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Singlet Cyclobutyne: A Relative Minimum on the C_4H_4 Potential Energy Hypersurface?

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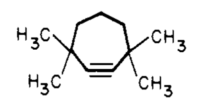
Abstract: The lowest singlet and triplet electronic states of cyclobutyne have been investigated by using the nonempirical molecular electronic structure theory. Initially, singlet cyclobutyne was studied with use of two-configuration self-consistent-field (TCSCF) methods and triplet cyclobutyne with single-configuration SCF theory. Three standard basis sets, of double-ζ (DZ) through double-ζ plus polarization (DZ+*P*) caliber, were employed, the largest being designated C(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p). Geometrical structures and harmonic vibrational frequencies were determined with use of analytic gradient techniques. Subsequently, the different stationary points were subjected to electron-correlation studies, including in a fully variational manner as many as 74 625 configurations. From purely geometrical considerations, the short carbon–carbon bond in singlet cyclobutyne may be labeled a weak (or long) triple bond, with $r_e(\text{C}{\equiv}\text{C}) = 1.258$ Å. For triplet cyclobutyne a much longer carbon–carbon distance (1.323 Å) is predicted, consistent with the sort of C=C double bond expected for this diradical species. The triple-bond CC harmonic stretching frequency for singlet cyclobutyne is predicted to be 1911 cm^{-1}, while the analogous stretching frequency for the triplet diradical species is 1779 cm^{-1}. Vibrational analyses demonstrate that (at the levels of theory considered) both singlet and triplet cyclobutyne are relative minima on the C_4H_4 potential-energy hypersurface. For the former, the lowest frequency predicted at the DZ+*d* TCSCF level of theory is 276 cm^{-1}, corresponding to the ring-puckering mode. These remarks notwithstanding, it is to be emphasized that singlet cyclobutyne is a highly energetic species, predicted to lie ~78 kcal above vinyl acetylene, $\text{HC}{\equiv}\text{C}{-}\text{CH}{=}\text{CH}_2$, the absolute minimum among C_4H_4 molecules. Finally, singlet cyclobutyne is predicted to lie 13 kcal below its triplet diradical.

Incorporating a carbon–carbon triple bond into a small cyclic system is an inherently difficult feat since the sp hybridization of the acetylenic carbon atoms prefers a linear $\text{CH}_2{-}\text{C}{\equiv}\text{C}{-}\text{CH}_2$ arrangement of the four carbon atoms. For this reason the question "what is the smallest otherwise saturated cyclic hydrocarbon that can accommodate a triple bond?" is of long-standing and fundamental interest.[1-4] The smallest unsubstituted cycloalkyne isolable (in gram quantities) is the eight-membered ring, cyclooctyne, first assuredly synthesized by Blomquist and Liu[5] in 1953. Although cyclooctyne has about 10 kcal of strain,[4] the carbon–carbon triple bond is reasonably normal, as reflected by its C≡C stretching frequency at 2210 cm^{-1} (typically 2100 cm^{-1} for alkynes[6]) and bond distance $r(\text{C}{\equiv}\text{C}) = 1.232 \pm 0.006$ Å. Moreover, the eight-membered ring is large enough that the C—C≡C bond angle need only distort from its preferred 180° to 158.5 ± 0.9°, according to an electron-diffraction study[7] of the structure of cyclooctyne.

Although cycloheptyne is apparently not isolable, the 3,3,7,7-tetramethyl analogue



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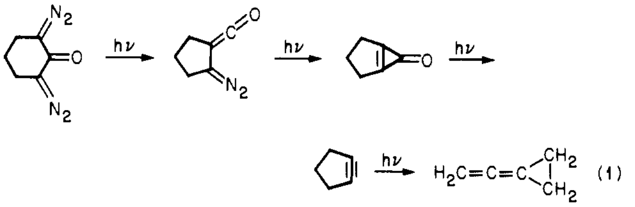
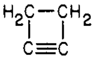
was synthesized by Krebs and Kimling[8] in 1971. The four methyl groups are seen to produce a drastic increase in the kinetic stability of the cycloheptyne system. Although no molecular structure appears to be available for **1**, the C≡C stretching frequency observed in the infrared at 2180 cm^{-1} confirms the existence of a genuine triple bond. There is ample evidence[1-4] for the transient existence of the unsubstituted cycloheptyne, cyclohexyne, and cyclopentyne. However, physical methods, specifically spectroscopic techniques, have not been used to detect these products in solution or in the gas phase. The evidence for the seven-, six-, and five-membered cyclic alkynes rests on the analogy to isolable cycloalkynes, on the expected reaction products derived from these intermediates, and on labeling and kinetic studies.[2]

Perhaps the most promising attempt to date at the spectroscopic identification of cyclopentyne was provided by the recent research of Chapman and co-workers.[9] They present evidence that the photolysis of 1,6-bis(diazo)cyclohexanone in frozen argon leads via the sequence



(1)

to the unsubstituted cyclopentyne. Unfortunately the last step in (1) was sufficiently rapid that the infrared spectrum of cyclopentyne was not recorded. The analogous pathway for cyclobutyne



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was not explored by Chapman, but should prove challenging, since at least two distinguished research groups[10,11] have failed to obtain

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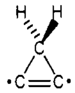
even the most indirect evidence for the transient existence of cyclobutyne.

From a theoretical perspective, cyclobutyne is expected to play a pivotal role among cycloalkynes. That is, C_4H_4 is probably either the smallest preparable unsubstituted cycloalkyne or the largest nonexistent monocyclic acetylene. Theoretical studies[12] show that although triplet cyclopropyne



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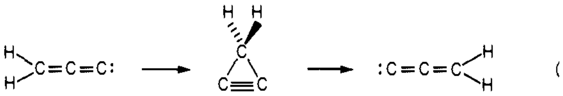
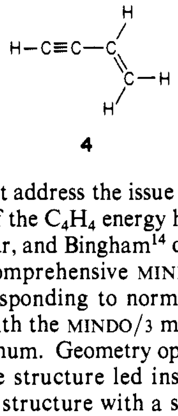
is a relative minimum on the C_3H_2 potential-energy hypersurface, the closed-shell singlet state is not. Specifically, singlet cyclopropyne appears to be a transition state for the degenerate rearrangement of propadienylidene



(2)

Thus the incorporation of a triple bond into an unsubstituted three-membered hydrocarbon ring would appear to be an unattainable goal, at least in the gas phase. Since there is solid evidence for the transient existence of cyclopentyne,[9] cyclobutyne remains as the single genuine mystery in the series of unsubstituted cycloalkynes.

Two previous theoretical studies of cyclobutyne should be noted here. Hehre and Pople[13] used minimum-basis-set self-consistent-field (SCF) theory to optimize the structure of this four-membered cyclic alkyne within the constraint of C_{2v} symmetry and found CC distances of 1.227, 1.596 (adjacent to the triple bond), and 1.528 Å (opposite the triple bond). As expected, cyclobutyne is a very high energy C_4H_4 isomer and was predicted to lie 117.5 kcal above the global minimum, vinylacetylene



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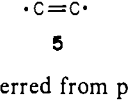
Hehre and Pople did not address the issue of whether cyclobutyne is a relative minimum of the C_4H_4 energy hypersurface. However, Kollmar, Carrion, Dewar, and Bingham[14] did consider cyclobutyne in this light in their comprehensive MINDO/3 study of all local minima of C_4H_4 corresponding to normal closed-shell species. These authors found with the MINDO/3 method that cyclobutyne is *not* such a local minimum. Geometry optimization starting with such a C_{2v} cyclobutyne structure led instead to an unexpected bicyclic "nonclassical" structure with a shortest carbon–carbon bond distance of 1.299 Å. Dewar and co-workers[14] concur with Hehre and Pople[13] that vinylacetylene (**4**) is the absolute energy minimum for the C_4H_4 system.

The primary goal of the present research was to make a definitive ab initio determination of whether or not cyclobutyne is a relative minimum on the C_4H_4 potential-energy hypersurface. However, the lowest triplet state of cyclobutyne



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which may perhaps be inferred from previous studies of triplet cyclopropyne **3** to be a local (or relative) minimum, was characterized in equal detail. A particular emphasis of this work is the prediction of vibrational frequencies for both the triplet and singlet cyclobutyne stationary point geometrical structures. This allows one to make definitive statements, within each level of theory, whether each stationary point is a true minimum, transition state (one imaginary vibrational frequency),[15] nor something more exotic.[16]

Theoretical Approach

The electronic configuration for the closed-shell structure **2** of cyclobutyne incorporating the carbon–carbon triple bond is

$$1a_1^2\,1b_2^2\,2a_1^2\,2b_2^2\,3a_1^2\,4a_1^2\,3b_2^2\,1b_1^2\,4b_2^2\,5a_1^2\,6a_1^2\,1a_2^2\,2b_1^2\,7a_1^2 \qquad (3)$$

and it is possible to carry out single-configuration self-consistent-field (SCF) studies of (3). However this may be imprudent. Specifically, the allowance for diradical character (of the type illustrated by **5**) requires a second configuration

$$1a_1^2\,1b_2^2\,2a_1^2\,2b_2^2\,3a_1^2\,4a_1^2\,3b_2^2\,1b_1^2\,4b_2^2\,5a_1^2\,6a_1^2\,1a_2^2\,2b_1^2\,5b_2^2 \qquad (4)$$

For this reason it was concluded that the simplest level of theory appropriate for singlet cyclobutyne was a two-configuration SCF procedure (TCSCF) involving variational determination of the coefficients of the configurations given in (3) and (4) as well as the molecular orbitals. For triplet cyclobutyne, a good qualitative description of the electronic structure is provided by the single configuration

$$1a_1^2\,1b_2^2\,2a_1^2\,2b_2^2\,3a_1^2\,4a_1^2\,3b_2^2\,1b_1^2\,4b_2^2\,5a_1^2\,6a_1^2\,1a_2^2\,2b_1^2\,7a_1\,5b_2 \qquad (5)$$

Three different basis sets of contracted Gaussian functions were used in the research. The first of these was the standard double-ζ (DZ) set of Huzinaga[17] and Dunning,[18] designated C(9s 5p/4s 2p), H(4s/2s). In the second basis, a set of *d*-like Cartesian functions (x^2, y^2, z^2, xy, xz, and yz multiplied by $e^{-\alpha r^2}$) was appended to each carbon atom. This basis is labeled DZ+*d* and may be designated C(9s 5p 1d/4s 2p 1d), H(4s/2s). To this were finally added a set of *p* functions (p_x, p_y, p_z) to yield a full double-ζ plus polarization (DZ+*P*) basis, designated C(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p). There are 148 primitive and 84 contracted Gaussian functions in the DZ+*P* set and the polarization function orbital exponents are $\alpha_d(\mathrm{C}) = 0.80$, $\alpha_p(\mathrm{H}) = 1.0$.

Analytic gradient techniques[19,20] were used here to determine the geometrical structure of singlet cyclobutyne with TCSCF wave functions and of triplet cyclobutyne with the single-configuration SCF method. These optimizations were carried out within the confines of C_{2v} symmetry, which is expected for cyclobutyne structures. Subsequently, however, the character of these constrained C_{2v} structures was tested via the determination, again with the analytic gradient method, of all quadratic force constants and the resulting harmonic vibrational frequencies. This manner of vibrational analysis was carried out at the DZ TCSCF and DZ+*d* TCSCF levels of theory for singlet cyclobutyne **2** and at the DZ SCF and DZ+*d* SCF levels for triplet cyclobutyne **5**.

Given the stationary point geometries obtained as described above, the effects of electron correlation were incorporated via the method of configuration interaction (CI).[21,22] Only the valence electrons were explicitly correlated; that is the four core-like (carbon 1s-like) molecular orbitals $1a_1$, $1b_2$, $2a_1$, and $2b_2$ were held doubly occupied in all configurations. Furthermore, the

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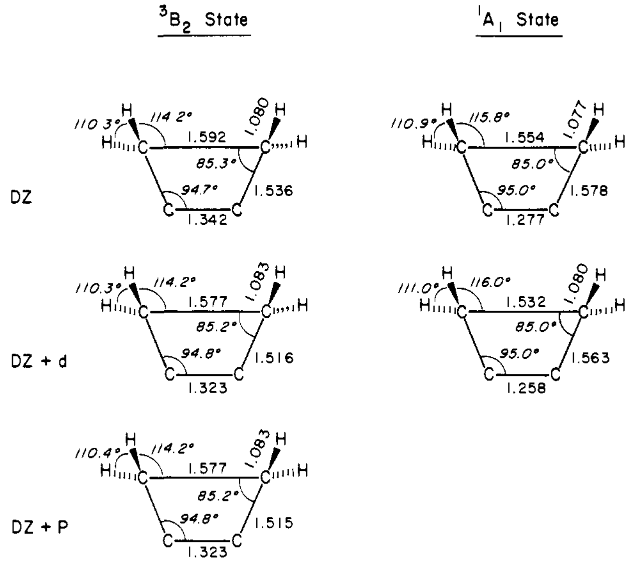

Figure 1. Predicted molecular structures, at several levels of theory, for singlet and triplet cyclobutyne. Singlet structures were determined with two basis sets from two-configuration SCF wave functions. Triplet structures were obtained with use of three different basis sets in conjunction with single-configuration SCF theory. All bond distances are in angstroms.

virtual orbital core counterparts within a DZ-type basis, the four highest unoccupied (virtual) orbitals, were deleted from the CI procedures. With these restrictions, all other singly and doubly excited configurations, relative to either reference configuration given in (3) or (4), were included in the correlated wave functions for singlet cyclobutyne. This amounts to 23 249 $^1A_1$ configurations with the DZ basis and 74 625 with the DZ+*d* set.

For triplet cyclobutyne, all Hartree–Fock interacting[23,24] single and double excitations relative to the SCF reference configuration given in (5) were included. For the DZ and DZ+*d* basis sets, the numbers of $^3B_2$ configurations for triplet cyclobutyne are 14 503 and 45 623, respectively. All correlated wave functions were obtained with use of the recently developed shape-driven[25] graphical unitary group approach.[26] Representative times for singlet C_4H_4 on the Harris Series 800 minicomputer were 64 min (DZ CI) and 306 min (DZ+*d* CI).

C_{2v} Geometrical Structures for Cyclobutyne

The predicted shapes of singlet and triplet cyclobutyne are given in Figure 1. This discussion will center on the $^1A_1$ structures first. Two structural features are of critical importance here, the $C{\equiv}C$ bond distance and the $C{-}C{\equiv}C$ bond angle, which as discussed earlier prefers being 180° when given a choice in the matter. The DZ and DZ+*d* TCSCF values of r_e ($C{\equiv}C$) are seen in Figure 1 to be 1.277 and 1.258 Å, respectively. Even the latter is significantly longer (by 0.055 Å) than the prototype $C{\equiv}C$ distance[27] in $HC{\equiv}CH$, namely 1.203 Å. However, the singlet cyclobutyne bond distance is even further removed (by 0.081 Å) from the prototype carbon–carbon double-bond distance of 1.339 Å in ethylene. Thus, strictly on the basis of bond-distance predictions, we would classify singlet cyclobutyne as possessing a weak triple bond.

Of necessity, the $C{-}C{\equiv}C$ bond angle in cyclobutyne must be less than the 180° called for by the classic sp hybridization on the acetylenic carbon atoms. At both the DZ TCSCF and DZ+*d* TCSCF levels of theory, this angle is predicted to be 95.0°, apparently not much wider than the 90° that would characterize a square. However, the C–C bonds adjacent and opposite to the triple bond are in fact very much longer than the latter. At the DZ+*d* TCSCF level of theory these distances are 1.563 and 1.532 Å, both within comfortable range of the standard C–C single-bond value, 1.54 Å. Thus we conclude that the $C{-}C{\equiv}C$ bond angle of 95.0° is essentially dictated by the long $C{\equiv}C$ triple bond and the three nearly normal C–C single bonds which compose the regular trapezoid of carbon atoms.

Comparison with the analogously predicted structure of singlet cyclopropyne,[12] the three-membered ring, is also of interest. The reader should keep in mind, of course, that cyclopropyne is *not* a minimum on its potential-energy hypersurface but rather a transition state, as indicated in eq 2. The structure of singlet cyclopropyne was predicted earlier at the DZ TCSCF level of theory and the $C{\equiv}C$ distance is 1.262 Å, which is actually 0.015 Å *less* than the comparable prediction for cyclobutyne. Furthermore, the other unique C–C distance in cyclopropyne is 1.556 Å, less by 0.022 Å than the analogous cyclobutyne C–C distance adjacent to the triple bond. Thus, in terms of bond distances, it is seen that those in the three-membered ring are somewhat more "normal" than those predicted here for cyclobutyne. The source of cyclopropyne's instability, then, is seen to lie clearly with its untenable $C{-}C{\equiv}C$ bond angle of 66.1°.

Turning to the predicted structures for triplet cyclobutyne, one sees first that the addition to the basis set of polarization functions on the four hydrogen atoms has virtually no effect on the predicted structure. The only changes in the reported geometrical parameters in going from DZ+*d* SCF to DZ+*P* SCF are a decrease of 0.001 Å in one of the C–C distances and an increase of 0.1° in the two equivalent HCH angles. For this reason, the more-time-consuming singlet TCSCF structural optimization was not carried out with the larger DZ+*P* basis set. As with the singlet structure, Figure 1 shows that the addition of a set of *d* functions to each carbon atom significantly decreases the C–C distances, by 0.019 ($C{\equiv}C$), 0.020 (adjacent to $C{\equiv}C$), and 0.015 Å (opposite), respectively. Further extension of the basis set will probably continue to decrease these C–C distances, but electron correlation will tend to exert a counterbalancing lengthening effect,[21] so the C–C distances predicted at the DZ+*d* SCF level should be reliable to ~0.02 Å. Thus one expects additional geometrical optimizations at higher levels of theory to be of decreasing value.

The DZ+*P* SCF value of the short carbon–carbon distance for triplet cyclobutyne is 1.323 Å, only slightly less than the standard double-bond value of 1.34–1.35 Å. Thus this triplet diradical species conforms quite well in this regard to the valence structure **5**. The C–C single-bond distance opposite to the double bond is somewhat long, 1.577 Å, but this stretching of ~0.03 Å beyond the standard single-bond value tends to lessen the ring strain associated with the double bond. Even so, the $C{-}C{=}C$ bond angle remains rather small at 94.8°, a result which is qualitatively inevitable for such a four-membered ring. The C–C distance adjacent to the double bond is seen in Figure 1 to be 1.515 Å, slightly short relative to the standard single-bond distance (1.54 Å).

Perhaps the most interesting comparison between the triplet and singlet cyclobutyne structures is the *reversal* of the order of the C–C single-bond distances. That is, one finds the relationships

$$\begin{array}{ll} \text{singlet} & r(\text{adjacent; } 1.563) > r(\text{opposite; } 1.532) \\ \text{triplet} & r(\text{opposite; } 1.577) > r(\text{adjacent; } 1.516) \end{array} \qquad (6)$$

Since the structure of a triplet cycloalkyne has never been determined experimentally, it is not obvious whether or not the relationship given in (6) is a general one. However, one can make a comparison with the structure of cyclobutene, which is "isostructural" with triplet cyclobutyne, in the sense of having one double bond and three single bonds within a four-membered ring. For cyclobutene the experimental carbon–carbon distances[28] are

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Table I. Predicted Vibrational Frequencies (in cm^{-1}) for the Lowest Singlet and Triplet Electronic States of Cyclobutyne

description		singlet ($^1A_1$)		triplet ($^3B_2$)	
		DZ TCSCF	DZ+*d* TCSCF	DZ SCF	DZ+*d* SCF
in-phase CH_2 asym stretch	B_1	3378	3370	3342	3329
out-of-phase CH_2 asym stretch	A_2	3362	3355	3326	3314
in-phase CH_2 sym stretch	A_1	3295	3294	3267	3262
out-of-phase CH_2 sym stretch	B_2	3286	3285	3256	3253
$C{\equiv}C$ stretch	A_1	1847	1911	1731	1779
in-phase CH_2 scissor	A_1	1635	1640	1636	1637
out-of-phase CH_2 scissor	B_2	1621	1612	1622	1614
out-of-phase CH_2 wag	B_2	1346	1320	1384	1375
in-phase CH_2 wag	A_1	1314	1311	1307	1298
out-of-phase CH_2 twist	A_2	1299	1301	1261	1257
in-phase CH_2 twist	B_1	1165	1163	1162	1155
out of-phase CH_2 rock	A_2	1079	1053	1119	1102
in-phase C–C stretch	A_1	1076	1100	1102	1127
out-of-phase C–C stretch	B_2	936	963	1025	1065
unique C–C stretch	A_1	885	916	897	922
in-phase CH_2 rock	B_1	871	855	884	854
ring deformation	B_2	716	618	910	878
ring puckering	A_2	320	276	381	371

1.342 (double bond), 1.517 (adjacent to the double bond), and 1.566 Å (opposite to the double bond). It is evident that the analogy between triplet cyclobutyne and cyclobutene bond distances is extraordinarily good in this respect.

Finally, it may be observed that the DZ SCF $C{=}C$ double-bond distance predicted earlier[12] for triplet cyclopropyne (1.298 Å) is notably less than that for triplet cyclobutyne (1.342 Å) at the same level of theory. The other C–C bond distance in triplet cyclopropyne is 1.567 Å, not far from the average (1.564 Å) of the two unique C–C single-bond distances of triplet cyclobutyne.

Cyclobutyne Vibrational Frequencies

Harmonic vibrational analyses for both the singlet and triplet C_{2v} structures of cyclobutyne are presented in Table I. At each level of theory, for both the singlet and triplet electronic states, all vibrational frequencies are predicted to be real, ensuring the existence of genuine relative minima on the respective potential-energy hypersurfaces. Thus at the two levels of theory considered (DZ TCSCF and DZ+*d* TCSCF), singlet cyclobutyne, unlike singlet cyclopropyne, is suggested as a possibly observable species. In this sense, cyclobutyne appears to be the smallest otherwise saturated monocyclic system in which it is possible to insert a triple bond. One must be cautious here, however, since the highest level of theory employed here (DZ+*d* TCSCF), although quite respectable, is by no means complete. Moreover, the fact that singlet cyclobutyne is a relative minimum tells us nothing about how deep or shallow this minimum is. The latter criterion of course is critical to the issue of whether singlet cyclobutyne can actually be observed in the laboratory. Nevertheless, the present ab initio structural prediction for cyclobutyne is in striking contrast with the suggestion from MINDO/3 that cyclobutyne is not a local minimum.[14]

The ordering of the vibrational frequencies is nearly the same for the lowest singlet and triplet electronic states of cyclobutyne. This result is predicted with use of either the DZ or DZ+*d* basis set. The only break in the ordering pattern arises from the fact that the B_2-ring-deformation frequency is much higher for triplet cyclobutyne (878 cm^{-1}) than for the singlet (618 cm^{-1}). This means that while the ring deformation is the second lowest frequency for singlet cyclobutyne, it is the third lowest for the triplet electronic state. This result is perhaps surprising since the singlet state incorporates the $C{\equiv}C$ triple bond and hence might be expected to be less susceptible to any distortion of the four-membered ring. However, the same qualitative result is seen for the ring-puckering mode, for which the singlet frequency (276 cm^{-1}) lies 95 cm^{-1} below that (371 cm^{-1}) for the triplet cyclobutyne.

The above vibrational-frequency relationships may profitably be interpreted in terms of the relative strengths of the C–C bonds adjacent to the multiple bond. Both the stretching frequencies (1127 cm^{-1} vs. 1100 cm^{-1} and 1065 cm^{-1} vs. 963 cm^{-1}) and the lengths (1.516 Å vs. 1.563 Å) of these bonds indicate that they are stronger for triplet than for singlet cyclobutyne. The ring-deformation mode may be viewed as an in-plane rotation of the C–C multiple bond in a manner opposite to that of the unique C–C single bond. Similarly, the ring-puckering mode is an out-of-plane rotation of these two bonds in opposite directions. The net effect of each of these two modes is to stretch (or compress) the C–C bonds adjacent to the multiple bond. In light of the earlier comments on the relative strength of these bonds, one is not surprised that these modes lie higher in energy for triplet cyclobutyne.

Before going further, it should be emphasized that the vibrational frequencies predicted here are anticipated to be significantly *higher* than those that (hopefully) will eventually be observed for cyclobutyne. For example, for the stable closed-shell molecules HCN, H_2CO, H_2O, and CH_4, the DZ SCF harmonic vibrational frequencies were found[29] on average to be 8.0% greater than the experimental harmonic frequencies. Moreover, harmonic vibrational frequencies are typically ~4% higher than the observed (anharmonic) fundamentals. Thus one can expect DZ SCF harmonic frequencies to be of the order of 12% higher than the experimental frequencies. Similar trends have been established recently by Pople and co-workers[30] using somewhat smaller basis sets. Although statistics have not been compiled for DZ+*d* vibrational-frequency predictions, these are also expected[29,30] to be ~12% higher than the observed fundamentals.

In general, the harmonic vibrational frequencies predicted here with the DZ+*d* basis set are in good agreement with those obtained with use of the smaller DZ set. The largest difference (98 cm^{-1}) occurs for the B_2-ring deformation of singlet cyclobutyne, the DZ and DZ +*d* values being 716 and 618 cm^{-1}, respectively. The latter value in such cases should of course be the more reliable. The addition of *d* functions to the basis set significantly increases the predicted carbon–carbon multiple-bond stretching frequency for both singlet (+64 cm^{-1}) and triplet (+48 cm^{-1}). This suggests that a considerably improved description of this triple (singlet) or double (triplet) bond ensues from the addition of such polarization functions to the basis set. Other frequencies significantly changed with the larger basis set are the singlet A_2-ring-puckering mode (−44 cm^{-1}) and the triplet B_2 out-of-phase C–C stretch (+40 cm^{-1}).

Even the casual reader will appreciate that the $C{\equiv}C$ stretching frequency in singlet cyclobutyne is of paramount importance here. This is predicted to be 1911 cm^{-1} at the DZ+*d* TCSCF level of theory, and an empirical correction of 12% would reduce this to 1682 cm^{-1}. For comparison, the observed $C{=}C$ double-bond

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(29) Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **73**, 2310 (1980).

(30) J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. Defrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quantum Chem., Quantum Chem. Symp.*, **15**, 269 (1981).

stretching frequency[31] in the structurally related cyclobutene molecule is 1566 cm^{-1}. Thus the C≡C stretching frequency in the cyclobutyne is empirically predicted to be only 116 cm^{-1} above the double-bond stretching frequency in the vastly more stable cyclobutene molecule. Of course even the straight ab initio prediction of 1911 cm^{-1} is significantly below the 2180-cm^{-1} frequency assigned[8] to C≡C stretching for the stable cycloalkyne 3,3,7,7-tetramethylcycloheptyne.

Also pertinent to the theoretical prediction of the C≡C stretching frequency in singlet cyclobutyne is the recent observation by Chapman[9] of the infrared spectrum of acenaphthyne

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This five-membered ring is the smallest incorporating a triple bond for which vibrational frequencies are available. Chapman has suggested that the IR band at 1930 cm^{-1} is a possible candidate for the carbon–carbon triple-bond stretch. Considering the highly constrained nature of **6** compared to the unsubstituted cyclobutyne studied here theoretically, it would appear to us that this very tentative assignment is quite reasonable.

The C=C double-bond stretching frequency predicted for triplet cyclobutyne at 1779 cm^{-1} (DZ+*d* SCF) is also of interest. Reduction of this frequency by 12% leads to an empirical prediction of 1566 cm^{-1}, which is serendipitously identical with the observed C=C fundamental in cyclobutene. This of course supports the view (as do the structural predictions discussed earlier) that triplet cyclobutyne is a seemingly normal cycloalkene species.

Comparison of the other predicted frequencies of singlet and triplet cyclobutyne with those observed for cyclobutene is also instructive. In particular the ring-puckering frequencies at 276 (singlet cyclobutyne) and 371 cm^{-1} (triplet) bracket the observed fundamental (325 cm^{-1}) for cyclobutene. The cyclobutene ring deformation at 875 cm^{-1} is in very close agreement with the analogous frequency (878 cm^{-1}) for triplet cyclobutyne, but much higher than the 618 cm^{-1} predicted for singlet cyclobutyne. The three cyclobutene C–C single-bond stretching frequencies are labeled "ring expansion" by Lord[31] and assigned as 1210 (B_2), 1182 (A_1), and 1113 cm^{-1} (A_1). However, Suzuki and Nibler[32] have reassigned the B_2 mode (out-of-phase C–C stretch) to 886 cm^{-1} and the two A_1 modes to 1113 and 986 cm^{-1}. The latter assignments are reasonably close to the present predictions for singlet cyclobutyne (A_1 1100, B_2 963, and A_1 916 cm^{-1}), although the ordering of the last two frequencies is reversed. The same theoretical order ($A_1 > B_2 > A_1$) is predicted for triplet cyclobutyne, with upward shifts in the absolute values of 27 (A_1), 102 (B_2), and 6 cm^{-1} (A_1). The most recent assignment of the C–C single-bond stretching frequencies is that of the Russian scientists Aleksanyan and Garkusha[33] and does agree with the theoretical ordering for cyclobutyne. Aleksanyan and Garkusha assign 1112 (A_1), 1009 (B_2), and 874 cm^{-1} (A_1) to the C–C single-bond modes.

Relative Energies from Correlated Wave Functions

Does singlet or triplet cyclobutyne lie lower in energy? This question has been addressed at four different levels of theory, and the effects of electron correlation have been incorporated variationally in two of these. Table II summarizes the theoretical predictions in this regard, and it is seen that the range of predicted singlet–triplet separations is rather small, namely 9.0–12.8 kcal. In every case singlet cyclobutyne is predicted to be the electronic ground state. At the highest level of theory considered, DZ+*d* CI, the singlet state lies 12.8 kcal below triplet cyclobutyne. Comparison with the lower levels of theory suggest that *d* functions on the four carbon atoms increase the singlet–triplet separation by ~1.5 kcal, while correlation effects result in a further increase of ~2.3 kcal.

Table II. Total Energies in Hartrees and Relative Energies in kcal/mol for the Lowest Singlet and Triplet Electronic States of Cyclobutyne

level of theory	no. of config	*E*, hartrees	Δ*E*(S–T), kcal
DZ TCSCF (singlet)	2	−153.54798	9.0
DZ SCF (triplet)	1	−153.53363	
DZ CI (singlet)	23 249	−153.85531	11.2
DZ CI (triplet)	14 503	−153.83741	
DZ+*d* TCSCF (singlet)	2	−153.62505	10.5
DZ+*d* SCF (triplet)	1	−153.60824	
DZ+*d* CI (singlet)	74 625	−154.05772	12.8
DZ+*d* CI (triplet)	45 623	−154.03731	
DZ+*P* SCF (triplet)	1	−153.61596	

Note of course that a vastly larger increase in the singlet–triplet separation would have been credited to correlation effects had we begun with a single-configuration treatment of singlet cyclobutyne. As pointed out earlier, a single-configuration description of the singlet state is simply inadequate, with a two-configuration SCF treatment instead comprising a proper zeroth-order starting point. For singlet cyclobutyne within the DZ+*d* TCSCF approximation the weights of configurations given in (3) and (4) are 83.5% and 16.4%. When the 74625-configuration wave function [single and double excitations relative to both (3) and (4)] is determined variationally, the weights of these two leading configurations are reduced to 75.5% and 11.0%, respectively. In contrast, triplet cyclobutyne is reasonably well described by the single configuration given in (5), which amounts to 86.7% of the DZ+*d* CI wave function. Note that the correlated wave functions quantitatively verify the need for two configurations in treating the singlet state of cyclobutyne. The two reference configurations given in (3) and (4) together account for 86.5% of the correlated singlet wave function. This percentage is virtually the same as the weight (86.7%) of the single configuration given in (5) in the correlated triplet wave function.

Cyclobutyne is certainly not expected to be an energetically low-lying species. For example, Hehre and Pople,[13] using STO-3G equilibrium geometries, find cyclobutyne to lie 117.5 kcal above vinylacetylene (**4**) at the 4-31G SCF level of theory. For comparison, the same method predicts tetrahedrane (the instability of which few would contend) to lie at 93.8 kcal, or 23.7 kcal lower than cyclobutyne. At its experimental geometry,[34] we have carried out several TCSCF calculations on vinylacetylene. The lowest energy is obtained for the wave function involving the Hartree–Fock configuration and the double excitation from HOMO to LUMO, i.e., $2a''^2 \rightarrow 3a''^2$. With the DZ+*d* basis set this TCSCF energy is −153.74912 hartrees, or 77.9 kcal below the comparable energy of singlet cyclobutyne. Thus while cyclobutyne remains a high-energy species, it lies significantly lower in energy than suggested by the earlier single-configuration SCF study.[13]

Concluding Remarks

In previous research[12] we have shown that it is *not* possible to incorporate a triple bond in the simplest otherwise saturated three-membered ring. Here it has been shown that it *is* possible to incorporate a triple bond in the simplest such four-membered-ring system, namely cyclobutyne. That is, singlet cyclobutyne does represent a relative minimum on the C_4H_4 potential-energy hypersurface. Triplet cyclobutyne is also predicted to be an energetic minimum, lying ~13 kcal/mol higher than the singlet ground state.

It must be stated that the carbon–carbon triple bond in cyclobutyne is not strong, as indicated by either bond distance (1.26

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[31] R. C. Lord and D. G. Rea, *J. Am. Chem. Soc.*, **79**, 2401 (1957).

[32] E. M. Suzuki and J. W. Nibler, *Spectrochim. Acta, Part A*, **30A**, 15 (1974).

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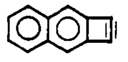
Å) or stretching vibrational frequency (~1700 cm^{-1}). Moreover, the electronic wave function for singlet cyclobutyne shows some signs of biradical character. For example, the coefficient of the second configuration in the two-configuration SCF wave function is 0.41, suggesting that this second configuration 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 ± 0.001 D[28]) of cyclobutene has been a matter of some discussion,[13,35] it is worth noting that the dipole moments of both singlet (DZ+d TCSCF μ = 2.37 D) and triplet (DZ+d SCF μ = 1.86 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 $C\equiv C$ 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.

Cyclobutyne is not going to be an easy molecule to make. It is predicted to lie ~78 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 identification[36] of the substituted molecule



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

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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 archtype 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 Chapman[6] 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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