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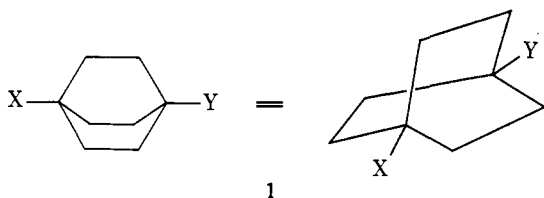
Molecular Orbital Studies of Organic Substituent Effects. Transmission of Charge and Energy Perturbations through Rigid Bicyclic Skeletons in a Model S_N2 Reaction

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Abstract: Substituent effects on model S_N2 exchange reactions of 4-substituted bicyclo[2.2.2]octylcarbonyl and cubylcarbonyl chlorides are examined in a series of CNDO/2 semiempirical molecular orbital calculations. The energetic trends produced by substitution in the two sets of aliphatic compounds are correlated with each other and with related experimental data; substituent effects in the two series were quite comparable. Interaction of substituents with the (charged) model transition state reaction site dominated a much smaller interaction with the (neutral) carbonyl chloride group. In all cases, the electron distribution in a carbonyl chloride and its corresponding model transition state were almost identically affected by a given substituent. An inductive pattern of charge perturbation (of uncertain energetic importance) was observed.

Rigid bicyclic molecules, especially those with the 4-bicyclo[2.2.2]octyl (BCO) skeleton (1), have played a central role

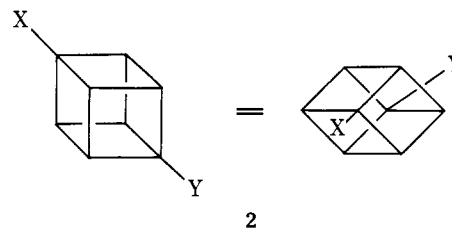


in experimental studies which attempt to separate the effects of substitution into components which differ in their origin and mode of transmission. Because these bicyclic compounds lack the aromatic π electron systems of benzene derivatives (in which substituent effects have been most thoroughly studied) but share the latter's rigidity, their properties have been used to assess the special transmission characteristics of those π systems.¹

The experimental studies do not allow an unambiguous evaluation of the relative importance of "inductive" and "resonance" contributions to observed substituent effects.² For one thing, *inductive* distortions of benzene π electrons seem to contribute significantly to observed substituent effects in at least some aromatic systems³ (though such distortions were not very important in a study of benzyl chloride S_N2 reactions analogous to this one⁴). For another, it has been suggested that *conjugative* transmission mechanisms may operate in the bicyclic saturated compounds. Analogous through-bond cou-

pling⁵ operates in similar systems and the BCO molecule (see Figure 1) has valence orbitals of symmetry appropriate to the coupling of either π or σ orbitals of substituent and reaction site.⁶ It has been argued⁷ that such coupling is not required to explain the available data but this question has not been thoroughly explored.

In another attempt to distinguish different modes of transmission, Stock⁷ has compared substituent effects in BCO derivatives with those in similar compounds in which the BCO framework has been replaced by the 4-cubyl skeleton (2). He



argued that because the spatial relationship of substituent to reaction site is quite similar in the two series, through-space electrostatic field effects⁸ should be similar, and that if this were the dominant mechanism of transmission measured substituent effects ought also to be rather comparable. If, on the other hand, the classical inductive effect (wherein successively polarized bonds carry the substituent's electrical disturbance to the reaction site⁹) were dominant, the cubane compounds ought to exhibit larger effects because there are

Table I. CNDO/2 Energies for Participants in Model S_N2 and Related Reactions of Bicyclo[2.2.2]octane Derivatives

X	$XC_8H_{12}CH_2Cl^a$	$XC_8H_{12}CH_2Cl_2^-^a$	$XC_8H_{13}^a$	$\Delta E(R3)^{b,c}$	$\Delta E(R4)^{b,c}$	ΔE^\ddagger^c	$\delta\Delta E^\ddagger^c$
H	92.1804	108.3407	68.0850	0.00	0.00	-35.58	0.00
NH ₂	104.6190	120.7794	80.5237	0.02	-0.01	-35.61	-0.03
CH ₃	100.8551	117.0158	76.7597	0.03	-0.23	-35.83	-0.25
F	119.1604	135.3259	95.0656	0.36	-2.90	-38.84	-3.26
CF ₃	181.8525	198.0209	157.7579	0.51	-4.56	-40.65	-5.07
NO ₂	139.9957	156.1679	115.9014	0.68	-6.75	-43.00	-7.42

^a Minus E_{total} , hartrees (valence electrons only). ^b For definitions of reactions R3 and R4, see text. ^c kcal/mol.

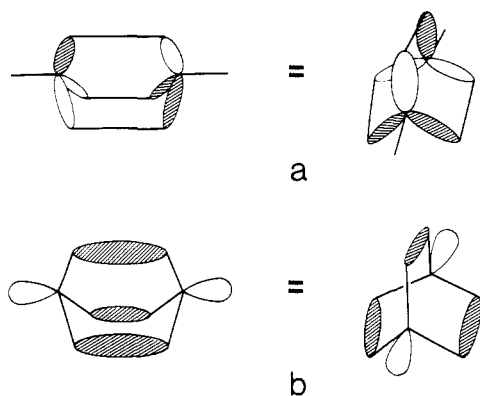


Figure 1. Valence orbitals of bicyclo[2.2.2]octane. Orbital a, one component of the E'' HOMO set, can couple π orbitals of substituent and reaction site; orbital b, only slightly lower in energy, can couple σ orbitals.

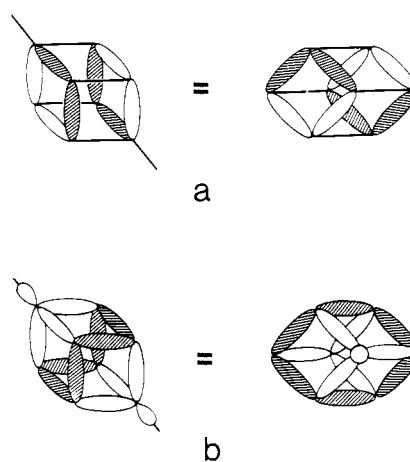


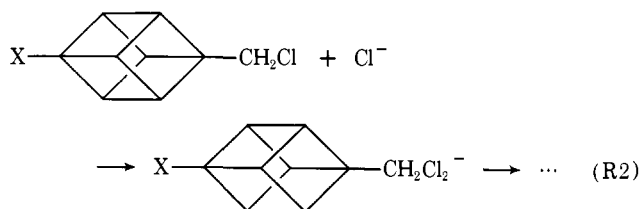
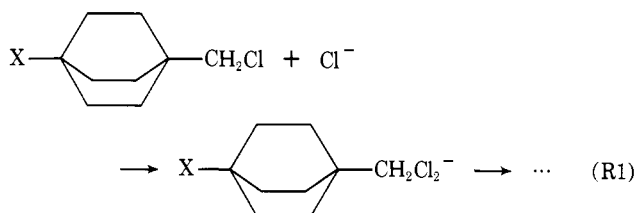
Figure 2. Valence orbitals of cubane. Orbital a is a component of the T_{2g} HOMO set which can couple π orbitals of substituent and reaction site; orbital b, another component of the same set, can couple σ orbitals.

more bond paths to do the transmitting.¹⁰ The different set of valence orbitals potentially available for conjugative coupling of substituent and reaction site by the cubane skeleton (see Figure 2) makes the comparison with BCO systems even more interesting.

This paper reports a series of all valence electron semiempirical molecular orbital calculations carried out to investigate the transmission of substituent effects in molecules containing the BCO and cubane skeletons.

Methods and Results

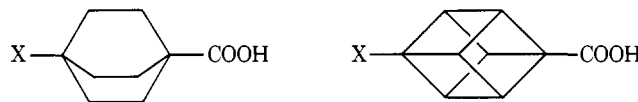
As in a previous paper on substituent effects in benzene derivatives,⁴ to which we will henceforth refer as I, CNDO/2 calculations¹² were carried out for reactants and model transition states in model S_N2 reactions (with X = H, NH₂, CH₃,



F, CF₃, NO₂). The reasons for our choice of this reactive system and of the CNDO/2 method for our calculations, as well as the geometry optimization procedure used in this work, are discussed in I. Skeletal geometries were optimized in the parent

hydrocarbons, reaction site geometries were adjusted to the aliphatic environment, and substituents were assigned the same NDO geometries used previously.¹³ As before, the ΔE^\ddagger 's calculated for R1 and R2 were negative, but the substituent effects, i.e., the changes of ΔE^\ddagger induced by substitution ($\delta\Delta E^\ddagger$), had reasonable signs and relative magnitudes.

Because both the rates of actual benzyl halide substitution reactions¹⁴ and calculated "activation energies" for the benzene analogue of R1 and R2 were highly correlated with Hammett σ constants (which are pK_a changes brought about by substitution in benzoic acids), we would have liked to correlate substituent effects on R1 and R2 energy changes with pK_a changes for the carboxylic acids below.



The calculated substituent effects ($\delta\Delta E^\ddagger$) are tabulated, along with other relevant energetic quantities, in Table I for BCO derivatives and in Table II for cubane compounds. High-precision pK_a measurements (in 50% w/w EtOH-H₂O) are available for some, but not all, of the substituted BCO acids of interest;^{7a,15,16} unfortunately, data for the relevant cubane acids could not be found in the literature. The rather satisfactory correlation (in the limited number of cases where direct comparisons were possible) is shown in Figure 3. The fit is slightly better than one calculated in a similar comparison of Hermann's computed CNDO/2 acid dissociation energies with the pK_{as} ;^{18,19} the slopes of the two correlations indicate that the model S_N2 reaction is considerably more sensitive to substitution than the acid dissociation.

Since appropriate experimental quantities were not available for the cubane compounds considered here, their substituent effects were compared with those calculated for the corre-

Table II. CNDO/2 Energies for Participants in Model S_N2 and Related Reactions of Cubane Derivatives

X	XC ₈ H ₆ CH ₂ Cl ^a	XC ₈ H ₆ CH ₂ Cl ₂ ^{-a}	XC ₈ H ₇ ^a	ΔE(R3) ^{b,c}	ΔE(R4) ^{b,c}	ΔE ^{±c}	δΔE ^{±c}
H	87.3785	103.5324	63.2683	0.00	0.00	-31.57	0.00
NH ₂	99.8349	115.9885	75.7247	0.03	0.19	-31.41	0.16
CH ₃	96.0644	112.2190	71.9543	0.09	-0.39	-32.05	-0.48
F	114.3596	130.5189	90.2500	0.41	-2.97	-34.95	-3.38
CF ₃	177.0598	193.2233	152.9508	0.77	-5.27	-37.62	-6.04
NO ₂	135.2035	151.3711	111.0949	0.98	-7.57	-40.12	-8.55

^a Minus E_{total} , hartrees (valence electrons only). ^b For definitions of reactions R3 and R4, see text. ^c kcal/mol.

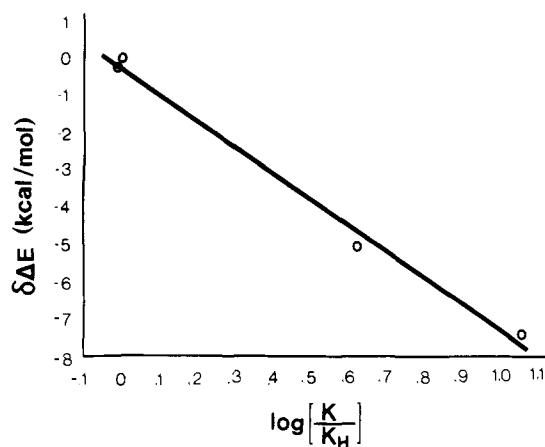


Figure 3. CNDO/2 substituent effects on bicyclo[2.2.2]octylcarbonyl S_N2 reactions vs. ΔpK_a for the corresponding carboxylic acids (in 50% w/w EtOH-H₂O). The least-squares line is $\delta\Delta E^\ddagger = (-7.0 \pm 0.3) \log(K/K_H) + (-0.3 \pm 0.2)$ kcal/mol. The correlation coefficient for the four data (H, CH₃, CF₃, NO₂) is 0.996.

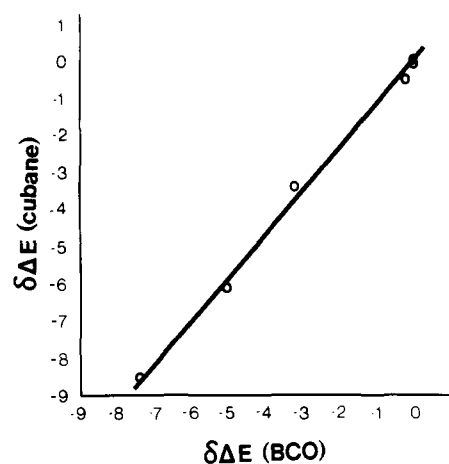
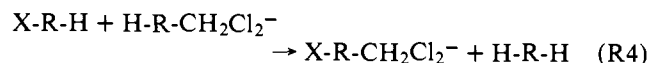
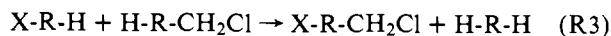


Figure 4. Comparison of calculated CNDO/2 substituent effects in bicyclo[2.2.2]octylcarbonyl and bicyclo[2.2.2]octylcarbonyl S_N2 reactions. The least-squares line is $\delta\Delta E^\ddagger(\text{cubane}) = (1.16 \pm 0.03)\delta\Delta E^\ddagger(\text{BCO}) + (0.05 \pm 0.11)$ kcal/mol. The correlation coefficient for the six data is 0.998.

sponding BCO derivatives; that comparison is shown in Figure 4. We find, as did Cole, Mayers, and Stock when they compared cubanecarboxylic acid pK_a s with those for BCO acids,^{7b} that substituent effects in the two series are linearly related, the slope of the straight line being not very different from unity. Our calculations thus provide additional evidence for their conclusion that the cubane and BCO skeletons do not exhibit major differences in transmission of the energetic effects of substitution.²⁰

The calculated substituent effects on activation energies are dominated by interaction of substituent and reaction site in the (charged) transition states; the corresponding interactions in the (neutral) carbonyl chlorides are much smaller. We base this statement on calculated energy changes for the reactions²¹



which are reported in Tables I and II.

The response of charge distribution to substitution in these two aliphatic systems is as similar as was energetic response. (There is some evidence²²—and widespread presumption—that charge and energy perturbations are in fact proportional to one another.) Calculated “regional” electron densities,²³ derived from Mulliken population analyses²⁴ and measured relative to formal densities for the atoms and groups, are presented in Table III and IV. As was the case for benzene derivatives in I, a given substituent produced essentially identical charge perturbations in each model transition state as it did in the corresponding carbonyl chloride, i.e., its influence on molecular charge distribution was essentially independent of the transformation of the reactive site by the process of reac-

tion. In each of the series of compounds, before the transformation the CH₂Cl group is a moderate electron acceptor from the skeleton (0.09 e⁻ was transferred in the BCO derivatives, 0.07 e⁻ in the cubane compounds); most of this electron density is lost by the carbon to which the reaction site is attached. In the model transition states, CH₂Cl₂⁻ has lost much of this attraction for skeletal electrons. In the BCO series, it is still slightly electron withdrawing (0.04 e⁻); in the cubanes it neither withdraws nor donates. In both cases, the net donation from reaction site to framework as the reaction proceeds is accompanied by some reorganization of skeletal charges; the carbon adjacent to the reaction site is left somewhat *more* electron deficient than it was at the beginning of the process.

In both series, the CH₃ group participates in little net interchange of electron density, NH₂ and CF₃ are moderate electron acceptors, and F and NO₂ withdraw electrons strongly. The magnitude of the charge disturbances (equal ones in carbonyl chloride and corresponding model transition state) set up by substituents in each of these aliphatic systems falls off monotonically with degree of removal from the point of attachment of the substituent in a manner reminiscent of the classical inductive effect; the perturbations do not follow the common pattern of charge alternation noted by Pople and Gordon,²⁵ by us in I, and by others. Among the BCO compounds, the pattern of disturbance does not extend beyond the carbon of attachment in the CH₃ compound, reaches only to the skeletal carbons β to the NH₂ and F substituents, and dies out at the γ positions in the CF₃ and NO₂ compounds. In the cubane series, CH₃ and NH₂ affect only the α and β skeletal carbons; F and CF₃ make their presence felt as far away as the carbons γ to their point of attachment. Only in the NO₂-substituted cubanes does the steadily decreasing disturbance actually reach the reaction site.

Table III. Total CNDO/2 Mulliken Electron Densities^{a,b} of Bicyclo[2.2.2]octylcarbinyl Chlorides and Model Transition States

Molecule	CH ₂	Cl	C ₁	(CH ₂) ₂	(CH ₂) ₃	C ₄	(CH ₂) ₅	(CH ₂) ₆	(CH ₂) ₇	(CH ₂) ₈	Subst
BCO carbinyl chloride (OC)	-9	18	-5	0	0	-4	0	-1	-1	0	2 ^c
Model transition state (TS)	-26	15	-6	-6	4	-4	4	-2	-2	4	5 ^c
Δ(TS-OC)	-16	-3	-1	-6	4	0	3	-1	-1	3	3 ^c
NH ₂ -OC	-9	18	-5	0	2	-14	1	-1	-1	1	8
NH ₂ -TS	-26	15	-6	-6	6	-13	4	-2	-2	4	11
Δ(TS-OC)	-16	-3	-1	-6	4	0	3	-1	-1	3	3
δ(NH ₂ -H)	0	0	0	0	2		1	0	0	1	
CH ₃ -OC	-9	18	-5	0	0	-5	0	-1	-1	0	3
CH ₃ -TS	-26	15	-6	-6	4	-5	3	-2	-2	3	7
Δ(TS-OC)	-16	-3	-1	-6	4	0	3	-1	-1	3	4
δ(CH ₃ -H)	0	0	0	0	0		0	0	0	0	
F-OC	-10	17	-5	-1	0	-23	1	-2	-2	1	24
F-TS	-26	14	-6	-7	5	-22	4	-3	-3	4	26
Δ(TS-OC)	-16	-3	-1	-6	4	0	3	-1	-1	3	2
δ(F-H) ^d	0	0	0	-1	0		0	-1	-1	0	
CF ₃ -OC	-10	17	-6	-1	-3	3	-3	-2	-2	-3	8
CF ₃ -TS	-26	14	-7	-7	1	3	0	-3	-3	0	11
Δ(TS-OC)	-16	-3	-1	-6	4	0	3	-1	-1	3	3
δ(CF ₃ -H)	0	-1	0	-1	-3		-3	-1	-1	-3	
NO ₂ -OC	-10	17	-5	-1	-3	-6	-4	-2	-2	-4	21
NO ₂ -TS	-26	14	-7	-7	0	-6	0	-3	-3	0	25
Δ(TS-OC)	-16	-3	-1	-6	4	0	3	-1	-1	3	4
δ(NO ₂ -H)	0	-1	0	-1	-4		-4	-1	-1	-4	

^a Relative to formal densities at each site. ^b In units of 0.01 electron. ^c Density at H₄. ^d "Regionalizing" this row of charge differences resulted in fortuitous cancellations at (CH₂)_{2,5,8}.

Table IV. Total CNDO/2 Mulliken Electron Densities^{a,b} of Cubylcarbinyl Chlorides and Model Transition States

Molecule	CH ₂	Cl	C ₁	(CH) ₂	(CH) ₃	C ₄	(CH) ₅	(CH) ₆	(CH) ₇	(CH) ₈	Subst
Cubylcarbinyl chloride (CC)	-10	17	-4	0	-1	-1	0	0	0	0	1 ^c
Model transition state (TS)	-26	14	-8	-3	1	0	3	0	3	0	3 ^c
Δ(TS-CC)	-16	-3	-4	-3	2	1	3	0	3	0	3 ^c
NH ₂ -CC	-10	17	-4	0	3	-13	2	-1	2	-1	6
NH ₂ -TS	-26	14	-8	-4	4	-11	4	-1	4	-1	9
Δ(TS-CC)	-16	-3	-4	-3	2	2	3	0	3	0	4
δ(NH ₂ -H)	0	0	0	0	3		2	0	2	0	
CH ₃ -CC	-10	17	-4	0	0	-4	0	-1	0	-1	2
CH ₃ -TS	-26	14	-8	-3	2	-3	3	0	3	0	6
Δ(TS-CC)	-16	-3	-4	-3	2	2	3	0	3	0	4
δ(CH ₃ -H)	0	0	0	0	1		1	0	1	0	
F-CC	-10	16	-5	-1	0	-20	0	-1	0	-1	22
F-TS	-26	13	-8	-4	2	-19	3	-1	3	-1	24
Δ(TS-CC)	-16	-3	-4	-3	2	2	3	0	3	0	2
δ(F-H)	0	-1	0	-1	1		1	-1	1	-1	
CF ₃ -CC	-10	16	-5	-1	-4	5	-3	-1	-3	-1	7
CF ₃ -TS	-26	13	-8	-4	-2	7	-1	-1	-1	-1	11
Δ(TS-CC)	-16	-3	-4	-3	2	2	3	0	3	0	4
δ(CF ₃ -H)	0	-1	0	-1	-3		-3	-1	-3	-1	
NO ₂ -CC	-10	15	-5	-2	-4	-3	-4	-2	-4	-2	20
NO ₂ -TS	-26	13	-8	-5	-2	-2	-1	-2	-1	-2	24
Δ(TS-CC)	-16	-3	-4	-3	2	1	3	0	3	0	4
δ(NO ₂ -H)	-1	-1	-1	-2	-3		-4	-1	-4	-1	

^a Relative to formal density at each site. ^b In units of 0.01 electron. ^c Density at H₄.

Conclusions

Transmission of the influence of polar substituents by the bicyclo[2.2.2]octane skeleton and by the cubane skeleton is similar in magnitude and probably in mechanism. If through-bond coupling via framework valence orbitals is important, it does not involve appreciable charge transfer and is comparable in the two systems. Calculated charge changes produced by substitution, which were essentially identical in

carbinyl chloride and corresponding model transition state for this S_N2 reaction, fell off monotonically at positions successively removed from the point of attachment of the substituent. Since in general the disturbance did not reach the reaction site, it is something of a matter of taste whether to call the result of this skeletal polarization a classical inductive effect. The present analysis does not allow estimation of the relative energetic importance of this polarization and the electrostatic field effect (experimental results^{7,11} indicate that the latter is

more significant²⁶). A more detailed examination of these and previous results using electrostatic calculations and perturbation theory is underway.

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- (20) This energetic observation does not provide direct evidence on the question of the importance of through-bond interaction of substituent and reaction site by admixture with the skeletal valence orbitals shown in Figures 1 and 2. If this coupling is important, it is comparable in the two series considered here, but the analysis of this paper (based on total energies and Mulliken charges) would detect such coupling only if it produced enhanced charge transfer between substituent and reaction site; no charge transfer was observed. Energetically important interaction which does not involve such transfer, e.g., exchange or polarization perturbation, would escape detection in this simple analysis. A self-consistent perturbation theory of substitution (SeCPeTS) under development in this laboratory should allow us to resolve this difficulty.
- (21) Use of these reactions to separate the two interactions was suggested by W. F. Reynolds (University of Toronto) in a private communication.
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Bonding in Acyclic Hydrocarbons. An FSGO Analysis and Computational Procedure

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Abstract: The FSGO method is used to study the nature of bonding orbitals in acyclic hydrocarbons. For a given local chemical environment, a bonding orbital's exponent and center are shown to depend linearly on bond length. Variations between different chemical environments are displayed and analyzed. The near-transferability of bond orbitals and chemical environments from molecule to molecule is demonstrated. Predictions for dipole moments and for certain bond lengths and stretching force constants in acetylene, ethylene, propene, ethane, propane, isobutane, butadiyne, vinylacetylene, propyne, 1,3-butadiene, butatriene, and allene are presented, and are shown to successfully monitor differences in similar chemical bonds. A procedure for determining orbital exponents and locations for FSGO wave functions, without explicit energy optimizations, is proposed. Calculations at fixed geometries, as reported for propyne, vinylacetylene, *cis*-1,3-butadiene, *trans*-1,3-butadiene, and isobutane, illustrate the speed of the proposed method, and demonstrate that the resulting wave functions are comparable in accuracy to explicitly optimized FSGO wave functions. Theoretical equilibrium geometries are computed for allene, propyne, *trans*-2-butene, *cis*-1-butene, and isoprene, to show the capabilities of the method. All calculations are ab initio in the sense that all integrals are evaluated and there is no recourse to experimental data.

I. Introduction

In 1967 Frost proposed¹ a quantum mechanical scheme, the floating spherical Gaussian orbital (FSGO) method, for generating crude ab initio molecular wave functions. This method avoids the LCAO approach and instead uses an absolutely minimal basis set of Gaussian core, lone pair, and

bonding orbitals. A number of investigators have since performed FSGO calculations on hydrocarbons. Their results demonstrate that accurate predictions can be made for molecular geometries,²⁻⁷ conformational preferences,²⁻⁸ orbital energy orderings,^{6,9} ESCA chemical shifts,¹⁰ charge densities,^{11,12} dipole moments,^{6,12} and polarizabilities and suscep-