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Attractive Nonbonded Interactions in Organic Molecules

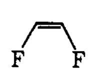
Nicolaos D. Epiotis

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received November 16, 1972*

Abstract: The interaction between lone pairs or between unsaturated bonds can be attractive in nature. This will occur whenever the orbitals of the lone pairs or the orbitals of the unsaturated bonds can interact through bonds with substrate orbitals of appropriate symmetry. The symmetry of the molecule determines in a major way whether nonbonded interactions will be attractive or repulsive in nature.

Molecular orbital theory has been applied to problems of organic chemistry very effectively. Some theoreticians have sought to correlate calculated quantities like electron densities, dipole moments, orbital energies, etc., with corresponding experimental observables. Some others have sought to interpret the results of molecular orbital calculations by using perturbation theory which allows the construction of a fully delocalized system from essentially localized parts. The latter approach has been eminently successful with organic reactivity problems where the knowns are the electronic properties of the parts, *e.g.*, the reactants, and the unknowns are the electronic properties of the system, *e.g.*, the transition state.[1,2] In this paper we report an approach of the latter type dealing with the nature of attractive nonbonded interactions in organic molecules and organic transition states.

There exist many examples in organic chemistry where the intuitive concept of nonbonded interelectronic repulsion fails to lead to correct predictions regarding the relative stability of geometrical or conformational isomers of organic molecules. For example, it is well known that *cis*-difluoroethylene is more stable than *trans*-difluoroethylene[3] and that *n*-propyl halides assume a preferred gauche rather than anti conformation.[4] In the examples given here two large groups display an affinity for each other contrary to expectations based on our intuition. Steric arguments, so frequently used by organic chemists to rationalize structural or reactivity patterns, clearly fail in these cases. The origin of such attractive effects has remained unclear.[5] We wish to present a simple interpretation of nonbonded attraction.



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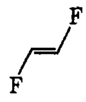

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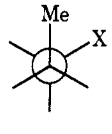

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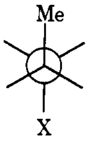

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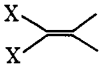
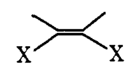
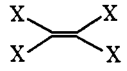
We will consider the interaction between two lone pairs, one occupying an atomic orbital ϕ centered on atom i and another occupying an atomic orbital ψ centered on atom j. In the language of quantum mechanics this interaction will be attractive in nature if the bond order element $P(\phi_i)(\psi_j)$ is positive and conversely.[6] Our problem is then reduced to identifying the way in which this bond order element varies for different geometrical arrangements of the atoms i and j which carry the lone pairs. We shall illustrate our approach by considering the three model systems shown below.







If X is fluorine, or, in general, a halogen, we have the most general case of two lone pairs per atom interacting. If X is NH_2, or, in general, a group YH_2 where

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(1) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968); G. Klopman, *ibid.*, **90**, 223 (1968); K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

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

(3) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969.

(4) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965.

(5) For speculations on the origin of these attractive interactions, see ref 3, ref 4, and G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968). For a quantitative discussion of the van der Waals and London forces involved, see M. M. Kreevoy and E. A. Mason, *J. Amer. Chem. Soc.*, **79**, 4851 (1957).

(6) In this and all subsequent discussions it is assumed that the two orbitals ϕ_i and ψ_j overlap appreciably and, hence, the bond order is a good index of bonding. This index is chosen because calculations have been carried out by the INDO method and bond orders rather than overlap populations are consistent with the INDO formalism.

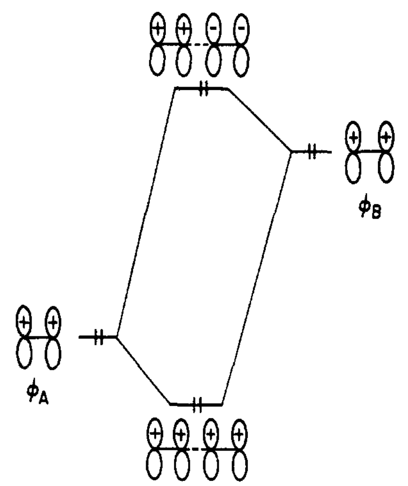

Figure 1. The interaction between two occupied olefinic orbitals. The interaction results in no net charge transfer.

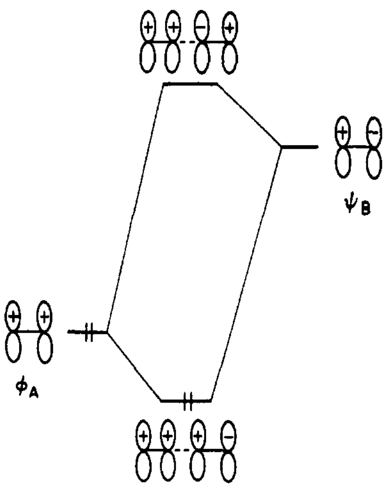

Figure 2. The interaction between an occupied and an unoccupied olefinic orbital. The interaction results in charge transfer from the occupied to the unoccupied orbital.

Y is N, P, etc., we have the least general case of a single lone pair per atom X interacting. We will consider the general case of the haloethylenes shown above. However, before we can proceed with our analysis it is necessary to consider the interrelationship among electron density, bond order, charge transfer, and orbital interactions.

Perturbation theory provides the framework for discussing orbital interactions. The energy of an isolated orbital ϕ_m becomes modified as a result of its interaction with other orbitals ψ_n. If there is no degeneracy between the interacting MO's, which will be the case of interest to us, the change in energy as a result of the orbital interaction is given by the expression

$$\delta E_m = \sum_n \frac{\langle \phi_m | \hat{P} | \psi_n \rangle^2}{E_m - E_n}$$

In the case of ground states, there are two important orbital interactions to be considered, namely, the interaction between two filled orbitals and the interaction between a filled and an unfilled orbital. The first type of interaction gives rise to no net charge transfer between the interacting orbitals. This is exemplified in Figure 1 for the interaction of the BMO's of two simple olefins. Here ϕ_A mixes with ϕ_B in a bonding combination and this amounts to charge transfer from ϕ_A to ϕ_B given by the expression

$$q_1 = n[\langle \phi_A | H | \phi_B \rangle / (E_{\phi_A} - E_{\phi_B})]^2 \quad n = 2 \tag{1}$$

On the other hand, ϕ_B mixes with ϕ_A in an antibonding combination and this amounts to charge transfer from ϕ_B to ϕ_A given by the expression

$$q_2 = n[\langle \phi_B | H | \phi_A \rangle / (E_{\phi_B} - E_{\phi_A})]^2 \quad n = 2 \tag{2}$$

As it can be seen from (1) and (2) there is no net charge transfer as a result of the orbital interaction because

$$q_1 = q_2 \tag{3}$$

The second type of interaction does give rise to net charge transfer between the interacting orbitals. This is exemplified in Figure 2 for the case of the interaction of the BMO of one olefin with the ABMO of the other olefin. Here, ϕ_A mixes with ϕ_B in a bonding combination and this amounts to charge transfer from ϕ_A to ψ_B given by the expression

$$q_3 = n[\langle \phi_A | H | \psi_B \rangle / (E_{\phi_A} - E_{\psi_B})]^2 \quad n = 2 \tag{4}$$

On the other hand, ψ_B mixes with ϕ_A in an antibonding combination and this amounts to zero charge transfer as can be seen from the expression below

$$q_4 = n[\langle \psi_B | H | \phi_A \rangle / (E_{\psi_B} - E_{\phi_A}]^2 = 0 \quad n = 0 \tag{5}$$

To summarize, the interaction of two filled orbitals results in no net charge transfer, while the interaction of a filled and an unfilled orbital results in charge transfer from the occupied orbital. We should now inquire as to how electron density is related to the bonding or antibonding character of a molecular orbital. In order to do that it is necessary to recall some simple relationships of elementary π molecular orbital theory[7] given below

$$\phi = c_1 p_1 + c_2 p_2 \tag{6}$$

$$Q = n(c_1^2 + c_2^2) \tag{7}$$

$$P_{12} = n c_1 c_2 \tag{8}$$

In the expressions above ϕ is a two-center π MO and c_1 and c_2 are the atomic orbital coefficients of p_1 and p_2, Q is the number of electrons occupying ϕ written in terms of the occupation number, n, and the atomic orbital coefficients, and P_{12} is the bond order element given in terms of the occupation number and the atomic orbital coefficients. For symmetrical cases we have

$$c_1 = c_2$$

and as a result we obtain

$$Q = 2|P_{12}|$$

because c_1 and c_2 can have opposite signs. This means that a bond order becomes increasingly positive as one feeds electrons in a BMO. Similarly, we can show that a bond order becomes increasingly negative as one

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(7) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1962; A. Liberles, "Introduction to Molecular Orbital Theory," Holt, Rinehart and Winston, New York, N. Y., 1966; A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961; A. Streitwieser and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965.

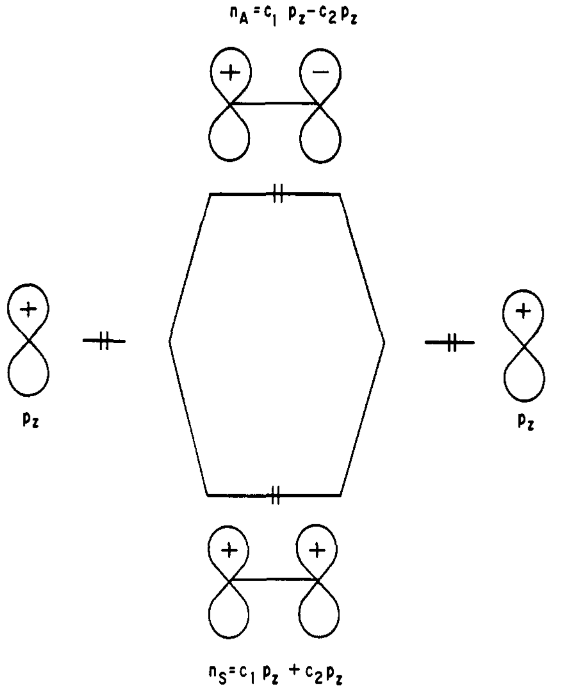


Figure 3. The interaction of two p_z lone pairs to yield a bonding, n_S, and an antibonding, n_A, combination.

feeds electrons in an ABMO. In the light of the above discussion it becomes clear that the bond order element between any two atomic centers will be affected by orbital interactions which result in the net transfer of electron density. This can be illustrated by considering the interaction of two lone pairs each occupying a p_z atomic orbital. This is shown in Figure 3. The bond order between the two orbitals is zero unless an unfilled orbital of S or A symmetry interacts with the n_S or the n_A orbitals, respectively. In the latter case the bond order will become positive while in the former case the bond order will become negative. Of course, this simple discussion neglects overlap. Inclusion of overlap will only shift the origin of the discussion, if we may say so. In such a case, the interaction between two lone pairs will be repulsive initially and orbital interaction will tend to render it even more repulsive or attractive.

A simple rule emerges: the interaction of two lone pairs will be attractive in nature if there is an antisymmetric (A) MO which can interact with the antisymmetric lone pair combination, n_A, and it will be repulsive in nature if there is a symmetric (S) MO which can interact with the symmetric lone pair combination, n_S. We shall now consider how this rule can be applied to cases of interest. It should be mentioned at this point that overlap populations, rather than bond orders, are better and more direct indices of bonding. In this paper we utilize bond orders consistent with the semiempirical computations employed to test our approach, and the importance of overlap in bonding is considered separately.

1,1-Dihaloethylenes

In 1,1-dihaloethylenes there is one lone pair occupying the p_z orbital of the halogen and one lone pair which can be localized mainly in a p_x or a p_y orbital. The lone pairs on one halogen atom will intereact with the lone pairs of the other halogen atom and with the orbitals of the olefinic bond as well. The type of interaction between the lone pairs and the olefinic bond will determine whether there will be net attraction or repulsion between the lone pairs. In this and subsequent discussions we shall consider the interaction of the lone pairs with the $2p\pi$ and $2p\sigma$ olefinic orbitals. Consideration of the additional interaction between the lone pairs and the $2s\sigma$ olefinic orbitals is omitted for brevity since the same conclusions are reached whether the latter interaction is considered or not.

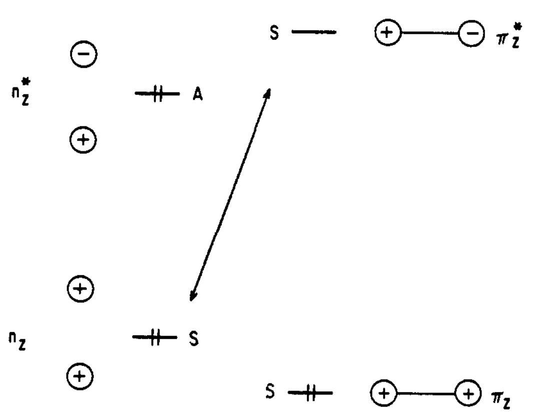


Figure 4. The interaction of the p_z lone pairs with the π_z orbitals of the ethylenic bond in 1,1-dihaloethylenes. Arrows indicate the interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

Consider the lone pairs occupying the halogen p_z orbitals. These lone pairs will interact since they are located in proximity to each other and their interaction will give rise to a bonding, n_z, and an antibonding, n_z^*, orbital. These orbitals can now interact with the π_z orbitals of the olefinic bond. In this case, there is an unoccupied π_z^* orbital which can interact with n_z giving rise to charge transfer from n_z to π_z^*. This renders the bond order between the two lone pairs negative and their interaction repulsive. The interactions between the filled orbitals are not considered because they do not affect the bond order of the lone pairs. This arises because there is no net charge transfer in the interactions between filled orbitals as discussed before. The arguments presented in this paragraph are best understood by reference to Figure 4.

Consider now the situation where the additional lone pairs are assumed to be mainly localized in the p_y halogen orbitals. By following the same reasoning as before we can determine that there is an empty σ_x^* orbital which can interact with the n_y orbital resulting in charge transfer and an empty π_y^* orbital which can interact with the n_y^* orbital also resulting in charge transfer. The latter interaction will be stronger than the former interaction since the energy separation of the interacting levels is smaller in the latter than in the former case. The net result of the two interactions is that the bond order between the two lone pairs becomes positive and their interaction attractive. The interaction diagram of Figure 5 provides a simple illustration of these considerations.

Finally, consider the situation where the additional lone pairs are assumed to be localized mainly in the p_x rather than the p_y halogen orbitals. The appropriate interaction diagram is given in Figure 6. This

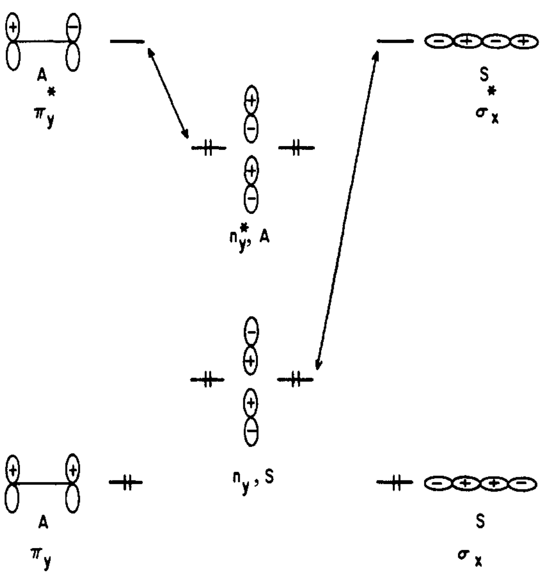


Figure 5. The interaction of the p_y lone pairs with the π_y and σ_x orbitals of the ethylenic bond in 1,1-dihaloethylenes. Arrows indicate the interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

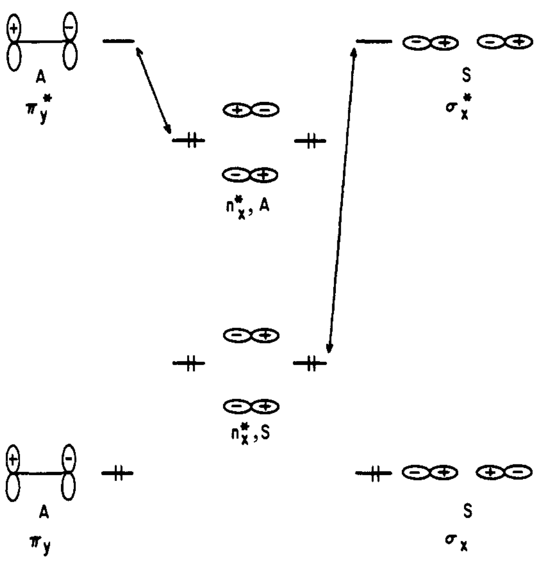
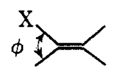


Figure 6. The interaction of the p_x lone pairs with the π_y and σ_x orbitals of the ethylenic bond in 1,1-dihaloethylenes. Arrows indicate the interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

case is identical with the previous one and it illustrates that whether the lone pairs are localized in the p_x or p_y halogen orbitals their interaction will be attractive in nature.

We have seen that the interaction of lone pairs occupying the p_z orbitals of halogen atoms will be repulsive in 1,1-dihaloethylene because there is a vacant olefinic π_z^* orbital which can interact with the bonding combination of the lone pairs. On the other hand, the interaction of lone pairs occupying the p_x or p_y orbitals of halogen atoms will be attractive in 1,1-dihaloethylene because there is a vacant olefinic π_y^* orbital which can interact dominantly with the antibonding combination of the lone pairs. On the basis of these considerations, it is clear that the two halogens in 1,1-dihaloethylene will attract or repel each other depending on the relative strength of the p_z–p_z repulsive interaction and the p_x–p_x or p_y–p_y attractive interactions. In haloethylenes, the lone pair of the halogen atom will be localized mainly in a p_x orbital as long as the angle ϕ is greater than 90°, a condition which is met in all normal olefins.



In such a case the ns and np_y orbitals of the halogen mix strongly and contribute mostly toward σ bond formation with the olefin while the lone pair becomes essentially localized in the p_x orbital of the halogen. We prefer to refer to the p_z–p_z lone pair interaction as the $p\pi$ interaction and to the p_x–p_x lone pair interaction as the $p\sigma$ interaction. In the case of interest the nature of halogen interaction will be determined by the relative magnitude of the $p\pi$ and $p\sigma$ bond orders.

We have carried out INDO calculations[8,9] on 1,1-difluoroethylene to determine the relative importance of $p\pi$ and $p\sigma$ lone pair interactions. The appropriate bond order information is contained in the density matrix and the results are shown in Table I. These results indicate that the attractive $p\sigma$ interactions clearly outweigh the repulsive $p\pi$ interaction. Table I contains both the total and the partial bond order between the p_x lone pairs of the halogens. The former involves summation of the p_x lone pair coefficient products over all occupied MO's while the latter involves summation of the same quantities over all the occupied MO's which are essentially "lone pair" in nature, *e.g.*, those MO's with a large coefficient for the halogen p_x orbitals. Obviously, the partial $p\sigma$ bond order is directly related to our analysis and the total $p\sigma$ bond order more remotely so. Net attraction or net repulsion between the two halogens will, of course, depend on the relative magnitude of the total $p\pi$ and $p\sigma$ bond orders. In the case of 1,1-difluoroethylene the degree of overlap between the two fluorine p_x orbitals is the same as the degree of overlap between the two fluorine p_z orbitals. Hence, it is predicted that there will be net attraction between the two halogens which is due to the p_x lone pair attractive interaction.

Table I. Bond Orders between the Lone Pairs of the Fluoroethylenes

Fluoroethylene	pπ bond order	Total pσ bond order	Partial pσ bond order
1,1-Difluoroethylene[a]	−0.0533	0.0873	0.0102
cis-1,2-Difluoroethylene[b]	0.0475	−0.0242	0.0066
Tetrafluoroethylene[c]			
Geminal fluorines	−0.0403	0.0978	
Vicinal fluorines	0.0403	−0.0381	

[a] Bond angles and bond lengths from ref 10b. [b] Standard bond angles and bond lengths from ref 9. [c] Bond angles and bond lengths from J. A. Young, *Diss. Abstr.*, **16**, 460 (1956).

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(8) The calculations were carried out on a CDC-6400 computer with the INDO program which is similar to the program of Pople and Dobosh.

(9) For an interesting discussion of approximate SCF methods the reader should consult J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

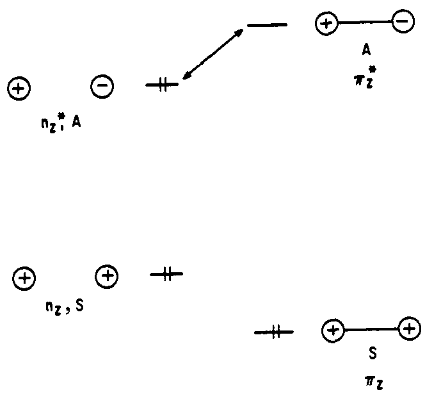


Figure 7. The interaction of the p_z lone pairs with the π_z orbitals of *cis*-1,2-dihaloethylene. Arrows indicate the orbital interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

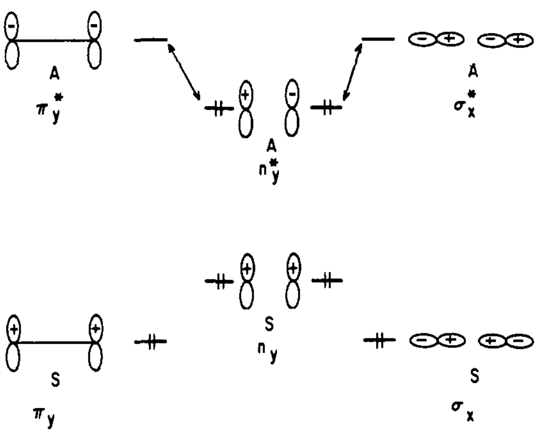
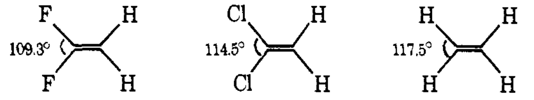


Figure 8. The interaction of the p_y lone pairs with the π_y and σ_x ethylenic orbitals of *cis*-1,2-dihaloethylene. Arrows indicate the orbital interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

It is interesting to test these predictions by reference to experimental data. Direct evidence for the attractive interaction of halogens in haloethylenes has been provided by spectroscopic studies. Specifically, it has been found that the XCX bond angle in dihaloethylenes is significantly less than 120° and, in any case, less than the HCH angle in ethylene.[10] However, it should be recalled that the FCF angle is smaller than normal in CH_2F_2 and, hence, the angle effect may not be specific for 1,1-dihaloethylenes. It is interesting to note that this bond angle effect in 1,1-difluoroethylene had been postulated to arise from p–p interaction of some sort.[11] As we have seen pπ interaction is actually repulsive in nature and it is the combined effect of pπ and pσ interactions which results in halogen attraction. What is noteworthy is that the nature of pπ interaction of the lone pairs could have been predicted by simple Hückel analysis. 1,1-Difluoroethylene is a six electron system isoconjugate to the trimethylenemethene dianion.[12] The bond order between two peripheral centers is negative and, hence, pπ interaction is repulsive. In a few words, orbital analysis, SCF calculations, and simple Hückel molecular orbital theory all yield the same clear-cut result with respect to pπ interaction.



cis-1,2-Dihaloethylenes

In *cis*-1,2-dihaloethylenes there will be lone pairs occupying the halogen p_z orbitals and lone pairs mainly localized in the p_x or p_y orbitals of the halogen. A lone pair on one halogen will interact with the lone pair of the other halogen and with the orbital of the olefinic bond as well. This latter interaction will determine whether the lone pairs on the two halogen atoms will have a bonding or antibonding character. The interaction of the lone pairs and the olefinic orbitals is considered below and the reasoning employed is similar to that of the previous cases.

Consider the lone pairs occupying the p_z halogen orbitals. These orbitals split into a bonding, n_z, and an antibonding, n_z^*, combination which can then interact with the orbitals of the olefinic bond. In this case, there is an unoccupied π_z^* orbital which can interact with n_z^* giving rise to charge transfer from n_z^* to π_z^*. This renders the bond order between the lone pairs positive and their interaction attractive. These considerations are illustrated in Figure 7.

Consider now the situation where the additional lone pairs are assumed to be mainly localized in the p_y halogen orbitals. The interactions of the n_y and n_y^* orbitals with the olefinic orbitals are shown in Figure 8. In this case the conclusions are straightforward. The σ_x^* and π_y^* orbitals of the olefinic bond can interact with n_y^* giving rise to charge transfer from n_y^* to σ_x^* and π_y^*. These interactions render the bond order between the lone pairs positive and their interaction attractive.

Finally, consider the situation where the additional lone pairs are assumed to be mainly localized in the p_x halogen orbitals. This case is identical with the previous case. The appropriate interaction diagram is shown in Figure 9. Again, whether the lone pairs are localized in the p_y or p_x halogen orbitals their mutual interaction is predicted to be attractive in nature. As we have seen before, the lone pairs of halogens attached to ethylene are essentially localized in the p_z and p_x halogen orbitals.

It should be pointed out that the interaction of the lone pairs and the olefinic bond occurs in both *cis*- and *trans*-1,2-dihaloethylenes. The magnitude of the interaction and, hence, the degree of charge transfer, is comparable in both isomers. This is due to a net balance of the size of the matrix element for the interaction and the magnitude of the energy separation of the interacting orbitals in each isomer. However, the interaction of the lone pairs and the olefinic bond can lead to nonbonded attraction in the cis but not the trans isomer.

It is interesting to note that the case of *cis*-1,2-difluoroethylene is quite different from the case of 1,1-difluoroethylene. In the former case both lone pair interactions, namely, pπ and pσ, are attractive in nature.

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(10) (a) R. L. Livingston, C. N. R. Rao, L. M, Kaplan, and L. Rocks, *J. Amer. Chem. Soc.*, **80**, 5368 (1958); (b) W. F. Edgell, P. A. Kinsey, and J. W. Amy, *ibid.*, **79**, 2691 (1957); (c) V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963); (d) J. M. Dowling and B. P. Stoicheff, *Can. J. Phys.*, **37**, 703 (1959); (e) M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, **69**, 4091 (1965).

(11) For example, see W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).

(12) Hückel wave functions can be found in ref 7.

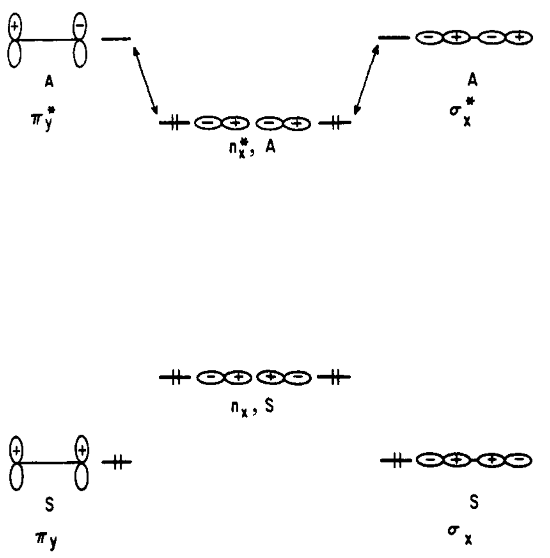


Figure 9. The interaction of the p_x lone pairs with the π_y and σ_x ethylenic orbitals of *cis*-1,2-dihaloethylene. Arrows indicate the orbital interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

Table II. Equilibrium Composition of Cis and Trans Isomers in XHC═CHY Molecules

X,Y	% cis at equil temp	Ref
F,F	63	*a*
F,Cl	70	*a*
F,Br	70	*a*
F,I	67	*b*
Cl,Cl	61	*c*
Br,Br	50	*d*
CH_3,Cl	76	*e*
CH_3,Br	68	*f*
CH_3,OPh	65	*g*
CH_3,OEt	81	*h*

[a] H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960). [b] A. Demiel, *J. Org. Chem.*, **27**, 3500 (1962). [c] R. E. Wood and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 1650 (1941); K. S. Pitzer and J. L. Hollenberg, *ibid.*, **76**, 1493 (1954). [d] H. G. Viehe and E. Franchimont, *Chem. Ber.*, **96**, 3153 (1963); **97**, 602 (1964). [e] J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963). [f] K. E. Harwell and L. F. Hatch, *J. Amer. Chem. Soc.*, **77**, 1682 (1955). [g] C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961). [h] P. Salomaa and P. Nissi, *Acta Chem. Scand.*, **21**, 1386 (1967).

Hence, the two halogen atoms in *cis*-1,2-difluoroethylene will tend to attract each other.

We have carried out INDO calculations on *cis*-1,2-difluoroethylene and the results are shown in Table I. It can be seen that the $p\pi$ bond order between the fluorine lone pairs is positive in agreement with our simple analysis. On the other hand, the total $p\sigma$ bond order is negative. This apparent anomaly arises from the fact that the p_x lone pair of fluorine is not completely localized in the p_x orbital. However, the partial $p\sigma$ bond order which is directly linked to our analysis and evaluated over all occupied MO's which are essentially "lone pair" in character is positive in accordance with our expectations. In any event, the $p\pi$ bond order is greater than the total $p\sigma$ bond order in absolute magnitude, and one can reasonably expect that there will be net attraction between the two halogen atoms. The overlap between the contaminated p_x lone pair orbitals is comparable to the overlap between the p_z lone pair orbitals.

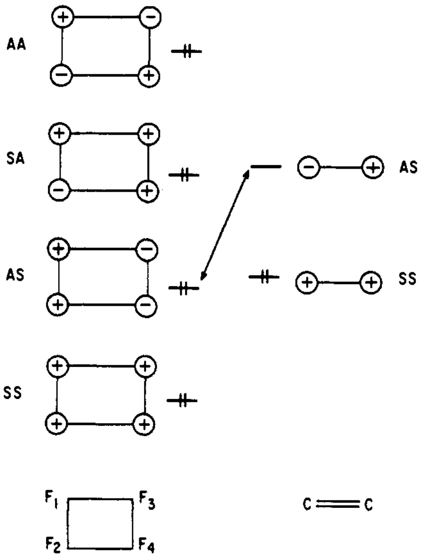
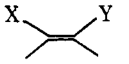
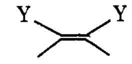


Figure 10. The interaction of the p_z lone pairs with the π_z orbitals of tetrafluoroethylene. Arrows indicate the orbital interactions which give rise to net charge transfer. Orbitals are classified with respect to *xz* and *yz* planes of symmetry.

Experimental evidence supporting our predictions is plentiful. Since there is net attraction between the two halogen atoms due to the $p\pi$ interaction, one expects that the cis isomer will be more stable than the trans isomer. This is so because the cis form can enjoy the additional stabilization provided by the attractive forces between the halogen centers, while the trans form cannot do so. The same conclusions are reached for molecules of the type shown below where X is a halogen and Y is a heteroatom with a single p_z lone pair. Experimental results are available, and in the case of the isomeric pairs listed in Table II the cis isomer has been found to be more stable than the trans isomer. In the examples of Table II it is assumed that the methyl group can be satisfactorily represented by the heteroatom model[13a] which, in effect, equates the methylene group with a doubly occupied p orbital.





It is interesting that the enhanced stability of the cis over the trans isomer of difluoroethylene had also been postulated to arise from some sort of p–p interaction. As we have seen $p\pi$ interaction is mainly the reason why *cis*-difluoroethylene is expected to be more stable than *trans*-difluoroethylene. The attractive nature of the $p\pi$ interaction in molecules like difluoroethylene could have been derived by simple Hückel molecular orbital theory. *cis*-1,2-Difluoroethylene is a six electron system isoconjugate to the cisoid butadiene dianion. The bond order between C_1 and C_4 in the butadiene dianion is calculated to be positive. This bonding situation between the two outer carbons will be present in the cisoid form where overlap occurs while it will be absent in the transoid form where overlap does not occur.[13b]

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(13) (a) F. A. Matsen, *J. Amer. Chem. Soc.*, **72**, 5243 (1950); D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966). (b) Obviously, the 1–4 π bond order itself will be the same in cisoid and transoid butadiene dianion according to Hückel type calculations but not so according to semiempirical or *ab initio* calculations. In the latter cases, the difference turns out, in general, to be small.

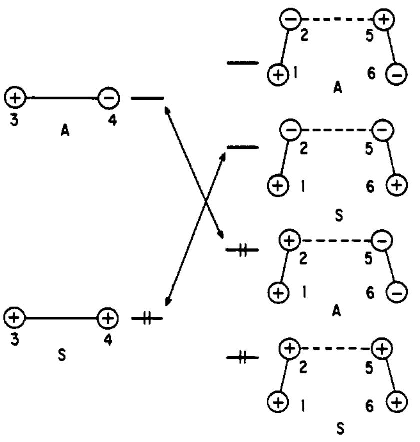


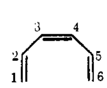
Figure 11. The interaction of the central π bond with the "outer" bonds in hexatriene systems. Arrows indicate the interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

Tetrahaloethylenes

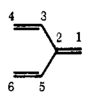
The nature of lone pair interactions in tetrahaloethylenes can be predicted on the basis of the previous discussions of 1,1- and *cis*-1,2-dihaloethylenes. In other words, the F_1–F_2 interaction will be similar to the interaction of the halogen atoms in 1,1-dihaloethylene and the F_1–F_3 interaction will be similar to the interaction of the halogen atoms in *cis*-1,2-dihaloethylene. This is illustrated in Figure 10 for the case of the p_z lone pairs and similar interaction diagrams can be constructed for the case of the p_y and p_z lone pairs. It can be seen from Figure 10 that the p_{1z}–p_{2z} lone pair interaction is repulsive exactly like in the case of 1,1-dihaloethylene and the p_{1z}–p_{3z} lone pair interaction is attractive like in the case of *cis*-1,2 dihaloethylene. We have carried out INDO calculations on tetrafluoroethylene and the results are similar to those obtained in the previous cases. Specifically, geminal fluorine interaction is predicted to be attractive in nature because of the predominance of the attractive pσ term, while vicinal fluorine interaction is also predicted to be attractive in nature because of the predominance of the attractive pπ term. The results are given in Table I. An interesting observation is that the partial pσ bond order is undefinable for tetrafluoroethylene because the lone pairs of the p_x halogen orbitals are extensively delocalized.

Hexatriene Systems

We are now prepared to extend the ideas described in the previous sections to other molecular types. Two common types of molecules are shown below. Molecule I can be treated as the interaction of the central olefinic bond with two symmetrically homoconjugated ethylenes. The interaction will be of the pπ variety and could in principle lead to attraction or repulsion between the two end double bonds. The interaction diagram of Figure 11 indicates that there will be a net attractive interaction between the two "end" double bonds.



I



II

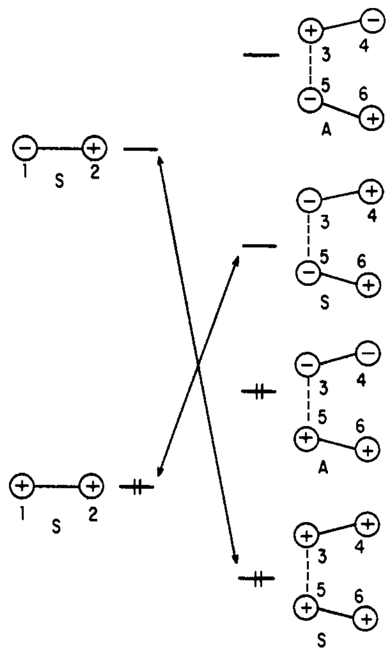
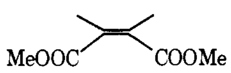


Figure 12. The interaction of a π bond with two adjacent π bonds in 1,1-divinylethylene systems. Arrows indicate the interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.

This will occur because charge transfer from ϕ_1 to ψ_3 and from ψ_2 to ϕ_2 increases the bond order between C_1 and C_6 and between C_2 and C_5. Molecule II can be treated in a similar manner and it is revealed that in this case there will be two different types of interaction, one reducing and one increasing the bond order between C_3–C_5 and C_4–C_6. Net attraction or repulsion will be determined by the relative strength of the two interactions. These considerations are illustrated in Figure 12.

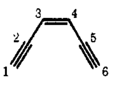
Experimental evidence regarding molecules of type I discussed in this section is available, but the interpretation is complicated by the presence of steric interactions between the ligands of the two outer double bonds. Thus, it is found that dimethyl fumarate is more stable than dimethyl maleate.[14] On the other hand, there is no experimental evidence which can be correlated with predictions regarding the interaction of the outer double bonds in type II molecules.

fumarate

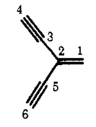


maleate

An interesting situation arises when the "end" double bonds are replaced by triple bonds. The linearity of the acetylenic unit prohibits the complicating steric interactions which occur with molecules of the type I and type II. By following the same reasoning as in the



III



IV

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(14) K. Mackenzie in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, and references cited therein.

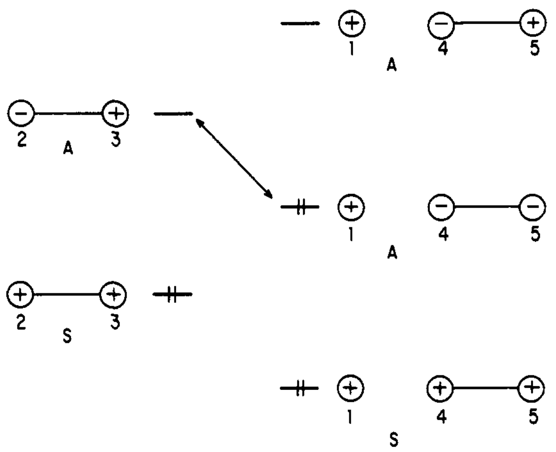


Figure 13. The interaction of a π bond with the adjacent π bond and heteroatom X. Arrows indicate the interactions which give rise to net charge transfer. The system is 1-X butadiene and the orbitals are classified with respect to plane of local symmetry.

previous case regarding the double bonds we arrive at the conclusion that in type III molecules there will be pπ and pσ attractive interactions between the triple bonds, while in type IV molecules there will be a pπ interaction which can be either attractive or repulsive and a pσ interaction which will be attractive in nature. In other words, the pπ interactions are similar for I and III and for II and IV but the acetylenic molecules display additional pσ interactions.

It is interesting to inquire whether the attractive interaction of the triple bonds in molecules of type III is actually manifested. In this respect, Huisgen has observed that in Diels–Alder reactions the trans isomer of a dienophilic pair reacts faster than the corresponding cis isomer.[15] For example, dimethyl fumarate reacts faster than dimethyl maleate in a typical Diels–Alder reaction. This is postulated to occur because in going from trigonal to tetrahedral carbon along the reaction coordinate you increase the nonbonded repulsions of the cis isomer more than those of the trans isomer. In molecules of type III such as *cis*- and *trans*-dicyanoethylenes one would expect that the attractive interaction of the two triple bonds will render the cis isomer more reactive than the trans isomer since in this case bringing the two cyano groups together along the reaction coordinate provides for better increased attractive interaction. The results shown below indicate

Dienophile	Trans/cis reactivity toward cyclopentadiene
$\mathrm{MeOOC{-}C{=}C{-}COOMe}$	117.8
$\mathrm{NC{-}C{=}C{-}CN}$	0.88

that the expected attractive effect between the triple bonds does operate albeit not to a great extent.

Pentadiene Systems

Two common types of molecules are shown below. Molecules V and VI can be treated as the interaction of the central olefinic bond with a homoconjugated atom X and a double bond. By going through the same reasoning as in the previous cases we conclude that there will be a net attractive interaction between the atom X and one center of the double bond in molecules of type V and a repulsive interaction between the corresponding centers in molecules of type VI. The interaction diagrams which lead to these conclusions are shown in Figures 13 and 14. We can replace the end double bond by a triple bond and this gives rise to molecules of types VII and VIII.

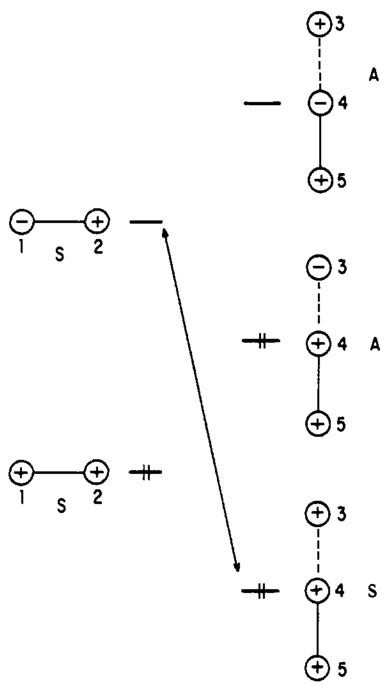
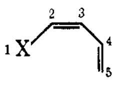
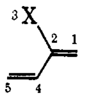


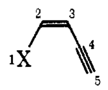
Figure 14. The interaction of a π bond with the adjacent π bond and heteroatom X. Arrows indicate the interactions which give rise to net charge transfer. The system is 2-X butadiene and the orbitals are classified with respect to plane of local symmetry.



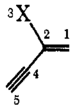
V



VI



VII



VIII

If X has one lone pair one is led to a situation similar to the one involved in type V and VI molecules since only pπ interactions obtain. If X has two lone pairs there will be an additional interaction between the acetylenic bond and the p_z lone pair of the heteroatom X. This interaction will be attractive for both type VII and VIII molecules. In the former case there will be net attraction between the triple bond and X because both pπ and pσ interactions are attractive, while in the latter case net attraction or repulsion will be determined by the relative strength of the pπ and pσ interactions. In short, VII and VIII are similar to *cis*-1,2-difluoroethylene and 1,1-difluoroethylene, respectively. Experimental data which confirm these expectations are given below for the unambiguous case of type VII molecules. The data in Table III show that the cis isomer has been found to be more stable than the trans isomer. It is interesting that the cis isomer is more stable than

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(15) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, and references cited therein.

Table III. Equilibrium Composition of Cis and Trans Isomers of XHC=CH—CH=CH_2 and XHC=CHCN Molecules

Molecule	% cis at equil temp	Ref
CH_3CN=CHCN	57	*a, b*
ClCH=CHCN	69	*a*
FCH=CH—CH=CH_2	62	*c*
ClCH=CH—CH=CH_2	70	*c*

[a] J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963). [b] J. N. Butler and R. D. McAlpine, *Can. J. Chem.*, **41**, 2487 (1963). [c] H. G. Viehe, *Angew. Chem.*, **75**, 793 (1963).

the trans isomer in the case of crotononitrile while the reverse holds for methyl crotonate.[16] The difference in behavior between the carbomethoxy and cyano groups is the same one encountered in the case of the isomeric dicarbomethoxy and dicyano ethylenes and it probably reflects the greater steric requirement of the carbomethoxy group.

Saturated Molecules

We now turn our attention to molecules like 1,2-disubstituted ethanes where the two substituents carry lone pairs. Consider, for example, the interaction of the lone pairs in 1,2-difluoroethane with the C–C bond. The lone pairs interact to form a bonding and an antibonding combination which can then interact with the σ and σ^* orbitals of the C–C bond. This is shown in Figure 15. It can be readily seen that charge transfer from the n_x^* orbital to the σ^* orbital renders the bond order between the p_x lone pairs positive and their interaction attractive. A similar analysis yielding the same results can be carried out with respect to the p_y halogen lone pairs.

There is impressive experimental evidence which supports the idea of attractive lone pair interactions in saturated molecules.[17–24a] This attractive interaction will be maximal for the syn eclipsed conformation and for the anti staggered conformation of molecules like 1,2-disubstituted ethanes, where the two substituents carry actual or formal lone pairs, an example of the latter type being the methyl group. Since the syn eclipsed conformation suffers from repulsive H–H interactions, a compromise is expected to result and the preferred conformation of many such molecules can be the gauche rather than the anti which one would have predicted on the basis of intuitive ideas regarding electron repulsions. Some experimental observations supporting these ideas are given below. A very large number of experimental facts which support these ideas has been collected by Wolfe[24b] in an excellent account of the so called "gauche effect." In addition this account includes extensive reference to recent theoretical work on rotational and inversion barriers. These theoretical studies done mostly within the *ab initio* framework deal with smaller molecules than the ones examined in this paper. It is very likely, however, that the ideas on nonbonded attraction described in this paper will be profitably used in discussing "attractive dominant" conformational barriers in a general qualitative manner.

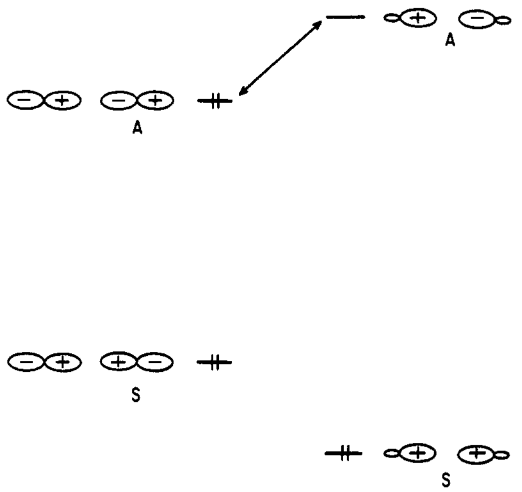
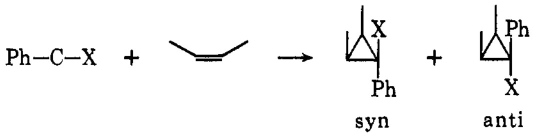


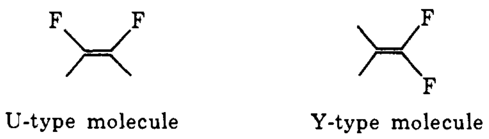
Figure 15. The interaction of the lone pairs of two heteroatoms with the σ orbitals of the carbon–carbon bond in systems of the type X-CH_2-CH_2-X in the syn eclipsed conformation. Orbitals are classified with respect to plane of symmetry.

Some additional interesting examples supporting these ideas can be found in the case of the reaction of phenylhalocarbenes with *cis*-2-butene. In such cases a significant regiochemical preference is observed to the extent that the halogen is oriented syn to the two methyl groups of *cis*-2-butene. Thus, the syn/anti ratio for the addition of phenylchloro carbene is 3.0[25] and the syn/anti ratio for the addition of phenylbromo carbene is 1.4.[26] The origin of this effect might very well be the attractive interaction between the halogen and the methyl group which is of the same type as the attractive interaction responsible for the preferred gauche conformation of *n*-propyl halides.



Conclusion

In this paper we attempted to show that there exist attractive interactions between lone pairs and these interactions are of both the pπ and the pσ type. Strong attractive interactions obtain in the case of U-type molecules and weak attractive interactions obtain in Y-type molecules. This arises from the difference in the symmetry classification of the interacting orbitals.



The analysis presented in these papers is a linear combination of three important concepts. (1) The con-

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(16) J. N. Butler and G. J. Small, *Can. J. Chem.*, **41**, 2492 (1963).
(17) P. Klaboe and J. R. Nielsen, *J. Chem. Phys.*, **33**, 1764 (1960).
(18) H. J. Bernstein, *J. Chem. Phys.*, **17**, 258 (1949).
(19) N. Sheppard, *Advan. Spectrosc.*, **1**, 295 (1959).
(20) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.
(21) Y. Morino and K. Kutchitsu, *J. Chem. Phys.*, **28**, 175 (1958).
(22) T. N. Sarachman, *J. Chem. Phys.*, **39**, 469 (1963).
(23) E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962).
(24) (a) T. Ukaji and R. A. Bonham, *J. Amer. Chem. Soc.*, **84**, 3631 (1962); (b) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972). It should be apparent that our analysis is an isolated molecule analysis and is directly relevant to gas phase data. It is possible that other effects contribute toward gauche conformational preference in solution.
(25) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).
(26) R. A. Moss and R. Gerstl, *Tetrahedron*, **22**, 2637 (1966).

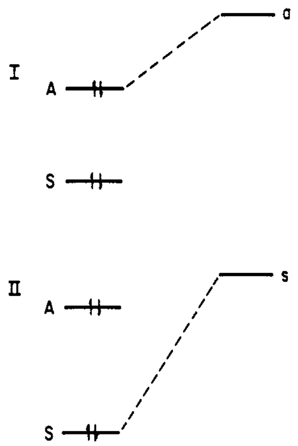

Figure 16. The two different cases of lone pair interactions with an adjacent system. In both cases there is net energy stabilization of the total system accompanied by either intrapair attraction (case I) or intrapair repulsion (case II).

cept of through space orbital interaction.[20] (2) The concept of charge transfer and its consequences on bonding properties of molecules.[27] (3) The concept of through bond orbital interaction.[2]

These concepts have been elegantly and simply stated by Hoffmann and his school and have been applied to organic structure and reactivity problems. In fact, Hoffmann and Olofson[28] as early as 1966 have discussed the dependence of conformational and isomer stability of polyene cations and anions on orbital occupancy in a manner which is essentially similar to our way of discussing the topics of this paper.

In this work we have employed calculations in order to test our analysis rather than generate numbers which could be compared with experiments. Nonetheless, it is of interest that the INDO procedure correctly predicts that difluoroethylene is more stable in the cis rather than in the trans form. In fact the calculated energy difference between the two isomers of difluoroethylene is 611 cal/mol, assuming standard bond angles and bond lengths, as compared with the experimental 928 cal/mol both favoring the cis isomer.

Professor Lionel Salem has made an interesting observation on the correspondence of the charge transfer viewpoint and the energetic viewpoint. This is illustrated in Figure 16. In case I the charge transfer point of view, *e.g.*, less antibonding density, so attraction between the lone pairs, agrees with the energetic point of view, *e.g.*, stabilization of the two A electrons. The situation is different in case II. Here, the charge transfer point of view, *e.g.*, less bonding density, so repulsion between the lone pairs, *seems* to disagree with the energetic point of view, *e.g.*, stabilization of the two S electrons. Of course, the answer here is that the disagreement is only apparent. Indeed, although the bond order between the two lone pairs decreases, the bond order between each lone pair and the system which carries the vacant orbital s increases. The latter is more important than the former and, hence, there is an overall *stabilization* which accompanies the intrapair *repulsion*.

Our analysis has been simplistic. It is a one-electron analysis with neglect of overlap where the interactions between filled orbitals are ignored. These drawbacks will manifest themselves in extreme cases. For example, diiodoethylene is more stable in the trans than in the cis form. Here, repulsions which are not given recognition by our approach upset our predictions. On the other hand, there is little doubt that the attractive interactions we alluded to obtain in most systems. More experiments and theoretical work will provide a better estimate of their importance relative to other effects.[29,30]

Acknowledgment. It is a pleasure to acknowledge the helpful comments of R. Hoffmann, L. Salem, and P. v. R. Schleyer. Professor R. Hoffmann kindly provided us with a preprint of related work in advance of publication. Professor E. R. Davidson graciously provided the computer facilities for this work. This work was made possible by the support of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation.

Appendix

Calculations by the INDO method were carried out on a CDC-6400 computer. The program used was essentially that of Pople and Dobosh described in ref 9 and adapted to the CDC-6400 computer by L. Stenkamp. The geometries of the haloethylenes were varied in order to determine the effect of structural variation on the sign and magnitude of the bond orders of interest. The qualitative results described in this paper are mostly independent of geometry choice.

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(27) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Gunther, *ibid.*, 5173 (1970).

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

(29) Professor Roald Hoffmann has discussed the possibility of "steric attraction" in a recent paper submitted for publication: R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Amer. Chem. Soc.*, **95**, 629 (1973).

(30) Subsequent to submission of this manuscript two interesting papers dealing with the nature of lone pairs in polyatomic molecules appeared in the literature: G. W. Schnuelle and R. G. Parr, *J. Amer. Chem. Soc.*, **94**, 8974 (1972); M. A. Robb, W. T. Haines, and I. G. Csizmadia, *ibid.*, **95**, 42 (1973).