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ROTATION OF GEMINAL ISOPROPYL GROUPS. DYNAMIC N.M.R. OF DIMETHYL—DIISOPROPYL CYCLOPROPANE

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Summary The title compound exists as an equilibrium of two conformations, that with isopropyls geared being slightly more stable than that where they clash. The interconversion barrier is 6.5 kcal/mol.

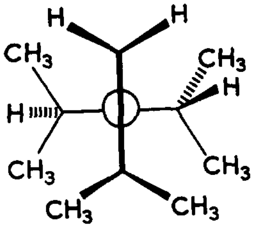
Isopropyl groups are sterically anisotropic, appearing small when encountered from one side, and large from the opposite side. The interplay of two adjacent isopropyl groups is particularly intriguing since 'small-1' interlocking with 'large-2' (static gearing[1]) seems a likely minimum on the rotational cycle and there is a second minimum when 'large-1' interlocks with 'small-2'. A likely maximum in the interconversion of these two occurs when 'large-1' more or less clashes with 'large-2'.

As a recent review has shown,[2] much novel information has emerged from the study of such groups attached to the same[3] or to neighbouring atoms[4] in a planar molecular framework. Likewise, two isopropyl groups attached to a single sp^3-hybridised centre turn out to have considerable conformational interest.[5] We now report an intermediate situation with two isopropyl groups attached to the same carbon atom of a cyclopropane ring, in which two different kinds of conformation are populated.

1,1-Dimethyl-2,2-diisopropylcyclopropane, 1, was obtained as a rearranged byproduct[6] of the acid catalysed dehydration of t-butyl-di-isopropylcarbinol. The proton nmr spectrum[7] of 1 is temperature-dependent. Below about -100 °, signals broaden, and on further cooling complex changes take place particularly in the methyl and methine region. Fortunately, the upfield ring-methylene region of the spectrum is less confused, the room-temperature single at δ = 0.13 becoming a doublet (δ = 0.37 and -0.14) and a singlet (δ = 0.10), of relative intensity 8.2:1.

The more stable conformation must have the two sides of the cyclopropane plane non-equivalent and is reasonably the one with the isopropyl groups statically geared, *i.e.* 2 or its enantiomer, or a somewhat skewed version of such structures.

The less stable conformation is more interesting, for the two sides of the cyclopropane ring are equivalent. A conformation like 3 where both isopropyl groups present their hydrogens towards the substituted ring or a skewed version thereof, *viz.* 4 or its enantiomer, are most likely. The free energy difference between the two kinds of conformation is 0.49 kcal/mol at -155 ° and the barrier to their interconversion is 6.5 kcal/mol at about -138 °.



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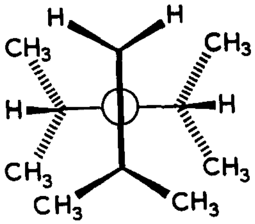

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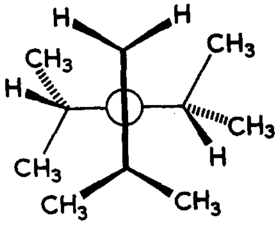

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The form with static gearing of isopropyl groups, 2, is thus the most stable, but the demands of the substituted ring are almost great enough to favour a form where both isopropyl groups gear with the ring and more or less clash with each other.[3]

REFERENCES

1. W.D. Hounshell, L.D. Iroff, D.J. Iverson, R.J. Wroczynski, and K. Mislow, *Isr. J. Chem.*, (1980), *20*, 65.
2. U. Berg, T. Liljefors, C. Roussel, and J. Sandström, *Acc. Chem. Res.*, (1985), *18*, 80.
3. I. Pettersson and U. Berg, *J. Chem. Soc. Perkin II*, (1985), 1365.
4. a. U. Berg and C. Roussel, *J. Amer. Chem. Soc.*, (1980), *102*, 7848.
   b. J. Siegel, A. Guttierez, W.B. Schweizer, O. Ermer, and K. Mislow, *J. Amer. Chem. Soc.*, (1986), *108*, 1569.
5. a. J. Reny, C.Y. Wang, C.H. Bushweller, and W.G. Anderson, *Tetrahedron Lett.*, (1975), 503. b. L. Lunazzi, D. Macciantelli, and L. Grossi, *Tetrahedron*, (1983), *39*, 305. c. J.E. Anderson, K.H. Koon, and J.E. Parkin, *Tetrahedron*, (1985), *37*, 4151.
6. A close analogy exists, G.J. Abruscato and T.T. Tidwell, *J. Org. Chem.*, (1972), *37*, 4151.
7. δ = 0.13,s,2H; δ = 0.96,d,$J\sim$7.5hz,6H; δ = 1.03,d,$J\sim$7.5hz,6H; δ = 1.20, s,6H; δ = 1.73,sept.,$J\sim$7.5hz,2H.

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