

References and Notes

- (1) D. M. Kern, *J. Chem. Educ.*, **14**, 37 (1960).
- (2) E. Magid and B. O. Turbeck, *Biochim. Biophys. Acta*, **165**, 515 (1968).
- (3) B. R. W. Pinsent, L. Pearson, and F. J. W. Roughton, *Trans. Faraday Soc.*, **52**, 1512 (1956).
- (4) B. Jönsson, G. Karlström, and H. Wennerström, *Chem. Phys. Lett.*, **30**, 58 (1975).
- (5) B. Jönsson, G. Karlström, H. Wennerström, and B. Roos, *Chem. Phys. Lett.*, **41**, 317 (1976).
- (6) B. Jönsson, G. Karlström, H. Wennerström, S. Forsén, B. Roos, and J. Aïmlöf, *J. Am. Chem. Soc.*, **99**, 4628 (1977).
- (7) P. Kabarle in "Modern Aspects of Electrochemistry", No. 9, Plenum Press, New York, N.Y., 1975, p 1.
- (8) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 209, 199 (1970).
- (9) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965). The hydrogen s exponents were multiplied by 1.34 as found by optimization on small molecules (B. Roos, private communication).
- (10) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).
- (11) J. Aïmlöf, USIP Reports 72-09 (Sept 1972) and 74-29 (Dec 1974), Institute of Physics, University of Stockholm, Sweden.
- (12) B. D. Sharma, *Acta Crystallogr.*, **18**, 818 (1965).
- (13) C. P. Baskin, C. F. Bender, C. W. Baushlicher, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **96**, 2709 (1974).
- (14) S. Scheiner, W. N. Lipscomb, and D. A. Kleier, *J. Am. Chem. Soc.*, **98**, 4770 (1976).
- (15) S. Lindskog, L. E. Henderson, K. K. Kannan, A. Liljas, P. O. Nyman, and B. Stranberg, *Enzymes*, **5**, 587 (1971).
- (16) K. K. Kannan, B. Notstrand, K. Fridborg, S. Lövgren, A. Ohlsson, and M. Petef, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 51 (1975).
- (17) H. Steiner, B-H. Jonsson, and S. Lindskog, *Eur. J. Biochem.*, **59**, 253 (1975).
- (18) R. G. Khalifah, *J. Biol. Chem.*, **246**, 2561 (1971).
- (19) S. H. Koenig and R. D. Brown, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2422 (1972).
- (20) R. G. Khalifah, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 1986 (1973).
- (21) S. Lindskog and J. E. Coleman, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2505 (1973).
- (22) B-H. Jonsson, H. Steiner, and S. Lindskog, *FEBS Lett.*, **64**, 310 (1976).
- (23) B. Jönsson and H. Wennerström, *Biophys. Chem.*, accepted for publication.
- (24) P. Wooley, *Nature (London)*, **258**, 677 (1975).
- (25) M. F. Dunn, *Struct. Bonding (Berlin)*, **23** (1975).

Relative Stability of Planar and Perpendicular Olefins

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Received July 25, 1977*

Abstract: The rotational barriers around carbon-carbon double bonds and the relative stability of the planar and perpendicular olefins were analyzed within the framework of the ab initio unrestricted Hartree-Fock theory in terms of electrostatic, exchange repulsion, polarization, charge transfer, and their coupling interactions. The olefins we have investigated are $CX_2=CH_2$ ($X = H, Li, F, CH_3, CN, BeH$ and Na), $CX_2=CY_2$ ($X = Li, CH_3$ and $Y = F, CN$), and polythioethylenes. The charge transfer and exchange repulsion interactions play an essential role in the stabilization of perpendicular olefins.

I. Introduction

A number of experimental investigations have been made on thermal rotational isomerizations about carbon-carbon double bonds as well as photochemical and catalytic isomerizations.²⁻⁴ The thermal rotation about a double bond is severely hindered and the planar olefin is more stable than the perpendicular form. There have been several ab initio calculations reported on the rotational barrier around a double bond in ethylene.⁵⁻⁷

The high rotational barrier of ethylene molecule should be lowered significantly by a proper selection of substituents. Their effects are thought to be both steric and electronic in origin.^{3,8} While bulky substituents can raise the energy of the planar form,⁹ electronic effects can stabilize the charge separation or biradicals in the perpendicular form.¹⁰ An effective combination of these two interactions could produce more stable perpendicular olefins.¹¹ A theoretical approach to this possibility was examined recently with an ab initio molecular orbital method.¹² It was found that the rotational barrier of 1,1-dilithioethylene not only is very low, but also the perpendicular form may actually be more stable than the planar form and that the carbon-carbon bond length does not change greatly during rotation.

Our purpose here is to analyze and find the origin, from the point of view of intermolecular interactions, of the rotational barrier around a double bond. Since in the supermolecule approach each molecule is treated as a whole, an interpretation of the spectrum of substituents tends to be obscured. Thus, we decided to view each molecule as an interacting system of two

fragments and decompose and interpret the rotational barrier in terms of five chemically meaningful interaction components—electrostatic (ES), exchange repulsion (EX), polarization (PL), charge transfer (CT), and their coupling (MIX) terms. Electron densities and Mulliken populations¹³ can also be divided into components. The molecules we have investigated systematically are $CX_2=CH_2$ ($X = H, Li, F, CH_3, CN, BeH$ and Na), $CX_2=CY_2$ ($X = Li$ or CH_3 and $Y = F$ or CN), and polythioethylenes.

II. Computational Aspects

All calculations reported here were performed within the framework of ab initio unrestricted Hartree-Fock (UHF) theory, employing a modified version of the GAUSSIAN 70 package.¹⁴ The split-valence 4-31G¹⁵ (5-21G for lithium atoms)¹⁶ and minimal STO-3G¹⁷ basis sets were used with the suggested standard parameters. As for the molecular geometries, standard bond lengths and angles proposed by Pople et al.¹⁸ were employed to systematically examine the substituent effects.

In our calculation a (substituted) ethylene molecule was considered to form as a result of interaction between two triplet (substituted) methylenes which have the geometry of the CH_2 part of ethylene. The partitioning is justifiable, for the two triplets can be coupled smoothly to form the ground state of ethylene.¹⁹⁻²¹ A restricted single-determinant representation of the ground state of ethylene becomes progressively less satisfactory as the rotation angle, θ , is increased from 0° (planar) to 90° (perpendicular). When the perpendicular form is

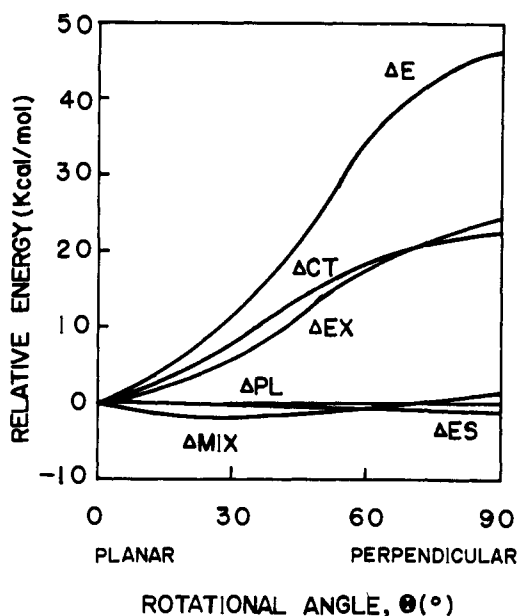


Figure 1. Variations of the rotational barrier of ethylene as a function of rotational angle, θ .

Table I. Energy Decomposition Analysis for the Binding Energy (E) of a Double Bond in Ethylene, α 4-31G Basis Set

	CH ₂ =CH ₂	
	Planar	Perpendicular
ES	-192.8	-193.8
EX	249.3	272.9
PL	-88.6	-88.5
CT	-228.9	-207.3
MIX	143.9	146.1
E	-117.1	-70.6

^a Values given in units of kcal/mol.

reached the bonding π and antibonding π^* orbitals become degenerate. The deficiency could be overcome within the single-determinant framework in the following way. By using the singlet coupling of the electronic configurations of two triplets in C_{2v} symmetry as the starting point of the UHF calculation, one obtains spatially different α - and β -spin orbitals for ethylene. Although these orbitals individually transform according to the C_{2v} symmetry, even in the planar form,²² the state symmetry remains A_1 . This unrestricted (or spin density wave) solution gives a lower energy than the restricted one in the symmetry-adopted approximation.²³⁻²⁵ In addition, it provides the correct description of orbital crossing²⁶ and dissociation curve.²⁷ Thus, the energy and charge decompositions into the ES, EX, PL, CT, and MIX terms²⁸ can be carried out within the UHF scheme.

The absolute values of energy components are sensitive to the approximation and the basis set.²⁸ The results we present in the following sections are therefore meant to be qualitative and interpretive rather than quantitative.

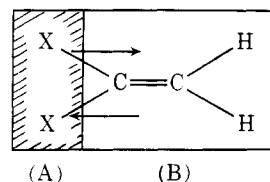
III. Results

A. Rotational Barrier around a Double Bond in Ethylene. We first examine the origin of the binding energy of a double bond in ethylene. The binding energy and its components calculated by the 4-31G basis set in the planar and perpendicular forms are given in Table I, where a negative (positive) value corresponds to a stabilization (destabilization). The binding energy of -117 kcal/mol²⁹ is a sum of large attractive (-510 kcal/mol) and repulsive (393 kcal/mol) terms. The attractive term consists of the electrostatic ES (38%), polarization PL (17%),

and charge transfer CT (45%). The repulsion comes from the exchange EX (57%) and coupling MIX (43%) terms. Though absolute values of contributions depend on the basis set and are not very meaningful, the importance of CT and ES interactions is evident from this analysis.³⁰ In the perpendicular form, the binding energy is reduced by 47 kcal/mol.³¹

In Figure 1 are shown the variations of the energy and its components calculated by the 4-31G basis set as functions of rotational angle, θ , relative to $\theta = 0$ (planar). The contributions of ES, PL, and MIX components to the barrier are small and almost constant throughout rotation. The energy increase for the rotation is thus ascribable to the destabilization caused by both a decrease in the CT stabilization and an increase in the EX repulsion. The former is due to the localization of the π electrons at the carbon centers rather than in the bonding region, i.e., the formation of the nonbonding biradical state. The overlap between CH₂ electrons cloud and the π electron on the other side and vice versa is responsible for the increase in EX. It is thus suggested that the stabilization of perpendicular olefins would depend strongly on how effectively this destabilization due to CT and EX could be reduced or removed. The destabilization could be partially relaxed by stretching the carbon-carbon distance.³² However, the effect is too small to stabilize the perpendicular form. We now turn to the effect of substituents on the CT and EX components.

B. Relative Stability of Planar and Perpendicular CX₂=CH₂. The influence of different substituents can be classified broadly into two types: electron-donating and -accepting groups. As is well known, the donor or acceptor character depends on the reference standard.³³ The simple classification merely implies the potentiality of the properties. It is useful to determine the donating and accepting powers of substituents in the olefins of interest. We define them as the quantity of electrons transferred to or from the C=CH₂ fragment. In the absence of interactions between the regions A and B, the region B



contains 2 π and 12 σ electrons, which are here taken as a reference. Interactions between the two regions change the number of electrons in the region B. Substituent X which increases (decreases) the number of electrons should be of donor (acceptor) character. In Figure 2 are shown the calculated donating and accepting powers of substituents. As is clear from Figure 2, the net donor or acceptor dominance decreases in the order of Na > BeH > Li > CH₃ and CN > F.

We first consider CLi₂=CH₂, where Li is an electron donor, and CF₂=CH₂, where F is an acceptor. In Table II are given the energy decomposition analyses for the binding energies in the planar forms using the 4-31G basis set. The point to be noted in the comparison of Tables I and II is that the Li substituent provides the smallest binding energy (-85 kcal/mol) which consists of the repulsive (732 kcal/mol) and attractive (-817 kcal/mol) energies, in spite of the considerable increase in the CT and PL interaction energies. The F substituent gives somewhat larger binding energy.

In Table III are given the relative stabilities (ΔE) of planar and perpendicular forms calculated by using the 4-31G basis set. These results show that the F substitution has rather undesirable influence on the stabilization of the perpendicular form with a small increase in the destabilization due to CT and EX interactions. However, the Li substitution dramatically reduces the CT and EX destabilization and the perpendicular form can be more stable than the planar. Here it should be noted that the relative stability by the STO-3G basis set is in

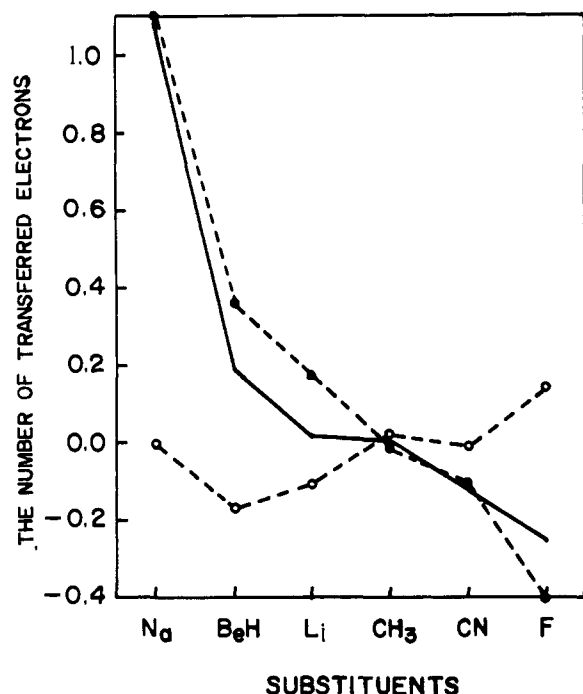


Figure 2. The number of electrons transferred from substituents. σ electrons (---●---), π electrons (---○---), and $\sigma + \pi$ electrons (—). Positive (negative) values indicate an increase (decrease) in electrons within the $\text{CH}_2=\text{C}$ fragment. STO-3G set.

Table II. Energy Decomposition Analysis for the Binding Energy (E) of a Double Bond in the Planar Forms of $\text{CLi}_2=\text{CH}_2$ and $\text{CF}_2=\text{CH}_2$,^a 4-31G Basis Set

	$\text{CLi}_2=\text{CH}_2$	$\text{CF}_2=\text{CH}_2$
ES	-215.3	-172.6
EX	335.6	232.7
PL	-239.6	-155.8
CT	-362.0	-232.3
MIX	396.2	204.6
E	-85.1	-123.4

^a Values given in units of kcal/mol.

Table III. Energy Decomposition Analysis for the Relative Stability of the Planar and Perpendicular $\text{CX}_2=\text{CH}_2$,^a 4-31G Basis Set

	$\text{CH}_2=\text{CH}_2$	$\text{CLi}_2=\text{CH}_2$	$\text{CF}_2=\text{CH}_2$
ΔES	-1.0	-0.7	-1.6
ΔEX	23.6	0.6	24.3
ΔPL	0.1	-2.3	-0.6
ΔCT	21.6	2.5	22.9
ΔMIX	2.2	-1.0	4.5
ΔE^b	46.5 (46.1)	-0.9 (-1.5)	49.5 (48.8)

^a Values, given in units of kcal/mol, are the energy of the perpendicular form relative to the planar form. ^b Values in parentheses are obtained by the STO-3G basis set.

agreement with that of the 4-31G basis set (Table III). This encourages us to use the more economical STO-3G basis set in the following larger systems.

In order to gain more insight into the substituent effect, all the substituents shown in Figure 2 were examined by the STO-3G basis set. In Figure 3 are presented the differences in the relative stability of the planar and perpendicular forms between ethylene and substituted ethylenes. The ES, PL, and MIX components play a minor role. However, the CT and EX

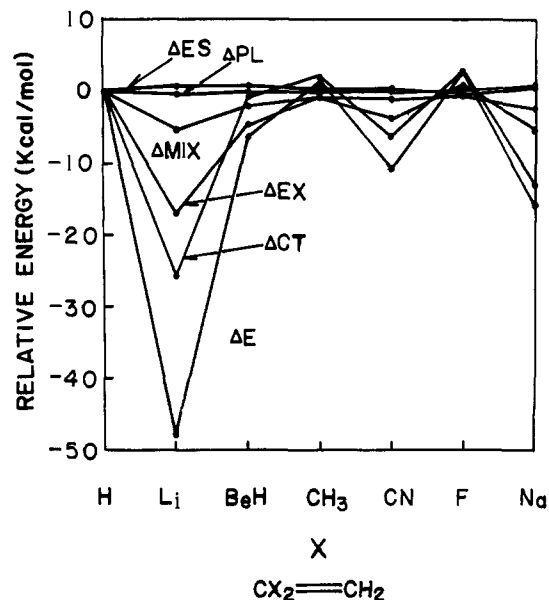


Figure 3. The relative stability of the planar and perpendicular forms of $\text{CH}_2=\text{CX}_2$ ($X = \text{Li}, \text{BeH}, \text{CH}_3, \text{CN}, \text{F}, \text{and Na}$) with respect to ethylene as the reference molecule. STO-3G set.

components play a significant role and govern the overall trends. While the substituents CN, Na, and BeH lower the barrier, ΔE , to a considerable extent, the effect of Li substituent is drastic and unique. Finally, substituents CH_3 and F have undesirable effects on the lowering of ΔE . Thus, the energy lowering effects decrease in the order of



The alkali metals have the most favorable influence on the energy lowering. The advantage of the Li substitution is due to the largest relaxation of the CT and EX destabilizations. As is seen in Figures 2 and 3, the order of the energy lowering seems to have no close relationship with that of donor and acceptor character.

C. Relative Stability of the Planar and Perpendicular $\text{CX}_2=\text{CY}_2$. We now examine the combined effects of the two different substitutions such as in $\text{CX}_2=\text{CY}_2$ ($X = \text{Li}, \text{CH}_3$ and $Y = \text{F}, \text{CN}$). Figure 2 suggests that the substituents Li and CH_3 are σ and π donors, respectively, while CN and F are σ acceptors. The combinations of these substituents produce highly polarized ethylene, for which we would expect a stabilization of the perpendicular form by the mixing of zwitterionic and biradical states.³⁴

The planar and perpendicular energy differences obtained by the STO-3G basis set are given in Table IV. As is seen in the case of $\text{C}(\text{CH}_3)_2=\text{CF}_2$ and $\text{C}(\text{CH}_3)_2=\text{C}(\text{CN})_2$, the combinations of π donor and σ acceptor do not have very good

Table IV. Energy Decomposition Analysis for the Relative Stability of the Planar and Perpendicular $\text{CX}_2=\text{CY}_2$ ^a

	$\text{CX}_2=\text{CY}_2$			
	$X = \text{CH}_3$ $Y = \text{F}$	CH_3 CN	Li F	Li CN
ΔES	-0.2	1.7	2.6	4.9
ΔEX	15.6	6.1	1.8	-8.6
ΔPL	-0.1	-0.1	-0.2	0.8
ΔCT	34.5	27.8	6.6	5.4
ΔMIX	-1.0	-0.6	-0.7	5.7
ΔE	48.8	34.8	10.1	8.2

^a Values, given in units of kcal/mol, are the energy of the perpendicular form relative to the planar form. STO-3G set.

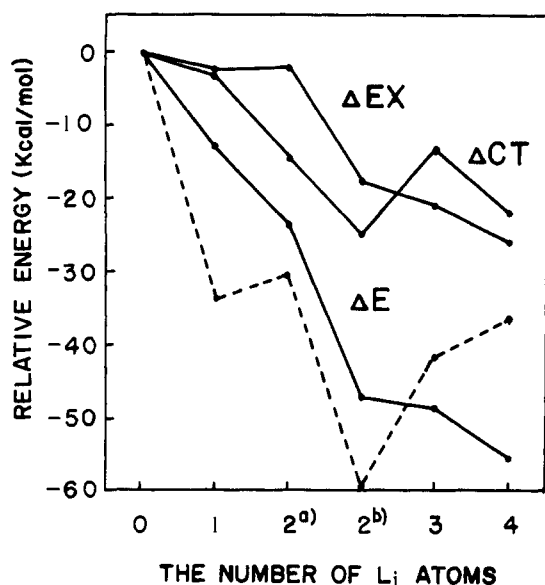


Figure 4. The relative stability of the planar and perpendicular polythioethylenes with respect to ethylene as the reference molecule. The energy lowering (scaled by 10) per Li atom is shown by the dotted line. (a) 1,2-Dilithioethylene; (b) 1,1-dilithioethylene. 4-31G set.

influence on the stabilization of the perpendicular forms, because of the insufficient reduction of the CT destabilization. However, the combinations of σ donor and σ acceptor in $\text{CLi}_2=\text{CF}_2$ and $\text{CLi}_2=\text{C}(\text{CN})_2$ can reduce effectively both the CT and EX destabilizations and give considerably small energy difference between the planar and perpendicular forms. The advantage of $\text{C}(\text{CH}_3)_2=\text{C}(\text{CN})_2$ over $\text{C}(\text{CH}_3)_2=\text{CF}_2$ or $\text{CLi}_2=\text{C}(\text{CN})_2$ over $\text{CLi}_2=\text{CF}_2$ is mainly due to their smaller EX destabilization.

D. Relative Stability of the Planar and Perpendicular Polythioethylenes. The Li substituent is particularly effective in lowering the energy difference between the planar and perpendicular forms. It is interesting to examine the effect of multiple substitution by the Li atom. The planar and perpendicular energy differences (kcal/mol) by the STO-3G basis set are $\text{CLiH}=\text{CH}_2$ (32.4), $\text{CLiH}=\text{CLiH}$ (21.7), $\text{CLi}_2=\text{CH}_2$ (-1.5), $\text{CLi}_2=\text{CLiH}$ (-3.5), and $\text{CLi}_2=\text{CLi}_2$ (-11.2). As is expected, the energy difference becomes small with the increase in the number of the Li atoms in the substituted ethylene. The effect of the multiple substitution becomes mild gradually as the number of Li atoms increases. In the disubstituted ethylene, the energy difference between the planar and perpendicular forms is smaller in $\text{CLi}_2=\text{CH}_2$ than in $\text{CLiH}=\text{CLiH}$.

In Figure 4 are shown the relative magnitudes of energy lowering as compared with ethylene. The first and second Li atoms in $\text{CLiH}=\text{CH}_2$ and $\text{CLi}_2=\text{CH}_2$ provide the most effective lowering of planar and perpendicular energy difference because of the sharp decrease in the EX and CT destabilizations. Evidently, the inefficiency of the second Li atom in

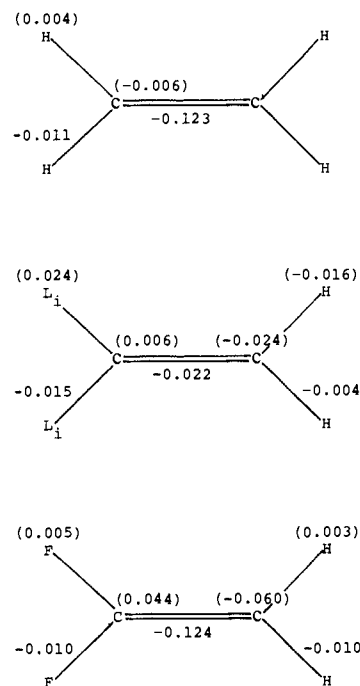


Figure 5. The relative electron populations in the planar and perpendicular forms. Values in parentheses indicate the gross atomic populations.

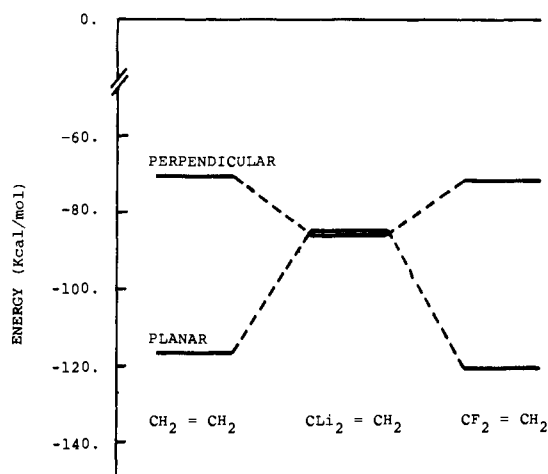


Figure 6. Energy diagram for the molecular formation from the isolated fragments (4-31 basis set).

$\text{CLiH}=\text{CLiH}$ is caused by a smaller reduction of CT and EX, especially the latter. The mild energy lowering as seen in $\text{CLi}_2=\text{CLiH}$ and $\text{CLi}_2=\text{CLi}_2$ is also due to the contributions of CT and EX components. The CT destabilization is increased in the trisubstituted ethylene. As can be seen in Figure 4, the energy lowering per Li atom is the most effective in $\text{CLi}_2=\text{CH}_2$, and becomes small in the order of $\text{CLi}_2=\text{CH}_2$

Table V. Component Analysis for the Bond Population Associated with a Double Bond in the Planar and Perpendicular Forms of $\text{CX}_2=\text{CH}_2^a$

	X =			$\text{CX}_2=\text{CH}_2$			
	H	Li	F	CH_3	CN	BeH	Na
ΔP_{EX}	-0.022	-0.003	-0.022	-0.024	-0.017	-0.019	-0.017
ΔP_{CT}	-0.104	-0.027	-0.106	-0.109	-0.074	-0.093	-0.065
ΔP_{MIX}	0.003	0.008	0.006	0.004	0.002	0.003	-0.006
ΔP^b	-0.123	-0.022	-0.124	-0.129	-0.093	-0.109	-0.088

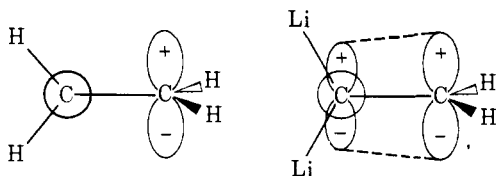
^a The difference between the perpendicular and the planar form. ^b $\Delta P = \Delta P_{\text{EX}} + \Delta P_{\text{CT}} + \Delta P_{\text{MIX}}$. STO-3G set.

$> \text{CLi}_2=\text{CLiH} > \text{CLi}_2=\text{CH}_2 > \text{CHLi}=\text{CHLi} > \text{CLiH}=\text{CH}_2$.

E. Charge Decomposition Analyses. Here we examine the electron distribution in the planar and perpendicular forms by use of the STO-3G basis set. In Figure 5 are shown the differences in the Mulliken electron population between the perpendicular and planar forms of $\text{CX}_2=\text{CH}_2$ ($X = \text{H, Li, and F}$). Considering the gross atomic populations we note that a small migration of electrons takes place from CH_2 to CX_2 parts in both $\text{CLi}_2=\text{CH}_2$ and $\text{CF}_2=\text{CH}_2$. Further, we find a large change in the C-C bond population. We first consider how the bond population of ethylene is formed by the interactions between two methylenes. All of the interactions except ES and PL can contribute to the bond population. In the planar case the contributions of EX, CT, and MIX interactions are -0.190 , 0.419 , and 0.322 , respectively. This suggests an antibonding contribution of the EX interaction and a bonding contribution of the CT and MIX interactions. In other words, the CT and MIX interactions increase the electron density between carbon atoms, while EX has an opposite effect. As a whole CT and MIX overshadow EX, a net positive bond population of 0.551 resulting between the carbon atoms. In the perpendicular case, we have an analogous situation, and the net bond population is again positive: $P(0.428) = P_{\text{EX}}(-0.212) + P_{\text{CT}}(0.315) + P_{\text{MIX}}(0.325)$. Note that the contribution of P_{CT} is reduced to a considerable extent and consequently the double bond character is substantially diminished.

We now turn to substituted ethylenes. In Table V are shown the component analyses for the bond population between carbon atoms in the planar and perpendicular forms. In all cases the bond population between carbon atoms is decreased in the perpendicular form. The extent of the decrease is related to the order of destabilization of the perpendicular form (Figure 3). The EX component decreases the bond population to some extent in the perpendicular form, while the MIX component tends to increase it. The change is, however, dominated by the CT component. The decrease in the bond populations, primarily caused by CT, is small in $\text{CX}_2=\text{CH}_2$ ($X = \text{Li, Na, or CN}$). The preservation of a double bond in $\text{CLi}_2=\text{CH}_2$ is now ascribable to the smallest decrease by the CT interaction.

We conclude by mentioning briefly the nature of bonding in the perpendicular forms of $\text{CH}_2=\text{CH}_2$ and $\text{CLi}_2=\text{CH}_2$. The unrestricted (symmetry-broken) molecular orbitals allow us to describe the bonding between the carbon atoms in a qualitative way. In the perpendicular form of $\text{CH}_2=\text{CH}_2$, a π bond is broken and a nonbonding biradical state is formed.



In the case of $\text{CLi}_2=\text{CH}_2$, however, a bonding orbital is formed within the Li-C-Li plane (but not within the H-C-H plane).

IV. Discussion

Our argument has been focused mainly on the energy difference between the planar and perpendicular forms of olefins. However, it seems important to examine the substituent effect on the energy of the planar and perpendicular forms separately. In Figure 6 is shown the energy diagram for the formation of $\text{CH}_2=\text{CH}_2$, $\text{CLi}_2=\text{CH}_2$, and $\text{CF}_2=\text{CH}_2$ from the isolated fragments. The small energy difference between the planar and perpendicular $\text{CLi}_2=\text{CH}_2$ is obtained by an increase in the energy of the planar form and a decrease in the energy of the

perpendicular form. The point to be noted here is that in this example the lowering of the energy difference is dominated mainly by the increase in the energy of the planar form. This trend is generally observed in substituted ethylenes we have investigated. The efficiency of the alkali substituents is in the fact that they lower the energy of the perpendicular form, whereas other substituents we examined raise it. This is why the lithium substituent is unique in making the perpendicular form more stable than the planar form. As the number of lithium atoms in substituted ethylene increases, the energy lowering of the perpendicular form is accelerated and becomes even the most dominant. In fact, the energy difference between the planar and perpendicular $\text{CLi}_2=\text{CH}_2$ is dominated by the decrease in the energy of the perpendicular form (not by the increase in the energy of the planar form).

Acknowledgment. The authors are grateful to Professor B. D. Joshi for critical reading of the manuscript and J. O. Noell for helpful discussions. They also wish to thank Professor P. v. R. Schleyer for bringing this problem to our attention. This research was supported in part by the National Science Foundation.

References and Notes

- (1) (a) The University of Rochester; (b) The Institute for Molecular Science.
- (2) K. Mackenzie In "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, N.Y., 1964, p 387.
- (3) H. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1973).
- (4) L. M. Jackman In "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, p 203.
- (5) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).
- (6) R. J. Buenker, *J. Chem. Phys.*, **48**, 1368 (1968); R. J. Buenker, S. D. Peyrimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, **11**, 65 (1971).
- (7) M. H. Wood, *Chem. Phys. Lett.*, **24**, 239 (1974).
- (8) A. P. Dowling, W. D. Ollis, and I. O. Sutherland, *Chem. Commun.*, 143 (1967); 1053 (1968); *J. Chem. Soc. B*, 111 (1969).
- (9) For example, see ref 8 and Y. Shvo, *Tetrahedron Lett.*, 5923 (1968).
- (10) See references cited in ref 3.
- (11) For a possible perpendicular olefin, see Eu. Müller and H. Neuhoft, *Ber. Dtsch. Chem. Ges.*, **72**, 2063 (1939); Eu. Müller and E. Tietz, *ibid.*, **74**, 807 (1941).
- (12) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 4332 (1976).
- (13) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
- (14) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Program 236, Quantum Chemistry Program Exchange, Indiana University, 1974.
- (15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
- (16) J. D. Dill and J. A. Pople, *J. Chem. Phys.*, **62**, 2921 (1975).
- (17) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (18) (a) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967); (b) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *ibid.*, **98**, 5419 (1976), and references cited therein.
- (19) H. Basch, *J. Chem. Phys.*, **55**, 1700 (1971).
- (20) S. Nagase and T. Fueno, *Theor. Chim. Acta*, **46**, 59 (1976).
- (21) For the orbital symmetry conservation in the coplanar approach of two triplet methylenes, see R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Am. Chem. Soc.*, **92**, 1460 (1970).
- (22) An ethylene molecule has D_{2h} symmetry in the planar form. Rotation around the double bond lowers the symmetry to D_2 . The symmetry is raised again to D_{2d} in the perpendicular form. By reducing an orbital symmetry to C_{2v} , the left-right electron correlation is taken into account in an approximate way.
- (23) In the restricted treatment, two π electrons of ethylene are forced to occupy an orbital represented as $\chi_a + \chi_b$. In the unrestricted case, however, two electrons occupy spatially different orbitals $\chi_a + \delta\chi_b$ and $\delta\chi_a + \chi_b$, respectively, which consequently take considerable parts of electron correlation into account.
- (24) For the instability of restricted solutions with respect to several different types of unrestricted solutions, see (a) D. J. Thouless, *Nucl. Phys.*, **21**, 225 (1960); (b) W. H. Adams, *Phys. Rev.*, **127**, 1650 (1963); (c) J. Čížek and J. Paldus, *J. Chem. Phys.*, **47**, 3976 (1967); **53**, 821 (1970); (d) J. Paldus and J. Čížek *ibid.*, **52**, 291 (1970); **54**, 2293 (1971); (e) R. A. Harris and L. M. Falicov, *ibid.*, **50**, 4590 (1969); **51**, 3153, 5034 (1969).
- (25) For the basis-set dependence of unrestricted solutions in the planar ethylene, see J. M. McKelvey and G. Berthier, *Chem. Phys. Lett.*, **41**, 476 (1976). However, the importance of unrestricted solutions should be emphasized in the perpendicular form.
- (26) K. D. Jordan and R. Silbey, *Chem. Phys. Lett.*, **18**, 27 (1973).
- (27) A. W. Salotto and L. Burnelle, *J. Chem. Phys.*, **52**, 2936 (1970).
- (28) (a) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); (b) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1976); (c) S. Yamabe and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 4458 (1975); (d) H. Umeyama and K.

- Morokuma, *ibid.*, **99**, 1316 (1977); (e) K. Morokuma, *Acc. Chem. Res.*, **10**, 294 (1977).
- (29) The calculated binding energy is comparable with the thermochemically estimated value (-120 kcal/mol) by U. I. Vendenev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich in "Bond Energies, Ionization Potentials and Electron Affinities", translated by W. C. Price, Edward Arnold, London, 1966.
- (30) In the present analyses, dispersion type interactions are not considered, though a part of electron correlation is taken into account through the UHF formalism. For the effects of electron correlation on binding energies, see C. Hollister and O. Sinanoğlu, *J. Am. Chem. Soc.*, **88**, 13 (1966).
- (31) The experimental barrier is found to be 65 kcal/mol by J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).
- (32) During the rotation from the planar to perpendicular form, the carbon-carbon bond distance changes from 1.36 to 1.49⁷ or 1.47 Å.⁸
- (33) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).
- (34) L. Salem, C. Leforestier, G. Segal, and R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975).

An ab Initio Molecular Orbital Study of Organic Reactions. The Energy, Charge, and Spin Decomposition Analyses at the Transition State and along the Reaction Pathway

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Abstract: Ab initio molecular orbital calculations have been performed in an effort to determine what types of chemical interactions play essential roles, and how effectively the charge and spin redistributions occur at the transition state and along the reaction pathway. The reaction barrier is expressed as a sum of the intramolecular deformation energy and the intermolecular interaction energy, which in turn consists of the electrostatic, polarization, exchange repulsion, charge transfer, and their coupling terms. The importance of the intramolecular deformation is especially emphasized in relation to the efficient intermolecular interaction. The charge transfer interaction plays a much more important role in chemical reactions than in molecular complexes such as electron donor-acceptor complexes and hydrogen bonds. Furthermore, it is found that the electrostatic and polarization interactions become significant as the ionic character of the reaction is increased. The specific reaction systems we have investigated are the additions of HCl, Cl⁺, CH₃⁺, H⁺, and H to olefins, the abstraction reactions involving CH₄ + H, CH₄ + Cl, and H₂ + ³CH₂, and the substitution reactions involving CH₄ + H⁻ and CH₃F + F⁻.

I. Introduction

For a theoretical investigation of reactivities in various organic reactions, it is extremely important to elucidate what types of chemical interactions play essential roles and clarify how effectively the charge and spin redistributions occur during the course of a chemical reaction. Many earlier theoretical studies which have dealt with the problem of chemical reactivities can be divided into three groups: the static, the localization, and the delocalization approach.² In these approaches only a portion of chemical interactions were explicitly considered. The applications of the HOMO-LUMO interaction scheme by Fukui³ and the symmetry rule by Woodward and Hoffmann⁴ have achieved great successes in the discussion of stereochemical reactions. The successes of these methods, in principle, rely on the importance of the charge transfer interaction.⁵ Some comprehensive treatments of chemical interactions have also been proposed based on the perturbation method.⁶⁻¹² However, the applications of such treatments have been limited to a rather early stage of reaction because of the inherent nature of the perturbation method. Furthermore, the effects of molecular deformations during the reaction were not considered explicitly. The molecular deformation becomes increasingly important with the progress of reaction and should have a significant influence on the reaction mechanisms.

In an effort to clarify the essential features of apparently complicated organic reactions, it seems of practical value to employ procedures which could give chemically meaningful visualization and interpretation of reactions. To this end, the reaction energy (ΔE) is expressed as a sum of the intramo-

lecular deformation (DEF) energy and the intermolecular interaction (INT) energy, which in turn consists of the electrostatic (ES), polarization (PL), exchange repulsion (EX), charge transfer (CT), and their coupling (MIX) terms. Our primary interest is on the qualitative determination of the relative importance of various interactions in the transition state and the reaction intermediate.

The specific reaction systems we have investigated are the additions of HCl, Cl⁺, CH₃⁺, H⁺, and H to olefins, the abstraction reactions of CH₄ + H, CH₄ + Cl, and H₂ + ³CH₂, and the substitution reactions of CH₄ + H⁻ and CH₃F + F⁻. These systems include the cationic, anionic, neutral, radical, and triplet reactions. Our hope is that the essential features of the interaction and bond interchange in these reactions can be understood from a unified point of view.

II. Computational Details

Computation. All calculations reported here were performed within the framework of the ab initio LCAO MO SCF theory, employing a modified version of the GAUSSIAN 70 programming system.¹³ The split-valence 4-31G basis sets were used with recommended exponents, contraction coefficients, and scale factors.¹⁴ The 4-31G basis set is flexible enough to give a reasonable estimate of the interaction energy and its components.¹⁵⁻¹⁷ However, it does have a tendency to exaggerate the polarity of molecules. Electron population analyses were carried out using the minimal STO-3G basis set¹⁸ for easier visualization.

Molecular Geometries. The molecular geometries of C₂H₄ + H and C₂H₃F + H were optimized using the STO-3G basis