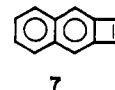


Å) or stretching vibrational frequency ($\sim 1700 \text{ cm}^{-1}$). Moreover, the electronic wave function for singlet cyclobutyne shows some signs of biradical character. For example, the coefficient of the second configuration in the two-configuration SCF wave function is 0.41, suggesting that this second configuration is 16.4% of the wave function. For an idealized diradical, of course, this contribution would be precisely 50%, while for the normal closed-shell vinylacetylene (4) molecule (an isomer of cyclobutyne) the second configuration amounts to only 2.9% of the TCSCF wave function.

Since the small dipole moment ($0.132 \pm 0.001 \text{ D}^{28}$) of cyclobutene has been a matter of some discussion,^{13,35} it is worth noting that the dipole moments of both singlet ($\text{DZ}+d \text{ TCSCF } \mu = 2.37 \text{ D}$) and triplet ($\text{DZ}+d \text{ SCF } \mu = 1.86 \text{ D}$) cyclobutyne are substantial. In both cases the triple-bond end of the molecule is of negative polarity. Despite these significant dipole moments, the acetylenic carbon atom Mulliken populations are modest, 6.08 for singlet and 6.03 Mulliken electrons for triplet cyclobutyne. Since the doubly occupied $7a_1$ orbital in (3) is a part of a $\text{C}\equiv\text{C}$ triple bond in singlet cyclobutyne, it is not surprising that removal of an electron from this orbital (into the $5b_2$ orbital to yield triplet cyclobutyne) would decrease the electron density in this part of the molecule and hence the magnitude of the dipole moment.

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Cyclobutyne is not going to be an easy molecule to make. It is predicted to lie $\sim 78 \text{ kcal}$ above vinylacetylene, which appears to be the absolute minimum among C_4H_4 molecules. Nevertheless there is a very recent unpublished report of the very tentative identification³⁶ of the substituted molecule



It is hoped that the present theoretical study will provide further impetus to the experimental characterization of the frontiers of cycloalkyne chemistry.

Acknowledgment. We thank Professors Orville L. Chapman and Michael J. S. Dewar and Dr. Michel Dupuis for helpful discussions. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The Berkeley minicomputer for theoretical chemistry is supported by the National Science Foundation, Grant CHE80-09320.

Registry No. Cyclobutyne, 1191-94-2.

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Ab Initio Second-Order Møller-Plesset Calculation of the Vibrational Spectra of Cyclobutadiene and Its Isotopic Derivatives

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Abstract: Optimum geometry, IR frequencies, and intensities were calculated for cyclobutadiene and seven isotopically substituted derivatives with use of SCF/6-31G* and MP2/6-31G* wave functions. Theoretical spectra agree well with experimental where they are known, except that a result that had been interpreted as showing cyclobutadiene to be square is reinterpreted in terms of a mixture of two nonequivalent dideuterio rectangular structures.

The question of the ground-state structure of cyclobutadiene, the smallest member of the antiaromatic $4n$ annulenes, has been of great interest to both the experimental and theoretical chemist over the past decade.¹ While benzene possesses significant thermodynamic cyclic stabilization and is considered the archetype of aromatic compounds, cyclobutadiene is computed to have significant cyclic *destabilization* and occupies an analogous position among antiaromatics. Benzene apparently is able to maximize its cyclic stabilization by adopting a regular hexagonal structure with equal CC bond lengths. It now appears that cyclobutadiene, on the other hand, in order to minimize the cyclic destabilization of its π electrons adopts a rectangular structure with strong bond alternation. In fact extensive ab initio calculations indicate cyclobutadiene should have CC single bonds that are even longer than a normal CC bond between two tetrahedral carbons.^{2,3}

Until recently the experimental evidence for the structure of cyclobutadiene was based almost entirely on the IR spectrum. This

spectrum and those of several isotopic derivatives were originally used as evidence for a square structure.⁴⁻⁶ However, Masamune concluded from an improved experimental IR spectrum that cyclobutadiene is not square but most likely rectangular.⁷ This is supported by the similarity found between Masamune's and the computed IR spectrum of rectangular cyclobutadiene.^{8,9} An earlier experiment of Chapman⁶ seemed to support the square structure since two dideuterio- α -pyrones that should have given distinct rectangular cyclobutadienes gave instead the same product.

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Table I. Calculated Optimum Geometries and Energies^a

	4-31G ^b	SCF/6-31G*	MP2/6-31G*
C-C	1.581	1.568	1.567
C=C	1.323	1.318	1.346
C-H	1.066	1.073	1.084
∠HCC ^c	134.7	134.8	134.9
energy	-153.409 300	-153.641 117	-154.137 722 ^d

^a Bond lengths are in angstroms, angles in degrees, and energies in atomic units. ^b Reference 10. ^c Exterior angle between the C-H and the longer C-C bonds (see Figure 1). ^d Inner shells and the four highest virtual MO's were not used in computing the correlation energy.

But we have now shown, by comparing theoretical IR spectra with those reported by Chapman, that he most likely had an equal mixture of rectangular [1,2-²H₂]- and [1,4-²H₂]cyclobutadienes in both cases.¹⁰

Hence these experimental and calculated IR spectra have played the central role in the verification of the rectangular structure of cyclobutadiene. To date the computed spectra have all been obtained at the SCF level with small- and medium-sized basis sets. The errors in computed force constants are well known,¹¹ and these are such that computed spectra are typically in error by 200–400 cm⁻¹. Nevertheless, when the computed spectrum of cyclobutadiene including the computed intensities is compared to the observed spectrum a striking similarity between the two is apparent.⁹ Due to the importance of IR spectra in resolving the structure of cyclobutadiene, we felt that it was highly desirable to go beyond the SCF level and obtain computed spectra with a wave function including electron correlation. We report here computation at the level of the second-order perturbation theory with Møller–Plesset partitioning of the Hamiltonian¹² (hereafter referred to as MP2) with use of the 6-31G* basis set. The force constants so obtained were used for the calculation of vibrational spectra of cyclobutadiene and several of its known isotopically labeled derivatives as well as those of a number of unknown labeled derivatives. Pople has previously shown that at this level there is excellent agreement between the computed and observed IR spectra of ethylene.¹³ In fact at this level, the error in computed frequencies is now reduced to the point that for most modes anharmonicity plays a significant role in the remaining differences.

Computational Details

Molecular-Orbital Calculations. Two standard basis sets developed by Pople's group,¹⁴ 4-31G and 6-31G*, were used. All 4-31G calculations reported in this paper originate from our earlier work.¹⁰ 6-31G* wave functions were used for the MP2 calculations. The four inner MO's of lowest energy and the four virtual MO's of highest energy are expected to make little contribution to bonding properties and hence were excluded from the computation of the correlation energy.

Geometry Optimization. Starting values for CC bond lengths in the MP2/6-31G* optimization were those Kollmar and Staemmler had obtained with use of the CEPA method.⁸ For CH bond lengths and ∠HCC angles starting values were obtained from optimization at the SCF/6-31G* level. To begin the optimization energies were computed for eight structures corresponding to plus and minus distortions along totally symmetric internal coordinates (see below) of the initial structure. From these energies the gradient of the energy and the diagonal force constants were evaluated numerically. The matrix of force constants was then completed with off-diagonal force constants taken from the 4-31G calculations and used, together with the energy gradient, in the first step of the force-relaxation method.¹⁵ At the resulting

Table II. The Three Theoretical Approaches Used in the Evaluation of Harmonic Vibrational Frequencies

	ref geometry	force constants	
		diagonal	coupling
4-31G	optimum 4-31G	4-31G	4-31G
SCF/6-31G*	optimum MP2/6-31G*	SCF/6-31G*	4-31G ^a
MP2/6-31G*	optimum MP2/6-31G*	MP2/6-31G*	4-31G ^b

^a The coupling constant $F_{11,13}$ is computed at the SCF/6-31G* level (see text). ^b The coupling constant $F_{11,13}$ is computed at the MP2/6-31G* level (see text).

Table III. Symmetry Coordinates^a

species	coordinate
A _g	$S_1 = 2^{-1/2}(r_1 + r_2)$
	$S_2 = 2^{-1/2}(d_1 + d_2)$
	$S_3 = 1/2(t_1 + t_2 + t_3 + t_4)$
	$S_4 = 1/2(\beta_1 + \beta_2 + \beta_3 + \beta_4)$
B _{3g}	$S_5 = 1/2(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4)$
	$S_6 = 1/2(t_1 - t_2 + t_3 - t_4)$
	$S_7 = 1/2(\beta_1 - \beta_2 + \beta_3 - \beta_4)$
B _{2u}	$S_8 = D(4 + 2D^2)^{-1/2}[r_1 - r_2 - D^{-1}(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4)]$
	$S_9 = 1/2(t_1 + t_2 - t_3 - t_4)$
B _{1u}	$S_{10} = 1/2(\beta_1 + \beta_2 - \beta_3 - \beta_4)$
	$S_{11} = R(4 + 2R^2)^{-1/2}[d_1 - d_2 + R^{-1}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4)]$
	$S_{12} = 1/2(t_1 - t_2 - t_3 + t_4)$
A _u	$S_{13} = 1/2(\beta_1 - \beta_2 - \beta_3 + \beta_4)$
	$S_{14} = 1/2(\tau_1 - \tau_2 + \tau_3 - \tau_4)$
B _{3u}	$S_{15} = 1/2(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4)$
	$S_{16} = 1/2(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)$
B _{1g}	$S_{17} = 1/2(\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4)$
	$S_{18} = 1/2(\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4)$

^a See Figure 1 for definitions of internal coordinates. D and R in coordinates 8 and 11 are respectively the equilibrium lengths of the shorter and longer CC bonds.

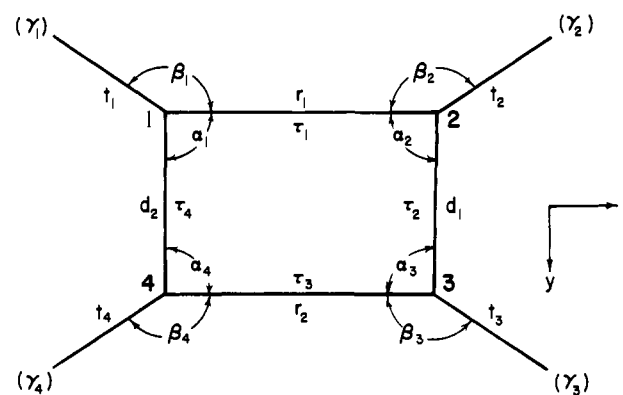


Figure 1. Definition of internal coordinates. γ_1 , γ_2 , γ_3 , and γ_4 are out-of-plane bending angles. τ_1 , τ_2 , τ_3 , and τ_4 are torsions τ_{4123} , τ_{2341} , and τ_{3412} .

geometry both the energy gradient and the diagonal force constants were updated and used in a second cycle that gave the final optimum MP2 geometry. The absolute values of the gradient components in the second step suggested that bond lengths are significant to three decimal places and bond angles to one decimal place. The final geometries are presented in Table I.

Vibrational Frequencies. The matrix of force constants was evaluated at three different levels of sophistication: 4-31G, SCF/6-31G*, and MP2/6-31G*. As seen in Table II, the three approaches differ in the reference geometry and in the set of diagonal force constants used. The set of coupling force constants, however, is the same in all three approaches and its use was motivated by experience accumulated¹⁶ in the literature where it has been found that coupling constants are affected rather little by electron correlation. Therefore the 4-31G set of coupling

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Table IV. Calculated Diagonal Force Constants^a

species	constant	4-31G	SCF/ 6-31G*	MP2/ 6-31G*
A _g	F ₁₁	4.260	4.568	4.319
	F ₂₂	11.259	9.858	9.295
	F ₃₃	6.448	6.022	5.905
	F ₄₄	0.892	0.883	0.798
B _{3g}	F ₅₅	2.144	1.863	1.758
	F ₆₆	6.414	5.975	5.885
	F ₇₇	0.866	0.833	0.723
	F ₈₈	1.302	1.563	1.344
B _{2u}	F ₉₉	6.430	5.988	5.882
	F _{10,10}	1.005	0.977	0.878
	F _{11,11}	7.391	5.499	5.159
	F _{12,12}	6.435	5.991	5.888
A _u	F _{13,13}	0.964	0.949	0.851
	F _{14,14}	0.631	1.670	1.208
	F _{15,15}	0.569	0.500	0.409
	F _{16,16}	0.338	0.288	0.211
B _{3u}	F _{17,17}	0.541	0.468	0.365
B _{2g}	F _{18,18}	0.314	0.248	0.168

^a Stretching force constants are in mdyn Å⁻¹ and bending and wagging force constants in mdyn Å rad⁻².

constants was used throughout with one exception. It is known that stretching–bending coupling constants are particularly sensitive to basis set,¹⁶ and we found this to be true in our case. The basis-set effect was large for coordinate 11 (double-bond stretching), and therefore the F_{11,13} constant was recalculated at both the SCF/6-31G* and MP2/6-31G* levels.

The reference geometries used in the 4-31G and MP2/6-31G* calculations were the respective optimum geometries. The optimum MP2/6-31G* geometry was also used for the evaluation of force constants at the SCF/6-31G* level in order to avoid additional time-consuming SCF/6-31G* runs.

The set of coordinates used is defined by Figure 1 and Table III. The redundancy in B_{2u} and B_{1u} coordinates was eliminated as suggested by Cyvin et al.¹⁷ For the B_{2u} species one constructs first the coordinates

$$S' = 2^{-1/2}(r_1 - r_2) \text{ and } S'' = 1/2(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4) \quad (1)$$

An orthogonal transformation of S' and S'' to give the zero coordinate

$$[2/(2 + D^2)]^{1/2}S' + D(2 + D^2)^{-1/2}S'' = 0 \quad (2)$$

also yields the final symmetry coordinate

$$S = D(2 + D^2)^{-1/2}S' - [2/(2 + D^2)]^{1/2}S'' \quad (3)$$

where D is the equilibrium C=C bond length. Similarly for the B_{1u} coordinate we obtain

$$S' = 2^{-1/2}(d_1 - d_2); S'' = 1/2(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4) \quad (4)$$

and

$$[2/(2 + R^2)]^{1/2}S' - R(2 + R^2)^{-1/2}S'' = 0 \quad (5)$$

$$S = R(2 + R^2)^{-1/2}S' + [2/(2 + R^2)]^{1/2}S'' \quad (6)$$

where R is the equilibrium C–C bond length. Diagonal force constants for the A_g species were evaluated numerically from energies at +ΔS_i and –ΔS_i for each coordinate. The diagonal force constants for the other coordinates were obtained from one-sided distortions since positive and negative distortions are equivalent. Distorted structures were generated by means of the BMAT link of the program TEXAS,¹⁸ and they therefore corresponded to displacements from the reference geometry along exact curvilinear coordinates. The displacements ±ΔS_i were chosen such that the bond-length distortions were ±0.05 au and the changes in angles

Table V. 4-31G Coupling Force Constants^a

species	constant	species	constant
A _g	F ₁₂ = 0.068	B _{2u}	F ₈₉ = 0.098
	F ₁₃ = 0.015		F _{8,10} = –0.342
	F ₁₄ = 0.061		F _{9,10} = –0.040
	F ₂₃ = 0.009	B _{1u}	F _{11,12} = –0.459
	F ₂₄ = –0.040		F _{11,13} = 0.886 ^b
B _{3g}	F ₃₄ = 0.073		F _{12,13} = –0.064
	F ₅₆ = –0.344	A _u	F _{14,15} = 0.299
	F ₅₇ = 0.449		
	F ₆₇ = –0.062		

^a Reference 10; stretching–stretching force constants are in mdyn Å⁻¹, bending–bending force constants in mdyn Å rad⁻², and stretching–bending force constants in mdyn rad⁻¹. ^b The SCF/6-31G* and MP2/6-31G* values are 0.446 and 0.450, respectively.

were ±3°. Calculated diagonal force constants are presented in Table IV. In Table V we present coupling constants that were obtained from our earlier 4-31G calculations.¹⁰ Vibrational wavenumbers were obtained by the standard GF matrix method.

Infrared Intensity. Integrated infrared band intensity for the kth fundamental

$$A_k = \frac{1}{cL} \int \log(I/I_0) dv \quad (7)$$

where c is concentration (mol L⁻¹) and L is the optical path (cm) was approximated by

$$A_k = \frac{\pi N_A}{3000c^2 \times 2.302581} |\partial\mu/\partial Q_k|^2 \quad (8)$$

where N_A is Avogadro's number (mol⁻¹), c is the light velocity (cm s⁻¹), and ∂μ/∂Q_k is the dipole-moment derivative with respect to the kth normal coordinate Q_k. The derivatives ∂μ/∂Q_k are expressed in D Å⁻¹ U^{-1/2}, U being the unified atomic unit M(¹²C)/12 = 1.660565 × 10⁻²⁷ kg. The intensity A is therefore expressed by (8) in km mol⁻¹. The derivatives of the dipole moment were obtained from SCF/6-31G* calculations and used in both SCF/6-31G* and MP2/6-31G* intensity calculations. Thus the intensity changes seen on going from SCF/6-31G* to MP2/6-31G* result from changes in force constants that lead to different normal modes. Changes in dipole-moment derivatives along a fixed direction are not taken into account. It was not thought that the additional computational effort required for a consistent MP2 treatment of the intensities would be warranted. If SCF predictions for relative intensities are compared with experiment or with results from correlated wave functions, the agreement is better than one might have expected from a consideration of the absolute intensities. For example, power series expansions of μ given by Rosenberg, Ermler, and Shavitt¹⁹ show that for the water molecule the values of |∂μ/∂Q_k|² are in the ratio 1:0.014:0.604 at the SCF level and 1:0.043:0.748 at the CI-SD level. Similarly, Botschwina²⁰ has reported for HCCC relative intensities of 1:0.020:0.636:0.001:0.001:0.382 with an SCF wave function and 1:0.016:0.577:0.001:0.001:0.364 with correlation included by the CEPA method. Even the relatively modest 4-31G basis gives SCF intensities for ethylene²¹ in the ratio 1:0.298:0.005:0.179:0.064 in comparison with experimental values of 1:0.312:0.007:0.169:0.122.

Discussion

Optimized Geometries. In the course of obtaining the vibrational spectra of cyclobutadiene the optimized geometry was determined, within the constraint of D_{2h} symmetry, at three levels of sophistication. Two were with an SCF wave function (4-31G and 6-31G*) and the third with a correlated wave function (MP2/

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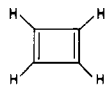
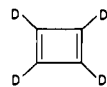
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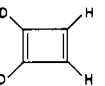
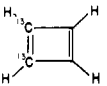
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Table VI. Vibrational Frequencies in cm^{-1} of Cyclobutadiene and $[1,2,3,4-^2\text{H}_4]$ Cyclobutadiene^d

symmetry ^a					
		6-31G*	MP2/6-31G*	6-31G*	MP2/6-31G*
B _{1u}	C-H(D) bend, in-plane	1129 (1)	1082 (1)	824 (0)	787 (0)
	C=C stretch	1699 (207)	1620 (203)	1629 (268)	1562 (254)
B _{2u}	C-H(D) stretch	3300 (1101)	3270 (1106)	2449 (437)	2422 (451)
	ring deformation ^b	793 (512)	721 (509)	661 (537)	604 (515)
	C-H(D) bend, in-plane ^c	1383 (1498)	1319 (1502)	1169 (506)	1113 (529)
B _{3u}	C-H(D) stretch	3306 (514)	3275 (513)	2434 (274)	2411 (272)
	C-H(D) bend, out-of-plane	669 (6891)	572 (6891)	491 (3715)	420 (3715)
A _g	C-H(D) bend, in-plane ^c	1022	984	766	731
	C-H(D) bend, in-plane ^c	1199	1153	1100	1067
	C=C stretch	1657	1606	1599	1552
	C-H(D) stretch	3344	3310	2522	2493
B _{1g}	C-H(D) bend, out-of-plane	963	851	770	680
B _{2g}	C-H(D) bend, out-of-plane	687	565	542	446
B _{3g}	ring deformation ^b	895	848	852	797
	C-H(D) bend, in-plane	1277	1200	1026	977
A _u	C-H(D) stretch	3287	3261	2415	2395
	C-H(D) bend, out-of-plane	803	736	575	527
	ring deformation	1336	1074	1320	1060

^a Species of *g* symmetry are Raman active. The A_u vibrations are neither IR nor Raman active. ^b Strongly coupled with C-H(D) in-plane bend. ^c Strongly coupled with ring deformation. ^d IR intensities in km mol^{-1} are in parentheses.

Table VII. Vibrational Frequencies in cm^{-1} of $[1,2-^2\text{H}_2]$ - and $[1,2-^{13}\text{C}_2]$ Cyclobutadiene^{c,d}

symmetry					
		6-31G*	MP2/6-31G*	6-31G*	MP2/6-31G*
A ₁	C-H(D) bend, in-plane ^a	793 (0)	757 (0)	1012 (0)	977 (0)
	C-H bend, in-plane	1054 (1)	1018 (1)	1126 (2)	1079 (1)
	C-H bend, in-plane ^a	1173 (0)	1128 (0)	1188 (0)	1140 (0)
	C=C stretch	1609 (70)	1557 (101)	1612 (37)	1555 (69)
	C=C stretch	1682 (167)	1613 (126)	1685 (160)	1614 (124)
	C-H(D) stretch	2485 (244)	2457 (250)	3294 (1085)	3264 (1087)
	C-H stretch	3323 (526)	3291 (530)	3338 (21)	3304 (24)
	C-H(D) bend, out-of-plane	516 (2458)	434 (2089)	667 (6780)	562 (180)
B ₁	C-H bend, out-of-plane	679 (2845)	568 (3214)	684 (91)	572 (6691)
	ring deformation ^b	716 (521)	653 (504)	782 (477)	711 (479)
B ₂	ring deformation ^b	879 (14)	830 (15)	880 (8)	834 (4)
	C-H(D) bend, in-plane	1092 (57)	1032 (57)	1270 (10)	1193 (9)
	C-H bend, in-plane ^a	1341 (932)	1275 (950)	1373 (1512)	1311 (1516)
	C-H(D) stretch	2425 (138)	2403 (137)	3281 (29)	3255 (43)
	C-H stretch	3296 (259)	3268 (258)	3302 (483)	3272 (469)
	C-H(D) bend, out-of-plane	643	586	802	735
A ₂	C-H bend, out-of-plane	913	812	958	846
	ring deformation	1328	1068	1312	1055

^a Strongly coupled with ring deformation. ^b Strongly coupled with C-H(D) in-plane bend. ^c IR intensities in km mol^{-1} are in parentheses. ^d All modes are Raman active.

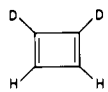
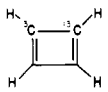
6-31G*). The geometric data in Table I show no distinct trends. While the C-C bond decreased in length with the inclusion of polarization functions on carbon at the SCF level, the addition of electron correlation had almost no effect on this particular bond length. On the other hand, the addition of polarization functions decreased the C=C length somewhat, but the addition of correlation led to a significant increase in this length (0.028 Å). This conforms to the known fact that at the Hartree-Fock limit multiple bonds may be too short by as much as 0.05 Å. The C-H bond distance showed an increase in length as the wave function was improved. All three levels gave very nearly the same value for the $\angle\text{HCC}$. Finally we note that the C-C and C=C lengths we obtained at the MP2/6-31G* level agree well with those found by Kollmar and Staemmler using the CEPA method,⁸ 1.57 and 1.34 Å, respectively. They did not optimize the C-H length or the $\angle\text{HCC}$ angle at that level.

Force Constants. The entries in Table IV show the anticipated trend for most force constants: on going from 4-31G to SCF/6-31G* and MP2/6-31G* the force constants became smaller in absolute value. The opposite trend with some force constants may

be explained as follows. It is well-known that a good description of multiple bonds requires more than two p-type functions in the valence shell and that potential curves for these bonds are poor unless a highly correlated wave function is used. Accordingly, the 4-31G basis greatly underestimates π bonding in the four-membered ring of cyclobutadiene. The C-C bond is too long (see Table I) and the C-C stretching force constants are too low (see F_{11} and F_{88} in Table IV). On improving the wave function the conjugation of the two bonds becomes more pronounced, and, as can be seen from the skeletal torsional force constant $F_{14,14}$ in Table IV, the skeleton more rigid. Since the 6-31G* basis set is not large enough to give a quantitative account of π bonding, the MP2/6-31G* vibrational frequencies for ring stretchings are, in contrast to other modes, still in rather large disagreement with experiment. Similar trends were found in the MP2 treatment of ethylene.¹³

Vibrational Spectra. In Table VI are listed the calculated vibrational frequencies and IR intensities at the 6-31G* and MP2/6-31G* levels, and in Figure 2 these theoretical IR spectra are plotted along with those obtained with use of STO-4G⁹ and 4-31G¹⁰ basis sets and that obtained experimentally by Masa-

Table VIII. Vibrational Frequencies in cm^{-1} of $[1,4\text{-}^2\text{H}_2]$ - and $[1,4\text{-}^{13}\text{C}_2]$ Cyclobutadiene^{c,d}

					
symmetry		6-31G*	MP2/6-31G*	6-31G*	MP2/6-31G*
A ₁	ring deformation ^a	691 (456)	635 (462)	782 (481)	712 (481)
	C-H(D) bend, in-plane ^b	917 (39)	869 (22)	1013 (4)	977 (3)
	C-H(D) bend, in-plane ^b	1118 (35)	1083 (43)	1187 (6)	1140 (7)
	C-H bend, in plane ^b	1319 (990)	1259 (995)	1373 (1514)	1310 (1515)
	C=C stretch	1627 (5)	1579 (4)	1627 (2)	1578 (2)
	C-H(D) stretch	2479 (148)	2452 (146)	3300 (499)	3269 (496)
B ₁	C-H stretch	3326 (248)	3293 (248)	3338 (13)	3304 (15)
	C-H(D) bend, out-of-plane	553 (4355)	475 (4419)	668 (6869)	571 (6869)
B ₂	C-H bend, out-of-plane	894 (948)	788 (884)	958 (1)	846 (1)
	ring deformation ^a	865 (0)	808 (0)	879 (0)	833 (0)
	C-H(D) bend, in-plane	912 (0)	879 (0)	1127 (2)	1080 (1)
	C-H bend, in plane	1224 (1)	1158 (0)	1270 (0)	1193 (0)
	C=C stretch	1665 (238)	1591 (229)	1670 (197)	1592 (193)
	C-H(D) stretch	2433 (210)	2409 (219)	3280 (121)	3254 (192)
A ₂	C-H stretch	3293 (558)	3265 (559)	3296 (985)	3267 (919)
	C-H(D) bend, out-of-plane	553	467	683	562
	C-H bend, out-of-plane	752	673	802	735
	ring deformation	1328	1066	1312	1055

^a Strongly coupled with C-H(D) in-plane bend. ^b Strongly coupled with ring deformation. ^c IR intensities in km mol^{-1} are in parentheses. ^d All modes are Raman active.

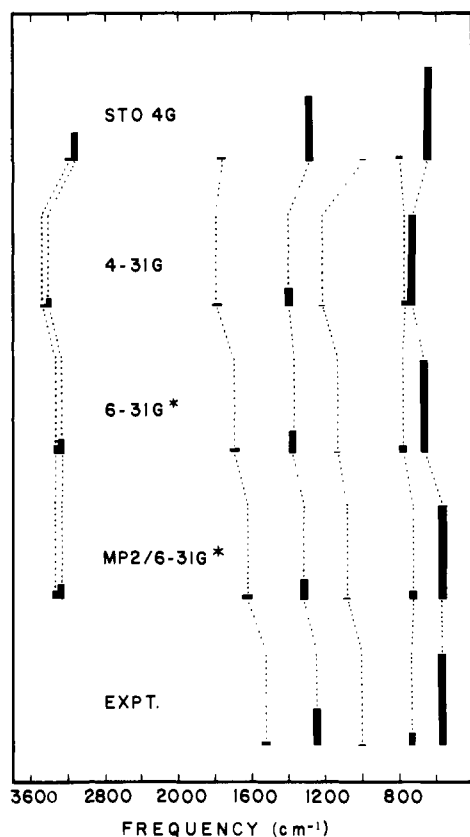
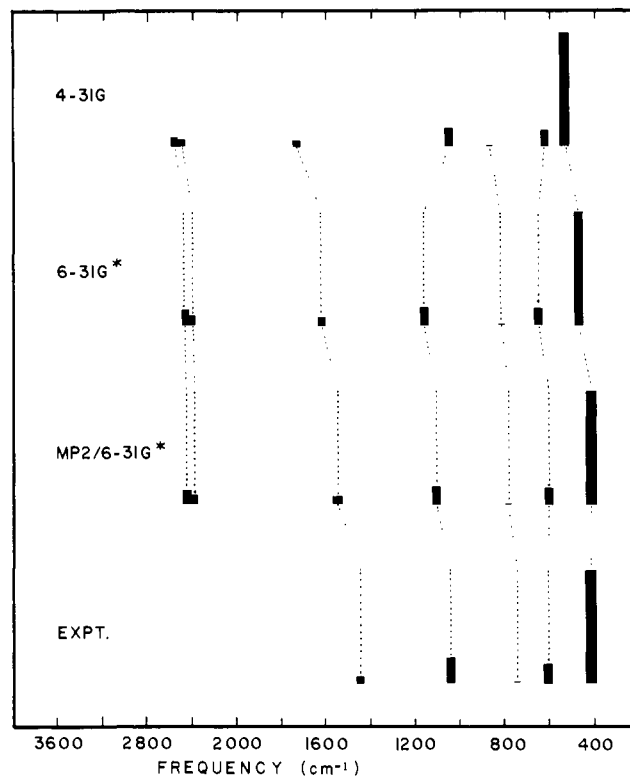


Figure 2. Calculated and experimental IR spectra of cyclobutadiene.

Figure 2. Calculated and experimental IR spectra of cyclobutadiene. While the frequencies computed with the STO-4G basis are in reasonable agreement with experiment except for the C=C stretch, it appears that the intensities are in rather poor agreement. On going to the 4-31G basis there is a significant improvement in the calculated intensities, but the calculated line positions are somewhat worse. Further improvement is obtained by adding polarization functions (6-31G*). Finally the computed spectrum obtained with the correlated wave function is even further improved with the greatest apparent error in the calculated frequency of the C=C stretch as noted above.

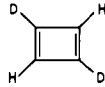
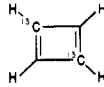
The calculated frequencies and IR intensities of the tetra-deuteriocyclobutadiene are also given in Table VI, and these are

Figure 3. Calculated and experimental IR spectra of $[1,2,3,4\text{-}^2\text{H}_4]$ -cyclobutadiene.

plotted in Figure 3. A comparison of Figure 2 with Figure 3 indicates very similar trends as the basis set is improved, and agreement of the correlated vibrational frequencies with experiment is virtually the same as in the case of the parent system.

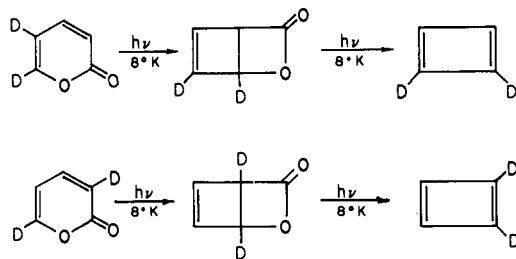
Tables VII and VIII contain the vibrational spectra of $[1,2\text{-}^2\text{H}_2]$ - and $[1,4\text{-}^2\text{H}_2]$ cyclobutadienes. These are of particular interest since Chapman⁶ had earlier prepared a dideuteriocyclobutadiene which he concluded had a square structure. However, we have shown¹⁰ that at the 4-31G level the computed IR spectrum of a 1:1 mixture of the 1,2- and 1,4-dideuteriocyclobutadienes has a pattern of frequencies that closely resembles that of the observed spectrum.^{6,18} A plot of the theoretical spectra for this mixture along with the observed spectrum is shown in Figure 4. Note that at the MP2/6-31G* level there is excellent agreement between

Table IX. Vibrational Frequencies in cm^{-1} of $[1,3\text{-}^2\text{H}_2]$ - and $[1,3\text{-}^{13}\text{C}_2]$ Cyclobutadiene^{d,e}

						
symmetry		6-31G*	MP2/6-31G*	6-31G*	MP2/6-31G*	
A _u	C-H(D) bend, out-of-plane	519 (3117)	451 (3479)	668 (6868)	571 (6868)	
	C-H bend, out-of-plane	751 (2156)	678 (1790)	802 (1)	735 (0)	
	ring deformation ^a	1328 (30)	1067 (33)	1312 (1)	1055 (2)	
B _u	ring deformation ^b	702 (495)	643 (491)	783 (484)	712 (483)	
	C-H(D) bend, in-plane	963 (6)	915 (1)	1127 (2)	1080 (1)	
	C-H bend, in plane	1314 (1004)	1255 (1019)	1373 (1521)	1310 (1523)	
	C=C stretch	1665 (255)	1591 (241)	1670 (198)	1592 (195)	
	C-H(D) stretch	2442 (365)	2417 (370)	3292 (959)	3262 (962)	
	C-H stretch	3303 (803)	3273 (806)	3304 (660)	3273 (661)	
A _g	ring deformation ^a	837	785	878	832	
	C-H(D) bend, in-plane ^c	892	856	1013	977	
	C-H(D) bend, in-plane ^c	1107	1068	1187	1139	
	C-H bend, in plane	1234	1170	1271	1194	
	C=C stretch	1627	1579	1627	1578	
	C-H(D) stretch	2469	2444	3281	3256	
	C-H stretch	3317	3287	3338	3304	
	B _g	C-H(D) bend, out-of-plane	589	487	683	562
		C-H bend, out-of-plane	893	785	958	846

^a Strongly coupled with C-H(D) out-of-plane bend. ^b Strongly coupled with C-H(D) in-plane bend. ^c Strongly coupled with ring deformation. ^d IR intensities in km mol^{-1} are in parentheses. ^e Species of *g* symmetry are Raman active.

the calculated and experimental frequencies and intensities for the six bands observed. The bands that were seen are in fact the six most intense bands in our calculated spectrum. The two remaining bands in the lower part of the spectrum that are of reasonable intensity we calculate will appear at frequencies close to 650 cm^{-1} . These two were not reported by Chapman.⁶ However, in the experimental spectrum this is precisely where there is strong CO_2 absorption that presumably masks these two bands and prevents their observation. The suggestion that Chapman observed a mixture of 1,2- and 1,4-dideuteriocyclobutadiene is consistent with the observations of Krantz,²² who demonstrated that the bicyclic lactone precursor of cyclobutadiene could not be labeled with ^{13}C at a single specific site when $[^{13}\text{C}]\text{-}\alpha\text{-pyrone}$ was photolyzed in solid matrices. Although specific ^{13}C -labeled bicyclic lactone can be prepared in solution at conventional temperatures by photochemical means, isotopic scrambling was found in matrices and attributed to rapid opening of the starting $\alpha\text{-pyrone}$ to an aldoketene which equilibrated terminal carbon atoms. By this same mechanism the expected synthesis of pure 1,2- and 1,4-dideuteriocyclobutadiene from 2-pyrone-3,6- d_2 and 2-pyrone-5,6- d_2 , respectively



is prevented by equilibration of the two pyrones.

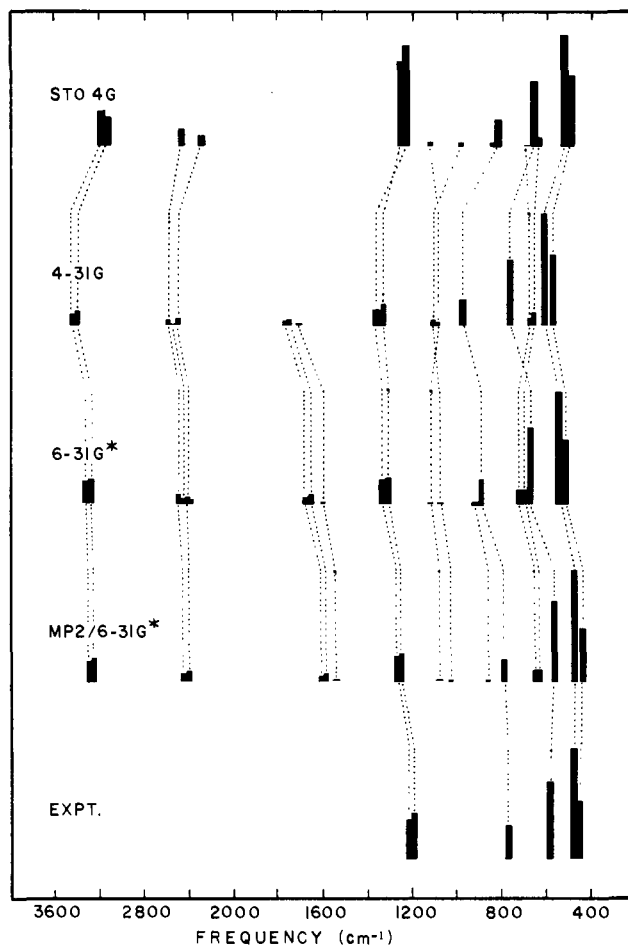
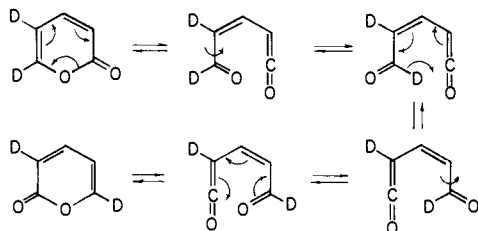


Figure 4. Calculated IR spectrum of a 1:1 mixture of $[1,2\text{-}^2\text{H}_2]$ - and $[1,4\text{-}^2\text{H}_2]$ -cyclobutadiene and the spectrum observed by Chapman on photolysis of either 2-pyrone-5,6- d_2 or 2-pyrone-3,6- d_2 .

In light of the good agreement we have found between the calculated and experimental spectra of cyclobutadiene and three of its isotopic derivatives, we conclude that cyclobutadiene is rectangular. We believe further verification of this can best be made by obtaining Raman spectra of cyclobutadiene and its derivatives for comparison with our calculated Raman spectra.

Finally, we have included calculated spectra for a number of other isotopically labeled cyclobutadienes in Tables VI-IX. While Chapman⁶ has obtained spectra of two of these, their isotopic purity is such that a comparison with our calculated spectra is not possible.

Acknowledgment. We should like to express our appreciation to the University Research Council, Vanderbilt University which provided travel funds and to the National Academy of Sciences

for its endorsement of Dr. Carsky's visit. We are especially grateful to Kaara Ettesvold at the Academy for her efforts in our behalf. We also thank Dr. Péter Pulay for making his program TEXAS available to us.

Registry No. Cyclobutadiene, 1120-53-2; [1,2,3,4-²H₄]cyclobutadiene, 56516-62-2; [1,2-²H₂]cyclobutadiene, 40522-77-8; [1,2-¹³C₂]cyclobutadiene, 84132-26-3; [1,3-²H₂]cyclobutadiene, 84132-27-4; [1,3-¹³C₂]cyclobutadiene, 84132-28-5.

Singlet Energy Transfer from the Charge-Transfer Excited State of Tris(2,2'-bipyridine)ruthenium(II) to Laser Dyes

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Abstract: Efficient singlet energy transfer from the charge-transfer (CT) excited state of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) to several laser dyes has been demonstrated. The limiting efficiencies of dye singlet state formation are 1.00 which shows the efficiency of formation of the sensitizing state of [Ru(bpy)₃]²⁺ is unity. For most of the dyes in methanol, energy transfer is shown to be predominantly by diffusion-assisted Förster transfer. For Rhodamine 101, however, energy transfer is predominantly by a contact exchange transfer. This result shows that the CT state of the sensitizer has a great deal of singlet character and should be referred to as a spin-orbit state.

Introduction

The photochemical and luminescence properties of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) and related complexes with α-dimine ligands are currently under intense investigation.¹⁻¹⁵ These systems are of fundamental interest^{1,6,7,9} and are potentially useful for solar energy conversion,^{2,4,5,8} for new laser dye systems,¹⁵ and for light intensity measuring systems.^{11,12} They exhibit a wealth of excited-state electron-transfer¹⁻⁵ and acid-base reactions.¹³

We have previously shown that very efficient singlet energy transfer (~100%) takes place from the emitting charge-transfer (CT) excited state of [Ru(bpy)₃]²⁺ to the lasing singlet state of the dye Rhodamine 101 (Rh101).¹⁴ We have also demonstrated very efficient singlet energy transfer from [Ru(bpy)₃]²⁺ to a variety of laser dyes at very low donor-acceptor concentrations (~10⁻⁵ M) in solutions in which aggregation is assisted by a suitable surfactant.¹⁵ In this study we provide experimental details of our previous work, new studies on other laser dyes in surfactant-free solutions, and interpretations of the results.

Experimental Section

[Ru(bpy)₃]Cl₂ (G. Frederick Smith Chemical Co.) was purified by three recrystallizations from water. The complex was spectroscopically pure as judged from its absorption and emission properties. Laser grade Rhodamine B chloride (RhB), Cresyl Violet acetate (CV), Oxazine 1 nitrate (OX1), and Rhodamine 101 perchlorate (Rh101) from Exciton Chemical Co. were used as received. Nile Blue A chloride (NBA) from

Eastman Kodak Chemical Co. was purified by recrystallization from chloroform and was chromatographically pure. Spectroquality solvents were used.

All energy-transfer experiments were carried out using equimolar concentrations of [Ru(bpy)₃]²⁺ and the dyes at room temperature (22 °C). Corrected optically dense excitation spectra were obtained on a microcomputerized luminescence quantum counter comparator.¹⁶ This system is an automated version of our earlier manual instrument.¹⁷ We briefly describe the instrument and its operation; full details are given elsewhere.¹⁶

The basic quantum counter comparator is shown in Figure 1A. Two 1-cm thick quantum counter cells were mounted side by side in front of the monitoring IR-sensitive photomultiplier tube (PMT) which viewed the sample luminescences from the rear face. Cutoff filters between the sample and the PMT blocked any transmitted excitation light and restricted the spectral region viewed by the PMT to the region of the [Ru(bpy)₃]²⁺ and dye emission. With filters it was not possible to discriminate against the emission contribution from [Ru(bpy)₃]²⁺. The excitation source was directed onto either the unknown sample or the reference quantum counter by an optical beam switcher. Automatic wavelength scans, signal averaging, ratio corrections, and compensation for the nonidealities of the reference quantum counter were all performed under computer control. The reference quantum counter was the previously calibrated optically dense RhB quantum counter (5 g/L in methanol).¹⁷

In operation the beam switcher alternately illustrated the reference and the sample. Automatic dark current compensation was obtained by deflecting the excitation beam onto a beam stop every cycle and reading the PMT dark current which was subtracted from both the sample and reference signals. The ratio of the sample to reference signals was then calculated. The process was repeated at 10-nm intervals over the 360-590-nm region. This ratio nearly equals the sample's relative photon yield at each wavelength except for the deviations in spectral flatness of the RhB reference counter. The data were then corrected for the small (±4%) variation of the quantum counter to yield the relative photon yield vs. wavelength.

Corrected emission spectra and photon yields were obtained on an SLM 8000 corrected spectrofluorimeter. Correction factors were obtained using a standard lamp.

The luminescence photon yields of [Ru(bpy)₃]²⁺ were determined using the standard optically dilute Parker and Rees method.¹⁸ The

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