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THE REACTIVITY OF NONCOPLANAR DOUBLE BONDS

William L. Mock

Department of Chemistry
Carnegie-Mellon University
Pittsburgh, Pennsylvania, 15213, USA

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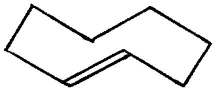
We wish to call attention to an aspect of double bond reactivity and its relationship to the concept of torsional strain. Nonplanarity in an unsaturated center may be deliberately induced in two ways. On the one hand, the trans substituents may be linked by a short chain; the best known example is *trans*-cyclooctene (**1**). On the other, relief of steric compression, as in *cis*-di-*t*-butylethylene (**2**), can likewise produce a torsion about the double bond. In each of



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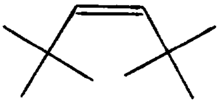

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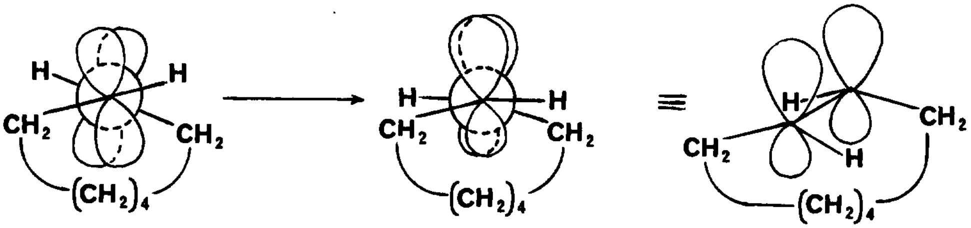
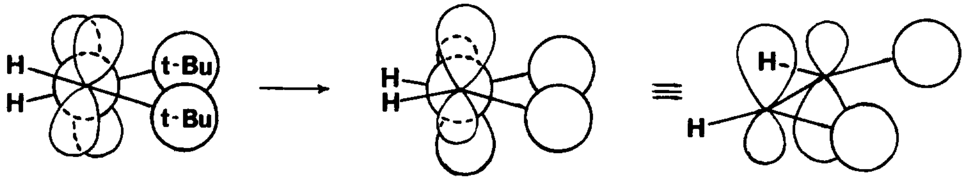
these cases there is an estimated strain energy of ≥ 9 kcal/mol.[1] To illustrate our point we shall make use of Newman projections. We make an initial approximation that both carbon atoms in a twisted double bond will retain sp^2 hybridization. The appropriate representations are given below (**1a**, **2a**):



1a **1b**

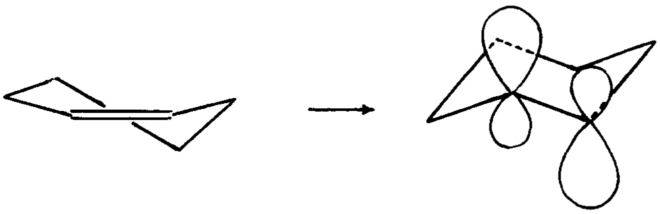


2a **2b**

The pertinent observation is that in **1a** and **2a** the axes of the 2p atomic orbitals of the pi bonds are not parallel, but are skewed relative to each other by an amount proportional to the "twist" in the pi bond. We submit that in order to attain better pi overlap the carbon atoms of the double bond will undergo modest rehybridization,[2] with the incorporation of some s character into the "lobes" of the pi bond.[2a] This is exemplified (if exaggerated) in **1b** and **2b**, in which the axes of the pi bonding atomic orbitals have been brought back into parallel, with attendant adjustment in the position of the hydrogen atoms on the double bond. However, note a characteristic difference in the two systems; in **1b** the lobes on the same face of the double bond are expanded,[2a] while in **2b** it is the lobes on opposite faces which are expanded. It follows that there should be marked differences in the propensities of these systems to undergo chemical reaction, in particular with respect to additions to the double bond. A system of the type **1b** will be relatively more susceptible to cis addition than to trans addition; the opposite will hold true for **2b** (trans rather than cis addition).

Experimental support of this hypothesis is not unambiguously available. One face of the double bond of *trans*-cyclooctene (**1**) is sterically shielded; trans addition is thereby suppressed. Furthermore, many trans additions proceed by way of bridged intermediates resulting from an initial cis addition. Naturally, steric bulk at the reaction site in *cis*-di-*t*-butylethylene (**2**) will also shield the double bond from attacking reagents; hence, comparisons with less strained systems are uncertain.

However, we note that the chemistry of strained systems is *consistent with* these suggestions.[2a, 3] In fact, we submit that these ideas have general applicability to alkene chemistry. For example, the strong tendency of cyclohexanes to adopt a chair conformation means that with regard to additions cyclohexene[4] will respond as in class **2a,b**, above.



Consequently, while there may be little torsional strain in the double bond of cyclohexenes (examination of recent X-ray crystallographic structures reveals six-membered ring C-C=C-C torsional angles of 0.5-5°),[5] the reaction paths leading to trans or cis addition might be expected to show a transition state differential amounting to several kcal/mol which could be attributed to this source. Naturally, the effect of this phenomenon cannot be separated from other aspects of double bond reactivity, but it should be recognized as a contributing factor in appropriate systems, for both additions[6] and eliminations.[7]

The generalized conclusion is that small ground state "torsions" about a double bond may be energetically inexpensive,[8] but that they may produce sizeable relative effects in the transition states corresponding to different modes of reactivity, particularly when the activated complex resembles the alkene.[9]

Notes and References

1. R. B. Turner and W. R. Meador, J. Amer. Chem. Soc., 79, 4133 (1957); R. B. Turner, D. E. Nettleton, and M. Perelman, ibid., 80, 1430 (1958). Actually, this is a minimal value, since it is a measured thermodynamic difference with a (not necessarily strain free) geometrical isomer in each case.

2. (a) N. L. Allinger, J. Amer. Chem. Soc., 80, 1953 (1958); (b) F. H. A. Rummens, Rec. Trav. Chim. Pays-Bas, 84, 5 (1965).

3. R. C. Fahey, J. Amer. Chem. Soc., 88, 4681 (1966); N. M. Weinshenker and F. D. Greene, ibid., 90, 506 (1968); J. R. Wiseman, H.-F. Chan, and C. J. Ahola, ibid., 91, 2812 (1969); J. A. Marshall and H. Faubl, ibid., 92, 948 (1970); J. R. Wiseman and W. A. Pletcher, ibid., 92, 956 (1970).

4. M. W. Lister, J. Amer. Chem. Soc., 63, 143 (1941); C. W. Beckett, N. K. Freeman, and K. S. Pitzer, ibid., 70, 4227 (1948).

5. Only structures with reasonable bond lengths were included in the survey: bromoarborinone, 4°, O. Kennard, L. R. di Sanseverino, and J. S. Rollet, Tetrahedron, 23, 131 (1967); anhydrodigitoxigenin, 0.5°, R. D. Gilardi and I. L. Karle, Acta Cryst., B26, 207 (1970); rimuene, 5°,

B. F. Anderson, D. Hall, and T. N. Waters, ibid., B26, 882 (1970); hinesol intermediate, 3°, J. Bordner and R. E. Dickerson, ibid., B26, 1618 (1970); diethylcarbamoylcyclohexenecarboxylic acid, 1°, C. Pedone, E. Benedetti, A. Immirzi, and G. Allegra, J. Amer. Chem. Soc., 92, 3549 (1970); a marginal example is pentachlorocyclohexene, 4°, R. A. Pasternak, Acta Cryst., 4, 316 (1951).

6. This represents an alternative explanation to the eclipsing effect recognized by Huisgen in cycloadditions: R. Huisgen, H.-J. Sturm, and H. Wagenhofer, Z. Naturforsch, 17b, 202 (1962); R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience, 1964, p. 820. It is conceptually preferable for reactions with early transition states: S. Hünig and H.-R. Müller, Angew. Chem. Intern. Ed. Engl., 1, 213 (1962).

7. This idea gives further insight into the "syn-anti dichotomy" of Sicher; for a discussion see D. S. Bailey and W. H. Saunders, Jr., J. Amer. Chem. Soc., 92, 6904 (1970). The special nature of six membered rings was demonstrated by M. P. Cooke, Jr. and J. L. Coke, ibid., 90, 5556 (1968).

8. This appears to us to be an area which has not been given adequate theoretical consideration: ref. 2b, 4; R. Bucourt and D. Hainaut, C. R. Acad. Sci., 258, 3305 (1964); R. Bucourt, Bull. Soc. Chem. Fr., 2080 (1964); N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, J. Amer. Chem. Soc., 90, 5773 (1968); G. Favini, G. Buemi, and M. Raimondi, J. Mol. Struct., 2, 137 (1968); N. C. Cohen, Tetrahedron, 27, 789 (1971); however, see following letter.

9. Attention is directed to a remarkable 16° double bond torsion found in 2,3-bis-(4-chloro-1-methylcyclohexyl)-*trans*-2-butene, which appears to fall in class 2a: D. Mootz, Acta Cryst., B24, 839 (1968). A more recent example of a similarly strained system has also been reported: W. E. Thiessen, H. A. Levy, W. G. Dauben, G. H. Beasley, and D. A. Cox, J. Amer. Chem. Soc., 93, 4312 (1971). A possible corollary to the hypothesis put forth in this communication is that torsionally strained double bonds which are unable to rehybridize as in **1b** and **2b** may not exhibit an exaltation in reactivity.