Corresponding Orbital Analysis of the Bonding of Some Monosubstituted Benzenes

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Abstract: A corresponding orbital analysis is used to study the nature of the interaction between the phenyl and substituent units of three monosubstituted benzenes; these are aniline, phenol, and fluorobenzene. The corresponding orbital eigenvalues clearly show significant trends in the σ symmetry charge donation from phenyl to substituent and the π symmetry donation from substituent to phenyl. The F substituent accepts the largest amount of σ change from the ring but also donates the smallest amount of π charge to it. At the other extreme, NH_3 is the poorest σ acceptor and the best π donor.

I. Introduction

Along with advances in obtaining accurate wave functions, corresponding orbitals[1] have received wider attention. They have primarily been used to simplify the evaluation of transition matrix elements. With corresponding orbitals, the invariance properties of full configuration interaction,[2] CI, or complete active space[3] wave functions can profitably be exploited in the construction of transition density matrices. The resultant simplifications make it possible to obtain matrix elements between initial and final state wave functions which are constructed from large configuration expansions.[2,3] However, besides their use as a technical tool, corresponding orbitals can be used to interpret the chemical changes that occur under different conditions. In ionization processes, for example, they make it possible to identify the "active" ionized orbital even when final state relaxation is taken into account and separate self-consistent-field, SCF, wave functions are used for the initial, neutral, and final ionized states.[4]

In the present work, we investigate the use of corresponding orbitals, CO's, as an interpretative tool for bonding. The CO's between the SCF molecular orbitals, MO's of a molecule, and its composite units (fragments) may show the symmetries and even the specific MO's which are most involved in the bonding.[5,6] In addition, the CO eigenvalues for a series of similar systems may display trends in the nature of the bonding in a clear and direct way. For these purposes, we consider CO transformations of the SCF occupied orbitals of the composite molecule and those for each of the appropriate units. The nonzero CO eigenvalues, ϵ, indicate the extent to which the CO is changed by or is involved in the interaction. Orbitals which have $\epsilon \approx 1$ are essentially unaffected by the interaction while those for which $\epsilon < 1$ are clearly changed by and, hence, involved in the interaction. It is possible to associate the reduction of the ϵ from 1 with charge transfer between the units of the composite system. The generation of the corresponding orbitals is straightforward and well-defined in the sense that the orbital eigenvalues converge toward a Hartree–Fock limit. This is in contrast to the Mulliken charge and bond order analysis which becomes ill-defined when large basis sets are used. This problem is particularly severe when the basis set includes diffuse functions with small exponents, e.g., to represent Rydberg character.[7]

In the previous studies, the CO analysis has been used to interpret the nature of the bonding between halogen atoms, F and Cl, and a Si surface[5] and between metals and CO.[6] In the present work, we consider the monosubstituted benzene derivatives, fluorobenzene, phenol, and aniline, in order to further explore the utility of corresponding orbitals for analysis of chemical bonding. In section II, we briefly review the relevant features of the CO transformation[1,4-6] and the computational details of the SCF calculations. In section III, we describe the bonding with special attention to differences and trends between the three systems. The

discussion in section IIIA is based on traditional considerations of population analyses and orbital energies. The CO analysis results are discussed in section IIIB. Finally, our conclusions are summarized in section IV.

II. Method

The sets of canonical Hartree–Fock orbitals for the fragments A and B and for the composite molecule AB are denoted ϕ^A, ϕ^B, and ϕ^{AB}, respectively. The elements of the overlap matrices, S^A and S^B between the fragment and composite molecule orbitals, are

$$S_{ij}^A = (\phi_i^A|\phi_j^{AB}) \qquad S_{ij}^B = (\phi_i^B|\phi_j^{AB}) \tag{1}$$

these are nonsquare matrices. There are two pairs of corresponding orbital sets which are denoted ψ^A and $\psi^{AB}(A)$ and ψ^B and $\psi^{AB}(B)$. These are formed by unitary transformations from ψ^A, ψ^B, and ψ^{AB}:

$$\psi^A = \phi^A U^A \qquad \psi_{(A)}^{AB} = \phi^{AB} V^A \tag{2}$$

$$\psi^B = \phi^B U^B \qquad \psi_{(B)}^{AB} = \phi^{AB} V^B$$

The unitary transformations, $U = (u_1, u_2 ..., u_p)$ and $V = (v_1, v_2, ..., v_q)$, are obtained as solutions of the eigenvector equations

$$SS^+u_i = \lambda_i u_i, \quad i = 1, ..., p \tag{3a}$$

$$S^+Sv_i = \lambda'_i v_i, \quad i = 1, ..., q \tag{3b}$$

where $p < q$ are the number of occupied orbitals of the fragment and composite molecules, respectively. Equation 3b has $q-p$ zero eigenvalues λ' and they are ordered as λ_{q+1} to λ_p; the remaining, nonzero, λ'_i (and λ_i) are ordered such that $i > j$ then $\lambda'_i > \lambda'_j$ ($\lambda_i > \lambda_j$). The nonzero eigenvalues have the following useful properties:

(1) $0 \leq \lambda'_i \equiv \lambda_i \leq 1 \qquad i = 1, ..., p$

(2) $\langle \psi_i^{AB}(A)|\psi_j^A \rangle = (\lambda_i^A)^{1/2}\delta_{ij}$ and

$$\langle \psi_i^{AB}(B)|\psi_j^B \rangle = (\lambda_i^B)^{1/2}\delta_{ij} \tag{4}$$

The corresponding orbital transformation brings the orbitals of

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Bonding of Some Monosubstituted Benzenes

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Table I. Electronic Configurations Used for the Fluorobenzene, Phenol, and Aniline SCF Wave Functions[a]

core and inner valence

$(X1s)1a_1^2$, $(C1s)2a_1^2$, $(C1s)3a_1^21b_2^2$, $(C1s)4a_1^22b_2^2$, $(C1s)5a_1^2$, $(X2s)6a_1^2$, $(C2s)7a_1^2$, $(C2s)3b_2^2$, $(C2s)8a_1^2$, $(C2s)4b_2^2$, $(C2s)9a_1^2$, $(C2s)10a_1^2$

outer valence

fluorobenzene: $5b_2^2$, $(\pi)1b_1^2$, $11a_1^2$, $6b_2^2$, $12a_1^2$, $7b_2^2$, $13a_1^2$, $(\pi)2b_1^2$, $8b_2^2$, $(\pi)1a_2^2$, $(\pi)3b_1^2$

phenol: $5b_2^2$, $11a_1^2$, $6b_2^2$, $12a_1^2$, $(\pi)1b_1^2$, $13a_1^2$, $7b_2^2$, $(\pi)2b_1^2$, $8b_2^2$, $(\pi)1a_2^2$, $(\pi)3b_1^2$

aniline: $5b_2^2$, $11a_1^2$, $6b_2^2$, $12a_1^2$, $7b_2^2$, $(\pi)1b_1^2$, $13a_1^2$, $8b_2^2$, $(\pi)2b_1^2$, $(\pi)1a_2^2$, $(\pi)3b_1^2$

[a] The configurations are divided into a common core and inner valence portion and an outer valence portion. For the former, X denotes the heavy substituent atom, X = N, O, F.

Table II. Bond Distance (in bohrs) and Bond Angles (degrees) Used (See Reference 8)

phenyl	phenyl substituent	substituent
C–C 2.710	C–F 2.466	O–H 1.909
C–H 2.022	C–O 2.778	N–H 1.935
∠HCH 120	C–H 2.778	∠HNH 113.9

Table III. SCF Orbital Energies, ϵ, for the Higher Valence Orbitals and the UPS Vertical IP's[a]

	SCF ϵ	UPS IP	
Aniline			
$3b_1$	8.90	$\pi(b_1)$	8.02
$1a_2$	10.43	$\pi(a_2)$	9.12
$2b_2$	12.54	n	10.78
$8b_2$	14.49	σ	11.88
$13a_1$	14.77	$\pi(b_1)$	12.48
$1b_1$	15.52		
Phenol			
$3b_1$	9.89	$\pi(b_1)$	8.56
$1a_1$	10.64	$\pi(a_2)$	9.28
$8b_2$	12.85	n	11.56
$2b_1$	13.61	σ	11.91
$7b_2$	14.69	$\pi(b_1)$	12.61
$13a_1$	15.25		
$1b_1$	16.02		
Fluorobenzene			
$3b_1$	10.69	$\pi(b_1)$	9.11
$1a_2$	11.02	$\pi(a_2)$	9.82
$8b_2$	14.95	σ	12.12
$2b_1$	15.34	$\pi(b_1)$	12.50
$13a_1$	15.69	σ	12.97
$7b_2$	17.14	n	13.85
		n	13.98

[a] For the UPS IP's, the orbital symmetry assignments of Debies and Rabalais[12] are also given. The ϵ's and IP's are in eV.

Table IV. Mulliken Gross Populations for the Substituent Groups in Fluorobenzene, Phenol, and Aniline[a]

substituent	F	OH	NH$_2$
symmetry			
a_1	−0.32	−0.36	−0.17
b_1	+0.07	+0.07	+0.09
b_2	+0.03	+0.00	−0.03
total	−0.225	−0.29	−0.11

[a] The populations are given as effective ionicities or changes of charge from that of the free substituent. The changes for each occupied substituent symmetry are given.

the fragment and composite molecules into maximum juxtaposition. For further details about the CO transformation see ref 1–6. The CO eigenvalues, λ_i, indicate the extent to which the orbitals of the fragments, or units, change when the composite molecule is formed. The CO's which have $\lambda_i \approx 1$ are essentially unchanged and are not involved in the chemical bonding; those which have λ_i significantly smaller than 1 are involved in the bonding. The CO's have the point group symmetry of the composite, and the eigenvalues indicate the extent to which orbitals of the different symmetries contribute to the bonding. By comparing the eigenvalues for a series of similar systems trends in the bonding can be determined.

We use the CO analysis to study the formation of aniline, phenol, and fluorobenzene from phenyl and the appropriate substituents; we denote the phenyl by A and the substituent by B. All the AB composites are assumed to have C_{2v} symmetry.[8] A common geometry is used for the phenyl fragment, and the same geometry is used for the NH$_2$ and OH fragments as for the AB composite. The phenyl, NH$_2$, and OH radicals are all $^2A_1$ open-shell systems; for the F radical, we place the open p shell in a$_1$ symmetry. Since the fragments are all open a$_1$ shell systems, we perform two types of CO transformations for this symmetry. For the first type, we exclude the fragment open shell from the set of Hartree-Fock orbitals, ψ_A or ψ_B. For the second type, we include the open shell in these sets. The difference in the λ_i for these two approaches gives an indication of the role of the open-shell orbital in the bonding.

The closed-shell electronic configurations for the self-consistent-field, SCF, wave functions of the composite molecules are given in Table I; these configurations have also been used in previous theoretical studies of these molecules.[9] The π orbitals are contained in the irreducible C_{2v} representations b$_1$ and a$_2$; the σ orbitals are in a$_1$. The bond distances and angles used are taken from ref 8 and are shown in Table II. The MOLECULE-ALCHEMY program[10] was used to perform restricted SCF calculations for the composite and fragment molecules. The calculations were carried out by using Gaussian basis sets given by Dunning and Hay.[11] For the

heavy atoms, C, N, O, and F, 9s and 5p elementary Gaussian functions were contacted to 4s 2p; for H, 4s functions were contracted to 2s.

III. Results and Discussion

A. General Features of the Bonding. The electronic structure of these molecules has been the subject of several theoretical studies based on ab initio wave functions.[9] Debies and Rabalais[12] have interpreted the bonding in these monosubstituted benzenes based on the analysis of their ultraviolet photoemission, UPS, data. They discussed the splittings and changes of the electron-binding energies in terms of inductive and resonant effects in the substituent–phenyl interaction. The features which they describe for the electronic structure of aniline have recently been confirmed in a high-resolution soft X-ray emission study.[13] The reader is referred to ref 9, 12, and 13 for detailed discussions.

In Table II, the UPS vertical ionization potentials, IP's, and the orbital assignments for the IP's of Debies and Rabalais[12] are compared to our SCF orbital energies, ϵ, for the higher lying valence orbitals. The order of the ϵ's of the highest π molecular orbitals, MO's, agrees with their assignment; however, the assigned order of the higher binding energy UPS IP's and the SCF ϵ's for these MO's do not agree. A Mulliken population analysis for the charge associated with the substituent group is given in Table IV. There, the gross populations are given as the ionicity; the total

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(10) The MOLECULE-ALCHEMY program package incorporates the MOLECULE integrals program written by J. Almlöf (unpublished) and the ALCHEMY SCF program written by P. S. Bagus and B. Liu (unpublished). The interfacing of the programs was performed by U. Walgren and P. S. Bagus (unpublished).

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Table V. Corresponding Orbital Eigenvalues between the Fragments, C_6H_5 or X, and the Composite Substituted Benzene, C_6H_5X

X	F	OH	NH_2
C_6H_5X-X			
a_1 closed fragment only	0.997	0.997	0.999
a_1 all fragment	0.896	0.883	0.874
b_1	0.988	0.985	0.977
b_2	0.996	0.997	0.999
$C_6H_5X-C_6H_5$			
a_1 closed fragment only	0.998	0.998	0.997
a_1 all fragment	0.643	0.651	0.786
b_1	0.997	0.998	0.998
b_2	0.999	0.998	0.997_5
a_2	1.000	1.000	1.000

[a] The smallest nonzero eigenvalue in each occupied symmetry is given. In a_1 symmetry, results are given both excluding and including the fragment open-shell orbital; these are called a_1 closed fragment only and a_1 all fragment, respectively.

ionicity is divided into its contributions from each symmetry of the substituent. In the $\pi(b_1)$ symmetry, charge is transferred from the substituent to the phenyl. This donation is from the filled substituent lone pair π MO to the phenyl; only half of the valence π orbitals arising for the phenyl fragment are occupied, and it is a π acceptor. A large charge transfer from the ring to the electronegative substituents takes place in $a_1(\sigma)$ symmetry. The charge transfer, as measured by the Mulliken population analysis, in the nonbonding b_2 symmetry is small for all three substituents. The splitting of the benzene $\epsilon(1e_{1g})$ π MO into its b_1 and a_2 C_{2v} components is largest for aniline, see Table III. Aniline also has the largest substituent to phenyl π donation; the splitting is generally described as a conjugative effect. The total charge transfer from the ring to substituent is smallest for aniline, and this is explained by the relatively small electronegativity of N. The molecules also have different first IP's; the largest is for fluorobenzene. This is described[12] as due to a resonant double-bond structure between C and F and related to the short C–F bond distance.

B. Corresponding Orbital Analysis. As we described in section II, we are concerned with two sets of corresponding orbitals. The first is between the substituted benzene and the phenyl radical, denoted $C_6H_5X-C_6H_5$; the second set is between the substituted benzene and the substituent, denoted C_6H_5X-X. The composite molecules, C_6H_5X, are closed-shell systems, and the separated fragments, C_6H_5 and X, are all $^2A_1$ states with an a_1 symmetry open shell. The corresponding orbitals of a_1 symmetry are obtained either by omitting the fragment open shell from the set of orbitals or by including it; the former CO calculation is called "closed fragment only" and the latter "all fragment". In Table V, we give the smallest, nonzero, corresponding orbital eigenvalues for each occupied symmetry for $C_6H_5X-C_6H_5$ and for C_6H_5X-X. The values not shown are very close to 1; in general they are ≥ 0.9999 although in a few cases they are smaller. The smallest CO eigenvalue not shown is $\lambda = 0.997$ for the a_1 all-fragment CO set for $C_6H_5X-C_6H_5$. The CO's which have these large λ's are fragment orbitals which are included essentially without change in the occupied space of C_6H_5X. These orbitals are not involved, to any significant extent, in the bonding between C_6H_5 and X. It is emphasized that the corresponding orbital analysis presented here concerns the role of occupied orbitals in the bonding. The influence of unoccupied orbitals, such as that manifested by a mixing of a HOMO orbital from one fragment with a LUMO from the other fragment, is thus not considered.

We consider first the CO λ's for a_1 symmetry. For the closed fragment only CO's, the smallest, nonzero, λ ranges between 0.997 and 0.999 for both $C_6H_5X-C_6H_5$ and C_6H_5-X. This shows that the closed-shell a_1 orbitals of the fragments, C_6H_5 and X, are contained essentially unchanged in the C_6H_5X occupied space. Only the fragment open shell can contribute to the bonding. In order to interpret the significance of the all-fragment a_1 symmetry smallest CO λ's, consider a model of a simple covalent bond involving the fragment open-shell orbitals. We denote these

Table VI. Expansion of the $\lambda = 0.643$ a_1 All-Fragment Corresponding Orbitals for $C_6H_5F-C_6H_5$ in Terms of the SCF MO's[a]

SCF-MO's	C_6H_5	C_6H_5F
$1a_1$	0.001	−0.083
$2a_1$	0.000	0.000
$3a_1$	0.000	0.000
$4a_1$	0.000	0.000
$5a_1$	−0.028	0.000
$6a_1$	0.025	0.807
$7a_1$	−0.032	−0.028
$8a_1$	−0.024	0.000
$9a_1$	−0.003	0.246
$10a_1$	0.022	0.316
$11a_1$	0.998	0.380
$12a_1$		0.023
$13a_1$		0.188

[a] The numbering of the SCF MO's is given in Table I and described in the text; for C_6H_5, $11a_1$ is the open shell.

orbitals as ϕ_1 and ϕ_2 and their overlap, at the C_6H_5X geometry, as $S = \langle \phi_1 | \phi_2 \rangle$. Neglecting charge transfer or donation between the fragments, the covalent closed-shell C_6H_5X orbital, ϕ, formed from ϕ_1 and ϕ_2 is

$$\phi = (\phi_1 + \phi_2)/[2(1 + S)]^{1/2} \qquad (5a)$$

and the overlap of either ϕ_1 or ϕ_2 is

$$\langle \phi_1 | \phi \rangle = \langle \phi_2 | \phi \rangle = [(1 + S)/2]^{1/2} \qquad (5b)$$

To a very good approximation, the remainder of the C_6H_5X a_1 occupied space is formed from the closed-shell a_1 orbitals of the fragments (see Table V, a_1 closed fragment only). If the closed-shell fragment space was completely unchanged, the smallest a_1 all-fragment λ would be just the square of $\langle \phi_1 | \phi \rangle$ or $(1 + S)/2$, see eq 4 and 5. In particular, the λ's for C_6H_5X-X and $C_6H_5X-C_6H_5$ would have the same value.

It is clear from Table V that this is not the case; the λ for C_6H_5X-X is larger than that for $C_6H_5X-C_6H_5$ for all cases. This is exactly the behavior that will follow from an ionic character for the a_1 covalent orbital. The C_6H_5X orbital, ϕ, is not as shown in eq 5a. A more appropriate description is

$$\phi = (a\phi_1 + b\phi_2) \qquad (6)$$

where if ϕ_1 is the substituent open shell then $a > b$; this corresponds to charge transfer from phenyl to the substituent. The ratio of the smallest CO eigenvalue, $R = \lambda(C_6H_5X-X)/\lambda(C_6H_5X-C_6H_5)$, provides a quantitative measure of the relative ionicities for the different X's; when R is greater, the phenyl to substituent charge transfer is greater. From Table V, the values of R are 1.394, 1.357, and 1.113 for C_6H_5F, C_6H_5OH, and $C_6H_5NH_3$, respectively. The phenyl to substituent a_1 charge transfer is similar for fluorobenzene and phenol; it is considerably smaller for aniline. This is close to the population analysis results in Table IV although the order of the transfer for fluorobenzene and phenol is reversed even though the difference is small. A population analysis provides only a qualitative guide to the charge distribuion because of arbitrariness in the assignments of basis functions and overlap populations to atomic centers. Thus, the ordering given by the ratio of the CO λ's is preferable.

The average of the $C_6H_5NH_2-NH_2$ and $C_6H_5NH_2-C_6H_5$ a_1 all-fragment λ's is larger than for the two other cases. This indicates that the overlap of the C_6H_5 and NH_2 open-shell a_1 orbitals, $\langle \phi_1 | \phi_2 \rangle$, is largest. This is not surprising since the NH_2 open-shell orbital has more lone pair character than do the orbitals of OH or F; it is more directed toward the phenyl fragment.

The expansion of the a_1 all-fragment CO eigenvectors in terms of the occupied SCF MO's gives further information. Representative CO eigenvectors with $\lambda = +0.643$ for $C_6H_5F-C_6H_5$ are given in Table VI. The numbering of the C_6H_5F a_1 SCF MO's is given in Table I. The numbering for C_6H_5 is obtained by deleting the F 1s and F 2s MO's from the list; the last, $11a_1$, MO is the phenyl open shell. The phenyl CO is almost entirely (0.998),[2] or 99.6%, the open-shell orbital. This further confirms our claim

that the other, closed-shell, phenyl orbitals are included essentially unchanged in the C_6H_5F orbital space. The situation is somewhat different for the C_6H_5F CO where five SCF MO's have coefficients larger than 0.1; this indicates that the bonding orbital of eq 6 is distributed over several SCF canonical MO's. The $6a_1$ SCF MO makes the largest contribution, 65%, to the CO. This deep MO with SCF ϵ = -45.2 eV has considerable C s-p and F s-p character; it is clearly a phenyl–F bonding orbital, and this is the reason for the large ϵ. However, the $9a_1$ to $11a_1$ and the $13a_1$ SCF MO's also make large contributions to this C_6H_5F CO: 6%, 10%, 14%, and 3.5%, respectively.

We consider next the CO λ's of π (b_1) symmetry. The C_6H_5X–C_6H_5 λ's are large, 0.997 or 0.998, showing that the phenyl fragment orbitals are, with only very small changes, included in the C_6H_5X space. The C_6H_5X–X λ's are somewhat smaller than 1.0; this corresponds to donation of charge from the substituent π lone pair into the empty, unoccupied, phenyl π MO's. From the CO λ's, the order of this donation is $NH_2 > OH > F$ which is consistent with the order given by the populations in Table IV.

The smallest CO values for the b_2 and a_2 symmetries are very near 1; the smallest is 0.996 for the b_2 symmetry of C_6H_5F-F. This is conclusive evidence that the fragment orbitals in these symmetries are essentially unchanged and uninvolved in the bonding.

IV. Conclusions

Differences in bonding properties of species such as those considered in the present study are most likely to be important in order to describe and understand differences in reactivity. In the present work, we have shown that a corresponding orbital analysis provides a useful description of the bonding. The corresponding orbital eigenvalues show that, at most, one corresponding orbital per symmetry is involved in the bonding. This is different from the SCF canonical orbitals where the bonding character may be distributed over several MO's. The smallest, nonzero CO eigenvalues also show the trends in the bonding for this series of substituted benzenes. The strongest bonding is in the $a_1(\sigma)$ space where the phenyl to substituent charge transfer is in the order $C_6H_5F \gtrsim C_6H_5OH > C_6H_5NH_2$. The bonding in the $b_1(\pi)$ space is weaker and the substituent to phenyl charge donation is in the order $C_6H_5NH_2 > C_6H_5OH > C_6H_5F$. These trends are consistent with those obtained from other studies,[9,12] and we emphasize the utility of the trends given by the CO eigenvalues. It is relevant to point out that the corresponding orbitals and eigenvalues are well defined and stable to increase in the size of the basis set used to describe the MO's. This is in sharp contrast to a population analysis which is increasingly ill defined for larger basis sets. The approach that we have presented for corresponding orbitals between a subunit and the total, composite, system does not require difficult calculations and can be evaluated in a straightforward fashion.

Toward the Laboratory Identification of Cyclopropenylidene

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Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Received February 13, 1984

Abstract: Nonempirical molecular electronic structure theory has been used to predict the geometries and energetics of the lowest singlet and triplet states of $\ddot{C}$—HC=CH. The closed-shell singlet ground state is predicted to lie about 70 kcal/mol below the lowest triplet state. Actually there are two low-lying triplet states, $^3B_1$ and $^3A_2$, which lie very close energetically. Ground-state cyclopropenylidene is predicted to have a dipole moment $\mu \sim 3.4$ D, making it a very nucleophilic carbene. Vibrational frequencies are predicted for all three low-lying electronic states at the double-ζ plus polarization (DZ+P) self-consistent-field (SCF) or two-configuration (TC) SCF levels of theory. A comparison of the predicted harmonic frequencies of singlet cyclopropenylidene and cyclopropene at the SCF level of theory is made. These predictions should assist in the identification of cyclopropenylidene from matrix-isolation infrared spectroscopy.

For the past two decades cyclopropenylidene and some of its derivatives have elicited much theoretical[1-7] and experimental[8-12] interest. The motivations behind these investigations have

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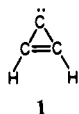
basically fallen into two categories. First, several studies have centered around the determination of the ground-state electronic structure of cyclopropenylidene. Theory[13,14] and experiment[15,16] are now in concurrence that methylene has a triplet ground state with a singlet–triplet energy difference, ΔE(S–T), of about 9 kcal/mol. However, CH_2 is the exception and numerous carbenes which have a singlet ground-state electronic structure have been

observed.[17] The primary factor which must be considered when comparing the energies of the singlet and triplet states is the

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