# Nonbonded Attraction in Organic Molecules and Substituent Effects on Nonbonded Attraction

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*Summary* Lone pairs can interact with each other and also with adjacent bonds, and this results in net lone pair attraction which is subject to substituent effects; experimental results are in agreement with these general qualitative conclusions.

THE interaction of nonbonded electrons[1] is responsible for certain mysterious effects in organic chemistry such as the small geminal angles in 1,1-disubstituted ethylenes[2] and the greater stability of the *cis* rather than the *trans* isomer of various olefins.[3] We report a simple molecular orbital interpretation of these effects.

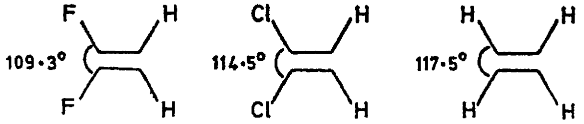
In 1,1-dihalogenoethylenes, the halogen lone pairs are contained in the $p_z$ and $p_x$ orbitals.† The $p_z$ lone pairs interact because of their proximity[4] to one another, and give rise to a bonding, $n_z$, and an antibonding $n_z^*$, orbital. The bond order between the two halogen $p_z$ orbitals is zero and the two lone pairs can be said to neither attract or repel each other. The $n_z$ and $n_z^*$ orbitals can then interact with the $\pi_z$ orbitals of the olefinic bond and there is an unoccupied $\pi_z^*$ orbital which can interact with $n_z$. A consequence of this interaction is charge transfer[5] from $n_z$ to $\pi_z^*$ and this now renders the bond order between the two halogen $p_z$ orbitals negative and the lone pairs can be said to repel each other (see Figure). Similarly the $p_x$ lone pairs will interact with each other and give rise to a bonding, $n_x$, and an antibonding, $n_x^*$, orbital. By following the same reasoning as before we find that there is an empty $\sigma_x^*$ orbital which can interact with the $n_x$ orbital resulting in charge transfer and an empty $\pi_y^*$ orbital which can interact with the $n_x^*$ orbital also resulting in charge transfer. The latter interaction will be stronger than the former 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 halogen $p_x$ orbitals becomes positive and the lone pair interaction attractive.‡

TABLE. *The effect of substituents on the stability of the geometrical isomers of* FXC=CXF *molecules*[a]

| Substituent X | $E_{\text{cis}} - E_{\text{trans}}$[b] (cal/mole) | $Fp_z$–$Fp_z$ Bond order |
|---|---|---|
| $NH_2$ .. .. | 1550 | 0·0376 |
| OH .. .. | − 283 | 0·0400 |
| H .. .. | − 611 | 0·0475 |
| CN .. .. | − 1392 | 0·0476 |

[a] Results of SCF–MO–INDO calculations. In all cases standard bond lengths and bond angles were used. [b] A plus sign indicates that the *trans* isomer is more stable and *vice versa*.

We have carried out INDO calculations[6] on 1,1-difluoroethylene in order to determine the relative importance of the $p_x$–$p_x$ attractive and $p_z$–$p_z$ repulsive lone pair interactions. It was found that the $p_x$–$p_x$ bond order is much more positive than the $p_z$–$p_z$ bond order is negative.§ Hence, the net effect of lone pair interaction in 1,1-dihalogenoethylenes is attraction. Direct evidence for the attractive interaction of halogens in halogenoethylenes has been provided by spectroscopic studies. Specifically, it has been found that the XCX bond angle in dihalogenoethylenes is significantly less than 120° and, in any case, less than the HCH angle in ethylene.[7] We can follow the same reasoning



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† In halogenoethylenes, the second lone pair 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 normal olefins. In such a case the *ns* and $np_y$ atomic orbitals of the halogen mix strongly and contribute mostly towards sigma bond formation with the olefin, while the lone pair becomes mainly localized in the $np_x$ atomic orbital of the halogen.

‡ It should be noted that if overlap is included, the interaction between the two halogen $p_z$ or $p_x$ orbitals will be repulsive and the lone pairs can be said to repel each other conforming to the classical picture. However, interaction of the lone pairs with the olefinic orbitals will tend to make this repulsive interaction either more repulsive or attractive, *e.g.* the qualitative conclusions remain unaltered whether or not overlap is included in the analysis.

§ The $p_z$–$p_z$ bond order was −0·0533 and the $p_x$–$p_x$ bond order was 0·0873 and the overlap integral in both cases is the same.

to analyse the lone pair interactions in 1,2-*cis*-dihalogenoethylenes. 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 $\pi_z^*$ orbital which can interact with $n_z^*$ giving rise to charge transfer from $n_z^*$ to $\pi_z^*$. This renders the bond order between the halogen $p_z$ orbitals positive and the lone pair interaction attractive. Similarly, it can be shown that the lone pairs localized in the $p_x$ halogen orbitals split into $n_x$ and $n_x^*$ orbitals as a result of through space interaction and $n_x^*$ can interact with the $\sigma_x^*$ and $\pi_y^*$ orbitals of the olefinic bond giving rise to charge transfer from $n_x^*$ to $\sigma_x^*$ and $\pi_y^*$ rendering the bond order between the halogen $p_x$ orbitals positive and the corresponding lone pair interaction attractive. Hence, the two halogen atoms in *cis* difluoroethylene will tend to attract each other. Since there is net attraction, 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 centres, while the *trans* form cannot do so. The same conclusions are reached for 1,2-disubstituted ethylenes where the two substituents are different heteroatoms possessing at least one lone pair.

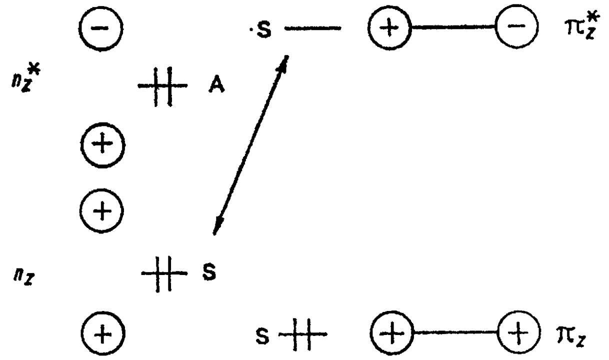

FIGURE. *The interaction of the $p_z$ lone pairs with the $\pi_z$ orbitals of ethylene in* 1,1-*dihalogenoethylenes. Arrows indicate the interactions which give rise to net charge transfer. Orbitals are classified with respect to plane of symmetry.*

We further tested this model by studying the effect of substituents on the degree of attraction between fluorine $p_z$ lone pairs in 1,2-disubstituted, 1,2-difluoroethylene molecules. Here, the attraction between the fluorine lone pairs depends on the magnitude of the fluorine $p_z$–$p_z$ bond order which, in turn, depends on the degree of charge transfer from $n_z^*$ to $\pi_z^*$. The latter is inversely proportional to the energy separation between $n_z^*$ and $\pi_z^*$ and, hence, substituents attached on *cis*-1,2-difluoroethylene which raise the energy of $\pi_z^*$ will tend to reduce the attraction between the two fluorine $p_z$ lone pairs and substituents attached on *cis* difluoroethylene which lower the energy of $\pi_z^*$ will tend to increase the attraction between the two fluorine $p_z$ lone pairs. Electron donor groups are substituents of the former type and electron acceptor groups are substituents of the latter type.[8] We have carried out INDO calculations to test our simple model and the results are shown in the Table.¶ As the electron donating power of the substituent increases, the $p_z$–$p_z$ bond order between the two fluorine atoms decreases and as this occurs the *cis* isomer becomes progressively less favoured energetically relative to the *trans* isomer. Hence, the relative stability of the two geometrical isomers is seen to be simply related to the relative attraction between the two fluorine $p_z$ lone pairs.

These ideas have been extended to pentadiene-like molecules, hexatriene-like molecules and to problems in conformational analysis and organic reactivity and these topics will be discussed in a full paper.

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¶ Substituents which are small in size were chosen for this study so that we could be reasonably certain that we were looking at a purely electronic effect.

[1] S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.

[2] W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' W. A. Benjamin, 1969.

[3] H. G. Viehe, *Chem. Ber.*, 1960, **93**, 1697; A. Demiel, *J. Org. Chem.*, 1962, **27**, 3500; R. E. Wood and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 1650; K. S. Pitzer and J. L. Hollenberg, *ibid.*, 1954, **76**, 1493; H. G. Viehe and E. Franchimont, *Chem. Ber.*, 1963, **96**, 3153; H. G. Viehe and E. Franchimont, *Chem. Ber.*, 1964, **97**, 602; J. W. Crump, *J. Org. Chem.*, 1963, **28**, 953; K. E. Harwell and L. F. Hatch, *J. Amer. Chem. Soc.*, 1955, **77**, 1682; C. C. Price and W. H. Snyder, *ibid.*, 1961, **83**, 1773; P. Salomaa and P. Nissi, *Acta Chem. Scand.*, 1967, **21**, 1386. In some of these examples, it is assumed that the methyl group can be equated to a doubly occupied $p_z$ atomic orbital according to the heteroatom model: F. A. Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5243.

[4] R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1, and references therein.

[5] M. J. S. Dewar, 'Hyperconjugation,' Ronald Press, 1962; R. Hoffmann, *Tetrahedron Letters*, 1970, 2907; H. Günther, *ibid.*, 1970, 5173.

[6] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, Inc., 1970.

[7] R. L. Livingston, C. N. R. Rao, L. M. Kaplan, and L. Rocks, *J. Amer. Chem. Soc.*, 1958, **80**, 5368; W. F. Edgell, P. A. Kinsey, and J. W. Amy, *J. Amer. Chem. Soc.*, 1957, **79**, 2691; J. M. Dowling and B. P. Stoicheff, *Canad. J. Phys.*, 1959, **37**, 703.

[8] For discussions of the effect of substituents on the electronic structure of olefins, see: H. H. Jaffe and M. Orchin, 'The Theory and Application of Ultraviolet Spectroscopy,' Wiley, 1962; K. Higasi, H. Baba, and A. Rembaum, 'Quantum Organic Chemistry,' Interscience, 1965; C. A. Coulson and E. T. Stewart in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, 1964.

[9] R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Amer. Chem. Soc.*, 1973, **95**, 629; see also: R. Hoffmann and R. A. Olofson, *ibid.*, 1966, **88**, 943.