counterion in $\mathbf{1a}^{-}\cdot$ or $\mathbf{1b}^{-}\cdot$. Such an enhancement is readily taken into account by setting the parameter α_O of this oxygen atom equal to $\alpha + (1.2 + \delta)\beta$ with $\delta > 0$. The coupling constants a_{H_μ} of the ring protons, calculated with $0.1 < \delta < 0.5$ by the same procedure as mentioned above ($\delta = 0$), are also given in Table V. They correlate nicely with their experimental counterparts found in the spectra of type *S* for the eight single ring protons (Table I). Moreover, the effect of increasing δ from 0.2 to 0.5 reproduces the trend in the paired coupling constants a_{H_μ} when K^+ is replaced by Na^+ and Li^+ as the counterion (Table II) or when the temperature is raised from 163 to 223 K (Table III).

The HMO model thus supports a structure of the ion pair in which the substantial localization of the π spin population on one of the two weakly interacting monoketone moieties is brought about by a close contact of the positively charged counterion with the oxygen atom in this moiety.

Concluding Remarks. The results of ESR and ENDOR studies reported above provide some insight into the mechanism of the electron transfer between the two formally nonconjugated π systems of the radical anion of *cis*-10,11-dimethyldiphensuccindan-9,12-dione (**1**). These results, in particular the *specific* line broadening in the type *I* spectra, leave no doubt with respect to the *intra*molecular character of such a transfer.[18] It is reasonable to assume that the counterion migration also takes place within the one and the same ion pair. This assumption is fully justified by the high dilution of the solutions (ca. 10^{-5} mol/dm^3) and is clearly supported by the finding that an increase in the concentration of $\mathbf{1}^{-}\cdot$ and its counterion does not change the type of the spectrum. Molecular models indicate that the migration of the cation between the preferred sites in the proximities of the two oxygen atoms is facilitated by the cis arrangement of the methyl groups.

The rates, $10^6\ s^{-1} < k < 10^9\ s^{-1}$, of the interconversion $\mathbf{1a}^{-}\cdot \rightleftharpoons \mathbf{1b}^{-}\cdot$, which have been found for the type *I* spectra with the solvent dimethylformamide, compare favorably with the analogous values reported for the *intra*molecular electron transfer in the ion pairs of the radical anions containing two phthalimide π systems separated by an alkyl chain.[19] The activation enthalpy, $\Delta H^{\ddagger} = 26$ kJ/mol, can be considered as the energy needed to separate the counterion (Et_4N^+) from the radical anion in the ion pairs of $\mathbf{1a}^{-}\cdot$ or $\mathbf{1b}^{-}\cdot$. Since in DMF such ion pairs are loose, this value represents rather a lower limit to $\Delta H^{\ddagger}$, and considerably higher activation enthalpies are expected with ethereal solvents where tight ion pairs are formed between the radical anion and its counterion. The positive sign of the activation entropy, $\Delta S^{\ddagger} = 23$ J/(mol K), means that, even in DMF, the gain achieved by separating the cation from the radical anion exceeds the loss caused by the increased solvation of the ions by the molecules of the solvent.

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Calculated Infrared and Raman Spectra of the ^1A_g Ground States of Rectangular Cyclobutadiene and Tetradeuteriocyclobutadiene

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Abstract: The IR fundamental frequencies were calculated for the rectangular ^1A_g ground states of cyclobutadiene and tetradeuteriocyclobutadiene using a single configuration SCF STO-4G basis and were found to be in good agreement with those observed experimentally for cyclobutadiene by Masamune and co-workers and with the previous calculations of Kollmar and Staemmler. Calculated IR intensities and Raman frequencies were also reported.

The observed IR spectrum of cyclobutadiene has been interpreted as indicating a square-planar structure for the molecule, originally because the number of bands agreed with the number expected,[1] and later because the frequencies also agreed with those calculated theoretically for a square ground state.[2] However, several good ab initio calculations of the ge-

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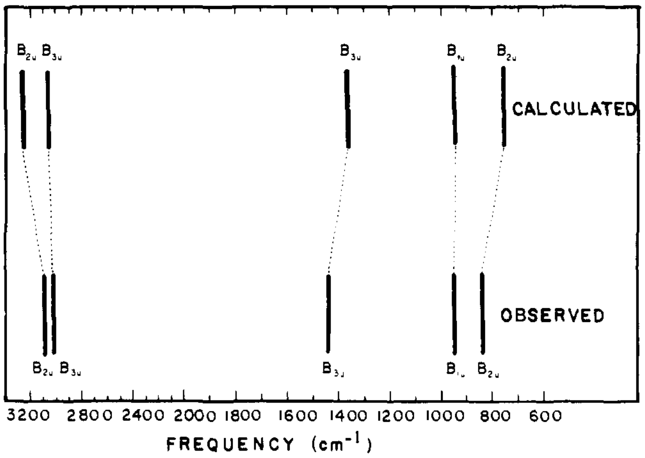

Figure 1. Comparison of calculated and experimental (ref 10 and 11) IR fundamental frequencies of ethylene.

Table I. Calculated Raman Frequencies of Ethylene, Rectangular Cyclobutadiene, and Rectangular Tetradeuteriocyclobutadiene[a]

symmetry	frequency, cm^{-1}		
	ethylene	C_4H_4	C_4D_4
A_g	1298	886	648
	1791	1178	1124
	3097	1785	1632
		3239	2592
B_{1g}		885	771
B_{2g}	925	678	538
B_{3g}	1172	915	840
	3254	1091	912
		3112	2287

[a] In addition to these and the vibrations shown in Figures 1, 2, and 4, there are calculated A_u fundamental frequencies at 563 and 869 cm^{-1} for C_4H_4, 464 and 744 cm^{-1} for C_4D_4, and 1078 cm^{-1} for ethylene which are neither IR nor Raman active.

ometry all agree in predicting a rectangular ground state instead.[3-5] To decide whether or not the observed IR spectrum might be consistent with that of a rectangular ground state, we have calculated the vibrational frequencies of this geometry by an ab initio SCF method.

As our calculations were being completed, two quite relevant papers appeared. First, Kollmar and Staemmler published a very similar calculation of the cyclobutadiene IR spectrum.[6] We report here only those of our results which supplement theirs, and refer the reader to their paper for more details of the problem. Second, Masamune and co-workers[7] subsequently presented a new Fourier transform IR spectrum of cyclobutadiene and concluded that the molecule is not square, but perhaps rectangular. We shall compare our computed spectrum with their new observations.

Like Kollmar and Staemmler we first tested the adequacy of our basis set by computing the vibrational frequencies of ethylene. The geometry of ethylene was optimized with a single configuration minimal STO-4G basis[8] to give a best total energy of −77.520 148 47 au at a C-C bond length of 1.3660 Å, a C-H length of 1.1680 Å, and an H C-H angle of 116.34°. Symmetry-adapted and mass-weighted combinations of Cartesian displacements of 0.01 au on each atom were used to approximate the elements of the force constant matrix. Using current values of the fundamental constants[9] the eigenvalues ϵ_i (in mass-weighted atomic units) of this matrix are related to the reciprocal wavelengths $1/\lambda_i$ (cm^{-1}) of the fundamental frequencies by

$$1/\lambda_i = 5140.4945\sqrt{\epsilon_i} \qquad (1)$$

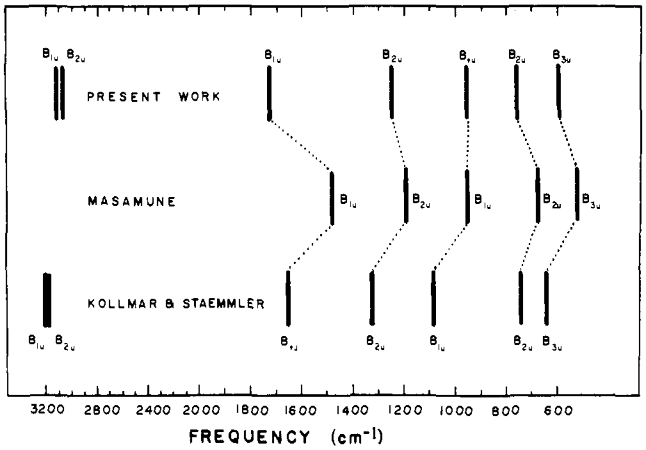

Figure 2. Comparison of cyclobutadiene IR fundamental frequencies from our calculations, those of Kollmar and Staemmler (ref 6), and the experimental values of Masamune (ref 7).

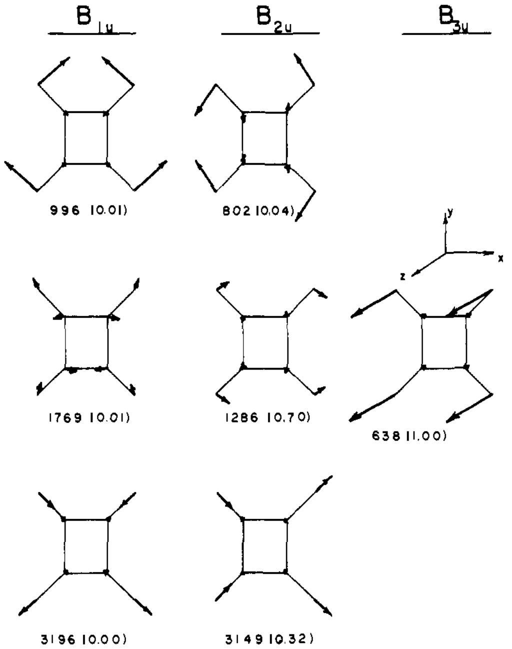

Figure 3. Calculated displacements at the classical turning points in the vibrational ground states of the IR-active normal modes of cyclobutadiene. Motions in the B_{1u} and B_{2u} modes are in the plane of the drawing; those in the B_{3u} mode are perpendicular to this plane and are shown in oblique projection. In all cases displacements are magnified by a factor of 150 compared to the scale of the undistorted molecule. Calculated frequencies (cm^{-1}) are shown below the drawings with calculated relative intensities in parentheses.

Calculated IR frequencies for ethylene are compared with experimental[10,11] in Figure 1, and satisfactory qualitative agreement is seen; in particular the symmetry of each band[12] is correct. Equally good agreement was obtained between experiment and our calculated Raman frequencies (Table I).

Using the same basis set, the optimum geometry obtained for cyclobutadiene was rectangular with a total energy of −152.694 709 62 au and C—C = 1.6297 Å, C=C = 1.3740 Å, C—H = 1.1713 Å, and the C=C—H angle = 135.75°. Again using 0.01-au Cartesian displacements to compute the force constant matrix led to the calculated IR frequencies compared in Figure 2 with those of Kollmar and Staemmler and with the experimental numbers of Masamune. We, like Masamune, have used a right-handed coordinate system in which the x axis is perpendicular to the molecular plane and

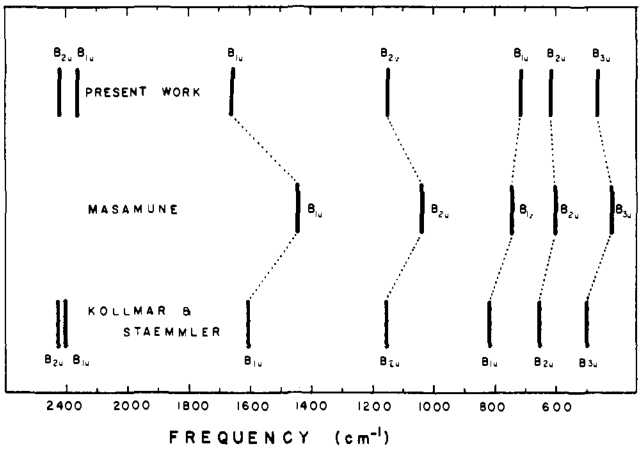

Figure 4. Comparison of calculated and experimental IR fundamental frequencies of tetradeuteriocyclobutadiene.

in which the z axis passes through the short side of the rectangle. Interchanging Kollmar and Staemmler's B_{1u} and B_{3u} symmetry designations brings their notation into agreement with this system. Figure 3 shows Cartesian displacements at the classical turning points of the calculated IR-active normal modes, together with calculated relative integrated band intensities.

Our calculated frequencies, those of Kollmar and Staemmler, and Masamune's experimental spectrum all agree in a reasonable qualitative way. Although Masamune reported no absorption corresponding to our predicted B_{1u} and B_{2u} lines near 3200 cm^{-1}, and the latter is calculated to be fairly intense, various components of the reaction mixture all absorb too strongly in this region to separate out these cyclobutadiene lines.[13] The most intense absorption is calculated to be the B_{3u} out of plane CH band, in agreement with Masamune's observation. The observed B_{2u} absorption at 1240 cm^{-1} is in agreement with our calculated line at 1286 cm^{-1}. As Figure 3 shows, and as Masamune concluded from the isotopic shift in C_4D_4, this vibration contains considerable in-plane CH bending and is not primarily a CC stretch, contrary to earlier experimental assignments. The CC stretch is the new and weaker B_{1u} band observed by Masamune at 1523 cm^{-1}. Our calculated frequency at 1769 cm^{-1} is in poor agreement, but Figure 3 does show this normal mode to be a C=C stretch with a low computed relative intensity.

The nine calculated Raman frequencies are listed in Table I. The 886-cm^{-1} A_g vibration is of special interest since motion in this normal mode would interconvert the two equivalent rectangular forms of cyclobutadiene. However, in the ground-state vibration the motion does not proceed far toward interconversion. At the classical turning point, the long bond has shortened only from 1.6297 Å to 1.5847 Å and the short bond lengthened from 1.3740 Å to 1.3900 Å. In accord with this is the fact that this ground vibrational level lies only 1.3 kcal above the potential minimum while the energy of the square singlet, which is presumably the transition state in rectangle–rectangle interconversion, is 14 kcal above this minimum.[3]

Calculated IR frequencies for rectangular tetradeuteriocyclobutadiene are compared to experimental in Figure 4, and again agreement is satisfactory. Calculated Raman frequencies for C_4D_4 are listed in Table I.

We conclude that theory and observation of the IR spectrum concur in favoring a rectangular over a square geometry for the ground state of cyclobutadiene, but we end with a caution. Ideally one would like to compute the molecular potential surfaces to sufficient accuracy so that one would know the vibrations to be accurate to perhaps ±10 cm^{-1}. This is currently impossible. Our cyclobutadiene electronic energy is about 1 au above the better result of Jafri and Newton,[5] which is in turn an unknown distance above the exact energy. Since 1 au $\approx$220 000 cm^{-1}, our absolute error exceeds by nearly two orders of magnitude the entire range of the IR spectrum of Figure 2. What one hopes is that the approximate surfaces will parallel the true and so give good vibrational levels. They appear to do so to an extent amazing in view of their absolute errors.

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