obtained from condensed phases and our results would seem to indicate that their interpretation through quantum mechanical calculations which do not explicitly the perturbation due to the solvent is fraught with danger. It is worth noting in this regard, that, consistent with our opening remarks with respect to the ubiquity of radial expansion of the electronic distribution upon excitation, even valence excitations like 31 ← 20 are shifted by 10 000 cm^{-1} in solution relative to the gas phase. Such large perturbations almost certainly have a significant effect upon the optical rotatory strength.

Registry No. Glycine, 56-40-6.

Small-Ring Cyclic Alkynes: Ab Initio Molecular Orbital Study of Cyclopentyne

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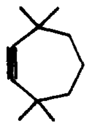
Abstract: The structure of the lowest energy singlet and triplet electronic states of cyclopentyne has been determined by ab initio MO theory at the GVB and ROHF levels, respectively, with the split-valence 3-21G basis set. Both electronic states prefer a C_s nonplanar structure, but the planarization energies are very small, indicating easy inversion. Harmonic force constant calculations on the optimized structures demonstrate that both singlet ($^1A'$) and triplet ($^3A''$) cyclopentyne are relative minima on the corresponding C_5H_6 potential-energy hypersurface. The triplet state is predicted to lie about 25 kcal/mol above the ground-state singlet. Harmonic vibrational frequencies are predicted for both electronic states. The triple-bond harmonic stretching frequency for singlet cyclopentyne is predicted to be 1828 cm^{-1}, whereas the analogous stretching frequency for the triplet state is 1622 cm^{-1}. These predictions should assist in the identification of cyclopentyne from matrix-isolation infrared spectroscopy.

Cyclic alkynes have been in recent times the subject of considerable interest, from either the theoretical or experimental point of view.[2-5] The integration of a triple bond into a small- or a medium-sized carbocycle is only possible through deviation of the C–C≡C–C moiety from the linear geometry, and this provokes an increasing destabilization of the system as the ring size decreases. The intriguing question is for the minimum ring size able to accommodate a triple bond, even for a transient existence. From an experimental point of view, cyclooctyne is readily available by dehalogenation of 1,2-dibromocyclooctene and exhibits a moderate stability.[6] The same is true for 3,3,7,7-tetramethylcycloheptyne (**1**),[7] but the parent compound, although easily generated, cannot be isolated.[6,8] No derivative of cyclohexyne has been reported with an appreciable lifetime in solution.[9] However, even the unsubstituted compound can be efficiently trapped as transition-metal complexes[10] and as Diels–Alder adducts.[11] Some five-membered ring cycloalkynes, like norbornyne (**2**),[12] 2,2,5,5-tetramethyl-1-thiacyclopentyne (**3**),[13] acenaphthyne (**4**),[14] and cyclopentyne (**5**),[15] have been generated. All of them have very short lifetimes in solution, but **4** has successfully been generated in an argon matrix at 15 K, and its UV and IR spectra have been recorded.[14] Indirect evidences on the generation of five-membered ring cycloalkynes include the isolation of the cyclotrimers of **2** and **4**[12,14] and the formation of the Diels–Alder adduct of **3** with 2,5-dimethylfuran and of the 1,3-dipolar cycloadduct of **3** with phenyl azide,[13] as well as the 2 + 2 cycloadducts of **5** with a variety of olefins.[15,16] All attempts to generate four-membered ring cycloalkynes have been up to now unsuccessful. The generation of cyclobutyne has never been substantiated,[17] and even the attempted synthesis of naphthocyclobutyne (**6**), postulated by similitude with **4** as a good candidate for a detectable cyclobutyne derivative, has not been confirmed.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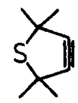
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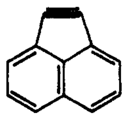
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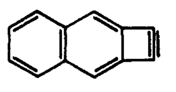
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It appears, therefore, that five-membered rings are the smallest able to accommodate a carbon–carbon triple bond in their structures and that, behind this limit, the energy cost of distorting the C—C≡C bond angles up to near 90° prevents the generation of cyclobutynes.

From the theoretical point of view, the problem of cyclic alkynes has been attacked in the opposite direction. Thus, Schaefer and co-workers have been interested in determining the smallest cycloalkyne whose singlet electronic state has a stable equilibrium

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geometry on the corresponding potential-energy hypersurface. Using a double-ζ-plus polarization (DZ+P) basis set, these authors have found that, at the two-configuration self-consistent-field (TCSCF) level of theory, singlet cyclopropyne is the transition state of the degenerate rearrangement of propadienylidene, whereas singlet cyclobutyne is a true relative minimum on the C_4H_4 potential-energy surface.[18,19] It is worth noting that both singlet species are calculated to have a remarkable diradical character.

Despite the interest of cyclopentyne as the smallest cycloalkyne ever detected, no detailed ab initio study of its electronic structure has been reported. Unpublished single-configuration MINDO/3[20] calculations by Gilbert and Baze[16] suggested that the C_{2v} structure of singlet cyclopentyne is a transition state linking two "π-complexes" of C_s symmetry. This theoretical result is in sharp contrast with the above-mentioned findings of Schaefer and coworkers on the existence of a stable C_{2v} equilibrium geometry for singlet cyclobutyne,[19] a considerably more strained molecule than cyclopentyne. However, a simple localized-bond picture shows that even in cyclopentyne one of the two formally equivalent acetylenic carbon–carbon π-bonds must necessarily be partially broken (i.e., the π-bond lying in the plane containing the four C—C≡C—C carbon atoms). As a consequence, the molecule is expected to have a considerable diradical character and cannot be adequately described by a single configuration wave function. A proper description requires a TCSCF wave function composed of the ground-state plus the HOMO → LUMO double excitation or an equivalent treatment. In fact, using a 3 × 3 CI wave function,[21] both MINDO/3 and MNDO[22] semiempirical methods predict that singlet cyclopentyne has a C_{2v} structure which is a genuine energy minimum on the C_5H_6 potential-energy surface.[23] A subsequent MNDO study of the 2 + 2 cycloaddition of cyclopentyne with ethylene (at the same level of theory) has allowed the understanding of the basic trends of its reactivity.[24]

Here we report the first comprehensive examination of the lowest singlet and triplet states of cyclopentyne at adequately high ab initio level. The present results confirm our preliminary predictions, based on the above-mentioned semiempirical methods and afford a more detailed picture of the structure and energetics of these species.

Computational Procedures and Results

Systems which are expected to have an important diradical character cannot be treated adequately at the closed-shell restricted Hartree–Fock (RHF)[25] level but require a multiconfiguration SCF (MCSCF) or an equivalent generalized valence-bond (GVB) treatment.[26] Therefore, we have optimized the geometry of singlet cyclopentyne at the GVB level by using a one-pair function to represent the acetylenic in-plane π-type bond. By contrast, a single-configuration SCF treatment of triplet cyclopentyne gives an acceptable description of this species. Consequently, the lowest energy triplet state of cyclopentyne was calculated by the ROHF (restricted open-shell Hartree–Fock) method.[27] All calculations employed the GAMESS program package[28] with suitable modifications.[29] Geometry optimizations used analytically calculated atomic forces in a Murtagh–Sargent multiparameter search routine.[30] To assess if the structure calculated for a given electronic state was a true energy minimum on the corresponding potential surface, the harmonic vibrational frequencies were determined by diagonalizing the matrix of the mass-weighted Cartesian force constants calculated numerically by finite differences of analytical gradients.[31] The small split-valence 3-21G basis set[32] was used in both the geometry optimizations and force constant calculations.

Table I. Optimized Molecular Structures[a,b] for the Lowest Singlet[c] and Triplet[d] Electronic States of Cyclopentyne

	$^1A_1$	$^3B_2$	$^1A'$	$^3A''$
C_1C_2	1.238	1.318	1.238	1.318
C_1C_3	1.514	1.515	1.515	1.517
C_3C_5	1.603	1.583	1.599	1.580
C_3H_6	1.081	1.082	1.081	1.081
C_3H_7	1.081	1.082	1.080	1.083
C_5H_8	1.081	1.080	1.082	1.080
C_5H_9	1.081	1.080	1.082	1.080
$C_2C_1C_3$	116.3	114.0	116.0	113.8
$C_1C_3C_5$	100.2	102.2	99.8	101.8
$C_3C_5C_4$	107.0	107.5	106.7	107.2
$H_6C_3H_7$	108.7	108.5	108.8	108.7
$H_8C_5H_9$	108.1	108.7	108.4	108.9
$C_3C_5H_8$	110.4	110.1	111.8	109.2
$C_3C_5H_9$	110.4	110.1	109.0	111.2
$C_1C_3H_6$	112.4	111.6	111.4	112.3
$C_1C_3H_7$	112.4	111.6	113.6	111.0
θ	0.0	0.0	13.1	12.9

[a] Geometrical parameters defined as in Figure 1. [b] Distances are in Å and angles in deg. [c] At the GVB/3-21G level of theory. [d] At the ROHF/3-21G level of theory.

Table II. Total Energies (in hartrees) and Singlet–Triplet Differences, ΔE(T–S) (in kcal/mol), for the Lowest Singlet and Triplet Electronic States of Cyclopentyne

state	level of theory	E, hartrees	ΔE(T–S), kcal/mol
$^1A_1$	GVB/3-21G//GVB/3-21G	−191.622 47	
$^3B_2$	ROHF/3-21G//ROHF/3-21G	−191.589 65	20.6
$^1A'$	GVB/3-21G//GVB/3-21G	−191.622 55	
$^3A''$	ROHF/3-21G//ROHF/3-21G	−191.589 72	20.6
$^1A'$	RHF/3-21G//GVB/3-21G	−191.559 95	
$^3A''$	ROHF/3-21G//ROHF/3-21G	−191.589 72	−18.7
$^1A'$	RHF/6-31G*//GVB/3-21G	−192.632 57	
3A″	ROHF/6-31G*//ROHF/3-21G	−192.662 87	−19.0
$^1A_1$	CISD/3-21G//GVB/3-21G	−192.020 32	
$^3B_2$	CISD/3-21G//ROHF/3-21G	−191.981 07	24.6

The first step in the present investigation was to determine the equilibrium geometries of singlet ($^1A_1$) and triplet ($^3B_2$) cyclopentyne within the constraints of C_{2v} symmetry. The most important geometrical details of the optimized structures found for these states are summarized in columns 1 and 2 of Table I (Cartesian coordinates of all optimized structures are available as supplementary material). The total energies and singlet–triplet energy separation are collected in Table II. The occupation numbers of the acetylenic in-plane π and π* natural orbitals in the GVB calculation of singlet cyclopentyne are given in Table III. The occupation number of the in-plane π* natural orbital reflects the amount of diradical character. For an idealized diradical this occupation number would be precisely 1.

It is to be noted that the ROHF/3-21G optimized structure found for the $^3B_2$ state is nearly identical with that previously calculated[23] by the unrestricted Hartree–Fock (UHF) method[33] with the 3-21G basis set, the energy difference being only 0.96 kcal/mol.

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Table III. Occupation Numbers of the Acetylenic In-Plane π and π^* Natural Orbitals in GVB/3-21G Calculations of Singlet Cyclopentyne

	natural orbital	
state	π	π^*
$^1A_1$	1.71	0.29
$^1A'$	1.71	0.29

The harmonic vibrational analysis showed that the 3-21G optimized structures for the $^1A_1$ and $^3B_2$ states of cyclopentyne have a weak ($\sim 104i$ cm^{-1}) imaginary frequency that correspond to a vibrational mode of b_1 symmetry which leads to a C_s structure. This implies that neither of the two states has a C_{2v} stable equilibrium geometry. To find the equilibrium geometries of the lowest energy singlet and triplet states of cyclopentyne, a C_s symmetry constrained geometry reoptimization was performed for both electronic states. The starting geometries of these calculations were the $^1A_1$- and $^3B_2$-optimized structures slightly modified according to the normal mode of imaginary frequency. These reoptimizations led to $^1A'$ singlet and $^3A''$ triplet states lying 0.04 and 0.05 kcal/mol below the $^1A_1$ and $^3B_2$ structures, respectively. The relevant geometrical details of the C_s-optimized structures are summarized in Table I. The total energies and the $^1A'$–$^3A''$ energy difference are given in Table II, and the above-mentioned natural orbital occupation numbers of the $^1A'$ state are included in Table III. The force constant analysis of the $^1A'$- and $^3A''$-optimized structures revealed that those are true energy minima on the corresponding potential-energy hypersurface. The harmonic vibrational frequencies calculated for these electronic states of cyclopentyne are listed in Table IV; the symmetry of each normal mode is also indicated in this table (normal modes in internal valence coordinates are available as supplementary material).

The influence of polarization functions (3d) at the carbon atoms on the $^1A'$–$^3A''$ energy separation of cyclopentyne was checked at the single-configuration SCF level by single-point calculations at the GVB/3-21G- and ROHF/3-21G-optimized geometries with the 6-31G* basis set.[34] The total energies and singlet–triplet energy gap calculated at this level of theory are included in Table II. Since the effects of polarization functions were found minor and GVB calculations in such a large basis would be very time consuming, we did not carry out single-point GVB/6-31G* calculations.

In an attempt to establish more reliable singlet–triplet separation, configuration interaction (CI) was performed at the GVB/3-21G and ROHF/3-21G optimum geometries. Since the separation for the $^1A'$ and $^3A''$ states was found to be identical with that calculated for the $^1A_1$ and $^3B_2$ states at the same level of theory (see Table II), and the number of configurations for CI generated from reference configurations of C_s symmetry ($^1A'$ and $^3A''$) is vastly much larger than the number of configurations generated from reference configurations of C_{2v} symmetry ($^1A_1$ and $^3B_2$), we decided to perform the CI calculations for the latter electronic states. The CI wave functions included all Hartree–Fock interacting[35,36] singly and doubly excited configurations (CISD) relative to the GVB ($^1A_1$) and ROHF ($^3B_2$) reference configurations. This amounted to 65 994 $^1A_1$ configurations for the singlet and 39 448 $^3B_2$ configurations for the triplet. The CISD calculated total energies and singlet–triplet energy gap are given in Table II.

Structure and Energetics

In comparing the optimized structures obtained for the singlet ($^1A'$) and triplet ($^3A''$) states of cyclopentyne, it is readily noticeable that the C_1C_2 bond distance is notably shorter (by 0.080 Å) in the case of the singlet. In the latter state, the distance has been lengthened by 0.035 Å with respect to the prototype C≡C distance in acetylene (1.203 Å). This result is consistent with the considerable amount of diradical character (ca. 29%; see Table III) shown by singlet cyclopentyne.

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

	symmetry	singlet ($^1A'$)	triplet ($^3A''$)
1	a'	82	83
2	a''	380	422
3	a'	686	695
4	a''	747	823
5	a'	798	826
6	a'	891	903
7	a''	934	970
8	a''	995	996
9	a'	1009	996
10	a''	1038	1048
11	a'	1143	1124
12	a''	1278	1287
13	a'	1346	1349
14	a''	1354	1350
15	a''	1416	1423
16	a'	1428	1428
17	a''	1462	1470
18	a'	1638	1635
19	a''	1650	1649
20	a'	1665	1663
21	a'	2054	1823
22	a'	3226	3228
23	a''	3252	3230
24	a'	3255	3256
25	a'	3268	3271
26	a''	3293	3272
27	a'	3303	3310

It is interesting to compare the structure calculated for singlet cyclopentyne with that found by Schaefer and co-workers for singlet cyclobutyne using an equivalent level of theory, namely a TCSCF wave function with a double-ζ (DZ) basis set.[19] At this level of theory the C≡C bond distance is predicted to be 1.277 Å, which is actually 0.039 Å greater than the value obtained for cyclopentyne. Thus, in terms of the C≡C bond distance, it is seen that the triple bond in singlet cyclopentyne is somewhat more "normal" than in singlet cyclobutyne. This result is also consistent with the larger diradical character predicted (ca. 34%) for the latter species. Another structural feature that is of critical importance in assessing the stability of cycloalkynes is the C—C≡C bond angle. This angle is predicted to be considerably wider in singlet cyclopentyne (116.0°) than in singlet cyclobutyne (95.0°). This result of course agrees with current intuition which attributes less strain to the former cycloalkyne.

Regarding the optimized structure of triplet cyclopentyne, it is noteworthy that the C_1C_2 distance is 1.318 Å, only slightly less than the standard carbon–carbon double-bond distance of 1.329 Å in ethylene. This result suggests, not unexpectedly, that in such triplet diradical species the acetylenic in-plane π-bond is completely broken. As found with the singlet state, comparison with the analogously calculated structure of triplet cyclobutyne shows that the C_1C_2 distance is significantly shorter (by 0.024 Å) in triplet cyclopentyne.

It is also interesting to compare the structures calculated for singlet and triplet cyclopentyne with those predicted in our previous semiempirical study.[23] The MINDO/3- and MNDO-predicted values for the C_1C_2 bond distance of triplet cyclopentyne (1.315 and 1.312 Å, respectively) are in remarkable good agreement with the ROHF/3-21G result. In the case of singlet cyclopentyne, however, the C≡C bond distances predicted by the above semiempirical methods at the 3 × 3 CI level of theory (1.278 and 1.263 Å, respectively) are notably longer than the GVB/3-21G value. In addition, the C–C bonds adjacent and opposite to the triple bond, in both the singlet and triplet structures, are found to be considerably longer by the present ab initio calculations than the values predicted by either the MINDO/3 or MNDO methods. However, it should be noted that the latter discrepancies between the predicted C–C bond distances are already found in the case

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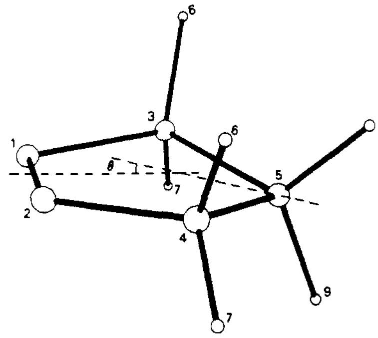

Figure 1. Computer plot of the optimized structure for the lowest energy singlet state ($^1A'$) of cyclopentyne.

of normal cycloalkanes when comparing the 3-21G calculated values with the results obtained by using the above semiempirical methods.

At first sight, the most striking structural differences found in comparing our previous semiempirical study of cyclopentyne with the present results is the small folding angle θ (see Figure 1) predicted for the equilibrium geometries of singlet and triplet cyclopentyne. However, it is readily seen from Table I that the geometrical differences, other than θ, between the planar and folded structures of both states are negligible. Therefore, although MINDO/3 and MNDO predict a planar arrangement of the five carbon atoms of cyclopentyne, rather than a folded structure, the real geometrical consequences of this shortcoming are irrelevant.

The singlet–triplet energy gap calculated at the GVB/RHOF level with the 3-21G basis set is 20.6 kcal/mol, the singlet being predicted to be the electronic ground state. One must be cautious here, however, since the level of theory employed, although being comparable for both electronic states, is by no means complete. Nevertheless, on the basis of the small effect of the polarization functions on the $^1A'$–$^3A''$ energy gap, determined approximately at the RHF/6-31G* level, and the estimated correlation effect (ca. 4 kcal/mol) on the $^1A_1$–$^3B_2$ energy gap, it seems unlikely that at higher levels of theory the relative energy ordering of the above states in cyclopentyne may be reversed. Moreover, we can report with some degree of confidence that the energy separation between the ground-state singlet ($^1A'$) and the lowest lying triplet ($^3A''$) in cyclopentyne is close to 25 kcal/mol. This singlet–triplet splitting is substantially larger than the values calculated for cyclopropyne and cyclobutyne (9.62 and 12.8 kcal/mol, respectively) at the CISD/DZ+P and CISD/DZ+d level, respectively.[18,19] The larger cyclopentyne singlet–triplet energy separation can be ascribed to the lesser diradical character shown by this species as compared with cyclopropyne or cyclobutyne. In this regard, it is interesting to recall that the estimated value of the adiatabic $S_0 \rightarrow T_1$ transition energy for acetylene is 46 kcal/mol.[37]

Finally, it should be noted that the singlet–triplet energy separation calculated from the heats of formation predicted in our previous semiempirical study of cyclopentyne is found to be exceedingly too small when compared with the present ab initio value. A recent study of Dewar and co-workers[38] on the performance of MNDO in calculating excited states has shown that the calculated energies of the lowest triplet states of the π,π^* type are systematically too negative. Therefore, it seems likely that the small singlet–triplet splitting predicted by the above semiempirical methods is due to an underestimation of the energy of the triplet cyclopentyne.

Vibrational Frequencies

When a symmetry analysis of cyclopentyne is performed, there arise 15 normal modes of the total symmetric irreducible representation, a′, and 12 normal modes of a″ symmetry. It is to be noted that the ordering of the vibrational frequencies (Table IV) is the same for singlet and triplet electronic states of cyclopentyne. Due to the high number of atoms that contribute to each normal mode, it is not possible to give a general description of the corresponding vibrational motion in terms of the conventional bond stretchings, bond–angle bendings, etc., except for some of them. Among the latter, it is of particular interest that the C≡C stretching in singlet cyclopentyne can be assigned to normal mode ν_{21}. This is predicted to be 2054 cm^{-1}. It should be noted here that the 3-21G SCF harmonic frequencies are expected to be of the order of 11% higher than the experimental frequencies.[39] Therefore, an empirical correction of 11% would reduce the calculated C≡C stretching frequency in singlet cyclopentyne to 1828 cm^{-1}. This value is reasonably close to the 1930-cm^{-1} frequency assigned tentatively by Chapman to the carbon–carbon triple-bond stretch **4**.[14] Note of course that **4** has a highly constrained structure compared to **5** and hence it is unlikely that the corresponding C–C stretching frequencies would be identical.

Comparison of the empirically predicted C–C stretching frequency in singlet cyclopentyne (1828 cm^{-1}) with those predicted or observed for other singlet cycloalkynes possessing either a higher or a lower number of carbon atoms in the ring is instructive. Thus, at the DZ TCSCF level of theory, Schaefer and co-workers[19] have calculated a C≡C stretching frequency of 1847 cm^{-1} for singlet cyclobutyne. Reduction of this frequency by 12%, the empirical correction suggested by the latter authors for DZ SCF harmonic frequencies, leads to an empirical prediction of 1625 cm^{-1}, which supports again the concurrent view that the carbon–carbon triple bond in singlet cyclopentyne should be stronger than in singlet cyclobutyne. Also, in going from singlet cyclopentyne to **1**, the stable seven-membered ring cycloalkyne, the expected changes occur. Thus, the frequency of 2180 cm^{-1} assigned to C≡C stretching for **1** is 352 cm^{-1} above that empirically predicted for singlet cyclopentyne, reflecting the expected relative strength of the C≡C bond in these cycloalkynes. Therefore, it seems to us that the frequency (1828 cm^{-1}) here predicted for the C≡C stretching in singlet cyclopentyne is quite reasonable. Since the most promising technique for the identification of singlet cyclopentyne in the near future is infrared matrix spectroscopy, we hope that the above frequency will prove to be a helpful result in aiding the identification of this species.

For triplet cyclopentyne the saving feature is the frequency predicted for the short carbon–carbon bond stretching (ν_{21}). This is calculated to be 1823 cm^{-1} at the ROHF/3-21G level of theory, and the above-mentioned empirical correction of 11% would reduce this value to 1622 cm^{-1}. For comparison, the observed C=C stretching frequency[40] in the structurally related cyclopentene molecule is 1618 cm^{-1}. Consequently, strictly on the basis of these carbon–carbon bond stretching frequencies, we would conclude that triplet cyclopentyne should be considered as a cycloalkene rather than a cycloalkyne. This is indeed just what was found in the case of cyclobutyne by Schaefer and co-workers.[19]

Finally, one more interesting result to be noticed is the small value of the lowest harmonic frequency (ν_1) predicted for both the singlet (82 cm^{-1}) and triplet (83 cm^{-1}) states of cyclopentyne. The vibrational motion associated to this frequency would lead to the planar C_{2v} structures calculated for these electronic states. The small value of the above frequencies is consistent with the extremely low potential energy change found in passing from the C_s structure to the C_{2v} one, for both electronic states.

Conclusions

The following points emerge from this study: (1) The lowest energy singlet and triplet electronic states of cyclopentyne prefer a C_s nonplanar structure, but the planarization energies are very small, indicating easy inversion. (2) The harmonic vibrational analysis of the optimized structures demonstrates that both electronic states are relative minima on the corresponding C_5H_6 potential-energy hypersurface. (3) Singlet cyclopentyne has a

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considerable amount of diradical character and cannot be adequately described by a closed-shell restricted Hartree–Fock method. (4) The triplet state ($^3A''$) is predicted to lie about 25 kcal/mol above the ground-state singlet $^1A'$. (5) The triple-bond harmonic stretching frequency for singlet cyclopentyne is predicted to be 1828 cm^{-1}, while the analogous stretching frequency for the triplet state is 1622 cm^{-1}.

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Registry No. Cyclopentyne, 1120-58-7.

Supplementary Material Available: Cartesian coordinates of the optimized molecular structures (C_{2v} and C_s symmetries) and harmonic frequencies and normal modes (in internal valence coordinates) for the lowest singlet (at the GVB/3-21G level of theory) and triplet (at the ROHF/3-21G level of theory) electronic states of cyclopentyne (13 pages). Ordering information is given on any current masthead page.

Electron Diffraction Investigation of Pseudorotation in 1,3-Dioxolanes

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Abstract: The gas-phase structures of 1,3-dioxolane, 2-methyl-1,3-dioxolane, and 2,2-dimethyl-1,3-dioxolane have been determined by least-squares analysis of gas-phase electron-diffraction patterns. Various rigid single conformer models, conformational mixtures of envelope and twist forms of the molecules, and pseudorotational models were tested. For 1,3-dioxolane the best results were obtained by using a pseudorotational model with a twofold barrier of about 0.3 kcal/mol. For 2-methyl-1,3-dioxolane a rigid model with the methyl group in the equatorial position gave the best fit. For 2,2-dimethyl-1,3-dioxolane a pseudorotational model with a twofold barrier of 1.1 ± 0.3 kcal/mol with the twist form being the more stable conformer gave the best agreement. These results are compared with previous experimental and theoretical results.

It is quite well-established that cyclopentane does not exist as static twist or envelope forms, instead it is constantly undergoing a large amplitude pseudorotational motion with nearly no barrier. We have recently been interested in the effects of exocyclic substitution on the pseudorotational potential function of cyclopentane. We have found that monosubstituted cyclopentanes like chlorocyclopentane[1] and cyanocyclopentane[2] have a hindered pseudorotational potential function which depends strongly on the nature of the substituents and that the stable conformers are the axial and equatorial forms. However, not enough experimental data are yet available to understand and predict the effect of substituents on the potential function.

One other way to influence the pseudorotational potential of cyclopentane is to make endocyclic substitution. Five-membered rings like tetrahydrofuran and 1,3-dioxolane are good candidates for these studies in that the oxygen atoms do not increase the barrier so much that only one conformer can be observed. For example, silacyclopentane has a twofold barrier of 4 kcal/mol,[3] and only the twist form is observed in the gas phase.[4] The molecular structure of tetrahydrofuran has been reported by Geise et al.[5] and the electron diffraction data were consistent with free pseudorotation. Other spectroscopic studies[6,7] have also shown this to be the case. We therefore decided to study the dioxolanes because there are available experimental and theoretical data for 1,3-dioxolane and for 2-methyl-1,3-dioxolane suggesting the presence of pseudorotational motion. The most stable form on the potential function of 1,3-dioxolane had not been resolved, and the twist, envelope, and a hybrid half-twist forms have all been proposed. We also felt that a more complete and perhaps detailed understanding of the pseudorotational motion could emerge if related dioxolanes were analyzed simultaneously by using the same procedures and programs. We have therefore chosen to study the molecular structures of 1,3-dioxolane, 2-methyl-1,3-dioxolane, and 2,2-dimethyl-1,3-dioxolane with particular attention paid to the pseudorotational motion of these compounds.

Cremer et al.[8,9] have employed ab initio molecular orbital calculations to study the effects of oxygen substituents in cyclopentane. Their findings indicated that nonadjacent oxygen substituents lowered the barrier to planarity but increased the barrier to pseudorotation while adjacent oxygen atoms raised both barriers. They found that the most stable forms in the first several members of the series were predicted to be twist instead of envelope. Cremer and Pople[8] noted that for 1,3-dioxolane the twist minimum was obtained by using 4-31G basis and that STO-3G gave the envelope form as minimum. However, the bond lengths and the methylene geometry in 1,3-dioxolane were fixed in these studies. Norskov-Lauritsen and Allinger[10] in their study on the treatment of

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