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Conformational Effects upon the Charge-Transfer Transitions of the Hexamethylbenzene–Tetracyanoethylene Crystalline Complex

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Abstract: Piezomodulated and direct reflection spectra from the (010) face of the hexamethylbenzene (HMB)–tetracyanoethylene (TCNE) electron donor–acceptor single crystal were measured from 10 000 to 45 000 cm^{-1} at 300 K. High-resolution spectra were obtained for the charge-transfer transition polarization direction over the visible region at 5 K. Results are compared to AIM-Xα-SCF calculations on the complex. Evidence for three separate charge-transfer transitions which may be associated with three specific triads of molecules is presented.

I. Introduction

A previous study[1] from this laboratory has shown that the interpretation and assignments of charge-transfer (CT) transitions in electron donor–acceptor (EDA) complexes can be greatly enhanced by the study of those complexes which display symmetry in the crystal. The case first considered, that of the EDA complex of anthracene with tetracyano-*p*-quinodimethane (TCNQ^0),[1] showed that, consistent with symmetry considerations, the lowest energy CT transition originated from the penultimately filled molecular orbital of anthracene and terminated with the lowest unoccupied molecular orbital (LUMO) of the TCNQ^0. The transition from the highest occupied molecular orbital (HOMO) of anthracene to the LUMO was found to be forbidden.

Of particular interest in the study of aπ–bπ EDA complexes have been the complexes of methyl-substituted benzenes with tetracyanoethylene (TCNE).[2,3] An interesting finding in earlier papers is the evidence for the presence of two charge-transfer bands in many of these complexes. This was rationalized by Voigt and Reid[3] and Orgel[4] as due to splitting of the doubly degenerate (e_g) highest occupied molecular orbitals of appropriately substituted benzenes (C_{3v} symmetry or higher) which is caused by the different interactions of the substituents and the degenerate orbitals. However, Voigt and Reid pointed out that another, albeit more subtle, effect could be induced by "geometric" perturbation where the C=C bond of the TCNE would have the plane containing the bond parallel to the plane of the ring but with the bond axis oriented with its projection on the ring plane either intersecting atoms or bisecting bonds. The energetics of the CT interaction would be

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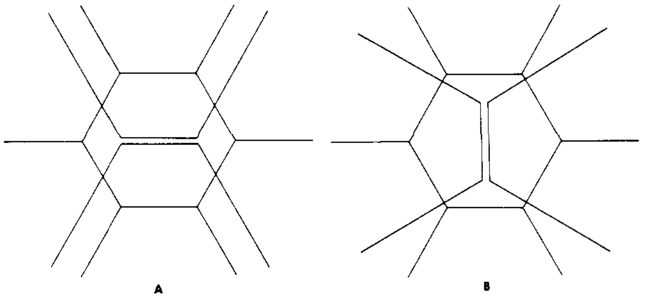

Figure 1. A and B conformations of HMB-TCNE dimers. The letters are also used to designate the orientation of the TCNE molecules relative to a given HMB molecule.

expected to be different and this has been substantiated by a CNDO calculation on the benzene-TCNE complex.[5]

The data for the methyl-substituted benzenes indicates that those complexes most likely to display multiple CT transitions are those where the donor molecule ring is substituted such that the symmetry is C_{3v} or higher. This is suggestive of influence of the splitting of the degenerate (e_g) HOMOs due to the geometrical isomerism mentioned above. An X-ray structure of the hexamethylbenzene-TCNE complex[6] permits an investigation of the influence of perturbations of complex geometry on the CT spectra.

We report the electronic spectra of the crystalline HMB-TCNE EDA complex obtained from near-normal incidence polarized specular reflection spectroscopy. The experimental data are compared to the results of Xα-SCF calculations which have been performed for the relevant geometries of the complex. Additional discussion of the energetics of the interactions between the three possible conformations of EDA complex "triads" is presented.

II. Experimental Section

A. Materials. The TCNE obtained from Eastman Organic Chemicals was purified by repeated vacuum sublimation. Hexamethylbenzene, which was obtained from the same supplier, was used without further purification. Equimolar amounts of the two compounds were used to prepare two separate solutions in reagent grade chloroform. The resulting purple solution formed upon mixing of the two solutions was allowed to stand until crystals formed. Lath-like crystals with a golden sheen were subsequently harvested and mounted for study.

The crystals formed had the appearance of bundles of much smaller filamentary crystals collected into larger crystalline structures. In contrast to most EDA complex crystals, which are fairly brittle, the HMB-TCNE crystals are quite plastic and may be bent without breaking. The crystals are easily cleaved parallel to the long axis of the crystal and frequently will separate into fibrous bundles if the cleavage is not true.

B. Crystal Data. The triclinic crystal is of the space group $P\bar{1}$ and there is one EDA complex in the unit cell where the molecular planes are perpendicular to the c axis which is also the long axis of the crystal.[6] Identification of the (010) face was made by X-ray diffraction measurements.

The crystal is disordered with a ratio of 3:1 between the so-called A and B forms. The A form with the projection of the TCNE central C=C bond bisecting the bond angles of HMB and the B form where the TCNE is rotated 90° to the TCNE in the A form are shown in Figure 1.

The point-group symmetry of the two complexes is C_{2v} and it is important to note that the irreducible representations of the TCNE molecules in the two forms will differ in the crystal owing to their 90° rotational difference. Both have C_1 site symmetry for the complex with each moiety at C_i sites.

Because of the high energies of both the HMB[7] and the TCNE molecular transitions,[8] the faces zonal to the c axis are spectroscopically equivalent over the wavelength region studied. Thus only the (010) face was studied. The principal directions for (010) were parallel and perpendicular to the crystal's long axis. No significant dispersion of principal directions was observed over the spectral region covered by this investigation.

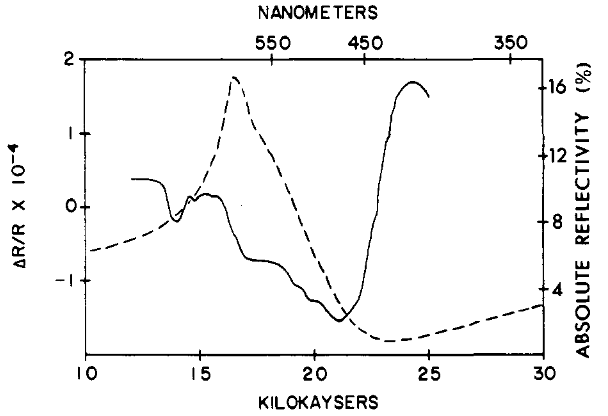

Figure 2. Direct (dashed line) and piezoreflection (solid line) spectra for light polarized parallel to the crystal c axis at 300 K.

C. Apparatus. The microspectroreflectometer used in this study has been described elsewhere.[1] The low-temperature spectra were taken in a variable-temperature cryostat with no liquid cryogens in the optical path. A 300-W xenon arc was used and light was rendered monochromatic by a Jobin-Yvon THR-1500 monochromator. The spectrum was taken with a point-by-point scan (4-cm^{-1} intervals) at 5 K with ensemble averaging by an on-line computer. Points obtained at both 5 and 300 K were accepted at a 95% confidence level.

Piezomodulation spectra were obtained at 300 K with previously described apparatus.[7] The induced strain was 10^{-4} and was isotropic in the plane of the crystal face being studied.

III. Results

The reflection spectra for light polarized parallel and perpendicular to the c axis for (010) were obtained at 300 and 5 K. Because the molecular planes of both the TCNE and HMB are perpendicular to this axis, the two polarizations will induce excitation of purely out-of-plane and in-plane transitions, respectively, if an oriented gas model of the crystal is assumed.

The direct reflection and modulated piezoreflection spectra at 300 K with light polarized along the c axis are shown in Figure 2. The piezomodulation spectrum shows low strain sensitivity. The structure to the red of 15 000 cm^{-1} is the result of modulation of the back reflection. There are two definite breaks in the spectrum which indicate the presence of at least two systems. The first is expected to be near 16 200 cm^{-1} and the second at 18 500 cm^{-1} as judged by comparison with the behavior of other piezoreflection spectra.[9] The presence of yet another system at ~21 000 cm^{-1} is also implied.

The absorption spectra for both polarizations were obtained by Kramers-Kronig transform of the reflection spectra and are shown in Figure 3. The $c_\perp$ direction is dominated by an edge which is also observed in the reflection spectrum. Because of the uncertainty of the location and reflectivity of the peak of the unobserved higher energy transition and its effect on the transform of structure near to it, little faith can be put in any other than the broadest interpretation of the absorptivity data obtained for this polarization. However, it is clear that the 35 000-cm^{-1} transition does not correlate well with S_1 observed for HMB in solution. In n-hexane, this transition is found to have a peak absorptivity of only 230 L/mol-cm, which is far below that observed in the crystal. It is improbable that this intensity would be in error by an order of magnitude. The validity of the intensity obtained from the crystal measurements is substantiated by the reflection spectrum of the band itself, which shows that it has relatively high reflectivity.

The most striking feature of the transform is found in the absorption spectrum for the c-axis low-energy transition. A

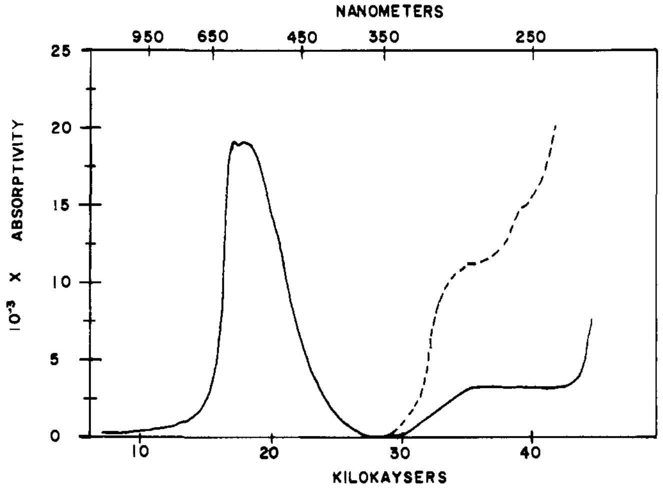

Figure 3. Absorption spectra obtained by Kramers-Kronig transforms of the c-axis (solid line) and $c_{\perp}$-axis (dashed line) reflection spectra at 300 K.

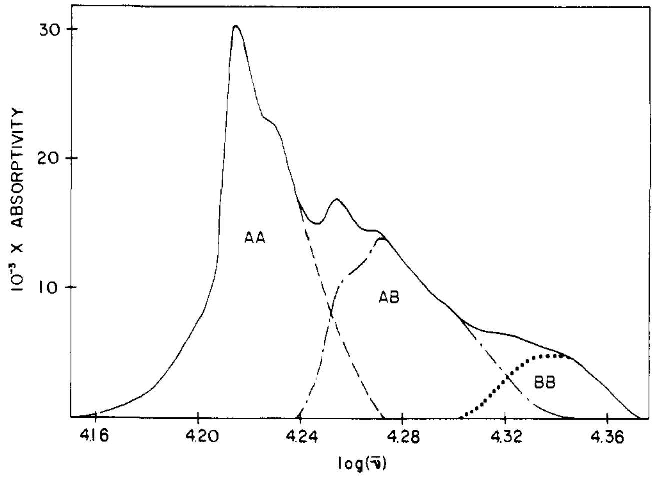

Figure 4. Deconvolution of the 5 K absorption spectrum for the c-axis polarization. Letter designations refer to the triad which may be associated with each transition.

Table I. Peak Molar Absorptivities and Equilibrium Constants for HMB-TCNE in Chloroform

method	$\epsilon_{\max}$, L/mol-cm	K_{eq}, L/mol
Benesi-Hildebrand[a]	8100	8.3
Scott[b]	6200	12.0
Foster-Hammick-Wardley[c]	7800	8.8

[a] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2704 (1949). [b] R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, **75**, 787 (1956). [c] R. Foster, D. L. Hammick, and A. A. Wardley, *J. Chem. Soc.*, 3817 (1953).

small but definite peak is observed at 17 100 cm^{-1} which is followed by a broader peak at 17 800 cm^{-1}. If one takes the peak of the band as $\bar{\nu}_{\mathrm{CT}}$ for purpose of comparison with solution and vapor-phase data, the crystal $\bar{\nu}_{\mathrm{CT}}$ is red shifted by 900 and 1300 cm^{-1}, respectively. The crystal dipole strength is 2.62 Å^2. Correction for geometrical factors and doubled cross section for the transition, because the donor molecule is sandwiched between two acceptors, gives a solution equivalent dipole strength of 0.44 Å^2. The estimated dipole strength reported for the complex in solution is 0.90 Å^2.[10]

Earlier work[2,10] on the spectra of the complex in solution indicated the HMB-TCNE complex to be strong with a K = 250 and ϵ 4390. Because the Benesi-Hildebrand procedure used in determining these constants involves extrapolation to high concentrations with attendant liability to large error, these constants were redetermined using the Liptay[11] method for weighting in the entire CT absorption band. Table I lists the results of the various analyses for molar absorptivity and K. The dipole strength obtained from the average of these procedures is 0.61 Å^2. In contrast, scaling the curves to the $\epsilon_{\max}$ value of the earlier data[10] gives a solution dipole strength of 0.50 Å^2. It should also be noted that the measurements reported here show an equilibrium constant (K = 9.7) reduced nearly 20-fold from that reported earlier.

Kramers-Kronig analysis of the 5 K CT reflection band was obtained by splicing the 300 K reflection data onto the measured 5 K spectrum at 20 500 cm^{-1}. Variation of the frequency at which the splice was made as well as alteration of the reflectivities and curvature of the spliced-on curve was not observed to have any significant effect on the band shape or position of the CT absorption band which is shown in Figure 4. This curve retains many of the general characteristics of the reflection band wherein two distinct band systems are observed. The peak molar absorptivity of 30 300 L/mol-cm is observed at 16 390 cm^{-1} with a shoulder at 16 900 cm^{-1}. The second system's peak at 17 950 cm^{-1} has an absorptivity of 16 900 L/mol-cm. Rather than another shoulder, however, a slight peak is observed at 18 550 cm^{-1} with an absorptivity of 14 500 L/mol-cm.

Another low-intensity and broad system is observed which is centered at ~21 000 cm^{-1}. This band showed some sensitivity in the transform to the high-energy spectrum which was spliced on at 20 500 cm^{-1}, but it was never possible to alter its intensity by more than ~10%. This would indicate that the structure is real and close examination of the reflection spectrum does reveal a very slightly positive curvature near 19 500 cm^{-1} which might cause such a structure in the transformed spectrum.

Comparison of the 300 and 5 K spectra reveal a ~1100-cm^{-1} red shift of the CT band in going to low temperature which is accompanied by a narrowing of the band. However, because the CT band apparently splits into at least two systems, it is difficult to obtain comparison. In fact, if the system at 20 500 cm^{-1} in the 5 K spectrum is considered, the low-temperature system has somewhat greater breadth than that observed at 300 K ($\Delta\nu_{1/2}$ = 5050 cm^{-1}). The half-width in solution is 5180 cm^{-1}.

Further, because of the large red shift upon cooling, the intensities obtained from the 5 K transform must be viewed with caution since the change of the unit cell dimensions upon cooling is not known. Since this will alter the molar concentration of the complex in the crystal, the values of the absolute intensities will contain significant error. The error in measured reflectivity at 5 K is quite high but the correct band shape and relative reflectivities are retained. Thus, any comparisons made with intensities from the same band will be valid.

In order to obtain the relative intensities for the CT bands at 5 K, some deconvolution of the spectrum is necessary. In Figure 4 is also shown the deconvolution chosen for this system. Other deconvolutions give similar results. As expected, the band shapes of the higher energy transitions are changed. The second system now has its major peak at 18 750 cm^{-1} with a lower energy and less intense peak at 18 100 cm^{-1}. The third system has its peak at 21 400 cm^{-1} but is otherwise structureless.

The integrated intensity of the first system is 0.36 Å^2 and that of the second is 0.23 Å^2. As mentioned previously, the third band system has been found to be sensitive to the Kramers-Konig transform since the intensity can be affected by the manner in which the transform is performed. However, the reflection spectrum supports the presence of structure in this frequency region and thus, while there is uncertainty with regard to intensity, it is taken to be real. The integrated intensity is small with a dipole strength of ~0.05 Å^2. Thus the total integrated CT dipole strength is 0.64 Å^2. The value compares favorably to both the 300 K crystal and solution values.

IV. Discussion

A. Comparison with AIM-Xα-SCF Calculations. Calculations were performed on both the A and B dimer configurations of HMB-TCNE using the AIM-Xα-SCF procedure discussed elsewhere.[12] Coordinates for the two complexes were taken directly from the X-ray crystallographic data but were symmetrized to give the complexes true C_{2v} symmetry. Calculations for both complexes were made with the customary value of $\alpha = 1.0$. Although finite computer time and funds precluded minimization with respect to the value of α, a calculation on the A configuration for $\alpha = 0.8$ was made for comparison. The total energy of the complex in this case was higher than that found for $\alpha = 1.0$, and the transition energies were higher and thus in greater agreement with experiment.

The results for $\alpha = 1.0$ for both configurations show that the total energy difference between the two 1:1 complexes is 0.0827 eV with the B configuration being the more stable. This is in agreement with previous calculations[5] utilizing a CNDO approach wherein it was found that the B form was stabilized by 0.79 eV over the A form at an interplanar distance of 1.75 Å. This difference was observed to diminish significantly with the increase of this distance.

Examination of the Xα orbitals indicates that the variance between the orbital energies differs only slightly throughout for the two conformations. However, a trend is observed in the LUMO which may be largely associated with the TCNE moiety and in the HOMO and penultimately occupied MO which may be associated with HMB. The LUMO associated with the B configuration is at a higher energy than that for A. The HMB orbitals are not affected energetically. This may be understood by realizing that the parent e_{2g} orbital has a nodal pattern which is consistent with both configurations. This means that the unperturbed degenerate irreducible representation would be the same in either configuration.

For both configurations, the LUMO is of b_1 symmetry while the HOMO is b_2 and the penultimate orbital is b_1. This differs from a previous analysis[13] of benzene-TCNE complex symmetries. Here the donor molecule has been rotated instead of the acceptor. This approach recognizes that the lower symmetry (no degenerate orbitals) molecule should fix the reference axial system.

The trend in the calculations indicates that the CT transition for the B configuration should come at higher energy than that for A. If the calculated transition frequency for the predominant A configuration is scaled to the vapor $\bar{\nu}_{\max}{}^{CT}$ and, if the $\bar{\nu}_{\max}{}^{CT}$ for the B configuration is scaled identically, then the latter is blue shifted by nearly 500 cm^{-1}. Of course, this can only be suggestive of a trend, since the calculations cannot be expected to be of the precision implied by these numbers nor is the electron repulsion necessarily the same for both geometries. The data are in agreement with a splitting between the origins of the $\bar{\nu}_{\max}{}^{CT}$ in A and B. There are two interpretations that may be applied to the data which are also consistent with the trends indicated by the calculation. The first is that the origins of the $\bar{\nu}_{CT}{}^{A}$ and $\bar{\nu}_{CT}{}^{B}$ in the crystal are only slightly displaced leading to a highly congested spectrum. The second is that the separation is large and the two absorptions are separated.

The data tend to support the latter hypothesis. Examination of the out-of-plane transitions at 5 K indicates two separate systems of quite similar band shape with an intensity ratio of ~3:2 which is close to the 3:1 ratio expected from the 3:1 ratio of A:B configurations observed in the crystal structure. Further, the band shapes would be expected to be quite similar since the potential wells for both systems are apparently nearly superimposable.[5]

B. Triads and Lattice Statistics. The data do not agree as well with these simple expectations as one could wish. The variance of both band shapes (admittedly obtained by arbitrary deconvolution) and intensities requires closer examination of the CT interactions.

It is of interest to consider the nature of the complexes in a given stack. Statistically, there are three times as many A conformations as B. Yet, in a given stack, there will be either A's neighboring A's, B's neighboring B's, or A's neighboring B's. Previous theoretical work[14] has suggested that triads of donors and acceptors are the fundamental unit in a mixed stack in EDA crystals. Although the crystal spectra of TCNQ-anthracene[1] did not completely support the calculations using this model, it nevertheless is worth considering in HMB-TCNE where the disorder imbeds different triads in the stack. Of the three types of neighbors, it is clear that the AB type will have a triad wherein a given HMB ring will be associated with two TCNE molecules which will have their central bond axes rotated at 90° to each other. The other two possible triads will have the HMB sandwiched between TCNE molecules which have parallel central bonds albeit with differing orientations with respect to the HMB. This suggests the possibility of a third CT transition of a frequency yet different from that of the other two configurations. The presence of diffuse and weak structure to the blue of the second CT system supports this conjecture. Unfortunately, the size of the triads prevents meaningful calculation of their energies and CT transitions using the AIM-Xα-SCF procedure.

The relative intensities can be calculated for this model. Because of the high A:B ratio, the most common triad should be of the AA type with the TCNE axis projection bisecting bond angles. The next in frequency should be the AB type with the HMB sandwiched by two TCNE molecules oriented 90° to each other. The least common triad would be the BB type where the TCNE molecules are rotated at 90° to those found in the AA conformation.

The triads imply the possibility of three different CT transitions each of which may be associated with a specific conformation. The situation is not unlike that of a binary alloy. The expected populations are $N_{AA}/N_{BB} = 9$ and $N_{AA}/N_{AB} = 1.5$ when one assumes that the occupation of sites is random but requires that the A-type TCNEs have thrice the population of B's. The observed intensity ratios from the deconvoluted spectrum are in excellent agreement with these ratios: $N_{AA}/N_{BB} = 7.2$ and $N_{AA}/N_{AB} = 1.6$.

This analysis supports the concept of triads as the basic unit of interaction in crystals of weakly interacting EDA complexes. It further suggests use of lattice statistics to estimate the interactions between the triads in a single stack by reducing it to a one-dimensional problem. Unfortunately, the dependence of the disorder upon temperature is not known so only the difference in energy of interaction of the AB system from the sum of the energies of the AA and BB forms can be computed; i.e., $\Delta E = 2E_{AB} - (E_{AA} + E_{BB})$. The E_{AA} and E_{BB} are the energies of the perfectly ordered AA- or BB-type crystals. The solution[15,16] to the problem is well known with

$$\Delta E = \frac{2kT \ln\left(\dfrac{1-s}{s}\right)}{(1-2s)}$$

where $s = N_A/(N_A + N_B) = 0.75$. Using $T = 298$ K gives $\Delta E = 0.113$ eV, which is somewhat more than half of the observed separation of the CT transitions for the AA and AB triads. However, this energy is a measure of interactions in the one-dimensional lattice and is not necessarily related to the optical transition frequencies. Such analysis is facilitated by the lack of rotation of the HMB in the lattice.[17]

C. Excitons. This complex also presents a problem which has been observed in other EDA complexes wherein the CT transition dipoles are collinear.[1,9] Simple exciton arguments lead to a prediction of a red shift and intensification of the CT band from its solution values. Indeed, this is observed in most cases (TCNQ–anthracene is a notable exception). If the total integrated intensities of the CT bands are used, a calculated (one-dimensional)[18] red shift of only 710 cm^{-1} from the solution CT peak is obtained which is less than the 1100-cm^{-1} shift which is observed. Tacit in this calculation is the assumption that the configurations and transitions observed in the crystal are directly related to those found in solution. The greatest deviations in energy would arise from the situation wherein the complexes in solution and the crystal possess quite different geometries. The fact that the solution and crystal CT transition intensities are similar offers, at best, weak support for the possibility that the geometries are similar.

V. Conclusions

The HMB-TCNE single crystal displays spectral structure in the visible which is attributed to three separate CT transitions which arise from the three different arrangements which are possible for a given HMB in the crystal stack. These configurations may be approximated by EDA complex trimers AA, AB, and BB which are expected to have slightly varying total energies as well as different CT transition frequencies. The spectra in the visible region form two distinct, structurally similar bands with a shoulder at higher energy which becomes a third transition upon deconvolution. These bands may be associated with $\bar{\nu}_{CT}$ for the trimers.

The model of binary alloys may be applied to the EDA stack and relevant statistics, when applied to the intensity ratios, support the hypothesis of EDA triads in the crystal. The treatment can be further extended to estimate the energy difference of the AB-type complex from that of the AA or BB type.

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Electronic Structure of the Lowest $^1A_1$ and $^3B_1$ States of Cyclopropenylidene

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Abstract: Multiconfiguration self-consistent field calculations have been performed at several geometries on the lowest $^1A_1$ and $^3B_1$ states of cyclopropenylidene. The effects of hybridization and electron correlation are analyzed at the various geometries. These model prototype calculations reveal strong correlation effects in the aromatic singlet state as well as a singlet–triplet potential surface crossing which may play a role in the chemical reactivity of analogous chemical reactions involving insertion of singlet or triplet reagents into triple bonds. It is demonstrated that multiconfigurational wave functions are absolutely necessary to obtain a qualitative description of the two spin states of these unsaturated carbenes.

I. Introduction

Considerable theoretical and experimental interest has been devoted to the chemistry of saturated and unsaturated carbenes. Theoretical research in our laboratory[1] and theoretical and experimental work in other laboratories[1-5,13] has focused on the very important question of singlet–triplet energy differences of isolated carbenes. Indeed, postulation of one-step stereospecific addition of singlet carbenes and two-step nonstereospecific addition of triplet carbenes to olefins has played a dominant role in the experimental determination of the spin state of carbenoid intermediates.[3] In this report, we attempt to gain a fundamental understanding of a particular carbene reaction that appears to involve a nonstereospecific singlet addition of a cyclic carbene.[4] Diphenylcyclopropenylidene appears to insert into both dimethyl maleate and dimethyl fumarate to produce the same spiropentene, thereby suggesting a triplet-like mechanism. However, the carbene itself is gen-

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