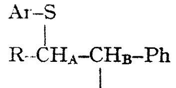
Conformation Involving *gauche* t-Butyl Groups

By D. C. BEST, GARY UNDERWOOD, and C. A. KINGSBURY*
(*University of Nebraska, Lincoln, Nebraska* 68508)

THE bulky t-butyl-group might be expected to impose severe conformational restraints in acyclic molecules[1], *cf.* cyclohexanes.[2] However, in n.m.r. studies of many acyclic pairs of diastereomers, very low vicinal coupling constants were found for t-butyl substituents quite unlike those for isopropyl or other large substituents (Table).[3]

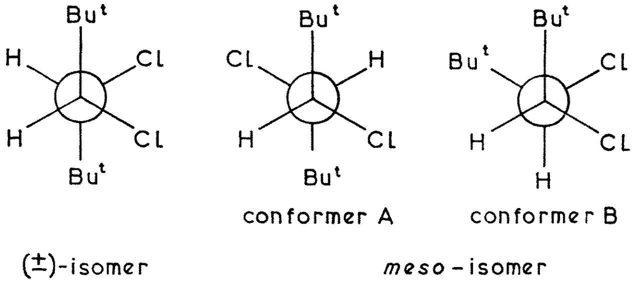


$\mathrm{R{-}CH_A(SAr){-}CH_B(Cl){-}Ph}$

R		Vicinal coupling constants J_{AB} (c./sec.)
erythro	isopropyl*	10·7
threo		6·1
erythro	t-butyl	4·7
threo		1·6

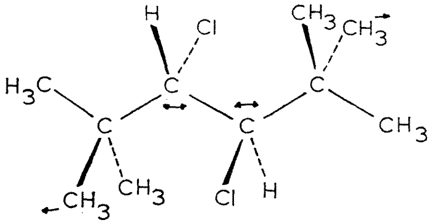
* Ar is 2,4-dinitrophenyl. The spectra have been duplicated by computer simulation.

For the *erythro* isopropyl compound, quite high conformational purity seems likely, with vicinal protons predominately *trans* (the phenyl and isopropyl groups must likewise be *trans*).[4] For the *erythro* t-butyl compound, the much lower J-value might indicate a substantial population of a conformer in which the t-butyl is *gauche* to another large group, in this case, phenyl. Possible angle deformations, involving the t-butyl group and the vicinal protons, could render the vicinal coupling constants a poor guide as to conformation.[5] Alternatively, it was possible that the equilibrium dihedral angles in the various conformers were grossly different from 60°.[6] In any case, other types of evidence are needed to corroborate the n.m.r. findings. In one system, 4,4-dimethyl-2,3-dibromopentane, dipole moment studies showed that both isomers possessed predominately *gauche* halogens; this is consistent with n.m.r. findings.[7,8]



For di-t-butyl systems, Fahey[9] reported a J-value of 0·8 c./sec. for (±)-3,4-dichloro-2,2,5,5-tetramethylhexane (very likely *gauche* protons and *trans* t-butyl groups). However, in the *meso* isomer, J_{AB} was 5·2 c./sec.,[9] much lower than the value (>10) expected for *trans* protons (and hence *trans* t-butyl groups). Again it seemed possible that a second conformer, with *gauche* t-butyl groups, was substantially populated (see, however, our previous reservations). If conformer B† were indeed populated, the dipole moment should be non-zero, due to vector addition of the C–Cl group moments.[8] We found a dipole moment of 1·9 D (cyclohexane),§ in reasonable agreement with the n.m.r. data.[9] The dipole moment of the $(\pm)$-isomer was 2·7 D, more or less as expected,‡ and also in agreement with n.m.r. data.

The reason that seemingly unfavourable conformations such as B are populated is obscure. However, conformer A is itself far from strain free, as the extended conformational diagram shows.† Two 1,3 non-bonded interactions are present between chlorine and methyl, somewhat analogous to 1,3 diaxial interactions in a cyclohexane system. We suggest that some angle widening has occurred. Alternatively, some lateral movement of the methyl groups may occur to reduce 1,3 interactions. In either case the *gauche* interaction between t-butyl groups would also be reduced, allowing an increased population of conformer B. However, these tentative ideas await more positive evidence, *e.g.* *X*-ray analysis.



(*Received, March 26th,* 1969; *Com.* 431.)

---

† Dihedral angles are shown as 60°, purely for convenience.

‡ A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, 1965, p. 206.

§ A check using fresh material and a slightly different technique gave a value of 2·20. The lower value is probably more reliable.

[1] G. Whitesides, J. Sevenair, and R. Goetz, *J. Amer. Chem. Soc.*, 1967, **89**, 1135.
[2] N. L. Allinger and A. Freiberg, *J. Amer. Chem. Soc.*, 1960, **82**, 2393.
[3] For other examples of divergent behaviour see: M. Buza and E. I. Snyder, *J. Amer. Chem. Soc.*, 1966, **88**, 1161; N. L. Allinger, H. Blatter, L. Freiberg, and F. Karkowski, *ibid.*, p. 2999; J. Sicher, M. Cherest, Y. Gault, and H. Felkin, *Coll. Czech. Chem. Comm.*, 1963, **28**, 22; L. P. Kuhn, *J. Amer. Chem. Soc.*, 1958, **80**, 5950.
[4] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1962, **84**, 743.
[5] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2780.
[6] R. J. Abraham, L. Cavelli, and K. Pachler, *Mol. Phys.*, 1966, **11**, 471.
[7] C. Kingsbury and D. C. Best, *J. Org. Chem.*, 1967, **32**, 6.
[8] See also J. Altona and C. Hageman, *Rec. Trav. Chim.*, 1968, **82**, 279.
[9] R. C. Fahey, *J. Amer. Chem. Soc.*, 1966, **88**, 4681.