can be extracted from the available information. A comparison of our ^{13}C chemical shifts of chlorophyll a with those of Katz and Janson[2] indicates that there are appreciable solvent effects on the unsaturated carbon chemical shifts. For example, the resonance of C-2b (peak 20 in Figure 3B) is downfield from that of P-2 (peak 21). In dioxane, the reverse has been reported.[2]

The 30 saturated carbons of chlorophyll a give rise to the 25 resonances upfield from chloroform (peaks 26–50 in Figure 3B). Peak 26 has been assigned to C-10.[2,6] Assignment of the rest of the saturated-carbon region is greatly facilitated by a comparison with the spectrum of phytyl acetate (Figure 3A). Peak 27 must be assigned to P-1. Peaks 31–36, 39–42, 44, 45, and 47 contain phytyl carbon resonances whose assignments (Table II) follow directly from the phytol assignments (Table I). Peak 45 is a three-carbon resonance, but only two phytyl carbons contribute to it. The 12 saturated carbons of chlorophyll a other than those of the phytyl group give rise (Figure 3B) to peaks 26, 28, 29, 37, 38, 43, 46, 48, 49, and 50 and one-carbon contributions to peaks 45 and 30. Peak 30 contains a chlorophyll resonance coincident with a strong methanol peak. The presence of a chlorophyll resonance at this position was inferred from spectra of chlorophyll a in dioxane[2] and in pure chloroform.[21] We have listed above a total of 12 peaks for 12 carbons. Variations in peak heights arise from differences in line widths and from partial saturation of some resonances that have long T_1 values (because of the relatively short recycle time used for recording the upfield region of the spectrum). Peaks 26, 28, 29, 30, 43, 46, and 50 can be assigned[2,6] to C-10, C-10b, C-7, C-8, C-8a, C-4b, and C-3a, respectively. However, the specific assignments of peaks 29 and 30 are tentative and could turn out to be inverted. Peaks 37 and 38 arise from carbons 7a and 7b.[2] Katz and Janson[2] specifically assigned peak 37 to C-7a but only tentatively. We confirmed this assignment by means of T_1 measurements. Resonance 37 has a much shorter relaxation time (about 0.18 sec) than resonance 38 (about 0.34 sec). C-7a should have a relatively short T_1 value because it is directly anchored to a bulky ring system.[9] C-7b, with its additional degree of internal rotation, should have a longer T_1 than C-7a.[9] The nonphytyl component of peak 45 can be assigned to C-4a, on the basis of the ^{13}C spectrum of methyl pheophorbide a.[2,5] Peaks 48 and 49 have been assigned to C-1a and C-5a but not on a one-to-one basis.[2]

Acknowledgment. This research was supported by the National Science Foundation (Grant GP-17966), by the donors of the Petroleum Research Fund, administered by the American Chemical Society, by the National Institutes of Health (Grant NS-10977), and by Eli Lilly and Co. One of us (E. O.) thanks the European Molecular Biology Organization and the Gilbert Foyle Trust of Great Britian for partial support. We thank Dr. D. Brune for his helpful suggestions about preparation of chlorophyll. We thank Dr. J. J. Katz for making available data in advance of publication.

---

(21) R. A. Goodman and A. Allerhand, unpublished results.

Attractive Nonbonded Interactions in 1-Substituted Propenes. Consequences for Geometric and Conformational Isomerism

N. D. Epiotis,* D. Bjorkquist, L. Bjorkquist, and S. Sarkanen

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105.

Received February 27, 1973

Abstract: Heteroatoms at the 1 position of propene can interact with the methylene group through space and through the olefinic bond. This interaction can be attractive in nature and responsible for both the lower energy of the cis isomer relative to the trans isomer and also the lower rotational barrier of the cis isomer relative to the rotational barrier of the trans isomer. The proposed model is tested by SCF–MO semiempirical calculations and the qualitative generalizations are found to be in good accord with the observed experimental trends.

Organic chemistry provides a number of instances where one cannot invoke the concept of steric or nonbonded repulsion to predict the relative stabilities of geometrical isomers of 1-substituted propenes. Various cases illustrating the general preference for the cis over the trans isomer of substituted propenes are listed in Table I. Furthermore, rotational isomerism in 1-substituted propenes is characterized by certain intriguing regularities. Specifically, it is found that in such molecules the rotational barrier of the cis isomer is significantly lower than the rotational barrier of the trans isomer. Experimental data pertaining to this interesting effect have been collected in an excellent

Table I. Equilibrium Composition of Cis and Trans Isomers of 1-Substituted Propenes

Compd	% cis at equil	Ref
$CH_3CH{=}CHOMe$	71	*a*
$CH_3CH{=}CHOEt$	81	*a*
$CH_3CH{=}CHOPh$	65	*b*
$CH_3CH{=}CHCl$	76	*c*
$CH_3CH{=}CHBr$	68	*d*

[a] P. Salomaa and P. Nissi, *Acta Chem. Scand.*, **21**, 1386 (1967). However, see ref 8. [b] C. C. Price and W. H. Snyder, *J. Amer. Chem. Soc.*, **83**, 1773 (1961). [c] J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963). [d] K. E. Harwell and L. F. Hatch, *J. Amer. Chem. Soc.*, **77**, 1682 (1955).

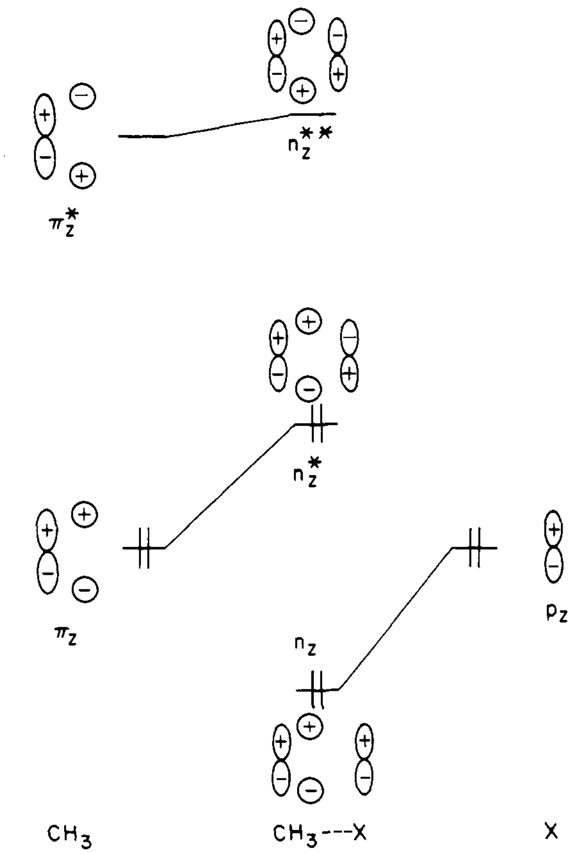
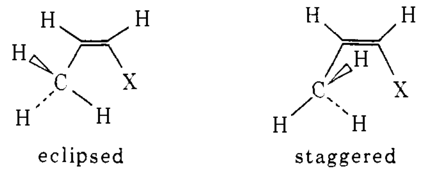


Figure 1. Through space orbital interaction between a lone pair p_z orbital and the π-type methyl orbitals.

review by Lowe.[1a] In this paper we extend our ideas on nonbonded attraction to these systems.[1b]

The approach will be illustrated with reference to *c*-MeHC=CHX, where X is a first row heteroatom group, *e.g.*, F, OH, NH_2, etc. In all cases the heteroatom has at least one lone pair housed in a p_z atomic orbital. The methyl group can assume either a staggered or an eclipsed conformation and these are shown below.



The orbitals of the methyl group have been discussed nicely elsewhere.[2] The p_z atomic orbital of the heteroatom which contains the lone pair can interact through space with the bonding π_z and antibonding π_z^* orbitals of the methyl group, irrespective of whether the methyl group is in a staggered or eclipsed conformation. The p_z–π_z orbital interaction is expected to be strong since the two interacting orbitals have similar energies. On the other hand, the p_z–π_z^* interaction is expected to be negligible since the energy separation of the interacting orbitals is huge (Figure 1). A consequence of the through space orbital interaction and the double occupancy of n_z and n_z^* is that the bond order between the p_z heteroatom orbital and the π-type methyl orbitals will be roughly equal to zero, unless an unfilled orbital of appropriate symmetry interacts with either the n_z or the n_z^* orbital or a filled orbital interacts with the n_z^{**} orbital. In our case, the only important interaction between a filled and an unfilled orbital is that between n_z^* and ϕ_2. The result of this interaction is net charge transfer of electron density from the n_z^* orbital into the ϕ_2 olefinic orbital[3] thereby rendering the net bond order between the lone pair p_z orbital and the π-type methyl orbitals positive and their interaction attractive. This effect is shown in Figure 2. One can use the same type of analysis for heteroatoms possessing in addition a p_x lone pair. In this case the lone pair p_x orbital will interact through space with filled and unfilled methyl orbitals of appropriate symmetry yielding n_x, n_x^*, and n_x^{**} orbitals. As in the previous case, charge transfer from n_x^* to the σ^* orbital of the olefinic bond will give rise to net attraction between the lone pair and the methyl group. However, this latter σ interaction is not going to be as important as the previous π interaction because σ^* lies high in energy and its interaction with n_x^* is weak.[4] It should be pointed out that, in general, the second lone pair of a halogen attached to ethylene is localized mainly in a p_x orbital as long as the geminal olefinic angle is greater than 90°, a condition which is met in all olefins. In such cases, the p_y atomic orbital of the halogen contributes mostly toward σ bond formation with the olefin, while the lone pair becomes mainly, *but not entirely*, localized in the p_x orbital.

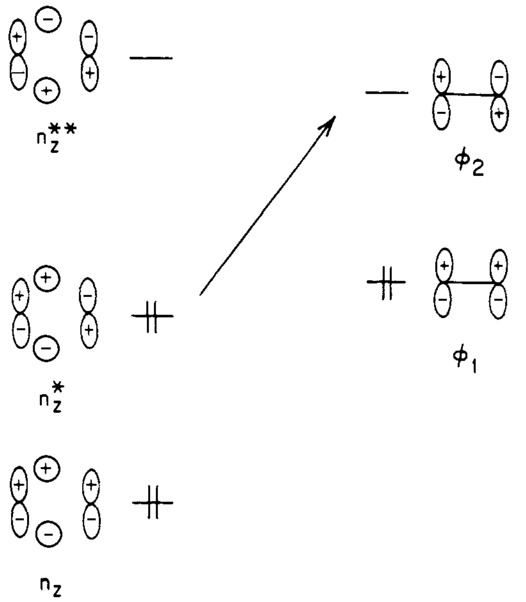


Figure 2. Through bond interaction in 1-substituted propenes. The arrow indicates the dominant orbital interaction which gives rise to charge transfer. Interactions between filled orbitals do not give rise to charge transfer.

---

(1) (a) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968). (b) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 3087 (1973); N. D. Epiotis and W. Cherry, *J. Chem. Soc., Chem. Commun.*, 278 (1973).

(2) B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 593 (1961).

(3) Intramolecular and intermolecular charge transfer, the result of orbital interactions, can have important chemical consequences. For example, see M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962; R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Günther, *ibid.*, 5173 (1970).

(4) According to well-known principles of perturbation theory, the magnitude of the interaction of two orbitals is inversely proportional to their energy separation. See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

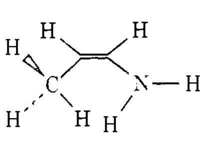
Table II. Bond Orders, Overlap Integrals, and Relative Energies of 1-Substituted Propenes

Compd	Methyl conformation	X_{p_z}–H_{1s} bond order	X_{p_z}–H_{1s} overlap	X_{p_z}–C_{p_z} bond order	X_{p_z}–C_{p_z} overlap	$E_{trans} - E_{cis}$[a] CNDO/2	$E_{trans} - E_{cis}$[a] INDO
$CH_3CH{=}CHF$	Eclipsed	0.0375	0.0006	−0.0004	0.0034	0.544	0.163
$CH_3CH{=}CHOMe$	Eclipsed	0.0441	0.0010	−0.0028	0.0052	0.755	0.490
$CH_3CH{=}CHNH_2$	Eclipsed	0.0524	0.0017	−0.0051	0.0083	−0.917	−1.004
$CH_3CH{=}CHF$	Staggered	0.0411	0.0041	−0.0062	0.0034	0.864	0.985
$CH_3CH{=}CHOMe$	Staggered	0.0494	0.0062	−0.0108	0.0052	1.155	1.889
$CH_3CH{=}CHNH_2$	Staggered	0.0603	0.0098	−0.0175	0.0083	1.866	0.591

[a] Energies in kcal/mol. A positive number indicates that the cis isomer is more stable than the trans. Bond orders and overlaps refer only to the CNDO/2 calculations.

The above simple analysis has been based on a simple one-electron approach with neglect of overlap. If overlap is included, then the interaction between the p_z atomic orbital of the heteroatom and the π-type methyl orbitals will be repulsive and charge transfer from n_z^* to ϕ_2 will tend to render this interaction attractive. In other words, the qualitative conclusions remain the same but an explicit determination of the magnitude of the charge-transfer effect becomes necessary.

We have tested the validity of these conclusions by CNDO/2 and INDO calculations.[5] We have calculated the cis and trans isomers of typical 1-substituted propenes[6] in both staggered and eclipsed conformations and the results are shown in Table II. It can be seen that in the case of the eclipsed conformer, the bond order between the lone pair p_z orbital of the heteroatom and the 1s hydrogen orbitals of the methylene group is positive and large while the bond order between the lone pair p_z orbital of the heteroatom and the p_z orbital of the methylene group is negligible.[7] This is in good accord with our predictions and shows that there is net bonding between the methyl group and the lone pair of the heteroatom in 1-substituted propenes. Furthermore, the calculations show that, with one exception, the cis isomer is more stable than the trans isomer, an effect which can be reasonably attributed to the bonding interaction between the methyl group and the heteroatom p_z lone pair. The one exception occurs when X is amino and it can be attributed to repulsion between the amino hydrogen and the in-plane methyl hydrogen.



In this and subsequent tables the bond orders X_{p_z}–H_{1s} for the trans isomers are omitted since they have no operational significance. Bond orders are meaningful only when there is overlap between two centers. In the cis form there is appreciable overlap between the methyl group and the heteroatom orbitals and the interaction is attractive as indicated by the bond order, while in the trans form there is negliglible overlap between the methyl group and the heteroatom orbitals. The greater stability of the cis isomer is due to nonbonded attraction present in the cis but absent in the trans form.

In the case of the staggered form, the same pattern of effects is observed. The only difference here is that the bond order between the lone pair p_z orbital of the heteroatom and the p_z orbital of the carbon of the methylene group is small but negative. In any event the antibonding X_{p_z}–C_{p_z} contribution is offset by a much stronger X_{p_z}–H_{1s} contribution and as a result there is net bonding between the methyl group and the heteroatom p_z lone pair. Another contributing factor to this effect is the better X_{p_z}–H_{1s} overlap relative to the X_{p_z}–C_{p_z} overlap in the staggered conformation. As expected on the basis of our analysis, calculations show that in all cases the cis is more stable than the trans isomer.[8a]

Additional support of this model comes from examination of the olefinic π bond order, C_{p_z}–C_{p_z}. As we have seen before, through space interaction between the p_z orbital of the heteroatom carrying the lone pair and the π-type methyl orbitals gives rise to two doubly occupied orbitals n_z and n_z^*. This through space interaction obtains in the cis but not the trans isomer. Hence, if through space interaction is strong, then the n_z^* orbital of the cis form will lie higher in energy than the heteroatom X_{p_z} and the methyl π_z noninteracting orbitals of the trans form. As a result, one may expect greater delocalization into the olefinic ϕ_2 orbital in the cis rather than the trans isomer. This is indeed what calculations show! In particular, the C_{p_z}–C_{p_z} bond order for the cis isomer is almost always *less* than the C_{p_z}–C_{p_z} bond order for the trans isomer for either staggered or eclipsed conformations. A typical example is given below.[8b]

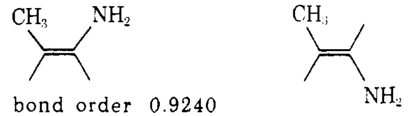
---

(5) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, 47, 2026 (1967); J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(6) In all cases standard bond lengths and bond angles were assumed.

(7) According to our experience, bond orders less than 0.005 can be considered insignificant. The small antibonding character of the X_{p_z} and C_{p_z} bond order is probably due to the weak ϕ_1–n_z^{**} orbital interaction.

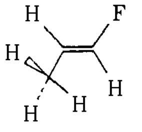
(8) (a) In these calculations, we have assumed a staggered conformation of the methyl group of OMe with respect to the double bond. In general, this is expected to be the situation if instead of OMe we have OR and R is a bulky alkyl group. Propenes of the type $CH_3CH{=}CHOR$, where R is a bulky group, are more stable in their cis form. In the case of $CH_3CH{=}CHOMe$, the methyl group of OMe is sterically forced to assume a staggered conformation in the cis isomer but is free to assume an eclipsed conformation in the trans isomer. This eclipsed conformation is another manifestation of nonbonded attraction. Hence, the greater stability of *trans*- relative to *cis*-1-methoxypropene reported by some workers may be attributed to the conformational effect of the methoxy group. See T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969); S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *J. Org. Chem.*, **35**, 3352 (1970); S. J. Rhoads and E. E. Waali, *ibid.*, **35**, 3358 (1970). (b) The difference of the bond orders is small and depends quantitatively, but not qualitatively, on geometry choice. For example, if the CCC and NCC angles are chosen to be less than 120, there will be greater through space interaction in the cis isomer and greater charge transfer into the olefinic ϕ_2 orbital will accompany this effect. On the other hand, the trans isomer will remain relatively unaffected.



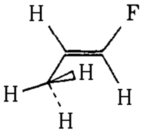
C_{p_z}-C_{p_z} bond order 0.9240 0.9262

In general, the result of strong through space interaction between the methyl group and the heteroatom X is that the π bond order of the two olefinic carbons will be greater in the trans isomer, while the π bond order of the methyl group and the adjacent olefinic carbons as well as the π bond order of the heteroatom X and the adjacent olefinic carbon will be greater in the cis isomer. However, the additional effect of nonbonded attraction between methyl and X which obtains in the cis but not in the trans isomer is the key interaction which renders the cis isomer more stable than the trans isomer, in many instances.

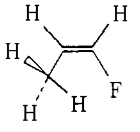
We now turn our attention to the problem of rotational isomerism in 1-substituted propenes.[9,10] We shall illustrate our approach by considering the rotational isomerism of cis and trans 1-fluoropropene. The barrier to rotation of the methyl group in the trans isomer can be taken to be the energy difference between the staggered S conformation and the eclipsed E conformation.[9,10] Similarly, the barrier to rotation of the methyl group in the cis isomer is the energy difference between the cis S and the cis E conformations. In the case of the trans isomer, the methyl group cannot interact with fluorine through space and the rotational barrier is determined, roughly, by the same factors which determine the rotational barrier in propene. In propene, as well as in *trans*-1-fluoropropene, the eclipsed conformer is the low energy form and the staggered conformer is the high energy form. Possible rationalizations of this effect have been offered elsewhere.[9] The π-type framework of propene is isoconjugate to the π framework of butadiene. The eclipsed conformation of propene corresponds to transoid butadiene (I) and the staggered conformation of propene to cisoid butadiene (II). In the isoconjugate butadiene, C_3 corresponds to the carbon atom of the methylene group of propene and C_4 to the two hydrogens of the methylene group of propene. It is known that the cisoid butadiene suffers from repulsive interactions between the p_z orbitals of C_1 and C_4 and, hence, is less stable than transoid butadiene where such repulsive interaction does not exist simply because the p_z orbitals of C_1 and C_4 do not overlap. In view of these considerations, the greater stability of eclipsed relative to staggered propene makes good sense. Similar considerations apply for the case of *trans*-1-fluoropropene. On the other hand, in the case of the cis isomer, the methyl group can interact with fluorine through space and the rotational barrier will now be determined by the same factors which determine the rotational barrier of propene and *trans*-1-fluoropropene but also by the nature of the methyl–fluorine interaction. This interaction is attractive in nature, as we have seen before, and stronger in cis S than in cis E because of the different spatial orientation of the out-of-plane methylene hydrogens and, hence, their proximity with respect to the fluorine p_z lone pair. The through space interaction between the methylene hydrogens and the p_z lone pair of fluorine is greater in cis S than in cis E because the resonance integral $\langle H_{1s}|H|F_{p_z}\rangle$ is greater in the former than in the latter case. This occurs because the resonance integral can be empirically assumed to be proportional to the corresponding overlap integral,[11] and there is better overlap in cis S than in cis E as shown in Table III. As a result, the interaction between $n_z{}^*$ and ϕ_2 is stronger in cis S than in cis E leading to greater charge transfer in the former than in the latter case. A consequence of that is that the bond order H_{1s}–F_{p_z} is expected to be more positive in cis S than in cis E. On the basis of these considerations, one expects that cis S enjoys greater through space attraction than cis E. Again, there is an alternative simple way of understanding these considerations. In particular, the π-type framework of cis S is isoconjugate with the π system of cisoid *cis*-1-fluorobutadiene (III), and the π-type framework of cis E is isoconjugate with the π system of transoid *cis*-1-fluorobutadiene (IV) (which see below). In the isoconjugate 1-fluorobutadiene, C_3 corresponds to the carbon atom of the methylene group of 1-fluoropropene and C_4 corresponds to the hydrogens of the methylene group of 1-fluoropropene. In III, the repulsion between the p_z orbitals of C_1 and C_4 is counteracted by the attraction between the p_z orbitals of C_4 and F, but the magnitude of the repulsion seems to dominate the magnitude of the attraction and cis S remains of



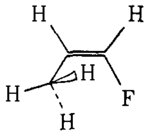
trans E



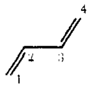
trans S



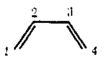
cis E



cis S



I



II

Table III. CNDO/2 Calculations of Rotational Barriers in Typical 1-Substituted Propenes

Molecule	Total energy, au	Relative energy, kcal/mol	H_{1s}–X_{p_z} overlap	H_{1s}–X_p bond order
	a. $CH_3CH{=}CHF$			
Trans S	−52.750667	1.859		
Trans E	−52.753639	0		
Cis S	−52.752044	1.539	0.0041	0.0411
Cis E	−52.754506	0	0.0006	0.0375
	b. $CH_3CH{=}CHOCH_3$			
Trans S	−52.896137	1.774		
Trans E	−52.898964	0		
Cis S	−52.897982	1.392	0.0062	0.0494
Cis E	−52.900119	0	0.0010	0.0441
	c. $CH_3CH{=}CHNH_2$			
Trans S	−38.217193	1.660		
Trans E	−38.219838	0		
Cis S	−38.220166	0	0.0098	0.0603
Cis E	−38.218377	1.123	0.0017	0.0524

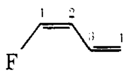
---

(9) (a) M. L. Unland, J. R. VanWazer, and J. H. Lechter, *J. Amer. Chem. Soc.*, **91**, 1045 (1969); (b) J. P. Lowe, *ibid.*, **92**, 3799 (1970).

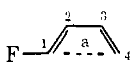
(10) For a theoretical discussion of the rotational barrier in propene and its fluoro derivatives, see E. Scarzafava and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 311 (1971).

(11) For example, see R. Hoffmann, *J. Chem. Phys.*, **40**, 2745 (1964).

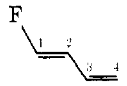
cis S
III



cis E
IV



trans S
V



trans E
VI

higher energy relative to cis E. In IV, neither repulsion between C_1 and C_4 nor attraction between C_4 and F obtains. According to the above discussion, it is expected that the barrier to rotation in *cis*-1-fluoropropene will be lower than the barrier to rotation in *trans*-1-fluoropropene, because attractive nonbonded interactions in the cis isomer tend to stabilize the high energy conformer S relative to the low energy conformer E. These conclusions can also be understood in terms of the isoconjugate models shown below. The interactions denoted by a are antibonding and those denoted by b are bonding.

SCF-MO calculations of the INDO and CNDO/2[5] variety confirm this model and the results are shown in Tables III and IV. It can be seen that: (a) there is better H_{1s}–F_{p_z} overlap in cis S than in cis E; (b) the bond order H_{1s}–F_{p_z} is greater in cis S than in cis E; (c) the rotational barrier is calculated to be lower in cis than in trans 1-substituted propenes, and this arises because the energy difference between trans S and cis S is greater than the energy difference between trans E and cis E; (d) there is an expected anomaly in the case of 1-aminopropene; here, the cis S conformation becomes the low energy form and the cis E conformation becomes the high energy form, because of steric repulsions between the in-plane hydrogens in the cis E conformation.

Table IV. INDO Calculations of Rotational Barriers in Typical 1-Substituted Propenes

Molecule	Total energy, au	Relative energy, kcal/mol
	a. $CH_3CH{=}CHF$	
Trans S	−50.680652	1.996
Trans E	−50.683832	0
Cis S	−50.681593	1.569
Cis E	−50.684092	0
	b. $CH_3CH{=}CHOCH_3$	
Trans S	−51.035756	1.891
Trans E	−51.038768	0
Cis S	−51.037325	1.395
Cis E	−51.039548	0
	c. $CH_3CH{=}CHNH_2$	
Trans S	−36.958769	1.761
Trans E	−36.961575	0
Cis S	−36.961778	0
Cis E	−36.959976	1.131

The general result of this qualitative analysis can be stated as follows: in 1-substituted propenes, where the cis isomer is found to be more stable than the trans isomer, one should also expect that the rotational barrier of the cis isomer will be lower than the rotational barrier of the trans isomer. Experimental results which are in striking agreement with these generalizations are given in Table V. In short, attractive nonbonded interactions seem to account for the striking difference of the rotational barriers in cis and trans 1-substituted propenes.

Table V. Relationship between Geometric and Rotational Isomerism in 1-Substituted Propenes

Molecule	% cis at equil	Rotational barrier Cis	Rotational barrier Trans
$CH_3CH{=}CHF$		1.06[d]	2.20[e]
$CH_3CH{=}CHCl$	76[a]	0.62[f]	2.17[g]
$CH_3CH{=}CHBr$	68[b]	0.23[h]	2.12[i]
$CH_3CH{=}CHOCH_3$	71[c]		
$CH_3CH{=}CHCN$	57[a]	1.40[j]	2.10[k]

[a] J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963). [b] K. E. Harwell and L. F. Hatch, *J. Amer. Chem. Soc.*, **77**, 1682 (1955). [c] P. Salomaa and P. Nissi, *Acta Chem. Scand.*, **21**, 1386 (1967). [d] R. A. Beaudet and E. B. Wilson, Jr., *J. Chem. Phys.*, **37**, 1133 (1962). [e] S. Segal, *ibid.*, **27**, 989 (1957). [f] R. Beaudet, *ibid.*, **40**, 2705 (1964). [g] R. Beaudet, *ibid.*, **37**, 2398 (1962). [h] R. A. Beaudet, personal communication cited in J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968). [i] R. A. Beaudet, paper presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, Sept 1966, Paper V12. [j] R. A. Beaudet, *J. Chem. Phys.*, **38**, 2548 (1963). [k] V. W. Laurie, *ibid.*, **32**, 1588 (1960).

The concept of long range attraction has undergone a slow evolution and now promises to become a major tool in the theoretical analysis of structural and reactivity properties of molecules. In this respect the contributions of Hoffmann[12,13] and his collaborators merit special attention. In this paper, we have shown that the concepts of through space and through bond orbital interaction[14] can be fruitfully applied to the discussion of molecular structure and can lead to interesting conclusions. The approach described here is qualitative.[15] A direct experimental testing of this model is in progress, and further theoretical work should provide additional valuable information about the range and magnitude of nonbonded attraction.[16]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for support of this work. We wish to thank Professor E. R. Davidson for making available his computer programs and Professors B. M. Gimarc and J. P. Lowe for their helpful comments.

---

(12) R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

(13) R. Hoffmann, C. C. Levin, and R. A. Moss, *ibid.*, **95**, 629 (1973).

(14) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(15) CNDO/2 and INDO calculations predict correctly the relative stability of the cis and trans isomers of a large number of 1,2-disubstituted ethylenes. For example, three possible conformational isomers of both *cis*- and *trans*-2-butene have been calculated and the trans isomer with both methyl groups in an eclipsed conformation was found to be the most stable isomer, in accordance with experimental results. The energy difference between the "best" trans isomer and the "best" cis isomers was 1100 cal in favor of the trans isomer. This and other results obtained by us indicate that CNDO/2 and INDO calculations provide a qualitatively adequate recognition of conventional interelectronic repulsion and can be used in the studies of the type reported here.

(16) One referee suggested that a comparison of the CNDO/2 and INDO one-electron orbital energies of the cis and trans isomers could further test the generality of the theory. Unfortunately, such comparisons cannot be made. One would have to know the one-electron energies of n_z, n_z^*, and n_z^{**} relative to the one-electron energies of the olefinic orbitals π_z and π_z^*. These "group orbital" energies are difficult to ascertain either directly or empirically. More importantly, our approach employs a Hückel-type Hamiltonian and the resulting one-electron orbital energies cannot be compared with SCF one-electron orbital energies since the SCF Hamiltonian contains the J and K terms which account for electron–electron interaction while the Hückel method employs an undefined interelectronic potential.