Conformation of Vinylic Methyl Groups

By WARREN J. HEHRE*
(*Department of Chemistry, University of California, Irvine, California* 92664)
and LIONEL SALEM
(*Laboratoire de Chimie Théorique, Université de Paris-Sud, Centre d'Orsay,* 91405 *Orsay, France*)

Summary A molecular orbital based model is constructed to show the observed tendency for eclipsing of vinylic methyl groups.

IT is well established that methyl hydrogens prefer to eclipse rather than to stagger unsaturated linkages, the resulting threefold rotational barriers generally falling in the range 1—3 kcal/mol.[1] This phenomenon, which seemingly contradicts simple steric arguments,[2] remains to be adequately explained.

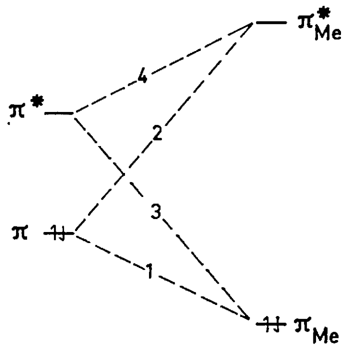

Figure 1

Considering the consequences of interaction of the orbitals of a double bond (occupied by two electrons) with those of appropriate π symmetry on the methyl,[3]† one of which is also doubly occupied [Figure (1)], four interactions may be depicted. The first (between π and $\pi_{\rm Me}$) is 4 electron destabilizing,[4] *i.e.*, the conformer [H-eclipsed or H-staggered, see Figure (2)] with the more effective overlap will be the more disfavoured. Inspection of the appropriate orbitals shows the (destabilizing) effect to be of lesser magnitude in the eclipsed form.

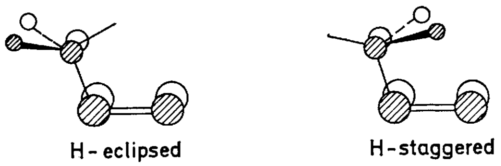
H-eclipsed H-staggered

Figure 2.

The eclipsed structure is also seen to benefit more from the 2 electron stabilizing interactions 2 and 3. Indeed, in the staggered conformation the large overlap between the carbon component of $\pi^*_{\rm Me}$ and π (or of $\pi_{\rm Me}$ and π^*)—which leads to a stabilizing second-order interaction in the eclipsed form—is strongly reduced by overlap of opposite sign between the H_2 component of $\pi^*_{\rm Me}$ and π (or of $\pi_{\rm Me}$ and π^*) [see Figure (3)].‡

Figure 3.

It is only interaction 4 which favours a staggered arrangement of the methyl hydrogens about the double bond. However, the π^* orbitals both on the double bond and on the methyl are formally unoccupied, and to a first approximation no net stabilization results. In $\pi\pi^*$ excited states, where interactions 1 (now 3 electron, approximately zero stabilizing), 2 (now only 1 electron stabilizing), and 3 (also 3 electron) are all much less effective, interaction 4 will certainly tend to diminish the preference of the methyl hydrogens to eclipse the double bond, and may even serve to reverse the observed stereochemistry.

The effect described here adds another example to a growing list of the conformational consequences of hyperconjugation.[3c,5]‡

W. J. H. thanks the Centre de Recherches, Roussel Uclaf for a fellowship.

(*Received*, 30*th May* 1973; *Com.* 758.)

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† We are aware that similar interactions exist within the manifold of σ orbitals. However, the energy gap between occupied σ and unoccupied σ^* orbitals is so large as to make effects of type 2 and 3 (see below) much smaller than the corresponding effects in the π manifold. Thus STO-3G wave functions for propene, suggest that the σ–σ^* energy separation is at least twice as great as that observed for π–π^*. As to the exclusion repulsion (effect 1), interaction between Me and the σ framework of the double bond can hardly account for the observed eclipsing of the two CH bonds.

‡ Our reasoning here is similar to that of Hoffmann and his co-workers in their treatment of contra-thermodynamic stereospecific processes (R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Amer. Chem. Soc.*, 1973, **95**, 629). For a related argument applied to the rotational barrier in ethane see ref. 3a. Our model suggests a lessening of the tendency for eclipsing as the polarity of the unsaturated linkage increases. Any localization of the electrons (for $X{=}Y$ where Y is more electronegative than X, the π orbital will be localized on Y and the π^* on X) will reduce the importance of the 2 electron interaction terms. This point is borne out by the observation that the rotational barrier in acetaldehyde (C=O) is smaller than in propene(C=C). A full discussion will be included in a future publication.

[1] For reviews see: J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1; G. J. Karabatsos and D. J. Fenoglio, *Topics Stereochem.*, 1970, **5**, 167; O. Bastiansen, H. M. Seip, and J. E. Boggs, *Perspectives in Structural Chemistry*, 1971, **4**, 60. Typical values for the barrier to rotation of the methyl group are: propene, 2·00 kcal/mol, D. R. Lide, jun. and D. E. Mann, *J. Chem. Phys.*, 1957, **27**, 868; F. Hirota, *ibid.*, 1966, **45**, 1984; acetaldehyde, 1·16 kcal/mol, W. Kilb, C. C. Lin, and E. B. Wilson, jun., *ibid.*, 1957, **26**, 1695.

[2] Note, however, that the bent bond picture of Pauling envisages a staggered arrangement of the in-plane methyl hydrogen with the "banana" components of the double bond: L. Pauling, 'Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960.

[3] (a) R. Hoffmann, *Pure Appl. Chem.*, 1970, **24**, 567; (b) B. M. Gimarc, *J. Amer. Chem. Soc.*, 1971, **93**, 593; (c) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *ibid.*, 1972, **94**, 6221; (d) For a detailed account see: W. L. Jorgensen and L. Salem, 'The Organic Chemist's Book of Orbitals,' Academic Press, New York, 1973.

[4] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543; K. Muller, *Helv. Chim. Acta*, 1970, **53**, 1112.

[5] N. Epiotis, *J. Amer. Chem. Soc.*, 1973, **95**, 3087; S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *ibid.*, p. 3806.