Ground States of Molecules. 36.[1] The Cyclobutadiene Problem and MINDO/3 Calculations of Molecular Vibration Frequencies

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Abstract: The energy relationships between the singlet and triplet states of cyclobutadiene are discussed in terms of MINDO/3 calculations and ab initio SCF calculations using the 4-31G basis set. Calculations of molecular vibration frequencies by MINDO/3 for ethane, ethylene, acetylene, benzene, singlet and triplet cyclobutadiene, and singlet and triplet monodeuteriocyclobutadiene are reported. The results support a recent suggestion that the $(CH)_4$ species obtained by photolysis in matrices at low temperatures is a metastable triplet. The role of configuration interaction in MINDO/3 calculations is discussed.

From the viewpoint of chemical theory, cyclobutadiene (**1**) is probably the most interesting compound in the whole of organic chemistry and the riddles it sets have still not all been solved. Its synthesis by Pettit et al.[2] after nearly 100 years of fruitless attempts by generations of organic chemists settled the primary question of its aromaticity. However, two almost equally important problems remained, and still remain. In the first place, all current theories predict **1** to have a very low lying triplet. Is this perhaps the ground state? And second, while nearly all theories predict the triplet to be square (D_{4h}) and the singlet rectangular (D_{2h}), theoretical studies by Buenker and Peyerimhoff[3] have suggested that the bond alternation in the singlet becomes less important as the calculations are refined. Is the actual stable form of the singlet then perhaps one with square (D_{4h}) geometry?


1

The chemical behavior[4] of **1** suggests very strongly that it has a singlet ground state. It undergoes stereospecific (Diels-Alder) cycloaddition to olefins whereas the triplet should add in steps, with at least partial loss of configuration in the olefin. Also the relative rates of addition to substituted ethylenes parallel the rates of analogous Diels-Alder reactions and are quite different from the relative rates for addition of radicals.

The behavior[5] of the vicinal diphenyl derivative of **1** indicates strongly that it not only has a singlet ground state but also exists as two distinct isomers **3** and **4**, the former being the more stable and its conversion to **4** being hindered by an activation barrier of ca. 7 kcal/mol. Recently these conclusions have been confirmed by the isolation of two stable, crystalline, monomeric cyclobutadiene derivatives, **5**[6] and **6**,[7] which certainly have singlet ground states and whose x-ray crystal structures[8,9] indicate the presence of a rectangular C_4 ring, two of the CC bonds having lengths similar to the double bonds in olefins while two are very long, longer than the C–C single bonds in polyenes. In the case of **5**, this distortion of the ring from a "polyene" structure could perhaps be due to steric effects but this is very unlikely in the case of **6**.


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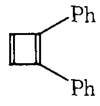

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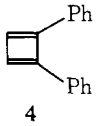

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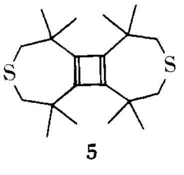

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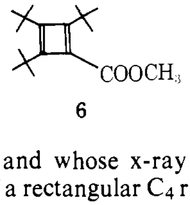

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These conclusions agree very well with those reached on the basis of calculations[10] using an SCF π approximation[11] which had been shown to give remarkably good estimates of geometries and heats of formation for a very wide range of conjugated hydrocarbons. This predicted **1** to have a rectangular (D_{2h}) structure with "single" C–C bonds that are much longer (1.512 Å) than those in classical polyenes (1.46–1.48 Å). Also **3** was predicted to lie 1 kcal/mol below **4**, in good agreement with the observed[5] equilibrium constant (at room temperature, $[\mathbf{3}]/[\mathbf{4}] = 7$).

On the other hand Chapman et al.[12] and Lin and Krantz[13] have obtained by photochemical reactions in matrices at low temperatures a species X which appears to be cyclobutadiene but has an infrared spectrum corresponding to a square geometry.[12-14] Since calculations[3,10,14-16] by a variety of theoretical procedures have all predicted singlet **1** to be rectangular, with C–C and C=C bonds differing greatly in length, it has been suggested that X must be triplet cyclobutadiene **2**. If so, one would have to explain why the substituents in **5** and **6** lead to a preference for the singlet and also why all attempts to detect ESR triplet absorption from X have failed. Almost all the theoretical calculations so far reported have predicted cyclobutadiene to have a singlet ground state.

A possible explanation of this apparent impasse has recently been suggested[16] on the basis of MINDO/3[17] calculations. These agreed with earlier theoretical work in predicting cyclobutadiene to have a rectangular singlet (**1**) ground state and in predicting the triplet to be square (**2**). They also implied, in agreement with previous work, that the singlet potential surface lies above the triplet for a square geometry. As a result, activation is needed to convert **2** into **1**. The calculated barrier was 2.3 kcal/mol. However, only one of the normal modes of vibration of **2** is effective in bringing about the interconversion; consequently the minimum activation energy required is equal to one quantum of this vibration, 3.5 kcal/mol[16] according to MINDO/3. An activation barrier of this height would completely suppress the reaction at the temperature (4 K) used in the matrix isolation experiments. Since moreover the crossing of the singlet and triplet potential surfaces lies only 9 kcal above **1**, the vibrational levels of **1** in that region should still be widely spaced. It is therefore likely that no level of suitable symmetry will match the appropriate level of **2** and in that case intersystem crossing should be strongly forbidden. These arguments suggest that the species observed by Chapman et al.[12] and by Lin and Krantz[13] might have been the triplet **2**, but *excited* triplet, its lifetime under the conditions used being extremely long. The formation of **2** rather than **1** could be explained either by photoproduction from triplet precursor or by an "allowed" photodissociation of **1** into acetylene. Acetylene was a major product in the reaction leading to **2.**

Subsequent MINDO/3 calculations[18] also accounted for the failure to observe triplet ESR absorption from X. These confirmed suggestions that the zero-field splitting of **2** might lie in the awkward region ($>0.2\ \mathrm{cm}^{-1}$) where ESR spectra can be observed only in very high magnetic fields. No study of **2** under such conditions has as yet been reported.

The possibility still remained, however, that the simple infrared spectrum of X might arise from accidental degeneracies of the vibrations of a rectangular species **1.** Krantz, Lin, and Newton[14] have reported calculations of vibration frequencies which seemed to indicate that even a slight distortion from a square geometry is excluded. However, these were based on assumed values for force constants derived from molecules of "normal" type while **1** is unique in being the only simple, planar, neutral antiaromatic cyclic polyene known. We therefore thought it of interest to calculate the vibration spectra of **1** and **2** directly, using MINDO/3. Since no MINDO/3 calculations of molecular vibration frequencies had yet been reported, we decided first to carry out such calculations for some simple molecules to test its potential in this respect. Since moreover few ab initio SCF calculations of cyclobutadiene have been reported in which the geometry was rigorously optimized, we also for comparison carried out such calculations using the 4-31G basis set.[19]

Procedure

The MINDO/3 method has been described in detail in part 25[17a] of this series. The present calculations were carried out using programs based on an approach similar to that used by McIver and Komornicki for MINDO/2. Here Cartesian coordinates are used instead of internal coordinates, as in the standard MINDO/3 program, and geometries are optimized by the Murtagh-Sargent procedure.[21] The use of Cartesian coordinates allows derivatives of the energy to be found analytically in a simple manner. As McIver and Komornicki[22] have pointed out, this enables second derivatives of the energy to be found by finite difference and hence the force constant matrix for Cartesian coordinates of the individual atoms. Diagonalization of this matrix then gives the force constants for the normal modes of vibration and the vibration frequencies can then in turn be calculated[22] by standard methods.

Previous MINDO/3 calculations for open-shell systems (e.g., ref 17) have used the "half-electron" method.[23] Here difficulties arise[16] in the calculation of derivatives of the energy and hence in the use of efficient geometry programs and the calculation of force constants. We therefore preferred to use the Pople-Nesbet[24] unrestricted formalism. Since this is based on a rigorous variational principle, no problems arise in the calculation of derivatives of the energy with respect to the nuclear coordinates.[20] The unrestricted wave function has the disadvantage in principle of not being an eigenfunction of the operator S^2. However, in the present calculations, the expectation value of S^2 indicated that the contamination by higher spin states was negligible.

The ab initio SCF calculations were carried out by standard methods, using the 4-31G basis set.[19] Geometries were found by cyclic variation of the coordinates.

Results and Discussion

(A) Structures and Energies of Singlet and Triplet Cyclobutadiene. We first carried out calculations (MINDO/3 and 4-31G) for **1** and **2**, to compare with previous studies. Our calculated geometries are shown in Table I (geometries are shown in Table I). Those for the singlet agree very closely with values recently reported by Haddon and Williams.[25]

The CC bond lengths for the triplet are almost identical and agree with the values given by the GVB method (1.434 Å[14]) and by "half-electron" MINDO/3 (1.433 Å[16]).

Table I. Optimized Geometries of Singlet (D_{2h}) and Triplet (D_{4h}) Cyclobutadiene

Species	Bond	MINDO/3	STO-3G[a]	4-31G
Singlet	*R*(C-C),[b] Å	1.535	1.569	1.580
	R(C=C),[b] Å	1.342	1.313	1.322
	R(C-H),[b] Å	1.095	1.081	1.066
	Angle (H-C-C), deg	138.3	136.2	135.2
Triplet	*R*(C-C),[b] Å	1.433		1.434
	R(C-H),[b] Å	1.095		1.066

[a] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975). [b] Bond length of indicated bond.

The 4-31G bond lengths for the singlet (1.322, 1.580 Å) show more alternation than do the MINDO/3 values (1.342, 1.535 Å) and are in better agreement with those found[8] in **5** (1.344, 1.600 Å). The latter are longer in each case by 0.02 Å, a difference that could reasonably be attributed to steric repulsions by the tertiary alkyl groups. The bond lengths in **6** also alternate though to a lesser extent, those of the "double" bonds being 1.376 and 1.406 Å and of the "single" ones 1.506 and 1.547 Å. Here again the bond lengths are clearly affected by steric interactions between the substituents, the shorter pair of bonds being those adjacent to the carbomethoxy group. The reduced alternation of bond lengths in **6**, compared with **5**, may well be due to conjugative interactions with the carbomethoxy group in the former. It is at any rate clear that the bonds do alternate very strongly, as all theoretical procedures have predicted.

Our MINDO/3 value (5.0 kcal/mol) for the singlet-triplet splitting (**1** vs. **2**) agrees well with the previous value (5.9 kcal/mol[16]). Recent work in these laboratories has shown that the "half-electron" and unrestricted versions of MINDO/3 give quite similar estimates for the energies of open-shell systems. On the other hand 4-31G predicts **2** to lie *below* **1** in energy, the singlet-triplet splitting (5.4 kcal/mol) being similar in magnitude to the MINDO/3 value but opposite in sign. As we have seen, the ground state of **1** is undoubtedly a singlet. The discrepancy in the 4-31G results reflects the tendency of single-configuration SCF treatments to overestimate the stabilities of triplets relative to singlets. For example, such treatments have uniformly predicted the triplet-singlet splitting in methylene to be ca. 30 kcal/mol[26-29] whereas the MINDO/3 value (8.7 kcal/mol[30]) agrees very closely with the results of two very detailed ab initio studies (11.5,[31] 9.2[32] kcal/mol). The experimental values accepted until very recently (8,[33a] 9[33b] kcal/mol) seemed to agree very closely with the latter, but now a somewhat larger value (19.5 kcal/mol) seems to have been established.[33c] This, however, is still a good deal less than the single-configuration values.[26-29] Likewise the Hartree-Fock method predicts[34] too large a separation (30.6 kcal/mol) between the ${}^3\Sigma_g{}^-$ and ${}^1\Delta_g{}^+$ states of O_2 (observed, 22.5 kcal/mol[35]) whereas the single-configuration MINDO/3 value (22.8 kcal/mol[17c]) agrees almost exactly. Also Buenker and Peyerimhoff[3] found that inclusion of CI lowers the energy of **1** below **2**.

Buenker and Peyerimhoff[3] also concluded that the singlet potential surface for cyclobutadiene lies below the triplet for all geometries, including the square geometry which is the equilibrium form of **2**. This, if true, would invalidate the identification[16] of the matrix-isolated species X as **2**. If CI is included in MINDO/3, the energy of square **1**, while still greater than that of **2**, is very close to it. We will defer until later further discussion of this point.

Our 4-31G calculations are also of interest in connection with current speculations concerning the stability of **1** relative to two molecules of acetylene (**7**). Our calculated 4-31G heat

Table II. Calculated Geometry of Triplet Acetylene (C_{2v} Symmetry)

	MINDO/3	4-31G
R(C-C), Å	1.285	1.318
R(C-H), Å	1.098	1.076
(H-C-C) angle, deg	133.5	129.2

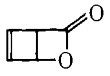
Table III. Comparison of Calculated and Observed[a] Vibrational Frequencies of Ethylene

Symmetry	Assignment[a]	ν(obsd)[b]	ν(calcd)[b]
a_g	3	1342	1296
	2	1632	1835
	1	3164	3544
a_u	4	1023	886
b_{1g}	6	1236	1024
	5	3103	3538
b_{1u}	7	949	979
b_{2g}	8	943	811
b_{2u}	10	826	697
	9	3106	3557
b_{3u}	12	1444	1306
	11	2989	3527

[a] T. Shimanouchi, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. **39** (1972). [b] Vibrational frequency (cm^{-1}).

$HC\equiv CH$

7



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of reaction for the dissociation of **1** into **7**, and the corresponding MINDO/3 value (from the results in ref 16 and 17b, which we have confirmed) are:

$$\rightarrow 2C_2H_2 \qquad (1)$$

$$\Delta H\text{ (MINDO/3)} = +21.2\text{ kcal/mol}$$
$$\Delta H\text{(4-31G)} = -8.6\text{ kcal/mol}$$

In this case there are no reliable indications from experiment.

It is true that **1** is stable for short periods at very high temperatures, having been formed[36] by flash pyrolysis of **8** at 800 °C. Unless the reaction is endothermic, it must involve a very high energy barrier. On the other hand the direct dissociation of **1** into **7** is a "forbidden" process which could very well have a very high activation energy. Thus the analogous dissociation of cyclobutane (**9**) into ethylene (**10**) has an activation energy of 62.5 kcal/mol[37] although the reaction is only moderately endothermic ($\Delta H = +14$ kcal/mol[38]).

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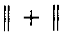

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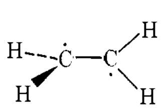

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Claims that **7** was formed in reactions when **1** might have been a precursor are also inconclusive since the **7** could well have arisen from some more reactive C_4H_4 species or by fragmentation of a precursor of C_4H_4.

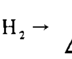
Analogy suggests that the MINDO/3 value in eq 1 is probably considerably too positive because while MINDO/3 gives better estimates of the strain energies of small rings than did MINDO/2,[39] it still tends to give heats of formation that are too negative. Thus the errors in the calculated heats of formation of cyclobutane and cyclobutene are −11.9 and −4.3 kcal/mol, respectively.[17b] On the other hand 4-31G seems[17b] to err in the opposite direction; e.g.:

Table IV. Comparison of Calculated and Observed[a] Vibrational Frequencies of Ethane (D_{3d})

Symmetry	Assignment[a]	ν(obsd)[b]	ν(calcd)[b]
a_{1g}	3	995	1196
	2	1388	1466
	1	2954	3460
a_{1u}	4	289	180
a_{2u}	6	1379	1328
	5	2896	3456
e_g	12	1190	1056
	11	1468	1308
	10	2969	3452
e_u	9	822	759
	8	1469	1314
	7	2985	3466

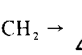
[a] T. Shimanouchi, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. **39** (1972). [b] Vibrational frequency (cm^{-1}).

$$CH_3CH{=}CH_2 \rightarrow \qquad (2)$$



$$\Delta H\text{ (obsd)} = 7.8;\ \Delta H\text{ (calcd)(4-31G)} = 12.5\text{ kcal/mol}$$

$$CH_2{=}C{=}CH_2 \rightarrow \qquad (3)$$



$$\Delta H\text{(obsd)} = 20.2;\ \Delta H\text{(calcd)(4-31G)} = 34.8\text{ kcal/mol}$$

Since the errors in the MINDO/3 results for cyclobutane and cyclobutene seem similar in magnitude, but opposite in sign, to those in the 4-31G ones for cyclopropane and cyclopropene, it seems likely that the true heat of reaction for **1** → **2** (**7**) is about half-way between the values in eq 1, i.e., +6.3 kcal/mol. This would correspond to a heat of formation of **1** of 104 kcal/mol compared with the MINDO/3 value,[16] 94.4 kcal/mol. The difference (10 kcal/mol) seems reasonable in relation to MINDO/3 results for other compounds containing small rings.[17b]

Given that **1** and **2** are certainly very similar in energy, it is obvious that **2** could not possibly dissociate into **7** without intersystem crossing. However, we thought it of interest to calculate the triplet state of **7**. Our calculated geometries (MINDO/3 and 4-31G) for the $^3B_2$ state with C_{2v} symmetry[40] are shown in Table II. The geometries calculated by both methods are very similar, as also are the singlet-triplet splittings (MINDO/3, 59.1 kcal/mol; 4-31G, 64.9 kcal/mol). These are less than the value (4.84 eV, 111.6 kcal/mol) reported by Kammer,[41b] possibly due to his failure to optimize geometries. The experimental values that have been reported (5.2,[42] 5.3[43] eV; 119.9, 122.2 kcal/mol) are also much greater. However, since the equilibrium geometry of the triplet is very different from that of acetylene itself, it would not be surprising to find that the experimental values were too high, referring more closely to vertical than adiabatic excitation. Subsequent work here[44] has shown that MINDO/3 agrees with other procedures in predicting a second stable (trans-bent) form of triplet acetylene to exist with a higher energy (by 18.2 kcal/mol) than that of the cis-bent isomer.

(B) Vibration Frequencies. Since no MINDO/3 calculations of molecular vibration frequencies have as yet been reported, we first carried out such calculations for some simple molecules to see how well MINDO/3 fares in this respect.

Tables III-VI show the calculated (MINDO/3) vibration frequencies for ethane, ethylene, acetylene, and benzene respectively, together with symmetry assignments and experimental values for comparison.

Cursory inspection shows that the agreement with experiment is quite good, except for CH stretches whose frequencies are systematically overestimated by ca. 500 cm^{-1}. Otherwise the agreement is usually within ±10%. The average error for all vibrations, other than CH stretches, is 10.0% and that in

Table V. Comparison of Calculated and Observed[a] Vibrational Frequencies of Acetylene

Upper state	Assignment[a]	ν(obsd)[b]	ν(calcd)[b]
Π_g	V_4	612	488
Π_u	V_5	729	885
Σ_g^+	V_2	1974	2237
	V_1	3374	3827
Σ_u^+	V_3	3287	3770

[a] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945. [b] Vibrational frequency (cm^{-1}).

Table VI. Comparison of Calculated and Observed[a] Vibrational Frequencies of Benzene

Symmetry	Assignment[a]	ν(obsd)[b]	ν(calcd)[b]
a_{1g}	2	993	1189
	1	3073	3507
a_{2g}	3	1350	1192
b_{2g}	5	707	590
	4	990	877
e_{1g}	6	846	820
e_{2g}	10	606	553
	9	1178	1113
	8	1600	1689
	7	3056	3482
a_{2u}	11	673	665
b_{1u}	13	1010	843
	12	3057	3474
b_{2u}	15	1146	1078
	14	1309	1191
e_{1u}	18	1037	1064
	17	1482	1484
	16	3068	3494
e_{2u}	20	398	389
	19	967	868

[a] V. J. Eaton and D. Steele *J. Mol. Spectrosc.*, **48**, 446 (1973); D. H. Whiffen, *Philos. Trans. R. Soc. London, Ser. A*, **248**, 131 (1955). [b] Vibrational frequency (cm^{-1}).

Table VII. Calculated Vibrational Frequencies of Singlet (D_{2h}) Cyclobutadiene

Symmetry	Assignment	ν, cm^{-1}	Description
a_g	4	988	In-plane C–H bend
	3	1264	In-plane ring deform.
	2	1744	C–C stretch
	1	3577	C–H stretch
b_{1g}	5	775	Out-of-plane C–H wag
b_{2g}	8	631	In-plane ring deform.
	7	1050	C–H bend
	6	3540	C–H stretch
b_{3g}	9	698	Out-of-plane C–H wag
a_u	11	424	Out-of-plane ring puckering
	10	760	Out-of-plane C–H wag
b_{1u}	14	922	In-plane C–H bend
	13	1211	C–C stretch
	12	3542	Asymmetric C–H stretch
b_{2u}	15	645	Out-of-plane C–H wag
b_{3u}	18	1007	In-plane C–H bend
	17	1738	In plane asymm. C–C stretch
	16	3556	C–H stretch

Table VIII. Calculated Vibrational Frequencies of Triplet (D_{4h}) Cyclobutadiene

Symmetry	Assignment	ν, cm^{-1}	Description
a_{1g}	2	1566	Symmetric ring breathing
	1	3580	C–H stretch
a_{2g}	3	1060	In-plane C–H wag
b_{1g}	5	705	Asymm. in-plane ring dist.
	4	3554	C–H stretch
b_{2g}	7	991	C–H wag
	6	1424	Asymmetric C–C stretch
e_g	8	372	Degenerate ring bend
a_{2u}	9	576	Out-of-plane C–H wag
b_{2u}	11	280	Ring puckering
	10	588	Ring puckering
e_u	14	697	In-plane C–H bend
	13	1085	In-plane C–H bend
	12	3536	C–H stretch

Table IX. Calculated and Observed Vibrational Frequencies (V_1, cm^{-1}) for Triplet Cyclobutadiene

		ν(calcd)		
Symmetry	ν(obsd)	This work	Ref 14	Description
a_{2u}	573[a]	576	576	CH out-of-plane wag
e_u	653[a]	697	661	In-plane bends
e_u	1236[a]	1085	1236	In-plane bends and CC stretch
e_u	3040[b]	3536		CH stretch

[a] Reference 14. [b] Reference 12.

the CH stretches, corrected by subtracting 500 cm^{-1}, is 2.1%.

Calculations of this kind would not in themselves be adequate for assigning spectra in the absence of other information unless it could be shown that the errors are due to systematic deviations (cf. the case of CH stretches, noted above). However, this level of accuracy may be sufficient for a number of applications, particularly in view of the ease with which the calculations can be carried out. The time required is little more than that needed for a single geometry optimization and MINDO/3 has already been used to optimize the geometry of a molecule containing fifty atoms (protonated LSD[45]). It may be noted that Pulay,[46] in studies using both semiempirical and ab initio SCF methods, has shown that vibrational frequencies can be in error by ±10%, even using procedures close to the Hartree-Fock limit. Such ab initio calculations are limited to quite small molecules by considerations of cost.

In view of these encouraging results, we proceeded to calculate the vibrational frequencies of cyclobutadiene, both of the rectangular singlet (**1**) and the square triplet (**2**). The results are shown in Tables VII and VIII, while Table IX compares our values for the triplet (**2**) with those observed for the species X in matrices of low temperatures.

The observed infrared spectrum of X could be attributed to the rectangular singlet **1** only if the vibration frequencies showed degeneracies similar to those expected for a square geometry. Our calculations show that this is not the case. Krantz, Lin, and Newton had arrived at a similar conclusion from a calculation based on force constants taken from other molecules. As noted above, this procedure is dubious in the case of a unique molecule such as **1**, though their calculated frequencies agreed well with experiment (Table IX).

As a further check, we calculated the spectra of monodeuterio derivatives of **1** and **2**. The results are shown in Tables X and XI. Isotopic substitution of one hydrogen atom by deuterium reduces the symmetry of **1** from D_{2h} to C_s and of **2** from D_{4h} to C_{2v}. In C_s there are 18 potentially active modes while in C_{2v} there are 17. The published spectrum[14] of monodeuterated X shows only five bands between 250 and 1400 cm^{-1}; these are listed in Table XI with possible assignments (cf. ref 14). Evidently most of the bands that become allowed in deuterated **2** remain extremely weak. This of course is not surprising since deuteration will affect only vibrations that involve considerable CH (CD) distortions.

Table X. Calculated Vibrational Frequencies of Singlet Monodeuteriocyclobutadiene

Symmetry	Assignment	ν(calcd)	Symmetry	Assignment	ν(calcd)
A′	9	560	A″	18	397
	8	625		17	734
	7	676		16	767
	6	737		15	942
	5	1198		14	997
	4	1259		13	1039
	3	1740		12	1707
	2	3541		11	2630
	1	3570		10	3550

Table XI. Calculated Vibrational Frequencies of Triplet Monodeuteriocyclobutadiene

Symmetry	Assignment	ν(calcd)	Symmetry	Assignment	ν(calcd)
A_1	7	689	B_1	14	641
	6	702		13	835
	5	1085		12	1022
	4	1544		11	1070
	3	2627		10	1424
	2	3547		9	3536
	1	3572	B_2	18	262
A_2	8	372		17	329
				16	532
				15	584

In the previous MINDO/3 study[16] it was suggested that the conversion of **2** to **1** might have a very low frequency factor, due to a mismatch of energy levels between **2** and **1** and a consequently low probability of intersystem crossing. According to MINDO/3, the conversion requires excitation of **2** by one quantum of the appropriate mode (ν_6 in Table VIII); the corresponding energy level lies ca. 9 kcal/mol above the ground state of **1**. Since **1** will presumably be formed with one quantum of the vibration corresponding to ν_6 of **2**, i.e., ν_3 in Table VII, the remaining energy (δE) must appear as a totally symmetric combination of vibrational modes.

The MINDO/3 values for ν_6 and ν_3, and for the difference in energy between **1** and **2**, lead to a value of ca. 1900 cm^{-1} for δE. Of course MINDO/3 is far too inaccurate for us to be able to tell whether or not there is in fact a totally symmetrical vibrational level of this energy; however, we can see that a mismatch is very likely because there are only five vibrations of the right symmetry in the range 1800-2000 cm^{-1}.

(C) **Role of Configuration Interaction.** The suggestion[16] that X is metastable **2** was based on the conclusion that activation is needed for the conversion of **2** to **1**, the square singlet lying above **2** in energy so that the singlet and triplet surfaces cross. This conclusion was, however, derived from a single-configuration treatment, the validity of which has been recently questioned.[47] Inclusion of CI in RH calculations is a device for allowing for electron correlation. In MINDO/3, however, electron correlation is taken into account via the parametrization, so inclusion of CI normally leads to an overcompensation for electron correlation and to energies that are consequently too negative. Exceptions occur in the case of biradical-like species where the ground state and lowest doubly excited configurations are degenerate or nearly degenerate and where the two MO's are composed of AO's of different sets of atoms. If, however, the two MO's are composed of AO's of the same set of atoms, with comparable orbital densities at each atom, as here, better estimates of the energy are obtained if CI is omitted. A full discussion of this important problem will be given elsewhere in due course.

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References and Notes

(1) Part 35: M. J. S. Dewar and I. J. Turchi, *J. Chem. Soc., Perkin Trans. 2*, 724 (1977).
(2) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965).
(3) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).
(4) (a) P. Reeves, J. Henery, and R. Pettit, *J. Am. Chem. Soc.*, **91**, 5888 (1969); (b) R. E. Davis and R. Pettit, *ibid.*, **92**, 716 (1970); (c) E. K. G. Schmidt, L. Brener, and R. Pettit, *ibid.*, **92**, 3240 (1970).
(5) P. Reeves, J. Devon, and R. Pettit, *J. Am. Chem. Soc.*, **91**, 5890 (1969).
(6) H. Kimling and A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **11**, 932 (1972).
(7) S. Masamune, N. Nakamura, M. Suda, and H. Ona, *J. Am. Chem. Soc.*, **95**, 8481 (1973).
(8) H. Irngartinger and H. Rodewald, *Angew. Chem.*, **86**, 783 (1974).
(9) L. Delbare, M. N. G. James, N. Nakamura, and S. Masamune, *J. Am. Chem. Soc.*, **97**, 1973 (1975).
(10) (a) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 3255 (1965); (b) M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *ibid.*, **93**, 3437 (1971).
(11) See M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).
(12) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 614 (1973); O. L. Chapman, D. De La Cruz, R. Roth, and J. Pacansky, *ibid.*, **95**, 1337 (1973).
(13) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 111 (1972).
(14) A. Krantz, C. Y. Lin, and M. D. Newton, *J. Am. Chem. Soc.*, **95**, 2744 (1973).
(15) N. L. Allinger and J. C. Thai, *Theor. Chim. Acta*, **12**, 69 (1968).
(16) M. J. S. Dewar and H. W. Kollmar, *J. Am. Chem. Soc.*, **97**, 2933 (1975).
(17) (a) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975); (b) *ibid.*, **97**, 1294 (1975); (c) *ibid.*, **97**, 1302 (1975).
(18) R. C. Haddon, unpublished work.
(19) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(20) J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971).
(21) B. A. Murtagh and R. W. H. Sargent, *Comput. J.*, **13**, 185 (1970).
(22) J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).
(23) M. J. S. Dewar, J. A. Hashmall, C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968).
(24) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).
(25) R. C. Haddon and G. R. J. Williams, *J. Am. Chem. Soc.*, **97**, 6582 (1975).
(26) J. F. Harrison and L. C. Allen, *J. Am. Chem. Soc.*, **91**, 807 (1969).
(27) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971); W. A. Lathan, W. I. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, **93**, 6377 (1971).
(28) J. F. Harrison, *J. Am. Chem. Soc.*, **93**, 4112 (1971).
(29) S. V. O'Neill, H. F. Schaefer, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971).
(30) (a) M. J. S. Dewar, R. C. Haddon, and P. K. Weiner, *J. Am. Chem. Soc.*, **96**, 253 (1974); (b) M. J. S. Dewar, R. C. Haddon, W.-K. Li, W. Thiel, and P. K. Weiner, *ibid.*, **97**, 4540 (1975).
(31) P. J. Hay, C. P. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972).
(32) V. Staemmler, *Theor. Chim. Acta*, **31**, 49 (1973).
(33) (a) H. M. Frey, *J. Chem. Soc., Chem. Commun.*, 1024 (1972); (b) W. L. Hase, R. J. Phillips, and J. W. Simons, *Chem. Phys. Lett.*, **12**, 161 (1971); (c) P. F. Zittel, G. B. Ellison, S. V. O'Neill, E. Herbst, W. C. Lineberger, and W. P. Reinharat, *J. Am. Chem. Soc.*, **98**, 3721 (1976).
(34) A. C. Hurley, *Adv. Quantum Chem.*, **7**, 315 (1973).
(35) G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed, McGraw-Hill, New York, N.Y., 1950.
(36) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Am. Chem. Soc.*, **91**, 1875 (1969).
(37) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968, Section 3.10.
(38) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.
(39) M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. J. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).
(40) Previous calculations[41] have shown this to lie below the ^3A_u state with C_{2j} symmetry.
(41) (a) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974); (b) W. E. Kammer, *Chem. Phys. Lett.*, **6**, 529 (1970).
(42) S. Trajmar, J. K. Rice, P. S. P. Wei, and A. Kuppermann, *Chem. Phys. Lett.*, **1**, 703 (1968).
(43) D. F. Dance and I. C. Walker, *Chem. Phys. Lett.*, **18**, 601 (1973).
(44) Unpublished work by H. S. Rzepa.
(45) M. J. S. Dewar and P. K. Weiner, to be published.

(46) P. Pulay, *Mol. Phys.*, **17**, 197 (1969); P. Pulay and W. Meyer, *J. Mol. Spectrosc.*, **40**, 59 (1971).
(47) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 5968 (1975).
(48) R. Parlser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
(49) B. S. Rabinsovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 2439 (1965).
(50) G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed, McGraw-Hill, New York, N.Y., 1950.
(51) Unpublished work in these laboratories.
(52) M. J. S. Dewar, R. C. Haddon, W.-K. Li, W. Thiel, and P. K. Weiner, *J. Am. Chem. Soc.*, **97**, 4540 (1975).

Ground States of Molecules. 43.[1] A MINDO/3 Study of the Rearrangement of Phenylcarbene to Cycloheptatrienacarbene

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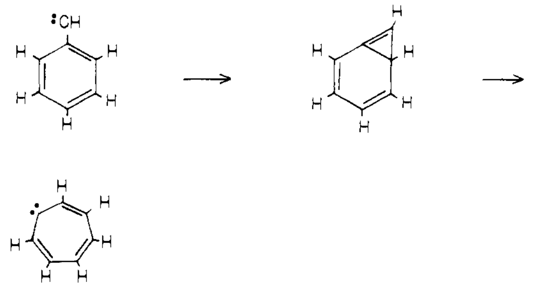
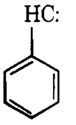
Abstract: The rearrangements of singlet and triplet phenylcarbene to the corresponding states of cycloheptatrienacarbene have been studied, using MINDO/3. The singlet state of cycloheptatrienacarbene is better represented as a standard cyclic tetraene than as a carbene. The singlet rearrangement ($\Delta H = -26.8$; $\Delta E^{\ddagger} = 6.3$ kcal/mol) involves bicyclo[4.1.0]heptatriene as a stable intermediate while the triplet reaction ($\Delta H = -8.0$; $\Delta E^{\ddagger} \geqslant 18.5$ kcal/mol) takes place in a single step.

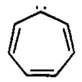
It now seems to be generally agreed[2,3] that phenylcarbene (**1**) and cycloheptatrienacarbene (**2**) occur as intermediates in certain gas phase pyrolysis reactions and that they can undergo interconversion under these conditions, but the mechanism of the interconversion is still a matter for discussion. Of those suggested, the most likely seems to be the one suggested by Baron et al.[3a] for the interconversion of the various isomeric monomethyl derivatives of **1** (Scheme I). Reversible interconversion of **1** and **2** by this mechanism should lead to scrambling of the six methine groups, without scrambling the methine and carbenoid carbon atoms. Hedaya et al.[3b] have shown by ^{13}C labeling that this is indeed the case, at temperatures below 600 °C.

Scheme I



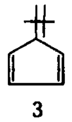


1

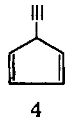


2

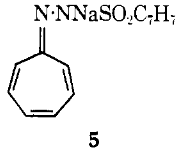
At higher temperatures, **1** undergoes ring contraction[3d,e] to fulvenallene (**3**) and 2-ethinylcyclopentadiene (**4**), and Crow and Paddon-Row[3c] have shown by ^{13}C labeling that hydrogen shifts occur in the conversion of **1** to **3** above 770 °C. However, the carbene interconversion (Scheme I), leading to ring expansion of **1**, appears to be faster than either the hydrogen shift or the ring contraction, even at the higher temperatures.



3



4



5

When **2** was generated in the gas phase by heating the sodium salt (**5**) of the tosylhydrazone of tropone, under conditions which led to the conversion of **1** to **3**, it was found that no ring contraction occurred. Crow and Paddon-Row[3c] have suggested that the **2** formed from **5** may be in a different electronic state from that formed from **1**, on the basis of MO calculations which predicted the singlet and triplet forms of **2** to be very similar in energy.

We recently reported[5] a MINDO/3[6] study of the conversion of benzyl cation (**6**) to tropylium ion (**7**) which led to apparently satisfactory conclusions. Since **1** and **2** are conjugate bases of **6** and **7**, respectively, and since MINDO/3 has been shown[7] to give good results for singlet and triplet carbene, we decided to use it to study the conversion of **1** to **2**.

Procedure

The calculations were carried out using the standard MINDO/3 procedure[6] together with the associated DFP geometry program.[6] Minimum energy reaction paths (MERP) were found by the usual reaction coordinate method.[7] The transition states located approximately in this way were refined by minimizing the scalar gradient of the energy.[8,9] Each stationary point located in this way on the potential surface was shown to be a true saddle point by calculating the corresponding Hessian (second derivative) matrix and establishing that it had one, and only one, negative eigenvalue.[8,9] Triplet surfaces were calculated using a spin-unrestricted version of MINDO/3 (UMINDO/3) in preference to the "half-electron" (HE) method for reasons stated in an earlier paper.[5] Studies of numerous open-shell systems have shown that both procedures lead to similar results.[11]

Results and Discussion

The geometries, heats of formation, and distributions of formal charge calculated for singlet **1** and singlet **2** are shown in Figure 1a–d.

The geometry of **1** differs in an interesting way from that calculated[5] for **6**. Both molecules are planar, but whereas the C_1–C_7 bond in **6** was very short (1.37 Å), corresponding to a