Stereoelectronic Effects, Tau Bonds, and Cram's Rule

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The fundamental role played by stereoelectronic effects in determining the paths of organic chemical reactions, clearly enunciated in the literature more than 30 years ago (*1*), is by now widely appreciated (*2, 3*). Nevertheless, the teaching of organic chemistry frequently suffers from the neglect of these ideas at the introductory level; and yet, to the extent that stereoelectronic effects commonly are treated in terms of interactions involving lone pair and sigma orbitals with antibonding orbitals, organic chemistry instructors perhaps have been correct in their hesitation to go beyond the most cursory discussion of the effects in introductory courses. It is the twofold purpose of this article to review a group of stereoelectronic effects and to outline the basis for a suggestion (*4*) that use of the "bent bond"—here called tau bond—model (*5–8*) for the double bond may be fruitful in helping students to visualize the effects. A simple model for Cram's rule (*9–14*) will be proposed as an example.

The Bent Bond or Tau Model for the Double Bond

The sigma/pi (σ/π) model of the double bond, and its extraordinary versatility in allowing discussion and rationalization of a wide variety of effects, need not be reviewed here. The stunning success of the theory of the conservation of orbital symmetry (*15*), which employs the σ/π model to such powerful effect, is in itself justification for the secure position of the σ/π model in organic chemistry.

An alternative description of the double bond is the one that was first put forward by Adolph Baeyer 100 years ago (*16*), was then used in organic chemistry for decades, and was ultimately placed on a quantum mechanical basis by Pauling (*5*). In this model the double bond is viewed as composed of two bent bonds or, as they were later also called, tau (τ) bonds (*17, 18*). For each atom of the double bond, the construction of the orbitals used to form the bonds simply involves further mixing of the sp^2 orbital and the p orbital that, in the σ/π model, are used to form the σ and π bonds. The result is two equivalent orbitals for each atom, having five parts p character and one part s character. Hence, two equivalent τ bonds may be formed.

The usefulness of the τ model in the simple prediction of bond lengths is well recognized (*8*). Perhaps less well appreciated is the fact that, as a result of its mode of construction, the τ model has the significant property of conveying information not only about the π but also about the σ component of a double bond in a pictorially instructive manner. The virtue of the τ bond orbitals is that they automatically mix the directional properties of σ and π orbitals. In the σ/π model of the double bond this information must be gleaned through the operation of σ/π mixing, qualitatively not such a straightforward process and therefore often neglected. The result is that chemists frequently use only the π component of the information, with a consequent impoverishment of understanding, as will be demonstrated in several instances in this article. We shall see, furthermore, that a particular strength of the τ bond model is that it allows easy recognition, through a graphically clear process, of staggered conformations in unsaturated molecules in their ground states.

It should be emphasized at the outset of this presentation of an alternative viewpoint that no attempt is being made here to promote the τ bond concept as a theory to be taken

more seriously than the σ/π theory. The σ/π model and the τ bond model are alternative descriptions whose goal it is to describe "reality". The two models are quantitatively equivalent (*19*). The qualitative use of either model must lead to some (not necessarily the same) loss of information. The observed directionality of the stereoelectronic effects to be described is qualitatively predicted by both models. Nevertheless, a case will be made that explanations of stereoelectronic effects are often more readily grasped at the introductory level when they are based on the τ bond model.

Conformation: The Anomeric and Gauche Effects

Stereoelectronic effects involve steric constraints on the fruitful interaction between donor and acceptor groups either in a ground state molecule or in a transition state. To begin with molecules in their ground states, a great deal of generalized experience in conformational analysis is summarized in the statement (*3*): "There is a stereoelectronic preference for conformations in which the best donor lone pair or bond is antiperiplanar to the best acceptor bond."
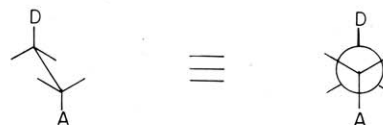

The classical anomeric effect (*3*) is the observation that for pyranose sugars and related molecules the equilibrium percentage of isomers axial at the anomeric center is greater than expected on steric grounds. In the case of D-mannopyranose the axial isomer predominates (68%). The anomeric effect is now generally perceived to be a consequence of the fact that only the axial isomer permits the σ^*_{C-O} orbital to accept electrons from an antiperiplanar lone pair on adjacent oxygen.
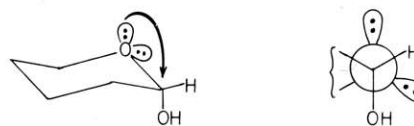

The gauche effect (*20*)—the observation that vicinal electronegative substituents favor gauche conformations—can be interpreted as a generalized anomeric effect (*3*). Thus, although the most stable conformation of *n*-butane is anti, that for 1,2-difluoroethane is gauche, the C–H bonds serving as donors and the C–F bonds serving as acceptors. An especially instructive example of the gauche effect is provided by the case of dimethoxymethane. Vapor phase electron diffraction (*21*) shows the conformation in which the substituents on each inner C–O bond are gauche as a result of a donor lone pair and an acceptor C–O, while the sterically unfavorable 1,3-dimethyl interaction—corresponding to a 1,3-diaxial interaction in a cyclohexane ring—is avoided. Bonds a are shorter than bonds b (1.382 Å vs. 1.432 Å), supporting the view of electron donation from the lone pair as donor to the σ^*_{C-O} as acceptor. It should be particularly stressed that the interpretation of these effects rests square-

ly on the principle that molecules prefer to exist in their staggered forms.
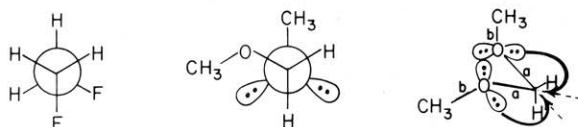
## Conformation: Carbonyl Groups and Tau Bonds

Some 25 years ago, using microwave spectroscopy, Wilson's group (22) determined the most stable conformations of acetaldehyde and propionaldehyde to have the carbonyl group eclipsed by hydrogen and methyl, respectively.
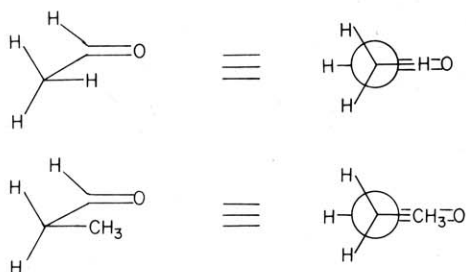

The stability of these conformations may again be attributed to donation of electron density from antiperiplanar bonds to a vacant antibonding orbital, this time $\pi^*_{C=O}$' whose directionality (not the directionality of the bonding π orbital) dictates the alignment of the bonds, and hence the conformation relative to the carbonyl group. Wiberg's recent theoretical study (23) suggests that in propionaldehyde the favored position of the methyl group may be the result of a dipole induced along the C–C bond of the ethyl group by the carbonyl dipole, leading to a stabilizing interaction.
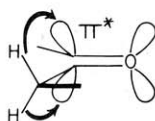
Use of the τ bond model dramatizes the importance of the concept of staggering in the interpretation of conformations involving double bonds. For example, the conformation of acetaldehyde can be clearly seen as staggered, with the best donor bonds antiperiplanar to the best acceptor bonds. In the case of chloroacetaldehyde (24) there is the additional possibility of donation to the C–Cl bond.
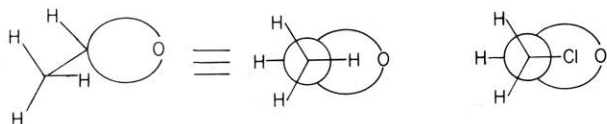
The favored conformation of propene (25) is also easily understood as staggered with respect to its τ bonds. Here the donor–acceptor interaction is exactly that which is considered to stabilize substituted olefins through hyperconjugation. Again, the directionality is important. Hyperconjugation is frequently incorrectly described and drawn in textbooks as though it were an interaction between a (filled) σ_{C-H} orbital and a (filled) $\pi_{C=C}$ orbital. Adherence to the τ bond notation decreases the likelihood of making this error.
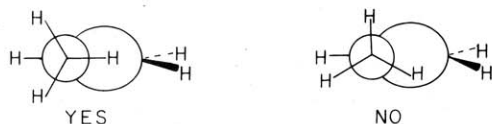

The favored conformations of enamines (26) and of enol ethers (27, 28) are also in accord with, and understood through, the principles delineated above. The lone pairs on nitrogen and oxygen, respectively, are found to be aligned so as to be antiperiplanar to the accepting τ bonds.


Transition States

Perhaps the most familiar example of a stereoelectronic effect in the general area of transition states of chemical reactions is that of the collinearity of the transition state in the S_N2 reaction. Given the extensive evidence for Walden inversion, it had long been assumed that coaxial attack from the rear was the optimum geometry for reactions undergoing this mechanism (although endocyclic transition states that render coaxial attack impossible were, and continue to be, frequently invoked—and not only by first-year students!). The experiment designed by Eschenmoser (29) confirmed that the donor lone pair of the nucleophile and the acceptor bond (σ^*_{C-X}) of the tetrahedral substrate should be collinear.
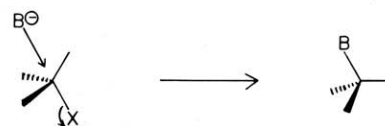
Essentially as familiar as the transition state for bimolecular substitution is that for bimolecular elimination. A moment's reflection, and inspection of the figures, will make it clear that the E2 process is closely related to the concepts that we have already developed. Indeed, bimolecular elimination is the end result when an electron pair, which in the textbook case will be liberated by the action of a base on a proton attached to carbon, finds itself antiperiplanar to a group able to function as a leaving group. It should be especially remarked how naturally the τ bond notation for the double bond thus formed falls out from the graphic formulation of the E2 mechanism.
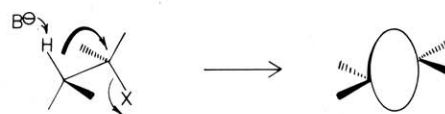

Now the two great groups of reactions undergone by the carbonyl functionality in the presence of bases are, first, nucleophilic addition, and second, removal of protons alpha to the carbonyl. These two classes in fact have the stereoelectronic characteristics of the S_N2 and E2 reactions respectively. In the first (S_N2) case the Bürgi–Dunitz trajectory, which is now accepted for nucleophilic addition to carbonyl (30), is qualitatively predicted by the τ bond model as well as by the σ/π model, and again with arguably less complication. It may be appropriately noted here that Baldwin, in the process of formulating his rules for ring closure (31), employed the τ bond model with the Bürgi–Dunitz trajectory when he extended, from tetrahedral to trigonal centers, the argument of a requirement for collinearity in displacement reactions.
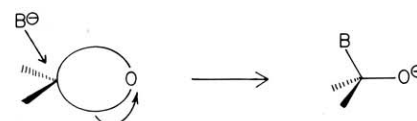
In the second (E2) case the stereoelectronic requirement for maximum acidity in the removal of a proton alpha to the carbonyl is apparent when one prescribes an antiperiplanar relationship between the hydrogen atom to be removed and a τ bond.


That a stereoelectronic requirement does in fact exist in these circumstances has been demonstrated, for example, in the case of protonated amidinium ions, where H or H_E, but not H_Z, are lost to solvent when deprotonation is rapid relative to $C-N^+$ bond rotation (32).
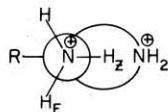

The details of the conformational dependence for maximum acidity of the C–H bond are not as yet known experimentally. An orthogonal relationship between the C–H bond and the carbonyl group is quite generally taken for granted, in spite of the fact that this view incorrectly portrays the axis of proton removal as guided by the (filled) π system rather than by $\pi^*_{C=O}$. It should again be emphasized that the two models, *when properly used*, yield identical predictions. However, the τ bond model very graphically suggests that (in the absence of steric constraints) the conventional picture should be questioned.


conventional picture τ bond model
for maximum acidity   for maximum acidity
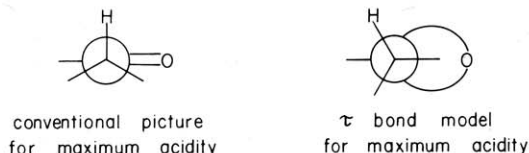
The vinylogous cases of Michael addition and of the removal of the gamma proton from an α,β-unsaturated carbonyl system are correspondingly formulated as follows.
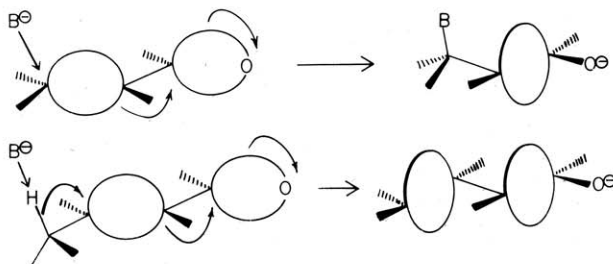

Through consideration of the S_N2' reaction, the stereochemical consequences in such vinylogous cases may be analyzed. When applied in conjunction with a staggered conformation, the τ bond model clearly and simply predicts that the leaving group in the S_N2' reaction should leave from the same side as the base attacks. This prediction of a syn outcome is in agreement with theoretical results (14, 33). The experimental evidence (34), although not entirely clear-cut, and subject to variance in individual examples, suggests that in general the course of S_N2' reactions is in fact syn. The prediction—not as yet confirmed by experiment (4)—of a particular angular relationship between the trajectory of the entering base and that of the leaving group should be noted.
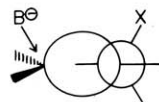
The E2', or 1,4-elimination reaction (4, 34, 35), is similarly treated. Again there is an angular prediction, of 60°, relating the incoming B–H–C axis and the outgoing C–X axis.
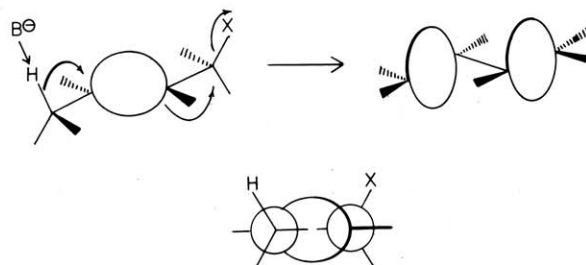

The S_E2' (allylic *electrophilic* substitution) reaction, if uncomplicated by interfering influences such as, for example, favorable cyclic transition state formation (36), proceeds in anti fashion (4, 36, 37).
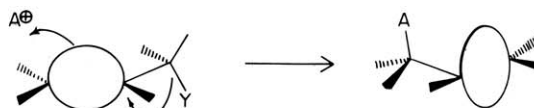

Concluding Case Study: Cram's Rule for Asymmetric Induction

By now it will be clear that the τ bond model can offer some substantial advantages to the teacher. Let us conclude by considering how the ideas that we have reviewed can be applied to a case that has generated wide interest over the years: Cram's rule for predicting the course of asymmetric induction in nucleophilic addition reactions of chiral aldehydes and ketones (9–14). What does the τ bond model predict for the reaction between an achiral nucleophile and a chiral aldehyde substituted at the alpha position with a small, a medium, and a large group?
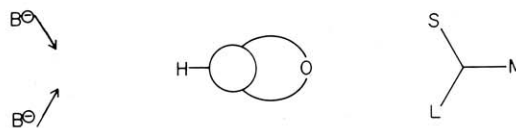

1. The path of the base is fixed. We are dealing with an S_N2 reaction and the Bürgi–Dunitz trajectory.
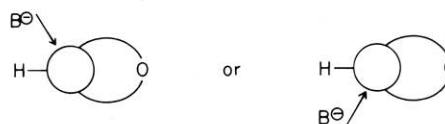
2. If the carbonyl substrate reacts in its most stable (staggered) conformation via the Bürgi–Dunitz trajectory, then the nucleophile is eclipsed with a vicinal bond in the transition state. Moreover, this eclipsing will be especially unfavorable, because the Bürgi–Dunitz trajectory is such as to force the base to effectively "lean in" toward the groups at the alpha position. However, the initial aldehyde conformation for a favorable reaction trajectory need not be the most stable one; we seek the lowest energy *transition state*, by the Curtin–Hammett principle (38). In the case at hand the two eclipsed conformations with the small and medium groups arranged to surround the base should provide the least resistance to the base on its trajectory and, furthermore, *correspond to staggered product*

conformations. This view is in accord with the theoretical contributions of Anh (*13*) and of Houk (*14*), who have established that staggered transition states, reflecting staggered products, should be the rule.
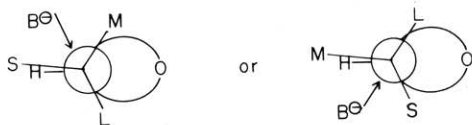
3. We minimize the interaction with the aldehyde hydrogen and are left with:

This model reproduces Cram's rule. It should be emphasized that individual cases will vary in conformational detail. The goal here has been to develop a model on a qualitative basis that can be readily used and understood by students. As has already been noted, the model is in fact identical to the one deduced through calculations (*13, 14*), differing not only from the pioneering Cram formulation (*9*) but also from the original Felkin model (*10*). The relationship of the model developed here (guided by the construction of τ bonds) to the Felkin model (guided by the π rather than the π^* orbital, that is, not modified by the Bürgi–Dunitz trajectory) is exactly the one that has already been mentioned several times in this article.

Cram   Felkin

In conclusion, the predictive power of the preceding arguments in the realm of stereoelectronic effects is substantial and reinforces the position that has already been taken on several occasions (*6–8*) in *this Journal: It is worth including the tau bond model of the double bond in the teacher's arsenal.*

Acknowledgment

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Literature Cited

1. (a) Corey, E. J. *Experientia* **1953**, *9*, 329. (b) Corey, E. J. *J. Am. Chem. Soc.* **1954**, *76*, 175. (c) Corey, E. J.; Sneen, R. A. *J. Am. Chem. Soc.* **1956**, *78*, 6269.
2. Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry;* Pergamon: Oxford, 1983.
3. Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen;* Springer–Verlag: Berlin, 1983.
4. Eschenmoser, A., personal communication. See also Vogel, E.; Caravatti, G.; Franck, P.; Aristoff, P.; Moody, C.; Becker, A. M.; Felix, D.; Eschenmaser, A. *Chem. Lett.* **1987**, 219.
5. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell: Ithaca, 1960; pp 136–142.
6. Walters, E. A. *J. Chem. Educ.* **1966**, *43*, 134.
7. Bernett, W. A. *J. Chem. Educ.* **1967**, *44*, 17.
8. Robinson, E. A.; Gillespie, R. J. *J. Chem. Educ.* **1980**, *57*, 329.
9. Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828.
10. Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199.
11. Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions;* Prentice–Hall: Englewood Cliffs, NJ, 1971.
12. Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2.
13. Anh, N. T. In *Topics in Current Chemistry*, No. 88; Springer–Verlag: Berlin, 1980; pp 145–162.
14. (a) Houk, K. N. *Pure Appl. Chem.* **1983**, *55*, 277. (b) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162. (c) Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y.-D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science* **1986**, *231*, 1108.
15. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry;* Verlag Chemie: Weinheim, 1971.
16. Baeyer, A. *Ber.* **1885**, *18*, 2269.
17. Hall, G. G.; Lennard-Jones, J. *Proc. Royal Soc. A* **1951**, *205*, 357.
18. Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry;* Benjamin: New York, 1964; pp 136–141.
19. See, for example, Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980.
20. Wolfe, S. *Accts. Chem. Res.* **1972**, *5*, 102.
21. Astrup, E. E. *Acta Chem. Scand.* **1973**, *27*, 3271.
22. (a) Kilb, R. W.; Lin, C. C.; Wilson, E. B., Jr. *J. Chem. Phys.* **1957**, *26*, 1695. (b) Butcher, S. S.; Wilson, E. B., Jr. *J. Chem. Phys.* **1964**, *40*, 1671.
23. Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035.
24. (a) Karabatsos, G. J.; Fenoglio, D. J. In *Topics in Stereochemistry;* Eliel, E. L.; Allinger, N. L., Eds.; Wiley–Interscience: New York, 1970; Vol. 5, p 167. (b) Karabatsos, G. J.; Fenoglio, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 1124.
25. Herschbach, D. R.; Krisher, L. C. *J. Chem. Phys.* **1958**, *28*, 728.
26. Brown, K. L.; Damm, L.; Dunitz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978**, *61*, 3108.
27. Owen, N. L.; Sheppard, N. *Proc. Chem. Soc.* **1963**, 264.
28. Mersh, J. D.; Sanders, J. K. M. *Tetrahedron Lett.* **1981**, *22*, 4029.
29. Tenud, L.; Farooq, S.; Seibl, J.; Eschenmoser, A. *Helv. Chim. Acta* **1970**, *53*, 2059.
30. (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563. (c) Bürgi, H. B. *Ang. Chem. Int. Ed. Engl.* **1975**, *14*, 460.
31. Baldwin, J. E. *J. Chem. Soc. Chem. Comm.* **1976**, 734, 738.
32. Perrin, C. L.; Johnston, E. R.; Ramirez, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6299.
33. Anh, N. T. *J. Chem. Soc. Chem. Comm.* **1968**, 1089.
34. Magid, R. M. *Tetrahedron* **1980**, *36*, 1901.
35. Hill, R. K.; Bock, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 637.
36. (a) Wetter, H.; Scherer, P; Schweizer, W. B. *Helv. Chim. Acta* **1979**, *62*, 1985. (b) Wetter, H.; Scherer, P. *Helv. Chim. Acta* **1983**, *66*, 188.
37. Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M.; *J. Amer. Chem. Soc.* **1982**, *104*, 4962.
38. Curtin, D. Y. *Record Chem. Progress* **1954**, *15*, 111.