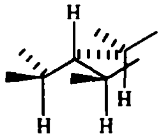
If all isopropyl groups have the hydrogen *gauche* to the unique hydrogen a conformation like 2 results. Note that Me groups need not be shown explicitly. We call this the (+g, +g, +g) conformation since looking along each bond towards the central carbon the (unique H)-C—C—H dihedral angle is positive. There is an enantiomeric (−g, −g, −g) conformation 3. When the isopropyl hydrogens are all *anti* to the unique hydrogen the (a, a, a) conformation 4 is obtained.



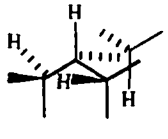
2(+g,+g,+g)



3(−g,−g,−g)

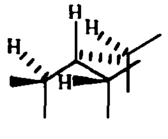


4(a,a,a)

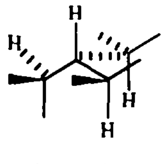


5(−g,−g,a)

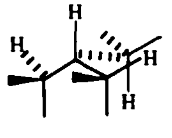
There are several other conformations 5 to 9, with different combinations of (+-*gauche*), (−*gauche*) and (*anti*) and there are various equivalent and enantiomeric forms of each. For example three equivalent forms of the (−g, −g, a) conformation exist, depending on which isopropyl group is *anti*; 5 is one of these. For each of these three, there is one enantiomeric (+g, +g, a) form.



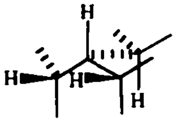
6(−g,−g,+g)



7(−g,a,a)



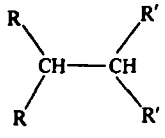
8(−g,+g,a)



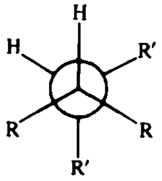
9(+g,−g,a)

It is not only the diversity of possible conformations however that makes tri-isopropylmethane notable, but also its relation to three problems of current interest.

Firstly, each of the isopropyl-to-carbon bonds in **1** can be considered in terms of a tetrasubstituted ethane **10a**. Recently, two other such ethanes **10b** 2,3-dimethylbutane[1] and **10c** tetra-t-butylethane[2] have been shown to have unexpected conformational properties, with *gauche* conformation **11** or **11′** uncommonly stable compared with the *trans*, **12**. Simple conformational analysis suggests that **12** with two R—R *gauche* interactions should be more stable than **11** or **11′** with three such interactions, but in **10b** the three conformations are found to be of equal energy[1a] at −160°, while for **10c** only *gauche* conformations can be detected[2a] at temperatures up to 200°. These results can be explained in terms of the opening of the R—C—R and R′—C—R′ bond angles to a greater or lesser extent depending on the size of R so that an *anti* conformation such as **13** has the groups R and R′ close together and a *gauche* conformation as in **14** minimises R—R′ interactions. In fact symmetrical (60°) representations **11** and **12** give a poor representation of the minimum energy conformations of the *gauche* and *anti* types. Tri-isopropylmethane **10a** with substituents R of size intermediate between **10b** and **10c** may illuminate this problem.



10a R = Me, R′ = *i*−Pr
10b R = R′ = Me
10c R = R′ = *t*−Bu



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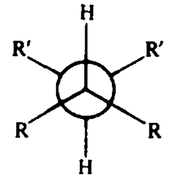

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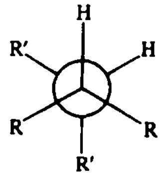
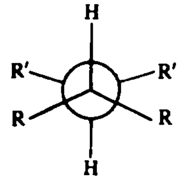


11′



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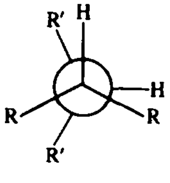

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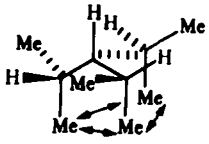
The second point of interest is the possibility of geared rotation of the iso-propyl groups—two adjacent isopropyl groups can minimise their interactions during rotation by moving in opposite senses as do gears.[3] This is important for tri-isopropylmethane for, whatever combination of −*gauche*, *anti*, and +*gauche* conformations has lowest energy—other than (*anti*, *anti*, *anti*)—there is an enantiomeric conformation of the same energy in which −*gauche* and +*gauche* conformations are interchanged. There will be a complex series of internal rotations of isopropyl groups which link these conformations. However, while two of the isopropyl groups may rotate together in opposite senses like meshed gears, the third, if it rotates so as to mesh with the first must inevitably clash with the second. Calculation of the barrier, to conformational interconversion and an experimental determination of it are thus of interest.

The third point of interest arises from an analysis of the interactions in conformations such as **2**, **4**, and **5**. In the (g, g, g) conformation, there are three methyl-hydrogen parallel-1,3-interactions[4] and three Me–Me ones; the latter are shown in **15**, an elaborated version of **2**. The (a, a, a) conformation **4** has three methyl-methyl parallel-1,3-interactions. The other conformations **5** to **9** each has a different combination of such interactions. It may be that such parallel-1,3-interactions are more significant than the more obvious *gauche* torsional interactions along the isopropyl-to-central-carbon bond. The best indication that such interactions are important would be that the molecule distorts to diminish them, and the easiest way of achieving this is that each isopropyl group rotates in the same sense, away from a symmetrical 60° conformation like **15**. Structure **16** when compared with **15** illustrates how parallel-1,3-interactions can thereby be reduced. It has been shown in certain cases,[2d,5,6] of which tri-t-butylmethane[5] and hexamethylethane are examples. that such torsional angles quite far removed from 60° do lead to reduced conformational energy.



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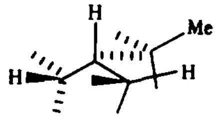

16

We have therefore carried out an NMR and molecular mechanics investigation of tri-isopropylmethane. At best NMR should give information on the stable populated conformations and the rate of interconversion among them. Molecular mechanics calculations[7] give estimates of the enthalpy of all conformations including unpopulated ones, by a minimisation procedure. It can thus be adapted to give a potential energy diagram for conformational interconversion. It is particularly reliable for calculating the enthalpy of conformations of hydrocarbons.

RESULTS AND DISCUSSION

Molecular mechanics

Table 1 shows the calculated enthalpies[8c] of the seven general types of conformation **3** to **9** for tri-isopropylmethane minimised by allowing bond angles, bond lengths and dihedral angles to relax, using the MM2 programme.[8] Also shown are the dihedral angles in the minimum energy structure of each conformation.

Table 1. Minimum energy staggered conformations[a] calculated energy and dihedral angles

Conformation	Calculated enthalpy, kcal/mol	Dihedral angles[b]		
−g, −g, a	17.36	−63.1	−95.5	179.0
−g, −g, −g	17.57	−81.8	−82.2	−80.0
−g, a, +g	19.36	−70.9	180.0	47.5
−g, −g, +g	19.70	−82.2	−84.1	50.0
−g, +g, a	20.40	−95.1	72.2	−171.4
−g, a, a	21.06	−78.9	−137.9	−180.0
a, a, a	25.51	−151.7	−151.5	−153.4

[a] For each conformation, there exists an equal energy enantiomeric conformation where −g and +g have been interchanged and +x° is replaced by −x° as the dihedral angle.

[b] The apparent angle between the isopropyl C—H bond and the unique C—H bond, when looking towards the central carbon atom from the isopropyl group.

The seven types can be divided into one high energy conformation (a, a, a) and then pairs of conformations of similar energy, see Table 1. The members of each pair differ by one interchange of *gauche* and *anti*.

The dihedral angles calculated are so different from 60° and 180° that it seems pointless to discuss these in terms of the parallel-1,3-interactions present in the idealised structures **3** to **9**. It is rather the extent to which these interactions can be relieved that determines the relative stabilities of conformations. Thus the (a, a, a) conformation is the least stable, yet as shown in **3**, it has the same number of Me–Me interactions as the (g, g, g) form and three fewer Me–H ones. In the (a, a, a) form however the Me–Me interactions reinforce each other in a buttressing sense which is much less marked in other conformations. A closer consideration of the two most stable conformational types is worthwhile.

In the (g, g, g) conformation, the reduction of non-bonded interactions is effected by rotation of each isopropyl group in the same sense by 20° or so, away from the 60° staggered position. As seems reasonable, this rotation is in the sense which increases the H—H dihedral angle, rather than in the opposite sense, since by this former means lesser eclipsing interactions are encountered. This means that in the (−g, −g, −g) conformation the rotation is in an anticlockwise sense, while it is clockwise in the (+g, +g, +g) conformation.

In the (g, g, a) conformation, the *anti* group and one of the *gauche* ones have near to normal values of the dihedral angle, while the second *gauche* conformation has a dihedral angle enlarged to greater than 90°. The (a, a, a) conformation is striking in that the dihedral angle is almost 30° removed from 180°, each group rotating in the same sense. The perfectly staggered (180°, 180°, 180°) conformation with its obvious Me–Me interactions (see **4**) is thus a transition state between two more stable conformations where rotation away from 180° is in either a clockwise or anticlockwise sense. We might better talk about (−a, −a, −a) and (+a, +a, +a) conformations on either side of (180°, 180°, 180°), separated by 56° rotation.

What the calculations suggest is that at ambient temperature there are substantial amounts of (g, g, g) and (g, g, a) conformations, and less than 5% of all others. We will use this as a basis for discussing the NMR results.

NMR Spetra

The 400 MHz spectrum of tri-isopropylmethane shows a coupling constant of 4.53 Hz between the unique hydrogen (at δ 0.83) and the three methine hydrogens (at δ 1.89), and a doublet (J = 7.0 at δ = 0.93) for the isopropyl methyl groups.[9] The methyl doublet broadens and splits into two signals of equal intensity at $\delta = 0.88$ and $\delta = 0.99$ below −135° indicating a conformational isomerisation occurring about 49 times per second at that temperature.

The vicinal coupling of the unique hydrogen was measured at −100° and at +201°. In the first case it was not sensibly different from the 4.53 Hz value found at ambient probe temperature, and at high temperature it was 4.4 Hz, very slightly less than the ambient value.[11]

The natural abundance ^{13}C-NMR spectrum of tri-isopropylmethane recorded with proton decoupling comprises three singlets at δ 22.06 (—$\underline{\mathrm{C}}\mathrm{H}_3$), δ 27.46 (CH_3—$\underline{\mathrm{C}}$) and δ 55.70 (i-Pr—$\underline{\mathrm{C}}$). On lowering the temperature below about −127° the methyl carbon signal splits to a doublet at δ = 19.30 and δ 25.08, but down to −158°, there is no further broadening of these or other signals which can be attributed to conformational processes. The proton–carbon one-bond coupling constants are 125.0 ± 1.0 Hz for the unique carbon, 125.3 Hz for the isopropyl methine hydrogens and 124.4 Hz for the Me groups.

The 4.53 Hz coupling constant of the unique hydrogen is the most useful experimental indication of the mixture of conformations adopted, since its magnitude depends on its *average* dihedral angle relationship to the isopropyl hydrogens. Since we know intuitively and calculations have also shown us that dihedral angles in *gauche* and *anti* arrangements are not 60° or 180°, respectively, it is useless to look for individual models of such a *gauche* or *anti* coupling constant.

Instead on the instigation of a referee we have chosen to accept the molecular mechanics values of $\mathrm{H}_{\mathrm{unique}}$-C—C—H dihedral angles shown in Table 1, and to calculate therefrom the average ^{3}J coupling constant to be expected for the (g, g, g) conformation and the (g, g, a) conformations using various available relationships of the Karplus type.[12a–d] The results obtained are shown in Table 2 and all suggest that there is rather more of the (g, g, a) conformation than the (g, g, g), if it be

Table 2. Calculated average coupling constants for the (g, g, a) and (g, g, a) conformations[a] and the conformational equilibrium position based thereon[b]

	Equations used	Calculated $^3J_{(g,g,g)}$ Hz	Calculated $^3J_{(g,g,a)}$ Hz	% (g, g, a)[b]	ΔG_0[c]
Garbisch[12a]	$J = 12.95\,(\cos^2\phi - 0.02\cos\phi)$	0.25	5.12	88	0.53
Karplus[12b]	$J = 7.76\cos^2\phi - 1.1\cos\phi + 1.40$	1.41	4.67	96	1.24
Altona[12c]	$J = 13.24\cos^2\phi - 0.91\cos\phi$	0.16	5.55	81	0.21
Pachler[12d]	$J = 7.19 - 1.65\cos\phi + 5.12\cos 2\phi$	2.06	6.56	55	−0.54

[a] Based on the equations shown and on the dihedral angles in Table 1.

[b] From these calculated ^3J values and the experimental ^3J value of 4.53 Hz.

[c] Assuming there are three equivalent (g, g, a) forms for each (g, g, g), then at 300 K, $\Delta G_0 = 2.3R \times 300 \log[(\%/3)/(100-\%)]$. A minus sign means that the (g, g, g) conformation is more stable.

correct to restrict discussion to those two types of conformation. When allowance is made for the fact that there are three possible (g, g, a) conformations for each (g, g, g) one, the former appears to be more stable than the latter by a few hundred calories/mol.[12e]

That the coupling constant is smaller at 200° suggests that the population of the (g, g, g) conformations is greater there, which accords well with that conformation being the less stable.

Minimum energy structures as calculated molecular mechanics bond angles and bond lengths

Table 3 shows bond angles for the (g, g, g) and (g, g, a) conformations and these calculated and measured for the even more crowded molecule tri-t-butylmethane.[5]

There is calculated to be little lengthening of bonds in **1**, the longest being the isopropyl to central carbon bond of 1.554 Å. Comparable lengthenings were calculated for tri-t-butylmethane which disagreed with markedly greater lengthenings actually found[5] in the electron diffraction structural determination, see Table 3.

The three isopropyl groups repel each other so that the i-Pr—C—i-Pr bond angle is 115.2°. The associated H—C—i-Pr angle is 102.9°. At the isopropyl methine carbon, the methyl groups do not appear to repel each other, since the bond angle is calculated to be 108.5°, but both Me—CH—CH bond angles do open up. At these centres it is once again the H—C—Me_3 and H—C—CH angles which are compressed. In individual methyl groups H—C—H bond angles are slightly compressed and the C—C—H bond angles are somewhat opened up.

It is interesting that some of the calculated bond angle and dihedral angle distortions are greater for tri-isopropylmethane than for tri-t-butylmethane. This is undoubtedly a consequence of the anisotropy of the isopropyl group which means that distortion to relieve

Table 3. Calculated geometric parameters for tri-isopropylmethane, and tri-t-butylmethane and electron diffraction results for the latter compound

	$(i\text{-}Pr)_3C{-}H$ calculated for		$(t\text{-}Bu)_3C{-}H$	
	(g, g, g)	(g, g, a)	calculated[b]	observed[5a]
C—H_{unique}	1.115	1.115	1.088–1.112	1.111
CH—C_3	1.554	1.558	1.538–1.601	1.611
C—CH_3	1.544 (g) 1.538 (a)	1.537–1.544	1.528–1.559	1.548
H_{unique}—$\hat{C}$—C	102.9	104.0 (g) 104.3 (g) 106.2 (a)	98.6–104.2	101.6
R—$\hat{C}$—R	115.2	112.0 (g) 113.9 (g) 115.1 (a)	114.2–117.2	116.0
C—$\hat{C}$—Me	111.6 (g) 115.8 (a)	112.5 (g) 114.0 (g) 116.0 (a)	112.5–115.2	113.0
Me—$\hat{C}$—Me	108.5	106.7 (g) 110.2 (g) 110.6 (a)	103.1–106.2	105.8
Δ_C(H_{un}—C—C—Me)[a]	21.1	13.2	13.7–16.4	10.8
Δ_C(C—C—C—H)	0.3 (g) 5.2 (a)	12.5	11.4–13.2	18.0

[a] The average amount by which dihedral angles differ from 60° or 180°.

[b] The numbers quoted are the upper and lower limits of the values given in Table 9 of reference 5*c* and Table 4 of reference 5*d*.

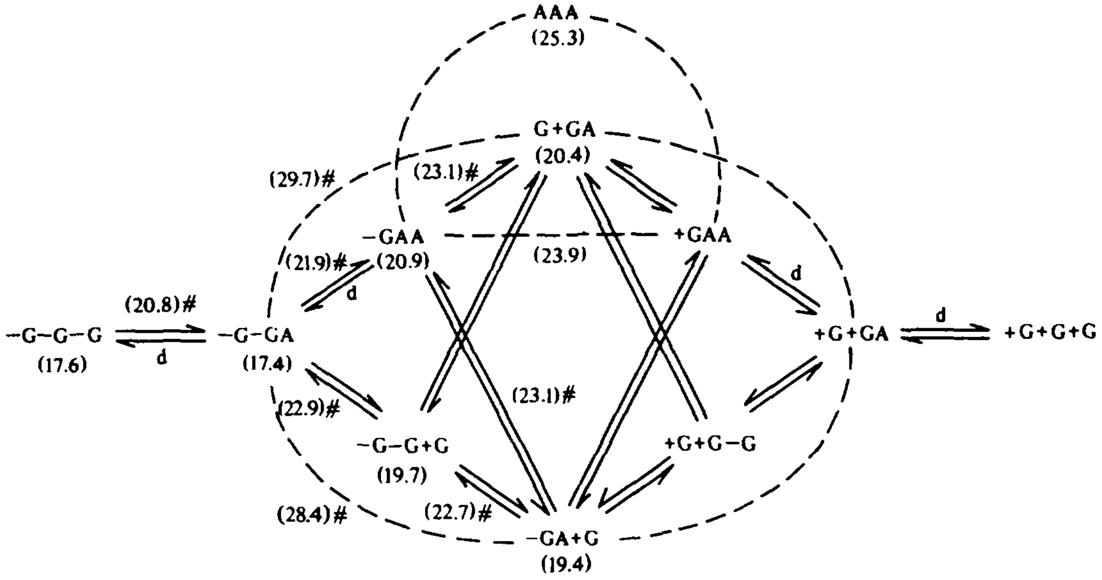

Fig. 1.

strain encountered by the methyl groups can go further because the concomitant increase in strain at the hydrogen of the isopropyl group is less.

Conformational interconversion in tri-isopropylmethane

The single relevant experimental observation we have made is that the methyls of an isopropyl group become nonequivalent in the NMR at low temperatures as a conformational interconversion process becomes slow on the NMR timescale. No other signals change so there is still a considerable degree of conformational averaging even at low temperatures.

The dihedral drive option in the MM2 programme[8] allows the calculation of the likely pathway and activation enthalpy for interconverting conformations, and using this we have obtained the extended diagram shown in Fig. 1. There is a plane of symmetry vertically through the middle, so all that is said about the left hand ('minus *gauche*') side applies *mutatis mutandi* to the right hand ('plus *guache*') side.

The first point to emerge is that there is a low barrier (3.4 kcal/mol by calculation) to the interconversion of the two stable conformational types (g, g, g) and (g, g, a).

The 'minus' set of conformations is separated from the 'plus' set by a succession of barriers, and intermediates which are the five other types of conformation **4**, **6**, **7**, **8**, and **9**. The high-energy point on these two sets is calculated to have a minimum value of 22.7–17.4 = 5.3 kcal/mol. There are several similar high energy points, so there are many more or less likely routes of interconversion.

Both the (− g, + g, a) and (− g, a, + g) conformations are metastable intermediates located symmetrically between the 'minus' and 'plus' sets. Any molecule arriving at these intermediate states is equally likely to return whence it came, or to go on to the enantiomeric set of conformations, hence a transmission coefficient of 0.5 ought to be used in relating the frequency of conformational exchange to the barrier which thus becomes 6.6 kcal/mol. The agreement between the calculated barrier, 5.3 kcal/mol, and the experimental one is not particularly good, but it is quite common that molecular mechanics calculations underestimate barriers.[6]

It is difficult to judge whether the entropy of activation is likely to be positive or negative, so complex are the possibilities for the ground state and transition state. In any case the quality of the spectra obtained at − 135°, does not encourage attempts to determine this parameter from the temperature-dependence of line shapes.

Thus the picture we derive is of two sets of conformations, the 'plus *gauche*' and the 'minus *gauche*'. Within these sets, two types of conformations, (g, g, g) and (g, g, a) are of rather greater stability than the others, and are populated to similar extents. A given molecule has a relatively long lifetime in one set (about 0.02 s at − 135°) during which it interconverts rapidly among principally the (g, g, g) and (g, g, a) conformations, before it interconverts to the other set. This interconversion is by way of an intermediate symmetric (− g, a, + g) or (− g, + g, a) conformation.

The various interconversion routes in the figure differ simply in the sequence by which each of the isopropyl groups pass through the two stages *gauche* → *anti* → opposite *gauche*. In principle, interconversion of sets could also be achieved by rotation through conformations where the isopropyl hydrogen eclipses the unique hydrogen. This directly interconverts 'minus *guache*' and 'plus *gauche*' conformations of the isopropyl group concerned, but calculation suggests that the barrier encountered in such a process is about 10 kcal/mol, which eliminates such a rotation as a likely route of interconversion.

It is worth noting that the conformational analysis of a compound with an identical range of conformations has recently appeared.[16] In the compound Me—C$(CH_2Cl)_3$, three conformations are populated. Defining them by the dihedral relationship of the chlorine atoms and the central methyl group, they are (a, + g, − g), 58%; (a, g, g), 34%; (g, g, g), 8%.

The calculations do not suggest that there is ever a concerted rotation of two isopropyl groups over a composite barrier, but that at most there are short areas of rotation where it is energetically favourable for two isopropyls to rotate together. In terms of the procedure of driving one dihedral angle which is how the programme operates, this means that for a time, as one dihedral angle moves away from a value that produces a local minimum, a second isopropyl group appears to be rotating in the minimising procedure. As driving continues however there is a discontinuity in energy, associated with a sudden change in the optimised dihedral angle of the second isopropyl group, which when considered in terms of rotation, has the characteristics of a gear slipping.

Returning to the first point of the introduction, and thus considering **1** as 1,1-dimethyl, 2,2-diisopropylethane, **10a**, once again *gauche* conformations seem to be particularly stable. Detailed analysis of the long-range interactions in the molecule explain this, and the fact that it is discrepant with what is found in butane hardly seems surprising.

There is strong support in the calculations for the third phenomenon mentioned in the introduction, that of dihedral angles quite different from 60° and 180°. While we do not doubt that such deviations, obtain in reality, those values reported in Table 1 are a direct reflection of the parameterisation of the MM2 programme to include such variations of dihedral angle.

There are several further aspects of the proton and ^{13}C-NMR spectra that merit discussion. The striking aspect of the proton NMR spectrum is that the unique hydrogen has a chemical shift $\delta = 0.83$,[9] much higher upfield than the tertiary hydrogen in many other trialkylmethanes and yet not as far as one or two others, see Table 4. When one adduces the downfield chemical shift of bridgehead protons in bicyclic hydrocarbons ($\delta = 2.20$ in norbornane, for example) it is clear that this highfield shift can be linked to there being on average relatively many C—C bonds *gauche* to the hydrogen in question, and relatively few *anti*. For **1** that means a relatively large population of *anti* conformations. The chemical shift in tri-t-butylmethane which must have three methyl groups *anti* to the unique hydrogen bears this out well.

The ^{13}C chemical shifts are only in moderately good agreement with those calculated on the basis of correlations with simpler hydrocarbons,[14] see Table 5. This no doubt reflects the distortion present in **1** and it is noticeable that the disagreement is in the same sense as but less marked than that of the more strained tri-t-butylmethane. The one bond coupling constant of the unique carbon, 125.0 ± 1.0 Hz, is in no way unusual and similar to that in tri-t-butylmethane.

Table 4. Chemical shift[13] of the methine proton in $R_1R_2R_3CH$

R_1	R_2	R_3	δ_{C-H}
Me	Me or Et	Me, Et, i-Pr or t-Bu	1.27 to 1.72 (7 examples)
i-Pr	i-Pr	i-Pr	0.83
Et	i-Pr	i-Pr	0.80
Et	Et	t-Bu	0.725
t-Bu	t-Bu	t-Bu	1.38

Table 5. Carbon-13 chemical shifts, observed[a] and calculated[b] for tri-isopropylmethane and tri-t-butylmethane

	$\underline{C}H_3$		$\underline{C}$-CH_3		H—$\underline{C}$—R_3	
	obs	calc	obs	calc	obs	calc
$(i\text{-}Pr)_3CH$	22.6	20.6	28.1	26.3	56.0	56.9
$(t\text{-}Bu)_3CH$	35.1	29.2	39.1	35.8	65.2	67.6

[a] This work and reference 5*e*.

[b] Using the parameters derived in reference 14.

EXPERIMENTAL

Compound **1**, was prepared by the original lit. method.[15] Proton NMR spectra were recorded at 400 MHz and 200 MHz, ^{13}C-NMR spectra at 50 MHz in approximately 1 : 1 $CHF_2Cl:CHFCl_2$ solns with solute concentration about 0.1 M (for H) and 0.5 M (for ^{13}C). Low temp spectra were recorded with a digitation of 3 points/Hz (^{13}C) and 6 points/Hz (^{1}H).

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since they allow a coupling constant of 0 Hz when the dihedral angle is 90°, at which point Karplus[12b] gives J = 1.40 Hz, and Pachler[12d] gives J = 2.00 Hz. We know of at least two hydrocarbons where J is less than 1 Hz, and our calculations predict several important dihedral angles near to 90°.

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