

Toward a Detailed Orbital Theory of Substituent Effects: Charge Transfer, Polarization, and the Methyl Group

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Abstract: Various molecular orbital calculations on propylene and toluene show little net electron transfer from the methyl group to the ethylene or benzene but a significant polarization of the π electron system. We analyze why this is so, in the process establishing some general conclusions on charge transfer and polarization. The natural formalism of perturbation theory is used, modified to take into account the nonorthogonality of the interacting orbitals. Second-order corrections to the wave functions are absolutely necessary to describe the polarization phenomenon. For instance the polarization of the propylene π system may be traced to a second-order mixing of the π^* orbital of the ethylene fragment into π via the interaction of both π and π^* with the hyperconjugating methyl group σ orbital.

The arrival on the contemporary scene of good molecular orbital calculations, semiempirical and *ab initio*, on chemically realistic systems has hardly created the heralded millenium of understanding of chemical processes. The calculations are so complex and the number of integrals so large that, even when the calculation yields the correct results for some observable, the reason for its giving that result usually escapes the human mind. Man then tends to abdicate to the computer and substitutes as a goal predictability for understanding.

The ideal computer, optimally programmed, could provide accurate wave functions from which the energy, dipole moment, chemical shift, or any other observable could be calculated. Various information reducing schemes could be applied to extract hopefully significant theoretical features of the electronic distribution: densities partitioned among atoms, bond orders, or overlap populations. The problem is understanding why the calculation came out the way it did. "Understanding" is here given an operational definition—we will say that we understand a molecular orbital wave function when we can qualitatively predict the shape (sign and size of coefficients) of every molecular orbital of the molecule prior to doing the calculation. The proper business of the computer is to translate our qualitative understanding into a quantitative prediction.

The particular focus of this paper is on substituent effects. The idea of substituent effects can be said to be part of the unique and beautiful logic of chemistry. One has a set of substituents, groups of atoms which, with more or less human difficulty, can be induced to replace each other on a molecular skeleton: H, D, CH₃, CH₂CH₃, CN, F, NO₂, etc. These discrete modifications have discrete effects on various observables. But the envelope of these effects traces a continuous curve. The curve, albeit distorted in various ways, can be transferred from one molecular framework to another.¹ We are thus able to characterize the chemical and physical properties and the reactivity of an infinity of molecules by the spectrum of their substituents, their functional groups, and their chromophores. The basic logical element here is a set of continuous

variations carried by discrete changes and transferable from molecule to molecule. The great strides of synthetic and mechanistic organic and, in recent years, inorganic chemistry are made possible by the logic of substituent effects.

Nothing like this logic comes out of molecular orbital calculations. Every molecule is treated as a whole, and no set of transferable properties associated with a functional group emerges. Moreover, in several cases the molecular orbital treatment has given results which are at variance with current preconceptions. Witness here the general MO results that a methyl group is not necessarily electron donating²⁻¹⁵ and that an electronegative substituent has an inductive effect which alternates in sign, instead of being damped uniformly, along a hydrocarbon chain, saturated or not.^{4,5,16,17}

The emphasis of this paper is on electron density and the concepts of charge transfer and polarization. The language will be quantum mechanical, and the specific tool perturbation theory. The approach follows the lines established in the pioneering work of Coulson and Longuet-Higgins¹⁸ and is related to the important anal-

(2) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(3) (a) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2367 (1966); (b) M. D. Newton and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **89**, 4261 (1967).

(4) (a) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); (b) W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2959 (1970); (c) W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970); (d) J. A. Pople, *Accounts Chem. Res.*, **3**, 217 (1970).

(5) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

(6) P. M. Kuznesof and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 1683 (1968).

(7) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **90**, 6537 (1968); **92**, 7007 (1970).

(8) N. C. Baird, *Can. J. Chem.*, **47**, 2306 (1969).

(9) M. L. Unland, J. R. Van Wazer, and J. H. Letcher, *J. Amer. Chem. Soc.*, **91**, 1045 (1969).

(10) T. P. Lewis, *Tetrahedron*, **25**, 4117 (1969).

(11) P. H. Owens, R. A. Wolf, and A. Streitwieser, Jr., *Tetrahedron Lett.*, 3385 (1970).

(12) H. Kollmar and H. O. Smith, *Angew. Chem.*, **82**, 444 (1970); *Theor. Chim. Acta*, **20**, 65 (1971).

(13) J. R. Grunwell and J. F. Sebastian, *Tetrahedron*, **27**, 4387 (1971).

(14) G. R. Howe, *J. Chem. Soc. B*, 981, 984 (1971).

(15) J. M. André, Ph. Degand, and G. Leroy, *Bull. Soc. Chim. Belg.*, **80**, 585 (1971).

(16) I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **95**, 165 (1971).

(17) The effect was also noted in extended Hückel calculations on saturated hydrocarbon chains and toluene in ref 2.

(18) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. Ser. A*, **191**, 39 (1947); **192**, 16 (1947); **193**, 447, 456 (1948); **195**, 188 (1948).

(1) As leading references on this subject see the articles by S. Ehrenson and C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1964.

yses of Dewar,¹⁹ Murrell and coworkers,²⁰ Godfrey,²¹ and Fukui and coworkers.²² Our final arguments will be qualitative. However, the derivation of the perturbational arguments is of necessity somewhat mathematical. The mathematics will not be hidden, but neither will it be used when it can be replaced by a simple verbal statement.

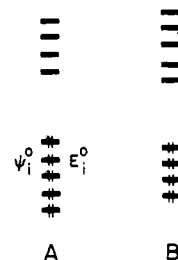
The Perturbational Formalism

Perturbation theory is a natural procedure for building up the molecular orbitals of complex molecules from those of simpler subsystems. The particular formulation we use is that of the simplest Rayleigh-Schrödinger perturbation theory for the nondegenerate case.²³ The formalism is applied within the framework of the extended Hückel method,^{2,24} the simplest semiempirical all-valence-electron procedure. The method has well documented deficiencies in the quantitative prediction of observables, but it does model faithfully, when compared to more sophisticated methods, the shape of the molecular orbitals of any molecule.²⁵ Since the method is not a self-consistent field procedure but a one-electron theory, the application of perturbation theory is particularly simple.²⁶ We can directly speak of the interaction of levels, neglecting the attendant interaction of electrons.

A complicating but essential feature of perturbation theory applied within an extended Hückel formalism is that the nonorthogonality of the basis set, the overlap integral, must be explicitly treated. This causes no fundamental difficulty, though the formulas may take on a somewhat unfamiliar appearance. The particular brand of perturbation theory with overlap which we use has been worked out by Imamura,²⁷ Salem,²⁸ Murrell,^{20e} and Fukui and Fujimoto.²⁹ Our own analysis has no new theoretical features and relies heavily on the

formalism of Imamura, as skillfully programmed by him.²⁷

Consider the interaction of the levels of two subsystems A and B, each with its characteristic set of orbitals. The unperturbed wave functions, ψ_i^0 , and energy levels, E_i^0 , are assumed known. The perturba-



tion here is defined as the interaction between the two groups and will be directly related below to their overlap. The general expression for the perturbed or new wave function is

$$\psi_i = \psi_i^0 + \sum_{j \neq i} c_{ji} \psi_j^0 \quad (1)$$

The second term can be factored into subsets of orbitals on A and on B

$$\psi_i = \psi_i^0 + \sum_{j \neq i}^A c_{ji} \psi_j^0 + \sum_k^B c_{ki} \psi_k^0 \quad (2)$$

making explicit the consequence of intra- and inter-group mixing. The former will assume a crucial role in our analysis of the polarization phenomenon.

Each mixing coefficient can be broken down into first- and second-order contributions, here denoted by a prime and double prime.

$$c_{ki} = c_{ki}' + c_{ki}'' + \dots \quad (3)$$

Higher order contributions are neglected. Wave functions to a given order in perturbation theory actually determine the perturbed energies to a higher order. However, while we will need wave functions to second order, we will not need the attendant energies beyond that order.

$$E_i = E_i^0 + E_i' + E_i'' \quad (4)$$

The following expressions for the first- and second-order corrections may be derived.

$$c_{ji}' = \frac{1}{E_i^0 - E_j^0} (H_{ji}' - E_i^0 S_{ji}') \quad j \neq i \quad (5)$$

$$c_{ii}' = -\frac{1}{2} S_{ii}' \quad (6)$$

$$E_i' = H_{ii}' - E_i^0 S_{ii}' \quad (7)$$

$$c_{ji}'' = \frac{1}{E_i^0 - E_j^0} \times \sum_{k \neq i} \frac{(H_{jk}' - E_i^0 S_{jk}')(H_{ki}' - E_i^0 S_{ki}')}{E_i^0 - E_k^0} \quad j \neq i \quad (8)$$

$$c_{ii}'' = -\frac{1}{2} \sum_{k \neq i} (c_{ki}')^2 - \sum_{k \neq i} c_{ki}' S_{ki}' \quad (9)$$

$$E_i'' = \sum_{k \neq i} \frac{(H_{ik}' - E_i^0 S_{ik}')^2}{E_i^0 - E_k^0} \quad (10)$$

It is worth repeating at this point that our notation is such that c_{ji} measures how much orbital j mixes into orbital i .

(19) (a) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3357 (1952); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(20) (a) D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1250 (1968); (b) M. Godfrey and J. N. Murrell, *Proc. Roy. Soc. Ser. A*, **278**, 64, 71 (1964); (c) J. N. Murrell and D. R. Williams, *Proc. Roy. Soc. Ser. A*, **291**, 224 (1966); (d) J. N. Murrell, S. F. Kettle, and J. M. Tedder, "Valence Theory," 2nd ed, Wiley, New York, N. Y., 1970; (e) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963.

(21) M. Godfrey, *J. Chem. Soc. B*, 799 (1967); 751 (1968); 1534, 1537, 1540, 1545 (1971).

(22) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954); K. Fukui, in "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 513; K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970), and references therein.

(23) See, for instance: A. Dalgarno in "Quantum Theory," Vol. 1, D. R. Bates, Ed., Academic Press, New York, N. Y., 1961, Chapter 5; or J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, in "Advances in Quantum Chemistry," Vol. 1, P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1964, p 255.

(24) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2189 (1962); **37**, 520 (1962).

(25) For a pictorial demonstration see the recent book by W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York, N. Y., 1973, p 55.

(26) The perturbational formalism within a self-consistent field has been developed by: (a) J. A. Pople, *Proc. Roy. Soc. Ser. A*, **233**, 233 (1955); (b) R. Lefebvre and C. Moser, "Calcul des fonctions d'onde moléculaire," Paris, Editions CNRS, 1958, p 109; (c) A. T. Amos and J. I. Musher, *Mol. Phys.*, **13**, 509 (1967); (d) R. Sustmann and G. Binsch, *Mol. Phys.*, **20**, 1, 9 (1971); (e) G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **8**, 165 (1967).

(27) A. Imamura, *Mol. Phys.*, **15**, 225 (1968).

(28) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968).

(29) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **41**, 1989 (1968).

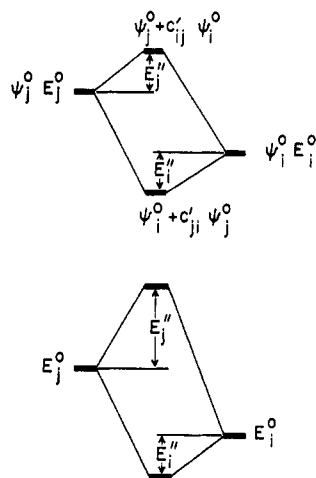


Figure 1. The interaction of two energy levels, with overlap neglected (top) and with overlap included (bottom).

There are several assumptions under which the above expressions were derived. We have assumed that the MO's are initially localized on each subgroup, with the subgroups at such a distance from each other that intergroup overlap is negligible. The perturbation then occurs as a result of moving one group toward the other, thus increasing intergroup overlap. We allow no change of geometry and no change of basis within a group, maintaining the original orthogonal group orbitals. We assume no change in intramolecular Hamiltonian matrix elements. A consequence of these restrictions is that $c_{ii}' = 0$, since $S_{ii}' = 0$. It also follows that $E_i' = 0$. This allows the simple expression for c_{ji}'' given in (8) above, since in the general case c_{ji}'' includes other terms.²³

Equations 5–10 show an explicit dependence on the overlap of the interacting groups. If S_{ji}' is set equal to 0, the more familiar perturbation expressions 11–16 are

$$c_{ji}' = \frac{H_{ji}'}{E_i^0 - E_j^0} \quad j \neq i \quad (11)$$

$$c_{ii}' = 0 \quad (12)$$

$$c_{ji}'' = \frac{1}{E_i^0 - E_j^0} \sum_{k \neq i} \frac{H_{jk}' H_{ki}'}{E_i^0 - E_k^0} \quad j \neq i \quad (13)$$

$$c_{ii}'' = -\frac{1}{2} \sum_{k \neq i} (c_{ki}')^2 \quad (14)$$

$$E_i' = H_{ii}' \quad (15)$$

$$E_i'' = \sum_{k \neq i} \frac{(H_{ik}')^2}{E_i^0 - E_k^0} \quad (16)$$

obtained. It should be noted that while these formulas do not contain the overlap explicitly, they would, in an extended Hückel calculation, possess an *implicit* dependence on the same overlap through the Wolfsberg–Helmholtz formula.

$$H_{ij}' = K \frac{(H_{ii} + H_{jj})}{2} S_{ij}' \quad (17)$$

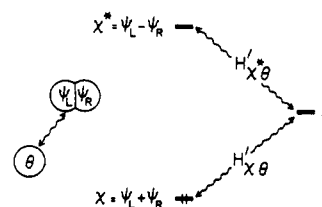
Why do we bother with two sets of perturbation formulas and why do we include the apparently complicated second-order corrections to the wave function? The answer to the first question lies in our desire to analyze group interactions both qualitatively and quantitatively.

The Imamura program mentioned above²⁷ implements the formulation with explicit overlap dependence (eq 5–10) in a quantitative way. We have found that semiquantitative results may be obtained from the simplified eq 11–16.

There are, however, obvious and crucial consequences of neglecting overlap. For instance, it is a well known^{18, 19, 28, 30, 31} result of implementing perturbation theory without overlap that, when two levels interact, the energy of perturbation is the same for both levels (the lower one is stabilized as much as the upper one is destabilized, $E_i'' = -E_j''$), and the first-order mixing is equal in magnitude (the lower orbital mixes into itself the upper one in a bonding way to the same extent that the upper one mixes into itself the lower one in an antibonding way, $c_{ji}' = -c_{ij}'$). This is illustrated at the top of Figure 1. When overlap is explicitly included, it can be shown (Appendix I) that the upper level is destabilized more than the lower one is stabilized, $|E_j''| > |E_i''|$, and that more of the lower level is mixed into the upper antibonding combination than there is of the upper level mixed into the lower bonding combination, $|c_{ij}'| > |c_{ji}'|$. This is shown at the bottom of Figure 1.

Though these important effects are due to inclusion of overlap, the most fundamental consequences of the orbital mixing, for example that c_{ij}' has the opposite sign to c_{ji}' and that the lower combination is in phase bonding, the upper antibonding, are present in the simplest variant of perturbation theory. The signs of the mixing coefficients are a direct consequence of the simple ordering of unperturbed energy levels. To obtain these signs, which will give the simplest qualitative picture of orbital interaction, we may use the perturbation theory version which neglects overlap.

The second question raised above concerns inclusion of the second-order corrections to the wave function. These are essential to describe the phenomenon of polarization. Consider a model two-orbital system at left below interacting with a model one-orbital, no electron perturber, θ . Let us assume the two-orbital



system has initially a twofold symmetry element interchanging its left and right sides (ψ_L , ψ_R). The initial wave functions χ and χ^* reflect the molecular symmetry. The perturbation is specified by the matrix elements $H_{X\theta}'$ and $H_{X\theta}^*$. Consider the effect of the perturbation on χ , the lower occupied orbital of the two-orbital system. In first order, χ mixes into itself θ

$$\chi' = \chi + c'\theta \quad (18)$$

where the mixing coefficient c' is a function of the orbital energies and $H_{X\theta}'$. The interaction so far has the consequence of electron transfer from χ to θ . But that electron transfer causes no asymmetry in the two-orbital system, since it occurs symmetrically from ψ_L and ψ_R .³²

(30) E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendung," Verlag-Chemie, Weinheim, Germany, 1968.

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

The place where the necessary asymmetry enters is in second order of perturbation theory

$$\chi' = \chi + c'\theta + c''\chi^* \quad (19)$$

when χ^* is mixed into χ . Our constraint to intergroup interaction only leads to a vanishing second-order mixing of θ into χ . The mixing coefficient c'' is a function of $H_{\chi\theta'}$ and $H_{\chi\theta''}$ and the various energy intervals. The sign of c'' is crucial, since in the two-orbital system the electron distribution is given by

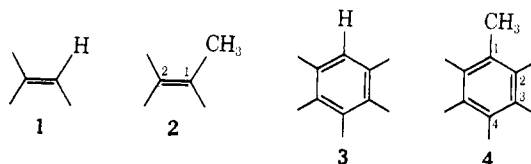
$$\chi' = \psi_L + \psi_R + c''(\psi_L - \psi_R) + \dots \quad (20)$$

If c'' is positive, then with the particular choice of representation of χ and χ^* the electron density is polarized so that it accumulates on the left side of the molecule. If c'' is negative, the polarization is reversed.

It is primarily in second order of perturbation theory that initially orthogonal subsystem wave functions begin to be mixed up with each other, polarizing the subsystem. The rules specifying the direction of polarization (for instance the sign of c'' above) can be made simple. The realistic example of the next section will help us to build an intuition for the polarization effect.³³

The Effect of a Methyl Group on a Double Bond

That methyl groups attached to π -electron systems are electron donors could be called a common prejudice of organic chemists. The first all-valence electron calculations by the extended Hückel method² compared the charge distribution in propylene with that of ethylene, and that of toluene with benzene. The net



charge transfer in propylene and toluene was very small; for instance, the total electron density in the olefinic C_2H_3 part of 2 was nearly the same as in the C_2H_3 fragment of 1. Nevertheless, the calculations showed a large charge reorganization in propylene and toluene. The β carbon of propylene, C_2 , became negative, as did the ortho and para positions of toluene. So the final charge distribution was similar to that expected on the basis of the preconception of methyl group donation. But it was achieved not by net donation but by a sizable polarization of the substituted π system.

Other semiempirical and *ab initio* procedures have put these conclusions on firmer ground.³⁻¹⁵ The most detailed analysis was given for the methylacetylene system by Newton and Lipscomb.^{3b} The dipole moments of molecules such as propylene, methylacetylene, and toluene are due not to electron donation by the methyl substituent but to the polarization caused in the π system.³⁴ The extended Hückel results parallel in

(32) In the general case, where the perturber possesses more than one orbital, it can exert a polarizing effect in first order. An example will occur in the next section.

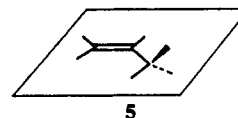
(33) The role of polarization has been stressed in ref 18-22. An excellent detailed analysis of polarization in the SN_2 reaction has been presented by J. P. Lowe, *J. Amer. Chem. Soc.*, **94**, 60 (1972); **93**, 301 (1971).

(34) Recent references to the controversy surrounding the electronic role of the methyl group include ref 35-50.

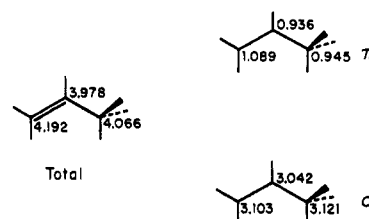
(35) T. L. Brown, *J. Amer. Chem. Soc.*, **81**, 3229, 3232 (1959).

detail the conclusions from more sophisticated calculations and will be analyzed here by the perturbational methods developed in the previous section.

Propylene is calculated in the C_s geometry, shown in 5 below, which corresponds to the equilibrium geometry



of the molecule. A Mulliken population analysis leads to the electron distribution⁵¹ shown at left below. The presence of a symmetry plane allows a partitioning of that charge distribution into a component symmetric with respect to the mirror plane and another component antisymmetric with respect to the same plane. We will call the former component σ and the latter π , with obvious reference to the double bond part of the molecule. The σ and π electron distributions are shown at right below.



It is clear that the charge reorganization in propylene originates primarily in the π system. The analysis is then greatly simplified, for we have in the π system only a set of four orbitals, two filled and two unfilled. We begin our analysis by considering these orbitals prior to interaction (Figure 2). At left in the figure are the π and π^* orbitals of the ethylene fragment. At right are the two methyl group orbitals of π symmetry, capable of mixing with the ethylene orbitals. These two orbitals, here called $\sigma\pi$ and $\sigma\pi^*$ are the familiar hyperconjugating set.⁵² They should properly be called

(36) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962); *J. Org. Chem.*, **35**, 951 (1970); W. M. Schubert and D. F. Gurka, *J. Amer. Chem. Soc.*, **91**, 1443 (1969).

(37) H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961); H. Kwart and T. Takeshita, *J. Amer. Chem. Soc.*, **86**, 1161 (1964).

(38) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963).

(39) R. C. Fort and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 4194 (1964); P. v. R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, **90**, 6528 (1968).

(40) J. A. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965); *J. Org. Chem.*, **36**, 204 (1971).

(41) V. W. Laurie and J. S. Muentzer, *J. Amer. Chem. Soc.*, **88**, 2883 (1966).

(42) F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **89**, 5677 (1967); A. Himoe and L. M. Stock, *J. Amer. Chem. Soc.*, **91**, 1452 (1969).

(43) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968); **92**, 5986 (1970); **93**, 3911 (1971); J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, **93**, 3914 (1971).

(44) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(45) E. W. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 1438 (1969).

(46) T. J. Broxton, L. W. Deady, A. R. Katritzky, A. Liu, and R. D. Topsom, *J. Amer. Chem. Soc.*, **92**, 6845 (1970).

(47) L. M. Jackman and D. P. Kelly, *J. Chem. Soc. B*, 102 (1970).

(48) P. M. E. Lewis and R. Robinson, *Tetrahedron Lett.*, 2783 (1970).

(49) J. F. Sebastian, *J. Chem. Educ.*, **48**, 97 (1971).

(50) S. Fliszár, *J. Amer. Chem. Soc.*, **94**, 1068 (1972).

(51) In the extended Hückel procedure the reference density for isolated carbon is 4.0 and for hydrogen 1.0 electrons. In ethylene, calculated with the same parameters, the densities are 4.103 and 0.949, respectively.

(52) R. S. Mulliken, *J. Chem. Phys.*, **1**, 492 (1933); **3**, 520 (1935); **7**, 339 (1939); see also ref 25, p 8.

How were the fragment orbitals obtained?

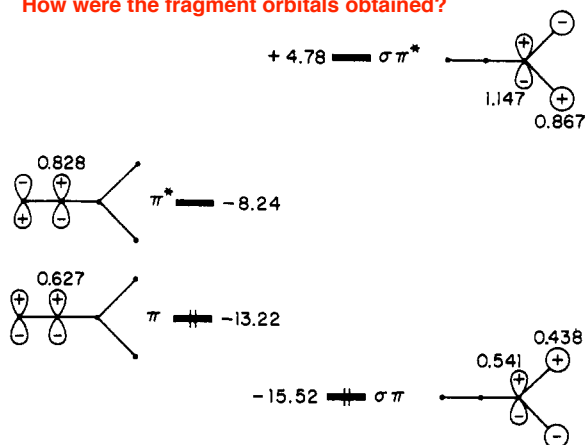


Figure 2. Energy levels of π symmetry of a double bond (left) and a methyl group (right) before interaction. The numbers in the middle are extended Hückel energies. The numbers next to the orbitals are atomic orbital coefficient magnitudes.

π_{CH_3} and $\pi^*_{\text{CH}_3}$, to emphasize their π character. However, we use the $\delta\pi$ notation to avoid multiple subscripts.

The perturbation is defined by the overlap matrix S' between the methyl and vinyl group orbitals. S' is the difference between the overlap in the normal geometry of propylene and the (zero) overlap when the two fragments are far apart, noninteracting. S' is given in Table I. It should be noted from Figure 2 and Table I

Table I. Group Overlap Integral Changes S' on Bringing Methyl and Vinyl Orbitals into the Propylene Geometry

	$\delta\pi$	π	π^*	$\delta\pi^*$
$\delta\pi$	0	0.116	0.116	0
π	0.116	0	0	0.101
π^*	0.116	0	0	0.091
$\delta\pi^*$	0	0.101	0.091	0

that the basis orbitals are so oriented that all of the overlap integrals are positive. This is convenient, but not necessary. In general the choice of the phase of the interacting orbitals is crucial and must remain consistent throughout a calculation.

We now proceed to estimate qualitatively and quantitatively the mixing of the basis orbitals produced by the interaction of methyl group orbitals. For the quantitative calculation we utilize the full set of eq 5–10. For a qualitative estimate we use the perturbation expressions without overlap (11–16). Let us begin with the latter, applied first to the perturbation of $\delta\pi$ by the other orbitals.⁵³

$$\begin{aligned}
 c_{\sigma\pi,\sigma\pi}' &= 0 \\
 c_{\pi,\sigma\pi}' &= K \frac{\langle \pi | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\pi}} \\
 c_{\pi^*,\sigma\pi}' &= K \frac{\langle \pi^* | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\pi^*}} \\
 c_{\sigma\pi^*,\sigma\pi}' &= K \frac{\langle \sigma\pi^* | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\sigma\pi^*}} \quad (21)
 \end{aligned}$$

(53) We use the bra-ket notation for overlap integrals in order to avoid excessive subscripts: $\langle \pi^* | \sigma\pi^* \rangle \equiv S_{\pi^*,\sigma\pi^*}$.

The approximation $H_{ij} = KS_{ij}$, with K negative, has been made in the above formulas. Since we are dealing with a heteronuclear (C,H) system, this reduction of the Wolfsberg–Helmholtz formula (17) is not quite correct. To the extent that we are using formulas without explicit inclusion of overlap as a qualitative guide, the approximation is adequate. The sign of the overlap integrals can be ascertained by inspection of the basis set of Figure 2 or by reference to Table I: $\langle \pi | \sigma\pi \rangle > 0$, $\langle \pi^* | \sigma\pi \rangle > 0$, $\langle \sigma\pi^* | \sigma\pi \rangle = 0$. The energy denominators can also be obtained from Figure 2. They are all negative. It follows that the nonvanishing first-order coefficients

$$c_{\pi,\sigma\pi}' > 0 \quad c_{\pi^*,\sigma\pi}' > 0$$

Moreover $c_{\pi,\sigma\pi}'$ should be greater in magnitude than $c_{\pi^*,\sigma\pi}'$ because $E_{\sigma\pi} - E_{\pi}$ is smaller than $E_{\sigma\pi} - E_{\pi^*}$.

The second-order mixing coefficients are

$$\begin{aligned}
 c_{\pi,\sigma\pi}'' &= \frac{K^2}{E_{\sigma\pi} - E_{\pi}} \times \left(\frac{\langle \pi | \sigma\pi^* \rangle \langle \sigma\pi^* | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\sigma\pi^*}} + \frac{\langle \pi | \pi^* \rangle \langle \pi^* | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\pi^*}} \right) \\
 c_{\pi^*,\sigma\pi}'' &= \frac{K^2}{E_{\sigma\pi} - E_{\pi^*}} \times \left(\frac{\langle \pi^* | \sigma\pi^* \rangle \langle \sigma\pi^* | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\sigma\pi^*}} + \frac{\langle \pi^* | \pi \rangle \langle \pi | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\pi}} \right) \\
 c_{\sigma\pi^*,\sigma\pi}'' &= \frac{K^2}{E_{\sigma\pi} - E_{\sigma\pi^*}} \times \left(\frac{\langle \sigma\pi^* | \pi \rangle \langle \pi | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\pi}} + \frac{\langle \sigma\pi^* | \pi^* \rangle \langle \pi^* | \sigma\pi \rangle}{E_{\sigma\pi} - E_{\pi^*}} \right) \quad (22)
 \end{aligned}$$

The first two coefficients vanish because they contain zero intragroup overlap factors. Taking into account the proper signs of overlaps and energy differences, we find the last mixing coefficient to be positive.

$$c_{\sigma\pi^*,\sigma\pi}'' > 0$$

The perturbed $\delta\pi$ orbital then becomes

$$\delta\pi' = \delta\pi + c_{\pi,\sigma\pi}'\pi + c_{\pi^*,\sigma\pi}'\pi^* + c_{\sigma\pi^*,\sigma\pi}''\delta\pi^* + c_{\sigma\pi,\sigma\pi}''\delta\pi \quad (23)$$

The last term is the qualitatively unimportant second-order self-correction, really a renormalization arising from eq 9 or 14.

The actual mixing coefficients, as they result from the full perturbation calculation, are given in Table II for

Table II. Mixing Coefficients for Propylene^a

j	c_{ji}'			
	$\delta\pi$	π	π^*	$\delta\pi^*$
$\delta\pi$	0	(-)-0.368	(-)-0.195	0
π	(+)+0.252	0	0	(-)-0.131
π^*	(+)+0.080	0	0	(-)-0.163
$\delta\pi^*$	0	(+)+0.030	(+)+0.071	0
j	c_{ji}''			
	$\delta\pi$	π	π^*	$\delta\pi^*$
$\delta\pi$	(-)-0.073	0	0	(+)+0.042
π	0	(-)-0.028	(+)+0.040	0
π^*	0	(-)-0.059	(-)-0.005	0
$\delta\pi^*$	(+)+0.005	0	0	(-)+0.006

^a The sign in parentheses is that predicted by inspection of the formulas without overlap.

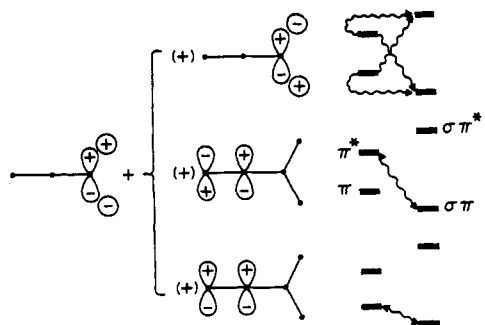


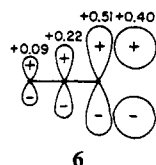
Figure 3. The composition of the perturbed $\delta\pi$ orbital. The sign of the mixing coefficient of each orbital mixed into $\delta\pi$ is given in parentheses. The actual magnitude of the mixing coefficients may be found in Table II. Next to each perturbing orbital is a sketch of the interaction it represents. Arrowheads connect orbitals mixed.

all the molecular orbitals. The first- and second-order contributions have been separated to show their complementary nature. Each column gives the correction coefficients for a given orbital. Thus

$$\delta\pi' = \delta\pi + 0.252\pi + 0.080\pi^* + 0.005\delta\pi^* - 0.073\delta\pi$$

Note that the signs of the mixing coefficients were correctly predicted from the formulas without overlap and that qualitative estimates of the magnitude of the coefficients are confirmed (for instance that $c_{\pi,\sigma\pi'}$ should be the largest perturbing coefficient).

The composition of the perturbed $\delta\pi$ orbital is shown schematically in Figure 3, and its final shape in 6 below. The numbers are the AO coefficients. We



will return below to a detailed analysis of the orbitals. Here we note only the obvious fact that some electron density has been transferred from the methyl group to both C_1 and C_2 , with more going to C_1 . The reader familiar with the π orbitals of butadiene will also be able to see a correspondence between 6 and the lowest π orbital of butadiene.

The perturbed π orbital of propylene becomes

$$\pi' = \pi + c_{\sigma\pi^*,\pi'}\delta\pi^* + c_{\sigma\pi,\pi'}\delta\pi + c_{\pi^*,\pi''}\pi^* + c_{\pi,\pi''}\pi$$

The coefficients may be read off from Table II as follows

$$\pi' = \pi - 0.368\delta\pi + 0.030\delta\pi^* - 0.028\pi - 0.059\pi^*$$

but it is again important to be able to estimate without a detailed calculation at least the sign of the coefficients. This is done for two of them below.

$$c_{\sigma\pi,\pi'} = K \frac{\langle \sigma\pi | \pi \rangle}{E_\pi - E_{\sigma\pi}} = (-) \frac{(+)}{(+)} = (-)$$

$$c_{\pi^*,\pi''} = \frac{K^2}{E_\pi - E_{\pi^*}} \times \left(\frac{\langle \pi^* | \sigma\pi \rangle \langle \sigma\pi | \pi \rangle}{E_\pi - E_{\sigma\pi}} + \frac{\langle \pi^* | \sigma\pi^* \rangle \langle \sigma\pi^* | \pi \rangle}{E_\pi - E_{\sigma\pi^*}} \right) \\ = \frac{(+)}{(-)} \left(\frac{(+)(+)}{(+)} + \frac{(+)(+)}{(-)} \right) \Rightarrow (-)$$

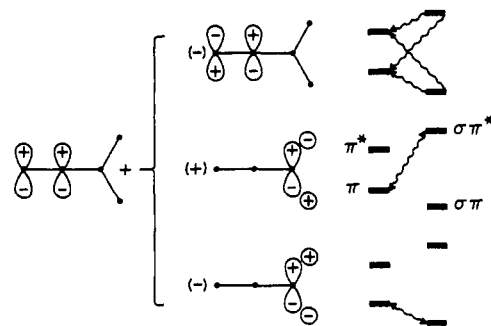
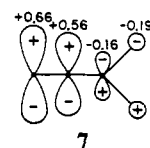


Figure 4. The composition of the perturbed π orbital. Conventions are the same as for Figure 3.

The first term in the expression for $c_{\pi^*,\pi'}$ dominates because $\delta\pi$ is much closer in energy to π than is $\delta\pi^*$.

The building up of the perturbed π orbital is shown in Figure 4, with the resultant 7. Some electron



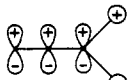
density has been transferred to the methyl group. The density in the ethylene part has diminished overall, but the partial density at C_2 has actually increased (compare the coefficient of 0.63 at C_2 in the unperturbed π orbital of Figure 2). Note the similarity, not accidental, of the perturbed π orbital to the second lowest π orbital of butadiene.

Our goal is to use the perturbation formalism to analyze what happens when a methyl group and an ethylene interact in propylene. It is important to establish that the analysis to second order in the wave functions is sufficiently accurate, and that it contains all the important effects. Table III has a comparison of the actual extended Hückel wave function with the perturbed wave functions to second order. The general agreement is good. That it is better for π^* and $\delta\pi^*$ than for π and $\delta\pi$ is probably a reflection of the faster convergence of the perturbation formalism due to the larger energy denominators in the perturbation terms for the former more isolated orbitals.

We now turn to a detailed analysis of the charge transfer and polarization effects in propylene. A Mulliken population analysis on the unperturbed, localized and the perturbed, delocalized $\delta\pi$ and π orbitals is given below.

Localized		Delocalized
$\begin{array}{c} \text{H} \\ \\ 1.000 \quad 1.000 \\ \text{C}=\text{C} \\ \\ \text{H} \end{array}$	π	$\begin{array}{c} \text{H} \quad 0.052 \\ \\ 1.067 \quad 0.795 \\ \text{C}=\text{C} \\ \\ \text{H} \quad 0.052 \end{array}$
$\begin{array}{c} \text{H} \quad 0.517 \\ \\ \text{C}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad 0.966 \quad \text{H} \quad 0.517 \end{array}$	$\sigma\pi$	$\begin{array}{c} \text{H} \quad 0.463 \\ \\ 0.022 \quad 0.142 \\ \text{C}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad 0.910 \quad \text{H} \quad 0.463 \end{array}$
$\begin{array}{c} \text{H} \quad 0.517 \\ \\ 1.000 \quad 1.000 \\ \text{C}=\text{C} \\ \\ \text{H} \quad 0.517 \end{array}$	Total	$\begin{array}{c} \text{H} \quad 0.515 \\ \\ 1.089 \quad 0.936 \\ \text{C}=\text{C} \\ \\ \text{H} \quad 0.945 \quad \text{H} \quad 0.515 \end{array}$

In $\delta\pi$, 0.160 electrons are transferred from the methyl group to the ethylene fragment. They are transferred

Table III. Comparison of Full Extended Hückel Wave Functions (EH) with Those Obtained from Perturbation Theory to Second Order in the Wave Functions (Pert)


		$\delta\pi$		π		π^*		$\delta\pi^*$	
C_2	C_1	C_3	H_1-H_2	Pert	EH	Pert	EH	Pert	EH
C_2				+0.092	+0.075	+0.659	+0.660	-0.797	-0.797
C_1				+0.224	+0.193	+0.560	+0.568	+0.849	+0.847
C_3				+0.507	+0.514	-0.164	-0.136	-0.024	-0.020
H_1-H_2				+0.402	+0.409	-0.187	-0.164	-0.147	-0.154
								+0.052	+0.054
								-0.217	-0.227
								+1.177	+1.178
								-0.855	-0.853

unsymmetrically to the two ethylene carbons, more going to C_1 than to C_2 . The polarization of the vinyl group, *i.e.*, the asymmetry of the charge distribution, is accomplished entirely in first order by mixing in of π and π^* with definite phases into $\delta\pi$. The donor methyl group is also polarized itself, now in second order by mixing in of $\delta\pi^*$ into $\delta\pi$. This last polarization is minute, $c_{\sigma\pi^*,\sigma\pi}$ being very small because of the large energy separation of $\delta\pi$ and $\delta\pi^*$.

In the π orbital 0.135 electrons are transferred to the methyl group. There is some first-order polarization of the methyl group, but the most important effect is the second-order polarization of the π level by mixing in of π^* . It should be noted that the mixing of π^* into π is not in absolute terms very large ($c_{\pi^*,\pi}$ from Table II is only -0.059; compare the coefficients in 7 with those of the unperturbed π orbital in Figure 2), but because it represents an additive term to a large coefficient it has a large net effect. The asymmetry between C_1 and C_2 electron densities is fully 0.26 electrons, with C_2 more negative than C_1 .

The perturbed orbitals $\delta\pi$ and π thus show entirely opposite effects. In one the electron drift is from methyl to vinyl and the vinyl group is polarized toward C_1 , the α position. In the other, the electron drift is from vinyl to methyl, and the vinyl group is polarized toward C_2 , the β position. The net charge transfer, +0.160 in $\delta\pi$, -0.135 in π , is a small +0.025 electrons from methyl to vinyl. But the polarization of the vinyl group in π is considerably greater than that in $\delta\pi$. The net result is a considerable charge reorganization with C_2 , the β position, more negative.

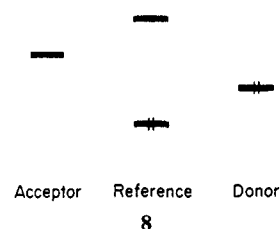
If one has to trace the polarization or charge distribution in propylene to a single factor, it is to the second-order mixing of π^* into π through the interaction of both with $\delta\pi$.

Before we leave the specific case of a methyl-substituted ethylene, we should observe that the rapidly developing field of photoelectron spectroscopy allows us to probe the polarization of each orbital individually. Consider a donor substituent on the double bond of propylene. If we could monitor the ionization potentials of the perturbed π and $\delta\pi$ levels and focus on the differential between C_1 and C_2 donor substitution, we should observe an opposite trend. In practice the experiment will be complicated by questions of assignment, but in principle the electron density distribution in each orbital could be inferred.

The Methyl Substituent and the General Donor-Acceptor Problem

We want to relate the case of the methyl group to a more general analysis of other substituents. In a

simplistic manner we can classify most substituents as donor or acceptor dominant, depending on whether it is an occupied orbital or an unoccupied one which is involved in the primary interaction.



Several cautions must be attached to such a definition.^{22,28,31,54} Obviously substituent groups have more than one orbital capable of interacting with the substrate or skeleton. The singling out of one orbital may be difficult and sometimes even misleading, but often it is easy and justifiable: the lone pair donor orbitals of NR_2 , OR, X; the low-lying π^* orbitals of NO_2 , NO, COR, CN. Even in the case of the methyl group we have seen that the $\delta\pi^*$ orbital is just too high up in energy to mix significantly. Methyl is then primarily interacting *via* its $\delta\pi$ level and can be said to be donor dominant. As we will show below, donor or acceptor dominance does not necessarily imply good donor or acceptor properties, merely the potentiality of such. In the case of the methyl group we saw explicitly that the donor character was minimal.

Another caution which should be kept in mind is that donor or acceptor character depends on the reference standard, in our special case the levels of ethylene. It may well be that attached to skeleton A a given substituent may be donor dominant, but attached to a different skeleton B it might interact *via* its (the substituent's) acceptor orbitals.

In the context of this paper the reference system is π -type, a polyene of some type. The specific two-orbital reference of this section is assumed to be an ethylene. Its occupied level is π ; its unoccupied level is π^* . The donor or acceptor orbital in our model will be called s (for substituent), whether it is occupied or not. It is clear that if s is to interact with the ethylene it must possess at the site of attachment an orbital component of π symmetry; that is, we are interested in π donors or acceptors.

We now will see what general conclusions can be drawn concerning charge transfer and polarization, and the specific way in which the methyl group fits into the general scheme.

(54) See also J. D. Bradley and G. C. Gerrans, *J. Chem. Educ.*, **50**, 463 (1973).

Consider the level scheme and basis set of Figure 5. The perturbed π level is given to second order by

$$\pi = (1 + c_{\pi,\pi'})\pi + c_{s,\pi'}s + c_{\pi^*,\pi'}\pi^* \quad (24)$$

Consideration of this level is sufficient for the acceptor case. In the donor case s is also occupied and must be evaluated.

$$s = (1 + c_{s,s'})s + c_{\pi,s'}\pi + c_{\pi^*,s'}\pi^* \quad (25)$$

The electron distribution is formed by squaring these wave functions. In the framework of a Mulliken population analysis, if we have a perturbed orbital located part in subgroup A, φ_A , part in subgroup B, φ_B ,

$$\psi = a\varphi_A + b\varphi_B \quad (26)$$

then the fraction of an electron located on A is

$$a^2 + abS_{AB} \quad (27)$$

The overlap density is arbitrarily divided equally among the interacting orbitals.

Proceeding along these lines, we assign as charge transferred to s that fraction of an electron in π (eq 24) given by

$$(c_{s,\pi'})^2 + c_{s,\pi'}(1 + c_{\pi,\pi'})S_{s,\pi'} + c_{s,\pi'}c_{\pi^*,\pi'}S_{s,\pi^*} \quad (28)$$

The last term in (28) is likely to be small compared to the first two. Since (neglecting overlap)

$$c_{s,\pi'} = \frac{H_{s,\pi'}}{E_s - E_\pi} \quad (29)$$

we can conclude that for an acceptor there will be an inverse energy gap dependence on the magnitude of the charge transfer. The lower in energy the acceptor orbital, the better the charge transfer, as would have been expected.

For the donor case we must also consider the reverse charge transfer from s to π and π^* implied by the form of eq 25. For donors with $E_s \cong E_\pi$ the charge transfer approximately cancels. However, as the donor capability increases, *i.e.*, s moves to higher energy, the charge transfer from s to π^* *via*

$$c_{\pi^*,s'} = \frac{H_{s,\pi^*}}{E_s - E_{\pi^*}} \quad (30)$$

increases. As expected, the better the donor, the more charge transfer to the olefin.

In the case of methyl $|E_{\sigma\pi} - E_{\pi^*}|$ is more than 7 eV; indeed $\sigma\pi$ is below π in energy. The extent of charge transfer is small. For donor substituents with low ionization potentials such as NR_2 , SR, and Cl, much greater donation is expected.

The next phenomenon to be analyzed is polarization. In the general case where two subgroups interact, each with its full set of occupied and unoccupied orbitals, a given orbital φ_i in group A can be written as

$$\varphi_i^A = \varphi_i^A(1 + c_{ii'}) + \sum_{j \neq i}^A c_{ji'}\varphi_j^A + \sum_k^B c_{ki'}\varphi_k^B \quad (31)$$

That is, φ_i in group A mixes into itself in second order other orbitals in A and in first-order orbitals of the other subgroup B. Polarization is achieved in two ways, by in-group mixing in second order and by charge

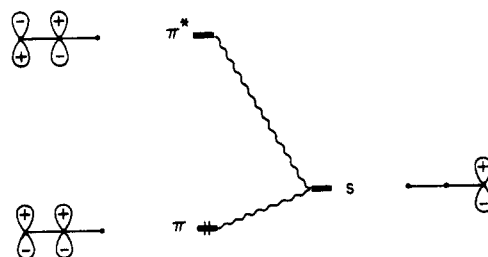
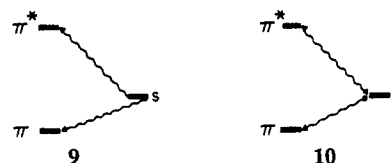


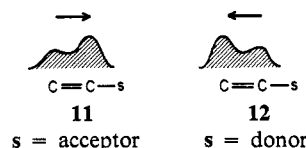
Figure 5. A model single orbital π perturber, s , at right, interacting with an ethylene π system at left.

transfer to the other group, which causes a polarization in B.

In the special case of a single orbital perturber, it is obvious that the perturber cannot be polarized by charge transfer to it nor can it polarize itself in second order. There are only two contributions to the polarization. π in (24) mixes into itself a little of π^* , as shown schematically in 9. s in (25) polarizes the ethylene by simultaneous charge transfer to π and π^* , as in 10.



The analysis of effects of polarization is straightforward and is given in Appendix II. There it is shown that an acceptor substituent always polarizes the ethylene so that electron density accumulates on the substituted carbon, as in 11. A donor produces the opposite polarization, shown in 12. The dominant factor



in the donor case is the second-order mixing of π^* into π . This was demonstrated explicitly above for the case of the methyl substituent. $c_{\pi^*,\pi'}$ depends on good overlap and proximity in energy of both the π^* and the π orbital to the substituent, and methyl fits these criteria well.

It should be noted that polarization is truly a second-order phenomenon, even when a component of it seems to be first order. If a wave function ψ is given by

$$\psi = c_1\varphi_1 + c_2\varphi_2 + \dots$$

then the electron density is associated with

$$\psi^2 = c_1^2\varphi_1^2 + c_2^2\varphi_2^2 + 2c_1c_2\varphi_1\varphi_2 + \dots$$

The first two terms are symmetric with respect to symmetry-equivalent sites in φ . The asymmetry, and thus the polarization, is introduced *via* the third, product, term. Referring back to our general system and (31), we note that in-group polarization will be measured by terms of the type $(1 + c_{ii'})(c_{ji'})$, while polarization *via* charge transfer will be measured by terms of the type $c_{ki'}c_{k'i'}$. In both cases the polarization takes a second-order form—a product of inter-

Table IV. Mixing Coefficients for Toluene. Second-Order Coefficients Are in Italics, First-Order Coefficients Are in Roman Type

<i>i</i>	$\delta\pi$	π_1	π_2	π_4	π_6	$\delta\pi^*$
$\delta\pi$	-0.121	-0.406	-0.268	-0.151	-0.090	+0.043
π_1	+0.339	-0.056	+0.076	+0.015	+0.004	-0.064
π_2	+0.174	-0.132	-0.013	+0.028	+0.006	-0.101
π_4	+0.062	-0.034	-0.039	-0.005	+0.010	-0.139
π_6	+0.028	-0.015	-0.015	-0.022	-0.006	-0.138
$\delta\pi^*$	+0.005	+0.011	+0.025	+0.061	+0.082	+0.003

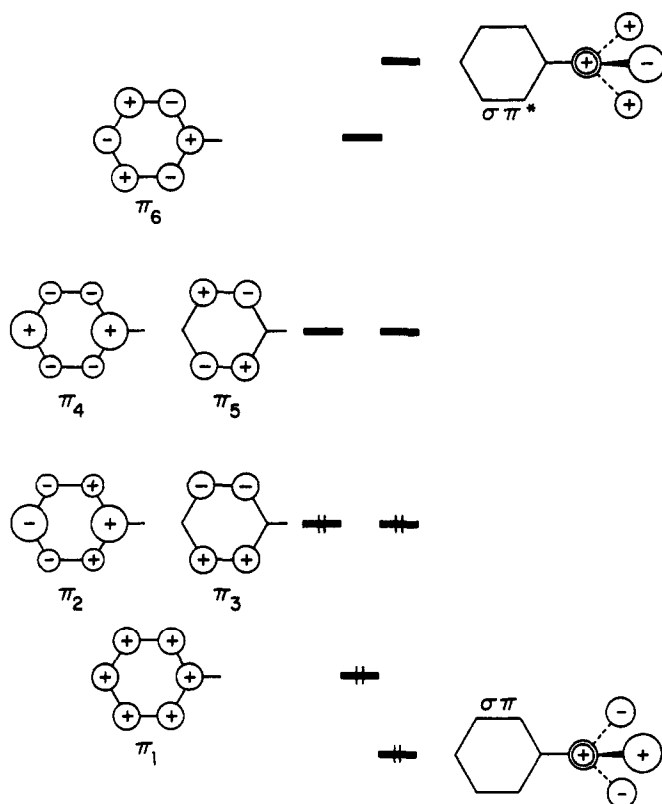
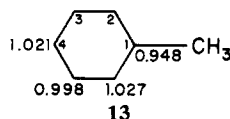


Figure 6. The basis set for the interaction of the π orbitals of a benzene ring (left) with the hyperconjugating σ orbitals of π symmetry of a methyl group. The signs of the carbon 2p orbitals are of the top lobe.

action matrix elements, divided by two energy differences.

Toluene, a Methyl Substituent on a Benzene Ring

Molecular orbital calculations agree in showing little charge interchange when a methyl group replaces a hydrogen in benzene.^{2-5,14,55} Toluene, like propylene, acquires its dipole moment through a polarization of its π system, a typical extended Hückel π electron distribution being shown in 13. A total of 0.019



electrons have been transferred from the methyl group, but the polarization that has resulted is more significant. Note the depletion in electron density at the ipso⁵⁶ (1) and meta (3) positions, and the enhancement

(55) Y. I'Haya, *Bull. Chem. Soc. Jap.*, **28**, 369 (1955).

(56) The nomenclature was introduced by C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, **93**, 3389 (1971).

of electron density at the ortho (2) and para (4) positions.

We will now trace the details of how the toluene charge distribution is produced. The basis set consists of the six familiar benzene π orbitals, labeled π_1 through π_6 , and the $\delta\pi$ and $\delta\pi^*$ orbitals of the methyl substituent (Figure 6). The presence of a vertical mirror plane through C₁ and C₄ of the ring simplifies the analysis somewhat, in that π_3 and π_5 , being antisymmetric with respect to the mirror, do not mix with the methyl group orbitals. Thus they contribute neither to charge transfer nor polarization.

The detailed perturbation analysis for the six-orbital problem that remains ($\delta\pi$, π_1 , π_2 , π_4 , π_6 , $\delta\pi^*$) is given in Table IV.

Table V gives the charge densities in the occupied π

Table V. Electron Densities in Toluene and Benzene (in Parentheses) Occupied π Orbitals

	4 para	3 meta	2 ortho	1 ipso	7 C	3H
π_3	— (—)	0.500 (0.500)	0.500 (0.500)	— (—)	— (—)	— (—)
π_2	0.623 (0.667)	0.127 (0.167)	0.215 (0.167)	0.606 (0.667)	0.022 (—)	0.066 (—)
π_1	0.394 (0.333)	0.360 (0.333)	0.278 (0.333)	0.179 (0.333)	0.062 (—)	0.082 (—)
$\delta\pi$	0.004 (—)	0.006 (—)	0.032 (—)	0.165 (—)	0.871 (0.701)	0.882 (1.299)

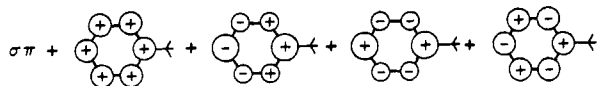
levels of toluene as they are obtained from a full extended Hückel calculation. The perturbation theory results to second order approximate well the calculated electron distribution. We proceed to analyze what happens to each orbital, making use of the corresponding electron distribution in an unperturbed benzene.

The methyl group orbital $\delta\pi$ transfers 0.245 electrons to the benzene π system. The ring is polarized by this transfer, with the qualitative shape of the orbital discernible without detailed calculations. $\delta\pi$ mixes into itself π_1 , π_2 , π_4 , π_6 in decreasing magnitude, as would be anticipated from the increasing energy denominator along the series. In the first-order mixing coefficient for any of these levels both the numerator and denom-

$$c_{\pi_i, \delta\pi} = \frac{H_{\pi_i, \delta\pi}}{E_{\delta\pi} - E_{\pi_i}} \quad (32)$$

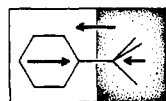
inator are positive. Therefore all the mixing coeffi-

cients are positive. The qualitative shaping of the orbital is given below. When the decreasing coeffi-



cients are taken into account, the resultant polarization shown in Table V is rationalized: density at $i > o > m > p$.

In second order the methyl group is internally polarized in the direction toward the benzene ring. Schematically the electron drift and polarization in this lowest orbital of π symmetry may be summarized in 14.

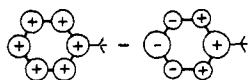


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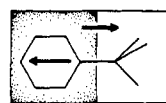
We turn to π_1 . This orbital transfers 0.144 electrons to the methyl group, primarily to $\delta\pi$. In second order π_1 is polarized primarily by mixing in of π_2 via $\delta\pi$. The requisite coefficient

$$c_{\pi_1, \pi_2}'' = \frac{H_{\pi_2, \sigma\pi} H_{\sigma\pi, \pi_1}}{(E_{\pi_1} - E_{\pi_2})(E_{\pi_1} - E_{\sigma\pi})} \quad (33)$$

is negative, leading to the mixing shown below.



The polarization is in the direction away from the substituent, summarized in 15.



15

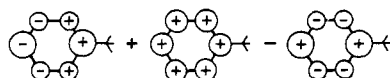
Finally we analyze π_2 . This orbital transfers 0.088 electrons to the methyl group, also polarizing it toward the hydrogens. Note the charge transfer is relatively small since π_2 is distant in energy from either $\delta\pi$ or $\delta\pi^*$. In second order π_2 is polarized by mixing into itself π_1 and π_4 (less). The signs of the mixing coefficients are predictable from the energy ordering.

$$c_{\pi_1, \pi_2}'' \sim \frac{1}{(E_{\pi_1} - E_{\pi_2})(E_{\pi_1} - E_{\sigma\pi})} > 0$$

$$c_{\pi_1, \pi_4}'' \sim \frac{1}{(E_{\pi_1} - E_{\pi_4})(E_{\pi_1} - E_{\sigma\pi})} < 0$$

(34)

π_2 is modified as follows.



The important result here is a definite electron shift, polarization, from m to o . Schematically



16

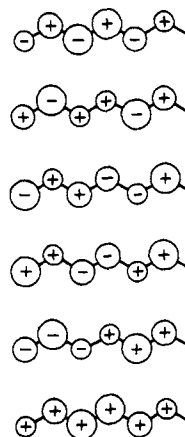


Figure 7. The π orbitals of a hexatriene, in order of ascending energy. The sign of the top lobe of the 2p orbital is shown.

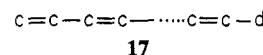
The details of the final electron distribution were given in Table V. With those details or even with the schematic diagrams 14, 15, and 16, we can trace the origins of the charge redistribution.

First, there is little net charge transfer. The shift from the methyl group in $\delta\pi$ is nearly balanced by the reverse transfer in π_1 and π_2 .

Second, there is considerable polarization of the benzene π system. The net result of the competing polarizations produced in the benzene part of $\delta\pi$ and π_1 is a concentration of electron density at the para position. This is because the second-order polarization in π_1 (toward p) greatly exceeds the reversed first-order polarization in $\delta\pi$ (away from p). The situation is very much like that which we found in propylene: a small polarizing correction to a large coefficient has much more "power," as far as charge shifts are concerned, than an equal correction to a zero coefficient. The correction in π_2 shifts electron density from the meta to the ortho position. This brings the ortho density to the level of the para, and accomplishes the depletion of the meta position. The net resultant of 13 is thus rationalized.

Polyene Substituent Effects

We have analyzed in great detail the interplay of charge transfer and polarization in propylene and toluene. Now we turn to another problem, the case of a donor substituent, a single occupied orbital, interacting with a general polyene of arbitrary length. To



sweep the range of realistic situations, the donor orbital will be allowed to vary in energy from an extreme where it is below all the polyene levels, through an intermediate situation where it lies among the π levels, to the other extreme where it is located above all of them. Some of the conclusions will be quite general, but they will be checked by model calculations with a hexatriene, whose orbitals are shown in Figure 7. Let the polyene orbitals be given as

$$\psi_j = \sum_k a_{kj} \varphi_k \quad (35)$$

where the a_{kj} is the coefficient of the k^{th} atomic orbital φ_k in the j^{th} molecular orbital. The donor orbital will be

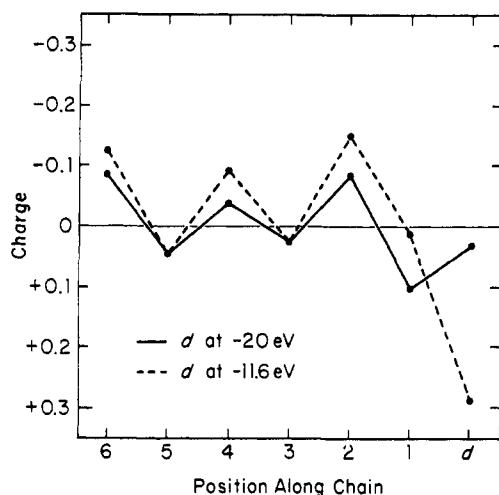


Figure 8. Charge densities along a hexatriene chain caused by a π -donor substituent, d . The charges are defined relative to a reference electron density of 1.0 for each hexatriene carbon and 2.0 for the donor orbital.

simply designated as d . The basis set is so chosen that polyene atom 1 is at the substitution site, and that all $a_{1j} > 0$. Then all interaction overlaps $S_{j,d'}$, which are controlled by the atomic overlap between φ_1 and d , are positive. Thus all $H_{j,d'}$ are negative.

We write the general expression for the perturbed donor orbital

$$d' = d + \sum_j c_{j,d'} \psi_j = d + \sum_j \frac{H_{j,d'}}{E_d - E_j} \psi_j \quad (36)$$

The interaction matrix element can be expanded into its component interactions between the atomic orbitals of the polyene and d

$$H_{j,d'} = \sum_k a_{kj} H_{k,d'} \quad (37)$$

and when substitution is at position 1 it may be a good approximation to retain only the controlling term

$$H_{j,d'} \sim a_{1j} H_{1,d'} \quad (38)$$

The perturbed polyene orbitals are given by

$$\psi_j' = (1 + c_{j,j'}) \psi_j + \frac{H_{d,j'}}{E_j - E_d} d + \sum_{k \neq j} \frac{H_{k,d'} H_{d,j'}}{(E_j - E_k)(E_j - E_d)} \psi_k \quad (39)$$

Note the absence of a second-order correction in d and its crucial presence in the π orbitals.

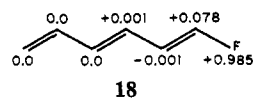
We begin by considering the situation when the donor level is far below all polyene levels, i.e., $E_d \ll E_j$. Then, after (36) and (38), and assuming orthonormal orbitals with overlap neglected,

$$\begin{aligned} d' - d &= \sum_j \frac{H_{j,d'}}{E_d - E_j} \psi_j \cong \frac{H_{1,d'}}{E_d} \sum_j a_{1j} \sum_l a_{lj} \varphi_l \\ &= \frac{H_{j,d'}}{E_d} \sum_l \delta_{1l} \varphi_l = \frac{H_{1,d'}}{E_d} \varphi_1 \end{aligned} \quad (40)$$

i.e., d is modified only by mixing in the atomic orbital at the site of attachment, and no charge transfer occurs to other polyene atoms.

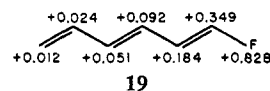
We checked this conclusion, as well as others to be

reported below, by a model extended Hückel calculation for d = a fluorine atom⁵⁷ with its Coulomb integral set arbitrarily at -25 eV. The coefficients in that orbital after interaction are shown in 18.



18

As the donor level moves up in energy, coming closer to the polyene levels, an increasing amount of electron density is transferred to polyene carbons further removed. There is a strict monotonic falloff of charge transfer with distance from the substituent, a representative wave function shown in 19 for a donor placed



19

0.3 eV below the lowest π level. Lest this behavior be identified with a classical inductive effect, the reader is reminded that we are discussing here but a single molecular orbital out of four π -type orbitals which are occupied. We will soon return to the very different behavior of the total electron density.

As the donor orbital moves up among the occupied π levels of the polyene, it becomes more and more difficult to identify. First-order interactions with polyene orbitals become strong and significant density at the substituent site is found in more than one molecular orbital.

We turn to the three polyene orbitals. On these the primary effect is one of polarization. Just as in the case of toluene, the composition of each orbital can be followed qualitatively or semiquantitatively by using the full perturbation formalism. Thus ψ_1 is primarily polarized by mixing in ψ_2 with a negative coefficient. ψ_2 mixes strongly with ψ_1 (positive coefficient) and ψ_3 (negative coefficient).

The net result, i.e., the total polyene electron distribution summed over the four occupied orbitals, is more constant than the individual orbital behavior would suggest. Figure 8 shows the electron density in the polyene at two disparate values of the donor energy. Note that an alternating polarization of the polyene has set in even at low donor energies. The polarization is maintained over the entire range of such energies. Over the same range the donor orbital progressively loses electron density. That density finds its way primarily to alternating chain atoms.

The regularities noted are at first surprising but in fact have been clearly explained some time ago. The extended Hückel calculation, when performed on the π system of a molecule, is nothing but a regular Hückel calculation with overlap included. This in turn is easily related to a simple Hückel calculation.^{58,59} The substituent can be modeled by a change in the Coulomb integral of the carbon at the site of attachment.^{18,19,58,60,61} The consequent changes in electron

(57) The C-F distance was taken as 1.31 Å, and the F2p Slater exponent as 2.425.

(58) G. W. Wheland, *J. Amer. Chem. Soc.*, **63**, 2025 (1941).

(59) B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc. Ser. A*, **201**, 196 (1950).

(60) G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.*, **57**, 2086 (1935).

(61) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

density along the chain may be obtained from the atom-atom polarizabilities

$$\pi_{r,s} = \frac{\partial q_r}{\partial \alpha_s} \quad (41)$$

first introduced by Coulson and Longuet-Higgins.¹⁸ In the second paper of their classic series on the electronic structure of conjugated systems, these authors utilized the explicit form of the linear polyene orbitals^{62,63} to reach some general conclusions concerning these polarizabilities. In particular, Coulson and Longuet-Higgins proved the generalization of the specific observation of Figure 8, namely that in substituted polyenes the electron density at the polyene carbons is alternately raised and lowered from 1.0. Similar conclusions were also reached by Dewar in his important series of papers on the application of perturbation theory to organic chemistry.⁶⁴ The alternation phenomenon is generally known as the π -inductive effect and has been the subject of much discussion.^{20,21,55,65-77} To the extent that a methyl substituent is donor dominant, its polarizing capability on ethylene and benzene, analyzed by us above, is consistent with the general effect of a donor on a polyene.

Acknowledgment. We are grateful to Akira Imamura for making his perturbation program available to us and to Hiroshi Fujimoto for some help in the calculations. Our research was generously supported by the National Science Foundation (GP 28137X) and the National Institutes of Health (GM 13468).

Appendix I

Consider the initial level ordering of Figure 1, with E_i^0 below E_j^0 . When overlap is neglected, it follows directly from eq 11 that $c_{ji}' = -c_{ij}'$ and from eq 16 that $E_i'' = -E_j''$ and that $E_i'' < 0$. That the in-phase bonding combination is at lower energy we cannot prove absolutely, but a plausibility argument³¹ is based on the usual opposite sign of H_{ij} to S_{ij} . For positive S_{ij} it then follows that $c_{ji}' > 0$.

When overlap is explicitly included, we obtain

$$c_{ji}' = \frac{H_{ji}' - E_i^0 S_{ji}'}{E_i^0 - E_j^0} \quad c_{ij}' = \frac{H_{ji}' - E_j^0 S_{ji}'}{E_j^0 - E_i^0} \quad (42)$$

(62) C. A. Coulson, *Proc. Roy. Soc. Ser. A*, **169**, 413 (1939).

(63) C. A. Coulson and A. Streitwieser, "Dictionary of π -Electron Calculations," W. H. Freeman, San Francisco, Calif., 1965.

(64) See ref 19, especially theorems 34-39.

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(69) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3539, 3541, 3546, 3548 (1962); M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, **88**, 354 (1966); M. J. S. Dewar and Y. Takeuchi, *J. Amer. Chem. Soc.*, **89**, 390 (1967); N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **91**, 352 (1969).

(70) D. P. Craig and G. Doggett, *Mol. Phys.*, **8**, 485 (1964).

(71) J. Burdon, *Tetrahedron*, **21**, 3373 (1965).

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(76) E. T. McBee, I. Serfaty, and T. Hodgins, *J. Amer. Chem. Soc.*, **93**, 22 (1971).

(77) W. Gründler and H. D. Schädler, *Monatsh. Chem.*, **104**, 206 (1973).

A direct proof that $|c_{ji}| < |c_{ij}|$ has not been found by us. The inequality would hold if

$$|H_{ji}' - E_i^0 S_{ji}'| < |H_{ji}' - E_j^0 S_{ji}'| \quad (43)$$

Within an extended Hückel type theory, where H_{ij} is taken as KS_{ij} , the above inequality would read

$$|(K - E_i^0)S_{ji}'| < |(K - E_j^0)S_{ji}'| \quad (44)$$

which requires that

$$|K - E_i^0| < |K - E_j^0| \quad (45)$$

K varies with the type of interaction, but typically (two carbon 2p orbitals) is around -20 eV. The above inequality is then satisfied if -20 eV $< E_i^0 < E_j^0$. This will be true for most energy levels.

For the energy level corrections

$$E_i'' = \frac{(H_{ji}' - E_i^0 S_{ji}')^2}{E_i^0 - E_j^0} \quad E_j'' = \frac{(H_{ji}' - E_j^0 S_{ji}')^2}{E_j^0 - E_i^0} \quad (46)$$

The conditions for $|E_i''| < |E_j''|$ are the same as those for the coefficients above.

Appendix II

We want to show that an ethylene perturbed by a substituent bearing a single orbital "s," will be polarized toward the substituent if "s" is unoccupied (acceptor), **20**, and away from the substituent if s is occupied (donor), as in **21**. The orbitals involved were shown in

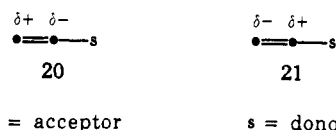


Figure 5, with E_s , the energy of the substituent level, variable, and s empty for an acceptor substituent, doubly occupied for a donor. Note the choice of phase is such that $S_{\pi,s}'$ and $S_{\pi^*,s}'$ are both positive and therefore $H_{\pi,s}'$ and $H_{\pi^*,s}'$ are both negative.

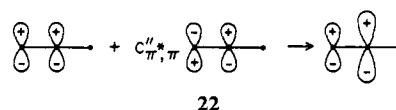
(1) **Acceptor Case, s Unoccupied.** The perturbed π is given to second order by eq 47.

$$\pi = (1 + c_{\pi,\pi}'')\pi + c_{s,\pi}'s + c_{\pi^*,\pi}''\pi^* \quad (47)$$

Polarization is achieved only through

$$c_{\pi^*,\pi}'' = \frac{H_{\pi s}' H_{s \pi^*}'}{(E_{\pi} - E_{\pi^*})(E_{\pi} - E_s)} \quad (48)$$

The numerator is positive, $E_{\pi} - E_{\pi^*} < 0$. $E_{\pi} = E_s$ is also negative for any reasonable acceptor. Therefore $c_{\pi^*,\pi}'' > 0$. Since $1 + c_{\pi,\pi}''$, the coefficient of the π orbital, is also > 0 , the polarization occurs as shown schematically in **22** below.



(2) **Donor Case, s Occupied.** This case is more complicated, since polarization is achieved in two ways, through second-order mixing in π , as well as through first-order mixing in s. The two effects operate in opposite directions. The form of π was given above in eq 47. Perturbed s is given by eq 49.

$$s = (1 + c_{s,s}'')s + c_{\pi,s}'\pi + c_{\pi^*,s}'\pi^* \quad (49)$$

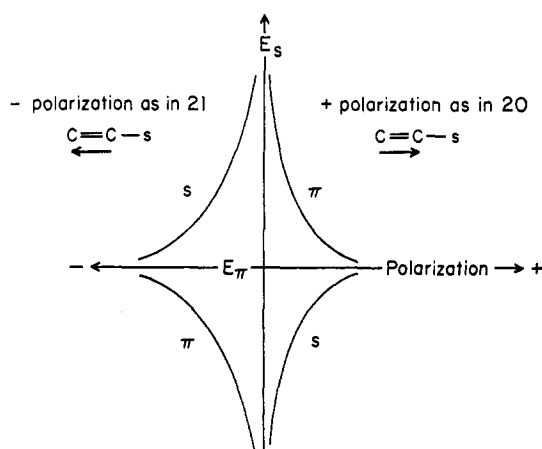


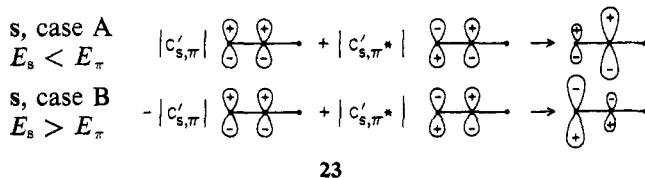
Figure 9. Polarization in s and π orbitals as a function of the position of the energy of the substituent orbital. The vertical scale is E_s , the energy of s . At the origin $E_s = E_\pi$. In the upper half plane $E_s > E_\pi$, which is case B. In the lower half plane $E_s < E_\pi$, which is case A. The horizontal axis measures the polarization, with + polarization as in 20.

Polarization in s is determined by the relative signs of $c_{\pi,s}'$ and $c_{\pi^*,s}'$.

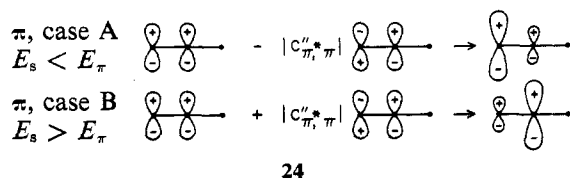
$$c_{\pi,s}' = \frac{H_{\pi,s}'}{E_s - E_\pi} \quad (50)$$

$$c_{\pi^*,s}' = \frac{H_{\pi^*,s}'}{E_s - E_{\pi^*}} \quad (51)$$

The numerators are negative. For all reasonable donors s is below π^* . Therefore $c_{\pi^*,s}' > 0$. We must distinguish, however, two cases, both realistic, for $c_{\pi,s}'$. In case A s is below π and $c_{\pi,s}' > 0$. In case B s is above π and $c_{\pi,s}' < 0$. The resultant polarizations are different in the two cases.



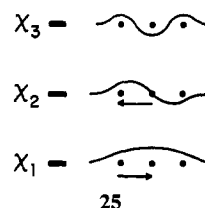
Proceeding to the two electrons in the π orbital, we have its form given by (47). $c_{\pi^*,\pi}''$, which determines the polarization of this orbital, is given by (48). The numerator is positive, $E_\pi - E_{\pi^*} < 0$. Again we must distinguish two cases depending on whether s is below π or above it. In case A, $c_{\pi^*,\pi}'' < 0$; in case B, $c_{\pi^*,\pi}'' > 0$. The resultant polarization in π is given below.



The methyl substituent we examined in the text of the paper was of type A, with $E_{\sigma\pi} < E_\pi$. The detailed polarizations of the perturbed $\sigma\pi$ and π levels should be compared with the formulas derived above.

The total polarization is due to the two electrons in s as well as the two electrons in π . The results then appear ambiguous, since the π polarization is of opposite sign to that of s . Moreover, the polarizations in each orbital change sign depending on the ordering of π and s . The situation is shown in Figure 9. There is a discontinuity in the polarizations at $E_s = E_\pi$. All of these points can be cleared up. The discontinuity at $E_s = E_\pi$ is an obvious artifact of the use of perturbation theory under the assumption of no degeneracy. The change in sign of polarization as s rises from below π to above is in fact necessary to preserve the nodal characteristics and shapes of orbitals. This may be seen by the following argument.

For a three-orbital system the shape of the molecular orbitals is the characteristic free electron set of 25.



The approximate shape of the orbitals is retained even when the system is heteronuclear. Now, if we consider the three-orbital system as built up from a two-orbital set at left (" π ") and a perturbing orbital at right (" s "), then χ_1 is clearly polarized toward s and χ_2 away from s . But whether χ_1 is derived from π or s depends on which orbital entered the perturbation scheme at lower energy. If s was above π , we identify χ_1 with π and χ_2 with s . Then π is polarized to the right and s to the left. If s was below π , the reverse polarization obtains; i.e., the final nodal structure of the orbitals remains the same, the switch in polarization is due to the arbitrariness of what we call π and what we call s .

Finally we can, despite the opposing nature of the effects shown in Figure 9, make a decision on which polarization effect dominates. If an orbital ψ shows a polarization

$$\psi = a\pi + b\pi^* + \dots \quad (52)$$

then the measure of that polarization is the product ab . The electron density is given by

$$\psi^2 = a^2\pi^2 + b^2\pi^{*2} + 2ab\pi\pi^* \quad (53)$$

and the asymmetry is introduced by the cross term. Corresponding to this cross term in the second-order polarization effect in π is $c_{\pi^*,\pi}'$ (see 22).⁷⁸ The cross term in the first-order polarization effect in s (see 23) is the product $c_{s,\pi}'c_{s,\pi^*}'$. These are given explicitly in eq 48, 50, and 51. It follows that

$$\left| \text{ratio of polarizations} \frac{\pi}{s} \right| = \left| \frac{c_{\pi^*,\pi}'}{c_{s,\pi}'c_{s,\pi^*}'} \right| = \left| \frac{E_s - E_{\pi^*}}{E_\pi - E_{\pi^*}} \right| \quad (54)$$

Reference to the energy ordering of the basis (Figure 5) shows that this ratio is greater than 1 when s is below π and less than 1 when s is above. In other words,

(78) The exact expression for the cross term is $c_{\pi^*,\pi}''(1 + c_{\pi,\pi}'')$; we neglect the product of the second-order corrections.

when $E_s < E_\pi$, the π polarization dominates. When $E_s > E_\pi$, the s polarization dominates. Reference to 23 and 24 translates this into case B for $E_s > E_\pi$ and case A for $E_s < E_\pi$. These are indeed both cases which result in polarization away from s , as in 21, and this completes the demonstration.

Finally we inquire about the energy dependence of the magnitude of the polarization. For the acceptor case the polarization is given by $c_{\pi^*,\pi}''$ from (48), which is larger the closer s lies to π , *i.e.*, the lower s lies for realistic acceptors. For the donor case the polar-

ization is proportional to

$$c_{\pi^*,\pi}'' + c_{s,\pi} c_{s,\pi^*}' = \frac{H_{\pi,s} H_{s,\pi^*}'}{E_\pi - E_s} \times \left(\frac{1}{E_\pi - E_{\pi^*}} - \frac{1}{E_s - E_{\pi^*}} \right) = \frac{K'}{(E_\pi - E_{\pi^*})(E_s - E_{\pi^*})} \quad (55)$$

This is larger in magnitude the closer s lies to π^* , *i.e.*, the higher s lies. Thus the "better" the donors or acceptors are, respectively, the more effective they should be at polarizing the π system.

Substituent Effects in the Bridging by Oxygen in Alkyl Radicals by Electron Spin Resonance

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Abstract: Trifluoromethoxy radicals generated photochemically from bistrifluoromethyl peroxide add to ethylene, propylene, and isobutylene, and the esr spectra of the adducts can be observed over a range of temperatures. Analysis of the β -proton hyperfine splitting and its temperature dependence indicates that the propylene adduct exists in a stable conformation in which the β oxygen eclipses the p orbital at the radical center. The adducts of PhCO_2 and PrOCO_2 radicals show similar conformational preferences, which are unusual since the β - CH_3O , n - BuO , HO , and $(\text{CH}_3)_3\text{SiO}$ analogs prefer stable conformations in which the β oxygen is staggered relative to the half-filled p orbital similar to the conformation of the *sec*-butyl radical. Homoconjugative and hyperconjugative interactions of the β - CF_3O , PhCO_2 , and PrOCO_2 groups to the radical center are discussed, but neither of them is sufficiently strong to force the ethylene adduct to a similar eclipsed conformation. Comparisons of the sulfur and other oxygen adducts indicate that bridging is much more important with sulfur. Bridging can be induced only when electro-negative groups are present on the oxygen center and are noticeable when energy differences between conformations are relatively small as in the β -substituted isopropyl radicals. A β -fluorine substituent is similar to β - CF_3O in this regard.

Stabilization of alkyl radicals and stereoselectivity in free radical reactions due to bridging and anchimeric assistance are subjects which have been discussed at length and are of current chemical interest.^{1,2} The dominant chemical effects are exerted by heteroatom substituents at the β carbon relative to the radical center, and they are especially pronounced with the halogens, bromine and chlorine, and sulfur.

The electron spin resonance (esr) spectra is an effective tool for the study of the structure and conformations of free radicals. The technique has been greatly aided by the development of procedures for the production of specific alkyl radicals in sufficiently high concentrations in solution to examine over a range of temperatures.^{3,4} The conformations and structures of a variety of β -sulfur substituted radicals have been examined by esr,^{5,6} but there is no example heretofore of an oxygen substituent involved in bridging. In order to determine whether a first row element in the

periodic table such as oxygen can participate in radical bridging, we examined the esr spectra of a variety of β -oxygen substituted alkyl radicals in solution.

Results

Photolysis of Bistrifluoromethyl Peroxide. The photolysis of bistrifluoromethyl peroxide in dichlorodifluoromethane (Freon-12) solutions at temperatures between -50 and -130° gave rise to no detectable esr spectrum. In order to optimize conditions for the observation of transient paramagnetic species, the



microwave power as well as the modulation amplitude were varied widely. The presence of trifluoromethoxy radical was undetected probably due to line broadening in the spectrum by relaxation effects described previously in attempts to observe alkoxy radicals in solution.⁷

Photolysis of bistrifluoromethyl peroxide in eq 1 probably proceeds by the same process involved in the previously studied di-*tert*-butyl peroxide.⁶ Moreover, we could find no evidence for photolytic scission at the C-O bond, since the spectrum of neither trifluoromethyl

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(2) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972.

(3) H. Fischer in ref 1, Chapter 19.

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