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

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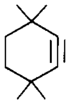
The structures of the lowest energy singlet and triplet electronic states of cyclohexyne have been determined by ab initio MO theory at the GVB and UHF levels, respectively, with the split-valence 3-21G basis set. Both electronic states prefer a C_2 nonplanar structure. Harmonic force constant calculations on the optimized structures demonstrate that both singlet (^{1}A) and triplet (^{3}B) cyclohexyne are relative minima on the corresponding C_6H_8 potential-energy hypersurface. The triplet state is predicted to lie about 42 kcal/mol above the ground-state singlet. Harmonic vibrational frequencies are predicted for both electronic states. The triple-bond harmonic stretching frequency for singlet cyclohexyne is predicted to be 2003 cm^{-1}, whereas the analogous stretching frequency for the triplet state is 1663 cm^{-1}. In terms of C$\equiv$C bond distance, diradical character, singlet–triplet energy separation, and C$\equiv$C stretching frequency, cyclohexyne should be considered as a normal, yet strained, alkyne.

Introduction

Cyclic alkynes are a subject of current interest, either from the experimental or theoretical point of view.[2-5] It now appears that the five-membered ring is the smallest one able to accommodate a carbon–carbon triple bond in its structure, since all attempts to generate cyclobutynes have failed,[3] and the generation of some cyclopentyne derivatives has been substantiated either by matrix isolation studies[4] or by trapping[5] and oligomerization[4,6] experiments. Moreover, the molecular and electronic structure[7] of the lowest singlet and triplet states of cyclopentyne as well its [2 + 2] cycloaddition with ethylene[8] have been studied from the theoretical point of view. Concerning the six-membered ring cycloalkynes, a great number of cyclohexyne derivatives have been reported.[2d] 3,3,6,6-Tetramethylcyclohexyne (1) has been generated in an argon matrix at 15 K and its IR spectrum has been recorded,[9] and even the parent compound (2) has been trapped in the form of platinum[10a-d] and zirconium[10e] complexes, or its formation inferred from the isolation of oligomerization and cycloaddition products.[11] On the other hand, as far as we know, no theoretical study on either the molecular or electronic structure of cyclohexyne has been reported.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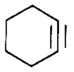
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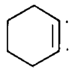
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Previous theoretical studies on the electronic structure of the lowest singlet state of cycloalkynes,[12,13] smaller than cyclohexyne have shown that in these strained molecules, due to the deviation of the C—C$\equiv$C—C group from the archetypal acetylenic linear geometry, one of the two formally equivalent carbon–carbon π-bonds is partially broken (i.e., the π-bond lying in the plane containing the four C—C$\equiv$C—C carbon atoms). As a consequence, these species have a considerable diradical character and cannot be adequately described by a single-configuration restricted Hartree-Fock (RHF) wave function.[14] A proper description requires a two-configuration self-consistent-field (TCSCF) wave function composed of the ground-state plus the HOMO → LUMO double excitation or the equivalent GVB treatment.[15] Since current intuition attributes a wider C—C$\equiv$C bond angle to cyclohexyne as compared with the aforementioned smaller ring cycloalkynes, a question arises on the importance of the diradical character in singlet cyclohexyne: Is the compound a "normal" alkyne and can it consequently be treated at the RHF level or is the diradical character of cyclohexyne still important as to require a TCSCF or the equivalent GVB treatment? In order to answer these questions, the present paper reports the results of an ab initio MO examination of the electronic structure of the lowest singlet state of cyclohexyne at both RHF and GVB levels of theory. For the sake of com-

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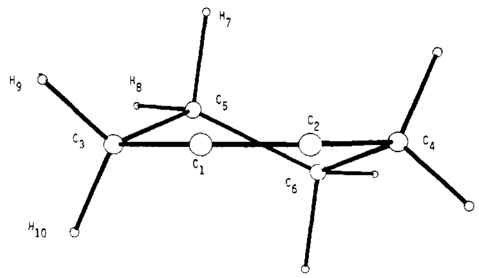

Figure 1. Computer plot of the optimized structure for the lowest energy singlet state (^{1}A) of cyclohexyne at the GVB/3-21G level of theory.

pleteness, we also report the results determined at comparable level of theory for the lowest triplet state of cyclohexyne.

Computational Details

The calculations reported in this paper were carried out within the framework of ab initio MO theory with the 3-21G split-valence basis set,[16] employing locally modified versions[17] of either GAUSSIAN80 system of programs[18] or GAMESS program package.[19] The lowest singlet state of cyclohexyne was calculated by the RHF method and, for comparison, by use of the GVB procedure with one-pair function to represent the acetylenic in-plane π-type bond. The spin unrestricted Hartree–Fock (UHF) method[20] was used for the lowest triplet state.

Geometries were initially optimized with the MNDO semiempirical SCF-MO method[21] and then further optimized with the 3-21G split-valence basis set, subject to specified molecular symmetry constraints, using analytical gradient methods.[22] Cartesian coordinates of all optimized structures of this investigation are available as supplementary material.

To assess if the structure calculated for a given electronic state was a true energy minimum on the corresponding potential-energy hypersurface, 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.[23]

Structure and Energetics

The first step in the present investigation was to determine the equilibrium geometry of singlet (^{1}A) cyclohexyne at the RHF level within the constraints of C_2 symmetry. The most important geometrical details of the optimized structure are summarized in column 1 of Table I, and the total energy is given in Table II. A singlet-point GVB calculation was then performed at the predicted RHF equilibrium geometry for the singlet state. As expected, the resulting GVB wave function showed an appreciable value (0.14) for the occupation number of the acetylenic in-plane π^* natural orbital, and the corresponding total energy was calculated to be 25.7 kcal/mol lower than the RHF one. Finally, a geometry reoptimization of singlet cyclohexyne was carried out at the GVB level. The relevant geometrical parameters of the resulting optimized structure are summarized in column 2 of Table I, and the total energy is given in Table II. The force constant analysis revealed that this optimized structure is a true energy minimum on the corresponding potential-energy hypersurface. A subsequent single-point RHF calculation at the GVB optimized geometry gave a total energy 27.8 kcal/mol higher than the calculated with the GVB wave function. The occupation number of the acetylenic in-plane π^* natural orbital in the GVB/3-21G optimized structure was calculated to be 0.16. For an idealized diradical, this occupation number would be precisely 1. Therefore, the lowest singlet state of cyclohexyne is predicted to have a 16% of diradical character.

Table I. Relevant Geometrical Parameters[a,b] of the Optimized Molecular Structures for the Lowest Singlet and Triplet Electronic States of Cyclohexyne

	^{1}A		^{3}B
	RHF/3-21G	GVB/3-21G	UHF/3-21G
distances			
C_1C_2	1.196	1.219	1.320
C_1C_3	1.484	1.488	1.505
C_3C_5	1.590	1.577	1.554
C_5C_6	1.562	1.558	1.554
C_5H_7	1.085	1.084	1.084
C_5H_8	1.084	1.084	1.084
C_3H_9	1.081	1.082	1.084
C_3H_{10}	1.083	1.083	1.085
angles			
$C_2C_1C_3$	132.8	131.0	125.1
$C_1C_3C_5$	101.1	103.1	109.4
$C_3C_5C_6$	114.6	113.6	110.6
dihedrals			
$C_3C_1C_2C_4$	4.3	1.7	1.2
$C_1C_2C_4C_6$	15.4	14.5	14.6
$C_3C_5C_6C_4$	58.6	41.1	45.8

[a] Geometrical parameters defined as in Figure 1. [b] Distances are in angstroms and angles and dihedrals in degrees.

Table II. Total Energies (in hartrees) and Relative Energies (in kcal/mol) for the Lowest Singlet and Triplet Electronic States of Cyclohexyne

state	level of theory	total energy	relative energy
^{1}A	RHF/3-21G//RHF/3-21G	−230.45034	26.7
^{1}A	GVB/3-21G//RHF/3-21G	−230.49128	1.0
^{1}A	GVB/3-21G//GVB/3-21G	−230.49289	0
^{1}A	RHF/3-21G//GVB/3-21G	−230.44858	27.8
^{3}B	UHF/3-21G//UHF/3-21G	−230.42603	42.0

A comparison between the RHF and the GVB optimized structures of singlet cyclohexyne shows only minor differences, the most significant change in bond distances being the lengthening of the C≡C bond as a consequence of the participation of the in-plane π^*-type bond in the GVB description. However, this participation is small, as indicated by the low value of the π^* natural orbital occupation number. Thus the GVB predicted C≡C bond distance (1.219 Å) is only slightly larger than the RHF/3-21G calculated C≡C bond distance in acetylene (1.187 Å).[24] Regarding the dihedral angles, both the RHF and GVB methods predict a nonplanar arrangement of the C—C≡C—C fragment, but the deviation from planarity is somewhat smaller in the GVB optimized structure (1.7°

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vs. 4.3°. In this context, the most important difference between the geometries optimized at the RHF and GVB levels of theory is in the predicted dihedral angles of the saturated moiety of the ring, the GVB treatment making it flatter by 17.5°. No X-ray diffraction data of cyclohexyne or other free six-membered ring cycloalkynes are available for comparison with the present theoretical results. However, the average value of $C{-}C{\equiv}C$ bond angles in [(cyclohexyne)Pt{$P(C_6H_5)_3$}$_2$][10c] and [(cyclohexyne)Zr{$P(CH_3)_3$}$(Cp)_2$][10e] is 125° and 127°, respectively, which are very similar to the predicted $C{-}C{\equiv}C$ bond angle in cyclohexyne.

Concerning the lowest energy triplet state of cyclohexyne, the C_2 symmetry constrained geometry optimization led to a structure which was shown to be a ^3B state. Although such a structure was computed using an UHF wave function, the calculated expectation value of the total spin angular momentum operator S^2 (2.003) indicated that the contamination by higher spin states was unimportant. The relevant geometrical parameters are summarized in column 3 of Table I, and the total energy is given in Table II. The force constant analysis revealed that the optimized structure is a true energy minimum on the potential-energy hypersurface associated to the electronic state ^3B.

Regarding the calculated structure for triplet cyclohexyne, the most interesting feature is the C_1C_2 bond distance of 1.320 Å, which is close to the experimental value of the carbon–carbon double-bond distance (1.335 Å) in cyclohexene.[25] This result suggests that in the triplet state, the acetylenic in-plane π bond of cyclohexyne is completely broken. The remaining geometrical parameters of the ^3B structure show only minor changes with respect to the equilibrium geometry calculated for the singlet state. However, it is to be noted that the C–C single bonds adjacent to the C_1C_2 bond have been lengthened by 0.018 Å, probably due to the diminution in the amount of s character of the hybridized orbitals of the C_1 and C_2 atoms in the triplet state, whereas the other C–C single bonds are somewhat shorter. The latter feature can be adscribed to the angular strain decrease in the triplet state, as compared with the singlet, reflected by the calculated $C{-}C{\equiv}C$ bond angle (125.1°) which is somewhat closer to the value (120°) attributed to an unstrained bond angle centered on a sp^2-hybridized carbon atom.

The ^1A–^3B energy separation calculated at the GVB/UHF level with the 3-21G basis set is 42.0 kcal/mol (Table II), the singlet being predicted to be the electronic ground state. This value, however, should be considered with caution since the level of theory employed, although comparable for both electronic states, is by no means complete. Indeed, it would be desirable to calculate the influence of both polarization functions and electron correlation on the above singlet–triplet energy gap. Because of computation-time limitations, we have not been able to carry out single-point energy calculations with the split-valence plus d-polarization (at the non-hydrogen atoms) 6-31G* basis set[26] using the configuration interaction approach, including all the singly and doubly excited configurations (CISD) relative to the GVB (^1A) and UHF (^3B) reference configurations, as we did for cyclopentyne.[7] Nonetheless, it is worth noting that in the latter cycloalkyne the singlet–triplet energy gap calculated at the GVB/ROHF level with the 3-21G basis set is 20.6 kcal/mol while at the CISD/6-31G* level it was estimated to be 25 kcal/mol.[7] Therefore, although it is likely that at higher levels of theory the calculated singlet–triplet energy gap in cyclohexyne may be somewhat different from 42.0 kcal/mol, we believe with some degree of confidence that it should be close to this value. In this regard, it is worth mentioning that the estimated value of the adiabatic $S_0 \rightarrow T_1$ transition energy in acetylene is 46 kcal/mol.[27]

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

ν	symmetry	^1A	symmetry	^3B
1	*b*	214	*b*	214
2	*a*	283	*a*	296
3	*a*	400	*a*	422
4	*b*	501	*b*	483
5	*a*	533	*a*	525
6	*b*	664	*b*	735
7	*a*	820	*a*	847
8	*a*	887	*a*	896
9	*b*	904	*a*	919
10	*a*	937	*b*	929
11	*b*	985	*b*	986
12	*b*	1013	*b*	1039
13	*a*	1060	*b*	1103
14	*b*	1140	*b*	1117
15	*a*	1189	*a*	1195
16	*b*	1287	*b*	1263
17	*a*	1298	*a*	1290
18	*a*	1377	*a*	1393
19	*b*	1385	*b*	1396
20	*b*	1449	*b*	1463
21	*a*	1478	*a*	1477
21	*b*	1497	*a*	1505
23	*a*	1503	*b*	1507
24	*a*	1638	*a*	1634
25	*b*	1645	*b*	1641
26	*b*	1646	*b*	1652
27	*a*	1655	*a*	1657
28	*a*	2251	*a*	1869
29	*b*	3197	*b*	3202
30	*a*	3201	*a*	3205
31	*a*	3228	*b*	3208
32	*b*	3229	*a*	3208
33	*a*	3240	*a*	3243
34	*b*	3245	*b*	3246
35	*a*	3271	*a*	3256
36	*b*	3274	*b*	3261

Vibrational Frequencies

In performing a symmetry analysis of cyclohexyne, there arise 19 normal modes of the totally symmetric irreducible representation, *a*, and 17 normal modes of *b* symmetry. The calculated harmonic frequencies for the lowest singlet (^1A) and triplet (^3B) states of cyclohexyne are listed in Table III; the symmetry of each normal mode is also indicated in this table (normal modes in internal valence coordinates are available as supplementary material). 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 $C{\equiv}C$ stretching in singlet cyclohexyne can be assigned to normal mode ν_{28}. This is predicted to be 2251 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.[28] Therefore, an empirical correction of 11% would reduce the calculated $C{\equiv}C$ stretching frequency in singlet cyclohexyne to 2003 cm^{-1}. This value is reasonably close to

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Table IV. Ab Initio Computational Results for the Lowest Singlet State of the First Four Cycloalkynes

ring size	basis set	C≡C bond distance[a]	C—C≡C bond angle[b]	C≡C stretching[c]	$\Delta E(S - T)$[d]	diradical character[e]
3[f]	DZ	1.262	66.1	1756[g]	8.2	26
4[h]	DZ	1.277	95.0	1644	9.0	33
5[i]	3-21G	1.238	116.0	1828	20.6	29
6	3-21G	1.219	131.0	2003	42.0	16

[a] In angstroms. [b] In degrees. [c] In cm^{-1}, with an empirical correction of 11%. [d] Singlet–triplet energy separation in kcal/mol. [e] In percent. [f] Reference 12. [g] Is not a true minimum.[31] [h] Reference 13. [i] Reference 7b.

the 2107 cm^{-1} frequency assigned by Krebs et al.[9] to the carbon–carbon triple-bond stretching of 1. Moreover, if one takes into account that the measured frequency of the C≡C bond stretching in 3,3,7,7-tetramethylcycloheptyne (2180 cm^{-1})[29] is reduced to 2121 cm^{-1} in cycloheptyne,[9] the expected frequency for the triple-bond stretching in cyclohexyne is ca. 2050 cm^{-1}, which is in better agreement with the aforementioned predicted value of 2003 cm^{-1}. Finally, it is worth noting that the predicted C≡C stretching frequency for cyclohexyne or, even more interestingly, that observed for the tetramethyl derivative 1, is close to the normal range of frequencies characteristic of standard carbon–carbon triple bonds.

For triplet cyclohexyne, the most remarkable feature is the frequency predicted for the C_1C_2 bond stretching (ν_{28}). This is calculated to be 1869 cm^{-1} at the UHF/3-21G level of theory, and the abovementioned empirical correction of 11% would reduce this value to 1663 cm^{-1}. For comparison, the observed C=C stretching frequency in the structurally related cyclohexene[30] molecule is 1649 cm^{-1}. A similar parallelism has been previously found between the corresponding short carbon–carbon bond stretching frequencies of triplet cyclobutyne and cyclobutene, and triplet cyclopentyne and cyclopentene. Thus, strictly on the basis of the predicted C_1C_2 bond-stretching frequencies, triplet cyclohexyne should be considered as a cycloalkene rather than a cycloalkyne, as it is also the case for the lowest triplet states of cyclobutyne and cyclopentyne.

Comparison of Cyclohexyne with Smaller Ring Cycloalkynes

It is instructive to compare the theoretical results obtained for cyclohexyne with those calculated for smaller ring cycloalkynes at a similar level of theory. Table IV summarizes the most relevant structural, energetic, and vibrational results calculated for the lowest singlet state of cyclopropyne,[12] cyclobutyne,[13] cyclopentyne,[7] and cyclohexyne, using either a double-ζ (DZ) for the 3-21G basis set with a TCSCF or the equivalent GVB wave function. It should be noted that the optimized structure obtained for singlet cyclopropyne is not a true energy minimum on the corresponding potential-energy hypersurface.[12,31]

One of the most important structural features in Table IV is that the larger decrease in the C≡C bond distance takes place in passing from cyclobutyne to cyclopentyne. Consequently, the latter species can be defined as the smallest "true" cyclic acetylene, namely, possessing a C≡C bond distance close to the standard triple-bond length in acetylene. Indeed, cyclopentyne is the smallest cycloalkyne for which transient existence has been inferred. Another structural feature that is of critical importance in assessing the stability of cycloalkynes is the deviation of the C—C≡C—C moiety from the linear geometry. As expected, the decrease in the amount of diradical character parallels the decrease in the angular strain along the series cyclobutyne, cyclopentyne, and cyclohexyne, as indicated by the increase in the C—C≡C bond angle. Thus the largest diminution of the calculated diradical character is found in passing from cyclopentyne to cyclohexyne. This result is consistent with the greater kinetical stability shown by the cyclohexyne derivatives as compared with five-membered ring cycloalkynes. Furthermore, the singlet–triplet energy gap calculated for cyclohexyne is approximately twice the value calculated for cyclopentyne.

Regarding the predicted C≡C stretching frequencies given in Table IV, it is to be noted a nearly constant increment in the series cyclobutyne, cyclopentyne, and cyclohexyne, accordingly with the diminution of the diradical character along this series and reflecting the expected relative strength of the C≡C bonds in these cycloalkynes.

Conclusions

The following points emerge from this study: (1) The lowest energy singlet and triplet electronic states of cyclohexyne are true minima on the corresponding C_6H_8 potential-energy hypersurface and both states prefer a C_2 symmetry nonplanar structure. (2) Singlet cyclohexyne has a moderate amount of diradical character and, therefore, from the geometrical point of view the single-configuration RHF description of this species seems to be acceptable. (3) The triplet state (^{3}B) of cyclohexyne is predicted to lie about 42 kcal/mol above the ground-state singlet (^{1}A). (4) The triple-bond harmonic stretching frequency for singlet cyclohexyne is predicted to be 2003 cm^{-1}, while the analogous stretching frequency for the triplet state is 1663 cm^{-1}. (5) In terms of C≡C bond distance, diradical character, singlet–triplet energy separation, and C≡C stretching frequency, cyclohexyne should be considered as a normal, yet strained alkyne.

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Supplementary Material Available: Cartesian coordinates of the optimized molecular structures and harmonic frequencies and normal modes (in internal valence coordinates) for the lowest singlet (at GVB/3-21G level of theory) and triplet (at UHF/3-21G level of theory) electronic states of cyclohexyne (18 pages). Ordering information is given on any current masthead page.

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