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Overlap Repulsion as an Important Contributor to Aromaticity

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Abstract: A Hückel aromatic molecule can be viewed in terms of one-electron MO theory as a system in which stabilizing orbital interactions are maximized and destabilizing overlap repulsions are minimized relative to a nonaromatic analogue. This latter conclusion is opposite to intuitive expectations and currently held viewpoints and it suggests yet another important factor which may favor "crowded" over "uncrowded" geometries. The results of semiempirical and ab initio calculations as well as experimental results drawn from the literature are presented to support the conclusions reached by an orbital symmetry based approach.

Simple perturbation theory arguments lead to the prediction that the π stabilization energies of the union of penta-dienyl with methyl to form benzene or hexatriene are: benzene, $\delta E = 4a\beta$; hexatriene, $\delta E = 2a\beta$, where the a 's are AO coefficients in the penta-dienyl NBMO and β is a standard resonance integral. According to this analysis, benzene is more stable than hexatriene and the difference in stability can be equated to what is traditionally referred to as "resonance energy".¹ In this work, we show that the greater stability of a Hückel aromatic cyclic molecule relative to its nonaromatic noncyclic analogue is only partly the result of greater stabilization of the cyclic geometry, and that *over-*

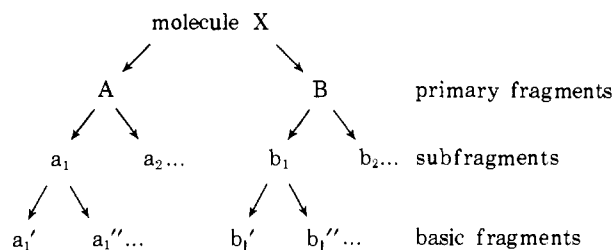
lap repulsion, contrary to any intuitive expectations, can destabilize the cyclic form less than the noncyclic one!

We have chosen to compare five diverse Hückel aromatic systems with their nonaromatic analogues and investigate by one-electron MO (OEMO) theory the origin of π Hückel aromaticity in these systems. The comparisons involve: (a) benzene vs. *trans*-1,3,5-hexatriene in its extended conformation; (b) *cis*- vs. *trans*-1,2-difluoroethylene; (c) the methyl rotational barrier in *cis*- vs. *trans*-1-fluoropropene; (d) the staggered and eclipsed conformations of dimethyl ether; (e) *cis*- vs. *trans*-2-butene in the staggered conformation. In all cases experimental results and ab initio calcu-

lations which bear on the problem are discussed in the light of our analysis.

Theory

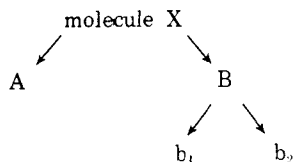
The theoretical analysis to be employed throughout this paper is based upon one-electron molecular orbital (OEMO) theory. According to this approach, a given molecule in a specified geometry is constructed by a sequential union of molecular fragments. A typical construction is illustrated below.



Once one knows the MO's of a set of basic fragments, he can construct the MO's of any molecule by means of relatively simple operations. A recent publication of Salem and Jorgensen² is a welcome addition to the library of any organic chemist, since it includes an extensive compilation of basic fragments and their MO's and provides illustrative examples of the theoretical manipulations involved in the construction of a total system from component fragments.

The union of any two molecular fragments is accompanied by an energy change which depends upon the interaction between the MO manifolds of the two fragments and is evaluated with respect to an effective one-electron Hamiltonian operator, the choice of the operator being such as to confer maximal simplicity to the analysis. This approach is ideal for comparing the relative stability of torsional isomers since one starts from the same building blocks and compares the energy changes which accompany their sequential union in two or more specified geometries.

In all cases examined in this paper, the sequential construction of molecules involves three basic fragments combined in the manner shown below:



The energies of the MO's of the "basic" fragments A, b₁, and b₂, which constitute the starting point of our analysis, were determined by SCF-MO-INDO calculations.³ The energy and AO eigenvectors of the MO's of B and X were developed by OEMO theory including overlap. The calculations of the energy changes accompanying MO interactions should be given qualitative significance only and are presented in order to illustrate general trends.

Benzene vs. *trans*-1,3,5-Hexatriene (Extended Conformation)

Consider the union of three π bonds A, B, and C to form a cyclic array equivalent to the π system of benzene (I) and a noncyclic array corresponding to *trans*-1,3,5-hexatriene (II). The former is a typical Hückel aromatic system and the latter a typical nonaromatic system.

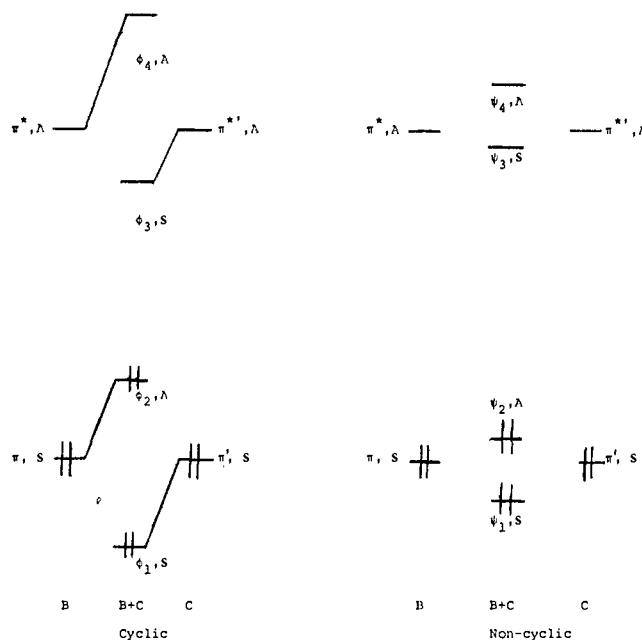
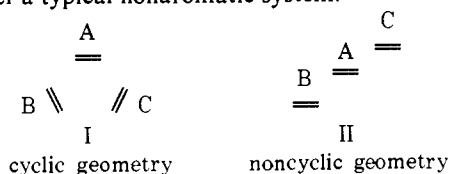


Figure 1. Interaction diagram for the orbital union B + C for the cyclic and noncyclic geometries.

Table I. Orbital Interaction Energies for A + (B + C) Union

Geometry	Orbital interaction	ΔE^4 , eV	ΔE^2 , eV
Cyclic ^a	$\pi-\pi'$	3.133	
Cyclic ^a	$\pi'-\pi^*$		-1.525
Cyclic	ϕ_1-w	2.309	
Noncyclic	ψ_1-w	3.234	
Cyclic	$w-\phi_3$		-4.834
Cyclic	ϕ_2-w^*		-3.167
Noncyclic	ψ_2-w^*		-1.749
Noncyclic	$w-\psi_3$		-1.632

^aFor the noncyclic geometry, these interaction energies are zero.

We shall analyze the orbital interactions which obtain in the union B + C and subsequently in the union A + (B + C) for each of the two geometries I and II.

The interaction diagram of Figure 1 shows the orbital interactions which obtain in the union B + C. In the case of geometry I, there is strong overlap and the two π bonds interact appreciably. The two-electron stabilizing interactions $\pi'-\pi^*$ and $\pi-\pi'^*$ compete with the four-electron destabilizing interaction $\pi-\pi'$. The two-electron stabilization energy is given by eq 1 and the four-electron destabilization energy is given by eq 2.⁴ In these expressions H_{ij} is the resonance integral of ϕ_i and ϕ_j , S_{ij} the overlap integral of ϕ_i and ϕ_j , E_i and E_j the one-electron energies of ϕ_i and ϕ_j , ϵ_0 the mean of E_i and E_j , and k an energy constant. In the derivation of the final form of eq 1 the approximation $H_{ij} = kS_{ij}$ has been made.⁵ We have explicitly calculated the energy change accompanying each orbital interaction alluded to before and the results are shown in Table I.

$$\Delta E^2 = \frac{(H_{ij} - S_{ij}E_i)^2}{E_i - E_j} = \frac{S_{ij}^2(k - E_i)^2}{E_i - E_j} \quad (1)$$

$$\Delta E^4 = \frac{4S_{ij}^2}{1 - S_{ij}^2} (\epsilon_0 - k) \quad (2)$$

In the case of geometry II, S_{ij} is approximately zero and the two π bonds do not interact to any significant extent. Therefore, the stabilization and destabilization energies are near zero. We conclude that there is greater stabilization as well as greater destabilization of the cyclic form relative to the noncyclic one. The destabilization outweighs the stabili-

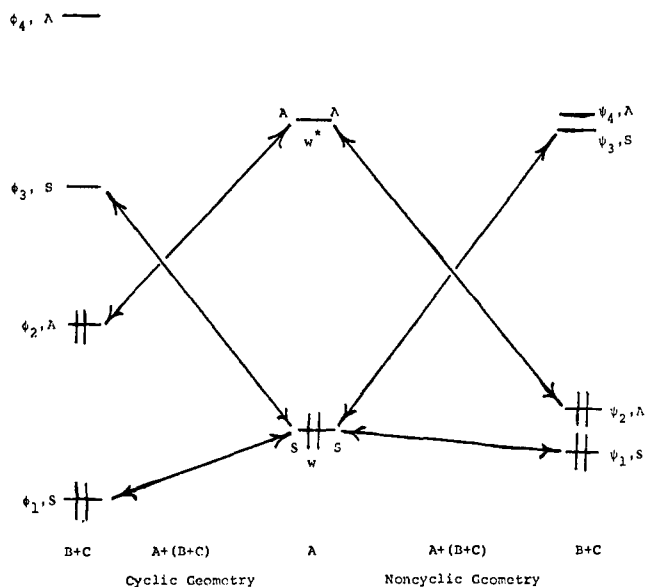


Figure 2. Interaction diagram for the cyclic and noncyclic union $A + (B + C)$.

zation and the noncyclic form is favored over the cyclic form, at this stage of the analysis.

Figure 2 shows the orbital interactions for the union $A + (B + C)$. The diagram allows us to decide unequivocally, and without regard to calculations, the relative degree of stabilization and destabilization of the two geometries. The following conclusions are readily apparent.

(a) The stabilizing interaction $w-\phi_3$ will be stronger than that of $w-\psi_3$ because $S_{w,\phi_3} > S_{w,\psi_3}$, E_w is common for both cases, and $E_w - E_{\phi_3}$ is smaller than $E_w - E_{\psi_3}$.

(b) The stabilizing interaction ψ_2-w^* will be stronger than the interaction ψ_2-w because $S_{\psi_2,w^*} > S_{\psi_2,w}$, E_{ψ_2} is less negative than E_{ψ_2} , i.e., $(k - E_{\phi_2})^2$ is greater than $(k - E_{\psi_2})^2$, and $E_{\phi_2} - E_{w^*}$ is smaller than $E_{\psi_2} - E_{w^*}$.

Thus, we have shown that an OEMO approach including overlap predicts that a cyclic geometry for $A + (B + C)$ union is stabilized relative to a noncyclic one, and explicit calculations show exactly that (Table I).

We now focus on the four-electron destabilizing interactions. A comparison of the destabilizing interaction $w-\phi_1$ and $w-\psi_1$ is very simple. The destabilizing interaction $w-\phi_1$ will be *smaller* than the destabilizing interaction $w-\psi_1$ because $S_{w,\phi_1} < S_{w,\psi_1}$ and $|(E_w + E_{\phi_1})/2| > |(E_w + E_{\psi_1})/2|$; the latter inequality arises from the fact that E_{ϕ_1} is more negative than E_{ψ_1} . We conclude, therefore, that *an OEMO analysis, including overlap, predicts that a cyclic geometry for $A + (B + C)$ union will be less destabilized than expected relative to a noncyclic geometry*, a conclusion which is in no way intuitively obvious.

We have calculated explicitly the various stabilization and destabilization energies which obtain in the $A + (B + C)$ union. On the basis of these calculations and the ones previously reported for the $B + C$ union, we have calculated that the *total* two-electron stabilization of the cyclic geometry relative to the noncyclic one is -6.145 eV while the total four-electron destabilization is only 2.210 eV. In other words, we can say that the cyclic form is not destabilized by overlap repulsion as much as one might have intuitively thought because of the orbital interaction pattern which obtains in the case of $A + (B + C)$ union. This orbital pattern arises in *all* comparisons of Hückel aromatic and nonaromatic systems.

1,2-Difluoroethylene

The π frameworks of *cis* and *trans*-1,2-difluoroethylene

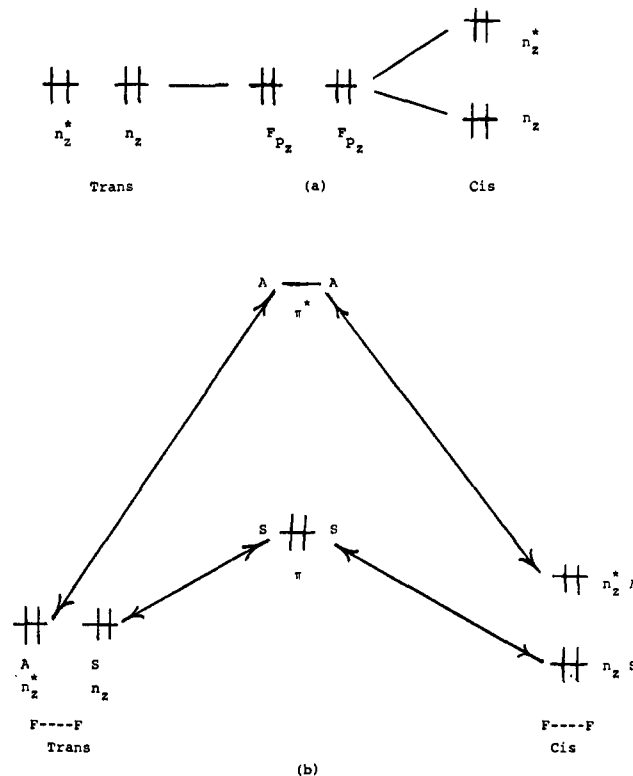


Figure 3. (a) Construction of the $F-F$ group π MO's from F_{p_z} AO's. Overlap repulsion is greater in the *cis* isomer. (b) Construction of the π MO's of 1,2-difluoroethylene. Arrows indicate the crucial two-electron and four-electron orbital interactions.

can be constructed from the group MO's spanning the two p_z "lone pair" AO's of the fluorine and the ethylenic π MO's. In the case of the *cis* molecule, the two fluorine AO's overlap and their through space interaction lifts the degeneracy of the two "lone pair" MO's. In the *trans* molecule, overlap is nearly zero and the two "lone pair" MO's are degenerate. The interaction diagram of Figure 3 contains all the necessary information for understanding why the *cis* isomer will be predisposed to be more stable than the *trans* isomer. We distinguish three types of interaction.

(a) A four-electron destabilizing interaction between the fluorine lone pairs. Since the overlap integral, S_{FF} , is non-zero in the *cis* but near zero in the *trans* molecule, we know that on the basis of eq 2 that the four-electron destabilization will be present in the *cis* but absent in the *trans* isomer.

(b) A four-electron destabilizing interaction between n_z and π . The quantity $S_{n_z\pi}$ is *greater* in the case of the *trans* isomer than in the *cis* because the normalization constant for the n_z MO has the form $(2 + 2S_{FF})^{-1/2}$ and will be smaller in the *cis* case since $S_{FF}(\text{cis}) > S_{FF}(\text{trans})$. Furthermore, ϵ_0 is more negative for the *cis* isomer and will lead to a smaller $(\epsilon_0 - k)$ value in the *cis* geometry. Hence, on the basis of eq 2, we conclude that this four-electron destabilization will be less for the *cis* than the *trans* isomer.

(c) A two-electron stabilizing interaction between n_z^* and π^* . The expression for this interaction is given by eq 1 and the following variations obtain: (1) the energy difference $\epsilon_{n_z^*} - \epsilon_{\pi^*}$ is smaller for the *cis* isomer; (2) the quantity $(k - \epsilon_{n_z^*})$ is greater for the *cis* isomer; (3) the overlap integral $S_{n_z^*\pi^*}$ is greater for the *cis* isomer because the normalization factor of the n_z^* group MO, given by the expression $(2 - 2S_{FF})^{1/2}$, is greater for the *cis* isomer. We conclude that the two-electron stabilization will be greater for the *cis* than the *trans* isomer.

A simple numerical calculation of the three types of MO interactions yields the results shown in Table II. It can be

Table II. Relative Destabilization and Stabilization Energies of *cis*- and *trans*-1,2-Difluoroethylene

	ΔE_{FF}^4 , eV	$\Delta E_{n_z\pi}^4$, eV	$\Delta E_{n_z^*\pi^*}^2$, eV
Cis	0.0014	0.0000	-0.0174
Trans	0.0000	0.0196	0.0000

Chart I

Isomer	E_{relative} , kcal/mol			
	INDO	MWH	Ab initio ¹⁶	STO-3G
cis	0.000	0.000	0.226	0.000
trans	0.611	0.051	0.000	0.431

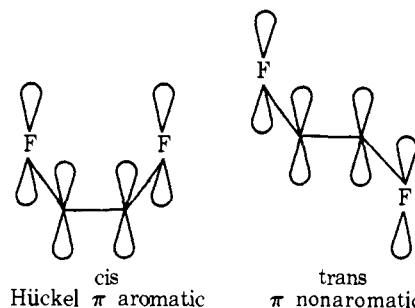
seen that the n_z - π four-electron destabilization favors the *cis* isomer and more than compensates for the four-electron F-F destabilization which favors the *trans* isomer. We conclude that the greater stability of the *cis* isomer in 1,2-disubstituted olefins is due to a greater n_z^* - π^* two-electron stabilization and a smaller n_z - π four-electron overlap repulsion in the *cis* isomer. In the previous comparison of benzene versus *trans*-1,3,5-hexatriene, we saw that overlap repulsion destabilized the cyclic form more than the noncyclic one by a small amount. Here, we find that overlap repulsion destabilizes the noncyclic form more than the cyclic form! The *cis* isomer of 1,2-difluoroethylene suffers from severe dipole-dipole (Coulombic) repulsion while the *trans* does not. Furthermore, internuclear repulsion is greater in the *cis* than in the *trans* isomer. Hence, the greater stability of the *cis* isomer is due to some important factor and in this discussion we have recognized a conspiracy of orbital interactions which maximize the stabilization and minimize the overlap destabilization of the *cis* relative to the *trans* isomer. In Figure 3, we recognize the orbital interaction patterns we first saw in Figure 2 and which is characteristic of the situations we discuss. Also, it is interesting to point out that the quantities ΔE^2 and ΔE^4 change by about the same amount (-0.017 and -0.018 eV, respectively) in the transformation *trans* \rightarrow *cis* so that, unlike the case of benzene vs. 1,3,5-hexatriene, the two-electron stabilization is not the exclusive factor determining the relative stability of *cis*- and *trans*-1,2-difluoroethylenes.

The results of SCF-MO-INDO,³ Mulliken-Wolfsberg-Helmholtz (MWH),⁶ and ab initio calculations are shown below for *cis*- and *trans*-1,2-difluoroethylene (Chart I). The calculations show that the energy difference between *cis*- and *trans*-1,2-difluoroethylene is small, a fact which is reflected in the ab initio computations where a change in basis sets gives a different result. However, the important point to be emphasized is that *cis*-1,2-difluoroethylene suffers from extreme dipole-dipole and internuclear repulsions leading one to expect the *trans* isomer to be much lower in energy than the *cis*. We attribute the comparable stability of *cis* and *trans*-1,2-difluoroethylene to stabilizing nonbonded interactions which obtain in the *cis* isomer and which counteract the severe destabilizing "steric" interactions.

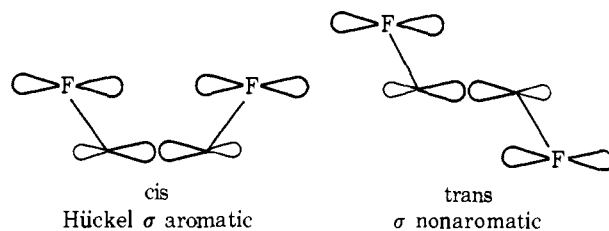
It should be pointed out that in 1,2-difluoroethylene the energy difference between the ethylenic π MO's and the fluorine-fluorine π group MO's, n_z and n_z^* , is large due to the high electronegativity of fluorine. Consequently, the primary stabilizing interaction, n_z^* - π^* , will be small and, hence, the one-electron factors favoring the *cis* isomer will be relatively weak resulting into comparable stability for the *cis* and *trans* isomers. We expect, therefore, that as the energy gap between n_z^* and π^* decreases, which will occur when the groups containing the lone pair electrons become

less electronegative, the one-electron factors favoring the *cis* isomer will increase resulting in a much lower energy, provided "steric" effects are not too large, for the *cis* than the *trans* isomer,

We can simplify the above discussion of 1,2-difluoroethylene by noting that *cis*-1,2-difluoroethylene resembles a 6π electron Hückel aromatic system while the *trans* isomer is a 6π electron nonaromatic system:



We have also pointed out previously^{7a} that σ interactions may also be important in contributing to the greater stability of the *cis* relative to the *trans* isomer. These interactions between the 2s and $2p_x$ lone pairs of fluorine and the σ component of the central double bond can be analyzed in exactly the same manner as the interactions between the $2p_z$ lone pairs of fluorine and the π component of the central double bond which were discussed before. Once more, the results of such an analysis can be conveyed in the language of the organic chemist by saying that the *cis* isomer constitutes a six-electron σ Hückel aromatic system and the *trans* is a six-electron σ nonaromatic system:



The greater stability of *cis*-1,2-difluoroethylene relative to the *trans* isomer is, therefore, a consequence of π aromaticity augmented by σ aromaticity which obtains in the former case but not in the latter. We shall see that π and σ aromaticity can compliment one another, as in 1,2-difluoroethylene, or work in opposite directions in which case one effect will dominate the other.

Rotational Isomerism in *cis*- and *trans*-1-Fluoropropene

The barrier to rotation of the methyl group in the *trans* isomer of 1-fluoropropene can be taken to be the energy difference between the staggered conformation TS and the eclipsed conformation TE.⁸ Similarly, the barrier to rotation of the methyl group in the *cis* isomer is the energy difference between the CS and CE conformations. In the case of the *trans* isomer, the methyl group cannot interact with fluorine through space and the rotational barrier is determined, roughly, by the same factors which determine the rotational barrier in propene. In propene as well as in *trans*-1-fluoropropene, the eclipsed or cisoid conformer is the low-energy form and the staggered or transoid conformer is the high-energy form. Possible rationalization of this effect has been offered elsewhere.⁹ On the other hand, in the case of the *cis* isomer, the methyl group can interact with fluorine through space and the rotational barrier will now be determined by the same factors which determine the rotational barrier of propene and *trans*-1-fluoropropene, but also by the nature of the methyl fluorine interaction. This interac-

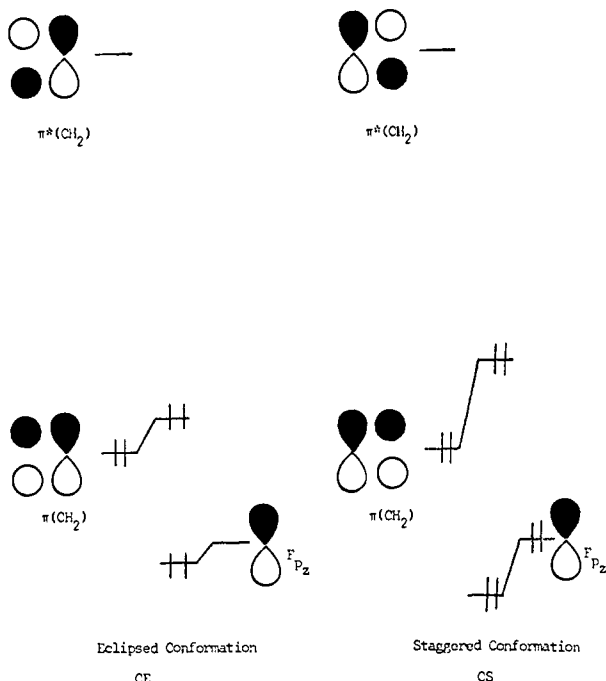


Figure 4. Construction of the n_z and n_z^* group MO's for CE and CS conformation of 1-fluoropropene.

tion is attractive in nature, and stronger in the CS than in the CE conformation because of the different spatial orientation of the out-of-plane methylene hydrogens and, hence, their proximity with respect to the fluorine p_z lone pair.

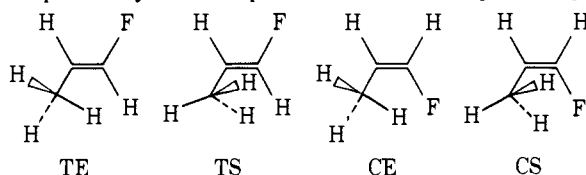


Figure 5. Interaction diagram for the union of the $(\text{CH}_3\text{--F})$ group π MO's and the π MO's of ethylene. Dominant orbital interactions are indicated by arrows.

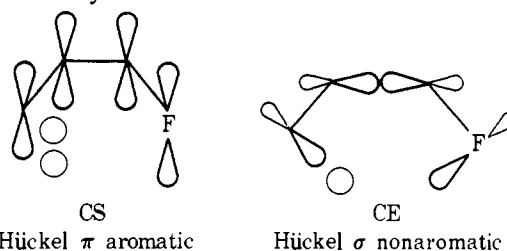
Table III. Orbital Interaction Energies for CS and CE Conformations of 1-Fluoropropene

Conformation	Interaction	ΔE^4 , eV	ΔE^2 , eV
CS	$F_{P_z} - \pi(\text{CH}_2)$	0.0296	
CE	$F_{P_z} - \pi(\text{CH}_2)$	0.0065	
CS	$n_z - \pi$	4.4500	
CE	$n_z' - \pi$	4.6220	
CS	$n_z^* - \pi^*$		-1.5400
CE	$n_z^{*'} - \pi^*$		-1.2990

Specifically, the through space interaction between the methylene hydrogens and the p_z lone pair of fluorine is greater in CS than in CE because there is greater overlap in CS than in CE leading to greater repulsion in the case of the CS isomer. These considerations are illustrated in Figure 4 where we have neglected the interaction of F_{p_z} with the π^* type MO of the $-\text{CH}_2$ since the energy separation of these two levels is large. Explicit calculations of the resulting four-electron destabilization energy are shown in Table III.

The interactions of the n_z and n_z^* group MO's with the ethylenic π bond are shown in Figure 5. Reasoning as before, we see that the CS conformation will enjoy a larger two-electron stabilization and a smaller four-electron destabilization relative to the CE conformation. Specifically, in the transformation $\text{CE} \rightarrow \text{CS}$ the total four-electron destabilization energy decreases by 0.1489 eV and the total two-electron stabilization energy increases by 0.2410 eV. Since ΔE^2 increases faster than ΔE^4 decreases, it is apparent that, in this case, ΔE^2 is the controlling factor in lowering the energy of the CS relative to the CE conformer. The final conclusion is that π nonbonded interactions lower the energy of the CS relative to the CE conformer, while such effects are absent in the trans isomer. σ nonbonded interactions of the σ type HOMO of the methyl group and the $2s$ and $2p_x$ fluorine lone pairs with the σ component of the double bond can be analyzed similarly. The final conclusion is that σ nonbonded interactions lower the energy of the CE relative to the CS conformer, an effect absent in the trans isomer and opposite in direction to the one due to π nonbonded interactions.

Once more we note that the CE and CS conformations correspond to six-electron σ and π Hückel aromatic systems, respectively, while the TE and TS conformations are nonaromatic systems:



The above analysis of the methyl rotational barrier in *cis*- and *trans*-1-fluoropropene can be simplified by taking into account the aromatic, nonaromatic, or antiaromatic character of the energy maxima and minima of the rotational curve. Specifically, the relative magnitude of the methyl rotational barrier can be determined by considering the aromaticity of the two maxima, CS and TS, and the two minima, CE and TE. In the former case, the energy maximum CS will be lower in energy than the energy maximum TS due to π aromaticity which obtains only in the CS conformer. In the latter case the energy minimum CE will be lower in energy than the energy minimum TE due to σ aromaticity which obtains only in the CE conformer. If the CS conformer is lowered in energy relative to the TS conformer by π aromaticity more than the CE is lowered relative to the TE conformation because of σ aromaticity, then the methyl rotational barrier in *cis*-1-fluoropropene will be lower than that in the trans isomer. This effect will arise from a greater change in energy in the transformation $\text{TS} \rightarrow \text{CS}$ than in the transformation $\text{TE} \rightarrow \text{CE}$.¹⁰

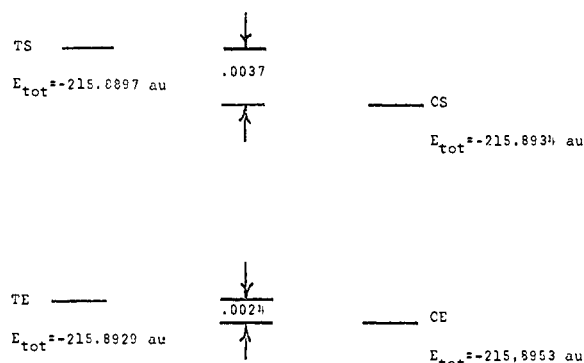
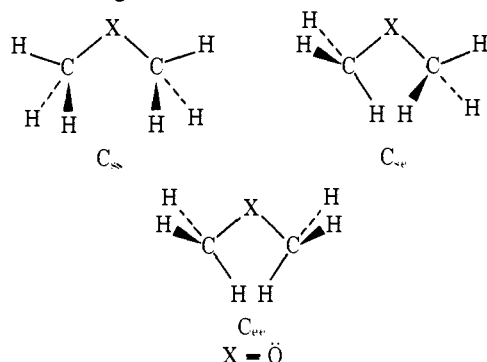


Figure 6. Factors affecting the methyl rotational barrier in *cis*- vs. *trans*-1-fluoropropene. Total energies taken from ref 10.

Ab initio calculations by Palke and English¹¹ on the methyl rotational barrier in 1-fluoropropene support the above theoretical analysis. Their results are summarized in Figure 6. It can be seen that the lower methyl rotational barrier in *cis*-1-fluoropropene relative to the *trans* isomer is due to the lower energy of the maximum CS relative to the energy maximum TS.

Dimethyl Ether

The three possible conformations of dimethyl ether are shown below along with the definition to be used in this sec-



tion. The π MO's of dimethyl ether can be constructed from the union of the methyl π group MO's and the $2p_z$ AO of oxygen. The methyl π group MO's for the C_{ss} and C_{ee} conformations are derived via the interaction diagram of Figure 7. In the case of the C_{ss} conformer, there is strong overlap between the methylene hydrogens and the methyl π MO's interact appreciably. This does not obtain in the C_{ee} conformer since the overlap of the methylene hydrogens is small. We expect, therefore, on the basis of eq 2 a larger four-electron destabilization in the C_{ss} conformer than in the C_{ee} conformation. The π_1 - π_2' two-electron stabilizing interaction will be small in both the C_{ss} and C_{ee} conformation because the magnitude of the overlap integral is decreased due to the nodal properties of the π_1 and π_2' MO's. Explicit calculations are shown in Table IV. As was the case in the benzene vs. *trans*-1,3,5-hexatriene we find that the C_{ss} conformation is destabilized relative to the C_{ee} at this point in the analysis.

The union of the methyl π group MO's and the $2p_z$ AO of oxygen for the C_{ss} and C_{ee} conformation is shown in the interaction diagram of Figure 8. By going through the same arguments as before we conclude that the C_{ss} conformation will be lower in energy than the C_{ee} conformation because it is stabilized *more* by the ψ_1 - ϕ_3 two-orbital-two-electron interaction and destabilized less by four-electron (ϕ_1 - ψ_1) overlap repulsion than is the C_{ee} conformation. Explicit calculations shown in Table IV show that this is indeed the case. Comparison of the total four-electron destabilization

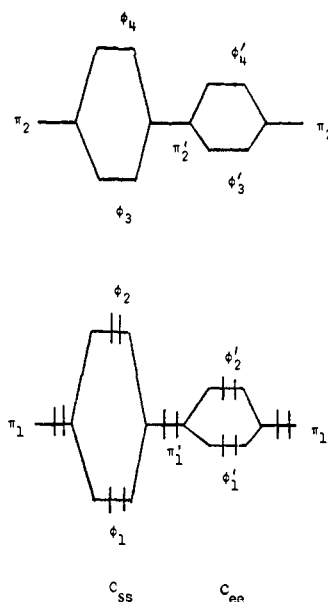


Figure 7. Construction of the $(\text{CH}_3)\text{-O-(CH}_3)$ π group MO's for the C_{ss} and C_{ee} conformations of dimethyl ether.

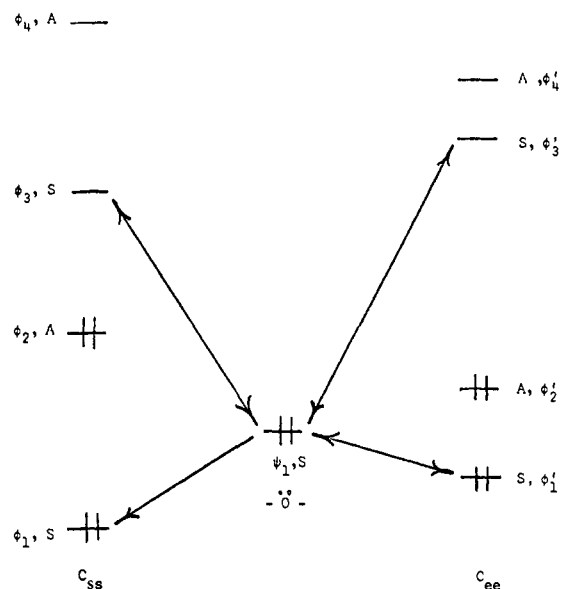


Figure 8. Union of the $(\text{CH}_3)\text{-O-(CH}_3)$ π group MO's and the oxygen p_z AO for the C_{ss} and C_{ee} conformations of dimethyl ether. Dominant orbital interactions are indicated by arrows.

Table IV. Orbital Interaction Energies for C_{ss} and C_{ee} Conformation of Dimethyl Ether

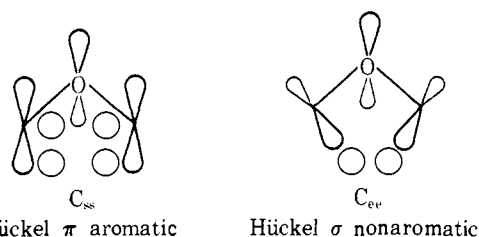
Conformation	Orbital interaction	ΔE^4 , eV	ΔE^2 , eV
C_{ss}	$\pi_1\pi_1'$	1.0590	
C_{ee}	$\pi_1\pi_1'$	0.3414	
C_{ss}	$\pi_1\pi_2' + \pi_1'\pi_2$		-0.0098
C_{ee}	$\pi_1\pi_2' + \pi_1'\pi_2$		-0.0082
C_{ss}	$\phi_1 - \psi_1$	3.299	
C_{ee}	$\phi_1 - \psi_1$	5.157	
C_{ss}	$\psi_1 - \phi_3$		-0.4099
C_{ee}	$\psi_1 - \phi_3$		-0.1630

and two-electron stabilization energies reveals that in the case of dimethyl ether the controlling factor in determining the preferred conformation is ΔE^4 . Specifically, the total four-electron destabilization energy decreases by 1.1404 eV in the transformation $C_{ee} \rightarrow C_{ss}$ while the total two-electron stabilization energy increases only by 0.2485 eV. The same

Chart II

X	C_{ss}	C_{se}	C_{ee}
C=O	0.0	0.75	2.22
C=CH ₂	0.0	1.93	4.31
-O-	0.0	2.98	7.00
-NH-	0.0	3.62	8.25
-CH ₂ -	0.0	3.70	8.77

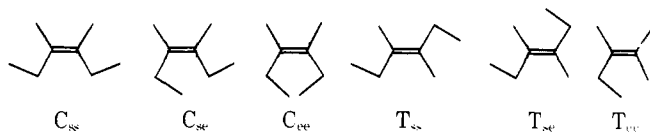
analysis can be used to compare the C_{ss} and C_{se} conformations. Proceeding as before, we can say that the C_{ss} conformation will be favored over the C_{se} conformation due to a larger 1,5 attractive interaction which arises from the 6 π electron cyclic aromatic geometry of the C_{ss} conformation.¹² Recently, Pople and his coworkers¹³ reported the results of an ab initio study (4-31 G basis set)¹⁴ of the conformational isomerism of CH₃-X-CH₃ type molecules where X is a substituent with two π electrons. The relative energies (kcal/mol) of the three possible conformations of such molecules for a variety of X groups are reproduced in Chart II. As can be seen, the ab initio results are in perfect agreement with the predictions reached by OEMO theory. In considering the aromatic character of the three conformations of dimethyl ether we recognize that the C_{ss} conformation resembles a 6 π electron Hückel aromatic system while the C_{ee} conformation resembles a 6 σ electron Hückel aromatic system:



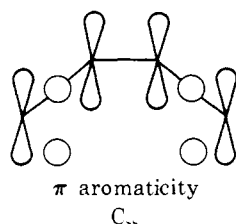
Since the ab initio calculations show that the C_{ss} conformation is more stable than the C_{ee} , it appears that in the case of CH₃-X-CH₃ molecules π aromaticity dominates σ aromaticity, a result which is reasonable in view of the fact that $n-\pi^*$ or $\pi-\pi^*$ stabilizing interactions are stronger than $n-\sigma^*$ or $\sigma-\sigma^*$ stabilizing interactions in these cases.

2-Butene

The six conformations of 2-butene are shown below along with definitions to be used throughout the rest of the present work, e.g., the label C_{ss} corresponds to the cis iso-



mer where the in-plane hydrogens of the methyl groups are staggered relative to the double bond. From our previous discussions we immediately recognize that the C_{ss} conformation is a 6 π electron Hückel aromatic system and should



profit to a greater degree, relative to the other conformations, from the one-electron factors which we have been discussing.

To illustrate our approach we shall compare the C_{ss} conformation with the T_{ss} conformation. The π MO's of 2-bu-

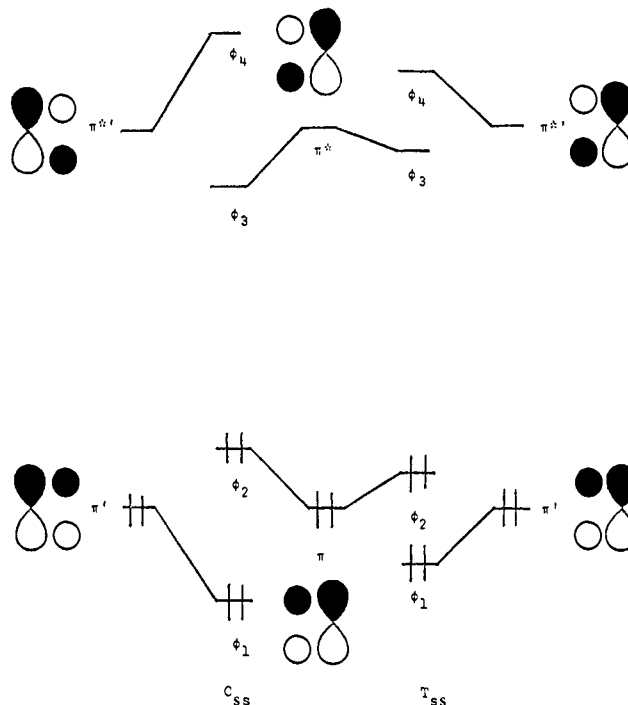


Figure 9. Construction of the (CH₃- -CH₃) π group MO's for the C_{ss} and T_{ss} conformation of 2-butene.

Table V. Orbital Interaction Energies for the C_{ss} and T_{ss} Conformation of 2-Butene

Conformation	Orbital interaction	ΔE^1 , eV	ΔE^2 , eV
C_{ss}	$\pi\pi^*$	0.549	
T_{ss}	$\pi\pi^*$	0.002	
C_{ss}	$\pi\pi^* + \pi'\pi'^*$		-0.005
T_{ss}	$\pi\pi^* + \pi'\pi'^*$		0.000
C_{ss}	$\phi_1-\pi$	5.048	
T_{ss}	$\phi_1-\pi$	5.610	
C_{ss}	$\phi_2-\pi^*$		-1.734
T_{ss}	$\phi_2-\pi^*$		-1.309
C_{ss}	$\pi-\phi_3$		-0.248
T_{ss}	$\pi-\phi_3$		-0.172

tene can be constructed from the union of the π group MO's which span the two vicinal methyl groups and the π MO's of the central ethylenic bond. The methyl π group MO's for the C_{ss} and T_{ss} conformation are derived via the interaction diagram shown in Figure 9. Since there is strong overlap between the methylene hydrogens in the C_{ss} but not in the T_{ss} conformation, we expect that the interaction between the methyl π MO's will be appreciable in the former case and small in the latter. Hence, we expect that the methyl-methyl through space interaction will destabilize the C_{ss} conformation more than the T_{ss} . This is indeed the case as shown in Table V.

The union to form the π MO's of the C_{ss} and T_{ss} conformations is shown in Figure 10. By following through with the orbital symmetry arguments outlined in the previous examples we can reach the following conclusions from the information contained in Figure 10: (a) the $\phi_1-\pi$ four-electron destabilization will be greater in the T_{ss} than the C_{ss} conformation; (b) the two-electron $\phi_2-\pi^*$ and $\pi-\phi_3$ stabilizing interaction will be greater for the C_{ss} than the T_{ss} conformation.

Explicit calculations shown in Table V confirm the above conclusions. Specifically, the C_{ss} conformation is predicted to be more stable than the T_{ss} conformation because of greater total two-electron stabilization energy and a smaller

Table VI. Relative Stabilization ($\Delta\Delta E^2$) and Destabilization ($\Delta\Delta E^4$) of "Aromatic" and "Nonaromatic" Systems

Aromatic	Nonaromatic	$\Delta\Delta E^2,^a$ eV	$\Delta\Delta E^4,^b$ eV
Benzene	1,3,5-Hexatriene	-6.1450	2.2100
<i>cis</i> -1,2-Difluoroethylene	<i>trans</i> -1,2-Difluoroethylene	-0.0174	-0.0182
1-Fluoropropene (CS)	1-Fluoropropene (CE)	-0.2410	-0.1489
Dimethyl ether (C _{SS})	Dimethyl ether (C _{ee})	-0.2485	-1.1404
2-Butene (C _{SS})	2-Butene (C _{ee})	-0.5060	-0.0150

^a $\Delta\Delta E^2 = \Delta E^2_{\text{Total}}(\text{aromatic}) - \Delta E^2_{\text{Total}}(\text{nonaromatic})$. ^b $\Delta\Delta E^4 = \Delta E^4_{\text{Total}}(\text{aromatic}) - \Delta E^4_{\text{Total}}(\text{nonaromatic})$.

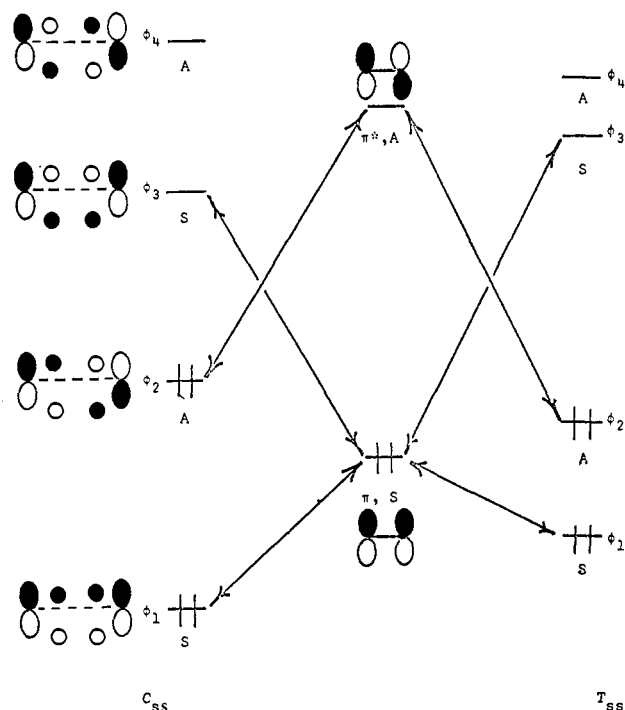


Figure 10. Union of the (CH₃- -CH₃) π group MO's and the π MO's of the central olefinic bond for the C_{SS} and T_{SS} conformations of 2-butene. Dominant orbital interactions are shown by arrows.

total four-electron destabilization energy, the changes being an increase of 0.506 eV and a decrease of 0.015 eV, respectively. In 2-butene, therefore, it is clear that the differential ΔE^2 is the controlling factor in stabilizing the C_{SS} relative to the C_{ee} conformer. Once again, we see that the more crowded geometry does not necessarily suffer from larger overlap repulsion relative to the noncrowded geometry.

A similar approach can be used for comparing the stabilization of the C_{se}, C_{ee}, T_{se}, and T_{ee} conformations relative to that of the C_{SS} conformation. Since appreciable overlap of the methylene hydrogens obtains only in the C_{SS} conformation, we would expect this conformation to have lower energy than the C_{se}, C_{ee}, T_{se}, and T_{ee} conformations, provided that steric effects are nearly the same in all cases. However, since steric effects are expected to be important, the relative energies of the six structures of 2-butene will be a result of a compromise between the one-electron factors we have discussed in this paper and steric repulsion, the balance to be determined by quantitative *ab initio* calculations. We have reported such computations at the 4-31G¹⁴ and STO-4G¹⁵ levels where the six conformations of 2-butene have been geometry optimized using a STO-4G basis set.¹⁷ The relative energies of the six geometries are shown below for both basis sets. As can be seen, the C_{SS} conformation is more stable than the T_{SS} conformation in accord with our expectations. Clearly steric effects favor the T_{SS} conformation but they are dominated by the π aromatic character of the C_{SS} conformation. That is, the one-electron factors we have discussed are the key electronic factors which favor the "more

Conformation	E _{relative} , kcal/mol					
	T _{SS}	C _{SS}	C _{se}	T _{se}	C _{ee}	T _{ee}
(4-31G)	3.71	2.85	2.31	1.81	1.86	0.0
(STO-4G)	3.03	2.64	2.16	1.50	1.85	0.0

crowded" conformation C_{SS}, over the "less crowded" T_{SS} conformation. The fact that the C_{SS} conformation is not *the* most stable conformer of 2-butene can be explained on the basis of steric effects dominating the one-electron factors which have been discussed.

Conclusion

It has been assumed by chemists that a molecule existing in a "crowded" geometry will be destabilized by "steric effects" and nonbonded overlap repulsions relative to an analogous molecule existing in a "noncrowded" geometry. In this work we have shown that when dealing with the stereochemical preferences of Hückel aromatic molecules these intuitive conclusions do not necessarily hold. In fact, we have seen that in the case of dimethyl ether the major factor favoring the "crowded" geometry is the differential four-electron overlap repulsion! In summary, we can say that the orbital interaction pattern of Hückel (or Möbius) aromatic systems, as shown in this paper, will tend, in general, to maximize two-electron stabilizing interactions and minimize four-electron overlap repulsions relative to nonaromatic analogues. We emphasize that in most cases, like in the example 2-butene, the two-electron stabilization is primarily responsible for "aromaticity" (see Table VI) and that the contribution of this work amounts to showing that four-electron overlap repulsion also contributes secondarily or even primarily toward aromaticity, the latter result being important simply because it runs against intuition.

The OEMO approach used in this paper ignores two-electron and coulombic internuclear repulsions and consequently one must always keep in mind the possibility that "steric" effects may dominate the one-electron factors discussed in this work. However, the agreement between *ab initio* calculations, where "steric effects" are explicitly accounted for, and our one-electron approach is sufficiently good so that it is quite clear that the orbital symmetry based one-electron factors discussed in this paper are of crucial importance in determining the stereochemical preferences of Hückel aromatic systems.

Now, a word of caution. Organic chemists are fond of using handy rules in the discussion of molecular structure and reactivity but, while such rules are useful and should be pointed out, an analysis, as outlined in this paper, should always accompany such simplified notions so that one can make appropriate distinctions where blind electron counting would be misleading. For example, the two molecules shown below have $4n + 2\pi$ type electrons but I is aromatic



while II is unstable. The difference between I and II could easily be understood by utilizing the approach presented in this paper.

An additional problem occurs in the case of σ aromaticity. Here, it is assumed that the closely spaced occupied σ MO's of the central bond act collectively as a single symmetric occupied MO and the closely spaced unoccupied σ MO's act collectively as a single antisymmetric unoccupied MO. These assumptions may break down depending upon the inductive nature of substituents, the nature of atoms constituting the central bond, and the type of calculation employed. Thus, σ nonbonded interactions should be discussed for each molecule separately although in most cases expectations based on a mere electron count, i.e., σ Hückel aromaticity, will be met. This is the situation with the molecules discussed in this work.

Finally, the ideas reported here can be used to understand why certain bond angles in molecules are surprisingly small, rotational barriers in molecules which have very high lying unoccupied MO's, and other problems of general interest.

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A Molecular Orbital Interpretation of the Static, Dynamic, and Chemical Properties of CH_2X Radicals

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Abstract: The effects of α substituents on the stability of radical centers are rationalized in terms of one-electron molecular orbital (OEMO) theory. The same treatment is used to rationalize the rates of radical reactions and the conformations of CH_2X radicals. Ab initio calculations of the preferred geometries of radicals of the type CH_2-X , wherein $X = O^-$, $-OH$, $-SH$, $-F$, $-Cl$, $-C\equiv CH$, $-C\equiv CF$, and $-CN$, are reported which substantiate the qualitative ideas developed on the basis of the OEMO treatment.

I. Introduction

Although the effects of substituents upon the stabilities of carbocations and carbanions are fairly well understood, their effects upon adjacent radical centers cannot be rationalized simply by the assumption that the behavior will be intermediate between that of carbocations and carbanions. Recent kinetic studies of the thermolyses of substituted azopropanes indicate that unsaturated substituents such as $-CH=CH_2$,^{3a} $-C\equiv CH$,^{3a} $-C\equiv N$,^{3b} and Ph ^{3c,d} stabilize an

adjacent radical center to the largest extent. Alkyl groups^{4a-c} and first-row heteroatoms such as OR ^{4a,c,d} have a small stabilizing effect, and second-row heteroatoms such as SR ^{4a,c} display intermediate effects.⁵

It should be emphasized that since these results have been obtained from kinetic studies, they reflect the effects of substituents on the stability of a radical center as it exists in the transition state of the reaction under study. Typical stabilization energies calculated from the data of ref 3 and 4 for a variety of substituents are collected in Table I. In