J. Am. Chem. Soc. **1987**, *109*, 5600-5605

Small-Ring Cyclic Alkynes: Ab Initio Molecular Orbital Study of 1,4-Dioxacyclohexyne (*p*-Dioxyne)

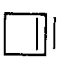
Santiago Olivella,*[1a] Miquel A. Pericàs,*[1a] Antoni Riera,[1a] Fèlix Serratosa,[1a] and Albert Solé[1b]

Contribution from the Departaments de Química Orgànica i Química Física, Universitat de Barcelona, 08028 Barcelona, Spain. *Received January 9, 1987*

Abstract: The structure of the lowest energy singlet and triplet electronic states of 1,4-dioxacyclohexyne (*p*-dioxyne) has 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) *p*-dioxyne are relative minima on the corresponding $C_4H_4O_2$ potential-energy hypersurface. Because of the considerable amount of diradical character exhibited by the ground-state singlet, the RHF approach predicts an artificial nonacetylenic Lewis structure for this state. The triplet state is predicted to lie about 13 kcal/mol above the ground-state singlet. Harmonic vibrational frequencies are predicted for both electronic states. The triple-bond harmonic stretching frequency for singlet *p*-dioxyne is predicted to be 1897 cm^{-1}, whereas the analogous stretching frequency for the triplet state is 1659 cm^{-1}. These predictions should assist in the identification of *p*-dioxyne from matrix-isolation infrared spectroscopy.

I. Introduction

Small-ring cyclic alkynes have been in recent years of considerable interest, either from a theoretical or experimental point of view, and this subject has been thoroughly reviewed.[2] Although high-level ab initio calculations[3] predict that cyclobutyne (**1**) is the smallest cyclic alkyne with a singlet ground state, only the five-membered ring homologues have been detected up to now.[4] In this theoretical context, we have recently reported an ab initio molecular orbital (MO) study of cyclopentyne (**2**), proving this species to possess a singlet ground state with a C_s nonplanar structure, which exhibits considerable diradical character.[5]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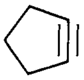
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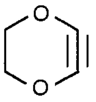
RO—C≡C—OR

3 R = $CH(CH_3)_2$

4 R = $C(CH_3)_3$

Our interest in acetylenic chemistry has been focused in recent times on the synthesis and synthetic applications of acetylene diethers,[6] the first stable members of this family of compounds, diisopropoxyethyne (**3**) and di-*tert*-butoxyethyne (**4**), having been prepared in our laboratories.[6a] Acetylene diethers were considered for a long time as "nonexistent compounds", but it is now clear that failure in the early attempts of synthesis of the lower members of this series was due to their tendency to undergo thermal polymerization at temperatures near 0 °C, and that this tendency to polymerization can be efficiently modulated by the steric bulk of the alkoxy substituents.[6a]

Within the framework of our research in the fields of acethylene diethers and cyclic alkynes, we decided to study the combined effects of distorting the O—C≡C bond angles and the lack of steric protection on the ynedioxy system. 1,4-Dioxacyclohexyne (*p*-dioxyne) (**5**) seemed to us a reasonable candidate either as the subject of a detailed theoretical study or as the target of subsequent experimental work.



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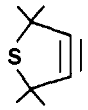

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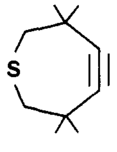

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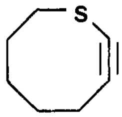

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Up to now, very little was known about small ring cyclic alkynes incorporating heteroatoms into the ring. Some reports have appeared on the synthesis of species such as 3,3,6,6-tetramethyl-1-thiacycloheptyne[7] (**6**) and 2,2,5,5-tetramethyl-1-thiacyclopentyne[8] (**7**), where the sulfur atom contributes to release strain due to the length of the C–S bonds, and only quite recently, 1-thia-2-cyclooctyne[9] (**8**), the first example of a cycloalkyne with a heteroatom directly bonded to the acetylenic group, has been reported. On the other hand, no theoretical study has been devoted to strained heterocyclic alkynes.

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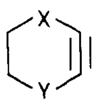
In a preliminary theoretical study on strained heterocyclic alkynes, we carried out semiempirical MNDO self-consistent-field (SCF) MO calculations[10] to elucidate the electronic and molecular structure of the series of compounds I.[11] To our surprise, when both atoms X and Y were first-row heteroatoms, the optimized structure of the lowest energy singlet state was predicted to be "nonacetylenic" in nature, being best described as a dipolar form corresponding to the Lewis structure II. Centering our study on the singlet state of p-dioxyne (I, X, Y = O), subsequent MNDO calculations using a 3 × 3 configuration interaction (CI) wave function[12] did not modify the results concerning the Lewis structure **5b** predicted for this state from the previous MNDO single-configuration calculations.



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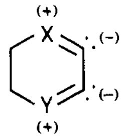

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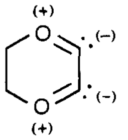

5b

In order to ascertain the true electronic nature of the ground state of p-dioxyne and to afford a more detailed picture of the structure and energetics of this species, here we report the first comprehensive ab initio MO examination of its lowest singlet and triplet states. In section II the results calculated for these states within the framework of the single-configuration (SCF) formalism are presented and discussed. In section III more reliable results obtained for the singlet ground state of p-dioxyne by the generalized valence-bond (GVB) treatment using one-pair function are analyzed.

II. Single-Configuration SCF Approach as a Starting Point

Computational Details. The calculations reported in this section were carried out within the framework of ab initio single-configuration SCF-MO theory with the small 3-21G split-valence basis set,[13] employing a locally modified version[14] of the GAUSSIAN 80 system of programs.[15] The restricted Hartree–Fock (RHF) formalism[16] was used for closed-shell singlet states and the spin-unrestricted Hartree–Fock (UHF) method[17] for triplet states.

Table I. Optimized Equilibrium Geometries (C_2 symmetry)[a,b] for the Lowest Singlet and Triplet Electronic States of p-Dioxyne

	^{1}A		^{3}B
	RHF/3-21G	GVB/3-21G	UHF/3-21G
	Bond Distances		
C_2O_1	1.348	1.372	1.372
C_6O_1	1.482	1.484	1.463
C_2C_3	1.410	1.229	1.313
C_5C_6	1.536	1.552	1.535
C_5H_7	1.079	1.079	1.080
C_5H_8	1.075	1.077	1.076
	Angles		
$C_3C_2O_1$	115.5	130.2	124.1
$C_3O_4C_5$	113.4	104.8	112.6
$C_5C_6O_1$	107.9	112.0	108.8
$H_7C_5H_8$	111.4	111.0	110.9
	Dihedral Angles		
$O_1C_2C_3O_4$	60.1	11.5	3.5
$C_2C_3O_4C_5$	25.3	7.3	14.0
$C_3O_4C_5C_6$	32.4	40.0	45.2

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

Table II. Total Energies (in hartrees) and Relative Energies (in kcal/mol) for Various Structures of the Lowest Singlet and Triplet Electronic States of p-Dioxyne

structure	symmetry	state	computational method	total energy	rel energy
5b	C_2	^{1}A	RHF/3-21G	−301.60499	31.5
5b	C_{2v}	$^1A_1$	RHF/3-21G	−301.58016	49.4
5	C_{2v}	$^1A_1$	RHF/3-21G	−301.58602	43.4
5c	C_2	^{3}B	UHF/3-21G	−301.63510	12.7
5c	C_{2v}	$^3B_2$	UHF/3-21G	−301.61864	23.0
5	C_2	^{1}A	GVB/3-21G	−301.65524	0
5	C_{2v}	$^1A_1$	GVB/3-21G	−301.64194	8.4

Geometries were initially optimized with MNDO subject to specified molecular symmetry constraints, then further optimized with the 3-21G basis set by either the Schlegel[18] or Murtagh–Sargent[19] multiparameter search routines, using analytically calculated forces.[20] 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 analytic gradients.[20] Normal modes in internal valence coordinates of all structures that were proven to be true energy minimum are available as supplementary material.

Singlet *p*-Dioxyne. We started our ab initio investigation by geometry reoptimization, within the constraints of C_2 symmetry, of the MNDO predicted equilibrium geometry **5b** for the lowest singlet electronic state (^{1}A) of p-dioxyne. The relevant geometric parameters of the resulting RHF/3-21G optimized structure are given in column 1 of Table I and its total energy in row 1 of Table II. The harmonic vibrational analysis showed that this stationary point is a true energy minimum on the corresponding potential-energy hypersurface.

Regarding the optimized structure calculated for the singlet state of p-dioxyne (^{1}A), it is worth noticing that the C_2C_3 bond distance has lengthened by 0.223 Å with respect to the RHF/3-21G predicted C≡C bond distance in acetylene (1.187 Å).[21] Another structural feature that is of critical importance in assessing the molecular structure found for the singlet state of p-dioxyne is the distance of C–O bonds adjacent to the C_2C_3 bond. This distance is predicted to be 1.348 Å, which is notably shorter than the value of 1.482 Å found for the carbon–oxygen single-bond distances C_5O_4 and C_6O_1. These results strongly suggest that the calculated RHF/3-21G equilibrium geometry for the singlet state

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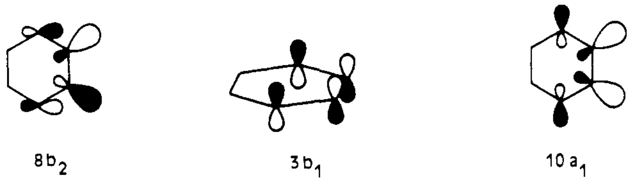
Chart I. Schematic Representation of the Atomic Orbitals of the Ynedioxy Group Which Make the Largest Contribution to the $10a_1$, $3b_1$, and $8b_2$ Molecular Orbitals in the $^1A_1$ State of *p*-Dioxyne



of *p*-dioxyne should be considered as the Lewis structure **5b** rather than the acetylenic structure **5**.

In an attempt to locate an isomeric acetylenic structure **5** for the singlet state of *p*-dioxyne, several C_2 symmetry constrained geometry optimizations were performed starting at different initial geometries with a C_2C_3 bond distance of 1.187 Å. All these calculations invariably led to the "nonacetylenic" structure **5b** already optimized. Finally, enforcing C_{2v} molecular symmetry, a structure with a C_2C_3 bond distance of 1.182 Å was located. The calculated total energy of this singlet state ($^1A_1$) is given in row 3 of Table II; from the relative energies given in the same table, it is predicted to lie 11.9 kcal/mol above the "nonacetylenic" singlet state ^1A. The harmonic vibrational analysis showed that the structure found for the $^1A_1$ state has one imaginary frequency that corresponds to a vibrational mode of a_2 symmetry which leads to a C_2 symmetry structure. To locate the corresponding equilibrium geometry, another C_2 symmetry constrained geometry optimization was performed starting at the above $^1A_1$ structure slightly modified according to the normal mode of imaginary frequency. Once more this optimization led to the singlet state (^1A) which has the Lewis structure **5b**.

At this point it is interesting to consider the valence electronic configuration calculated for the acetylenic $^1A_1$ singlet state of *p*-dioxyne. With the a_1 and b_2 irreducible representations denoting the in-plane symmetries, this electronic configuration can be written as follows:

$$4a_1^2\,4b_2^2\,5a_1^2\,6a_1^2\,5b_2^2\,1b_1^2\,7a_1^2\,6b_2^2\,8a_1^2\,1a_2^2\,7b_2^2\,2b_1^2\,9a_1^2\,2a_2^2\,10a_1^2\,3b_1^2\,8b_2^0 \qquad {}^1A_1 \quad (1)$$

The atomic orbitals (AOs) which make the largest contribution to the $10a_1$, $3b_1$, and $8b_2$ MOs are shown in Chart I. Since this singlet state has a symmetry plane containing the six-membered ring atoms, it is convenient to classify the valence MOs as symmetric or antisymmetric with respect to reflection in this plane. From the electronic configuration 1, it can be seen that the acetylenic singlet state $^1A_1$ has five occupied antisymmetric MOs: three essentially formed from linear combination of the out-of-plane p AOs of the six-membered ring atoms, and two from the s AOs of the hydrogen atoms. Consequently, this planar acetylenic singlet state possesses a six π-electron system. Furthermore, a simple localized-bond picture shows that four of the six π electrons can be ascribed to the lone pairs on the oxygen atoms and two to the "acetylenic" π bond orthogonal to the aforementioned plane of symmetry.

Promotion (relative to configuration 1) of the two $3b_1$ electrons to the empty $8b_2$ orbital gives rise to another singlet state possessing a four π-electron system. Again, a simple localized-bond picture shows that these four π electrons can be ascribed to the C_2O_1 and C_3O_4 π bonds. This π-bonding picture formally corresponds to the Lewis structure **5b**. Therefore, it appears that within the C_{2v} molecular symmetry there are two possible low-lying electronic singlet states for *p*-dioxyne: one with the ynedioxy group formally containing six π electrons (**5**) and the other with four π electrons on this group (**5b**).

In order to estimate the energy of the singlet state which has the Lewis structure **5b**, we calculated an approximate RHF wave function for such a closed-shell electronic state by starting with a density matrix generated from an orbital guess corresponding to an electronic configuration related to (1) in which the $8b_2$ orbital was doubly occupied rather than the $3b_1$ one. Admittedly, from the theoretical point of view, such a nonadiabatic electronic wave function is of limited significance. This arises from the fact that the above closed-shell singlet has the same symmetry (A_1) as the lower energy singlet state possessing the acetylenic structure **5**. Therefore, to obtain a true variationally optimized wave function for the "nonacetylenic" (**5**) singlet state, it is required that its wave function remain orthogonal to that of the lowest singlet state (**5**). Unfortunately, since a proper SCF calculation including this orthogonality constraint cannot be done with the standard version of GAUSSIAN 80, the geometry optimization of the second $^1A_1$ state (**5b**) was performed with the above-mentioned approximate wave function. The resulting structure showed an abnormally large C_2C_3 bond distance (1.689 Å), while the value of C_1O_2 and C_3O_4 bond distances was found to be 1.314 Å, which is actually 0.041 Å shorter than the value calculated for the acetylenic singlet state $^1A_1$. On the basis of the antibonding C_2C_3 character of the doubly occupied $8B_2$ orbital (see Chart I), the unusually long distance found for the C_2C_3 bond is not surprising. The calculated total energy of this second $^1A_1$ state is given in row 2 of Table II; from the relative energies given in the same table, it is predicted to lie 6 kcal/mol above the acetylenic singlet state $^1A_1$ and 17.9 kcal/mol above the lowest singlet state ^1A. The harmonic vibrational analysis showed that the optimized structure for the second $^1A_1$ singlet state has an imaginary frequency that corresponds to a vibrational mode of a_2 symmetry which leads to a C_2 structure.

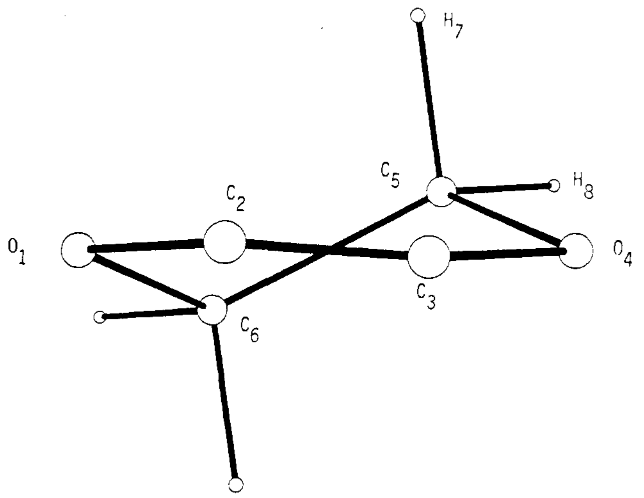


Figure 1. Computer plot of the optimized structure for the lowest energy singlet state (^1A) of cyclohexyne at the GVB/3-21G level of theory.

Obviously, when the molecular symmetry of *p*-dioxyne is lowered from the C_{2v} point group to the C_2 one, the symmetry plane that allows one to distinguish between the σ and π electrons vanishes, and, consequently, both $^1A_1$ states collapse to the lowest singlet state (^1A).

It is interesting to compare the electronic configuration 1 with the valence electronic configuration calculated for the lowest singlet state (^1A), which can be written in short form as follows:

$$\ldots\,10b^2\,12a^2\,11b^0 \qquad {}^1A \qquad (2)$$

By comparison of the topology of each one of the MOs which define the electronic configurations 1 and 2, it was found that the $10a_1$, $3b_1$, and $8b_2$ MOs correlate with the 12a, 11b, and 10b, MOs, respectively. Therefore, within the C_2 molecular symmetry the hypothetical acetylenic singlet state of *p*-dioxyne corresponds to the electronic configuration:

$$\ldots\,12a^2\,11b^2\,10b^0 \qquad {}^1A \qquad (3)$$

Consequently, in lowering the molecular symmetry from C_{2v} to the C_2 point group, double occupation of the formerly $8b_2$ MO (10b in C_2 symmetry) appears to be energetically more favorable than double occupation of the formerly $3b_1$ MO (11b in C_2 symmetry). This is illustrated in the MO correlation diagram given in Figure 2a. It is likely that such a reversal of the orbital occupation pattern obtained within the C_{2v} molecular symmetry is due to the fact that in the highly nonplanar structure adopted

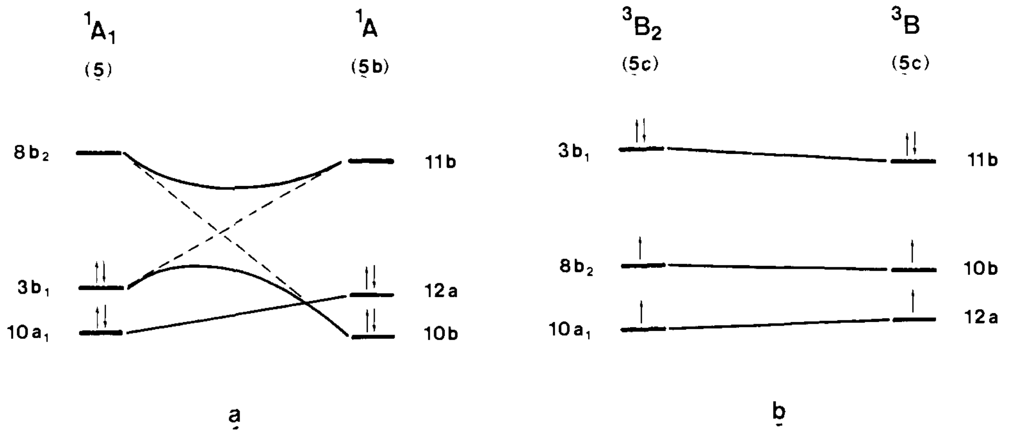


Figure 2. Molecular orbital correlation diagrams showing the effect of the molecular symmetry lowering ($C_{2v} \rightarrow C_2$) on the electronic configuration of the lowest energy singlet (a) and triplet (b) states of *p*-dioxyne.

Table III. Calculated Harmonic Vibrational Frequencies (in cm^{-1}) for the Lowest Singlet[a] and Triplet[b] States of *p*-Dioxyne

	symmetry	^1A	symmetry	^3B
1	b	304	b	125
2	a	307	a	315
3	a	471	a	469
4	b	525	a	511
5	a	554	b	553
6	b	831	b	858
7	a	875	a	902
8	a	916	b	939
9	b	997	b	999
10	a	1095	b	1081
11	b	1101	b	1150
12	b	1161	a	1173
13	a	1184	a	1202
14	a	1353	b	1360
15	b	1375	a	1389
16	a	1503	a	1514
17	a	1508	b	1520
18	b	1645	a	1656
19	a	1646	b	1657
20	b	2132	a	1864
21	a	3277	a	3256
22	b	3282	b	3260
23	a	3335	a	3328
24	b	3348	b	3334

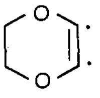
[a] At the GVB/3-21G level of theory. [b] At the UHF/3-21G level of theory.

by the atoms of the six-membered ring in the C_2 structure **5b** (reflected by the large value of dihedral angle $O_1C_2C_3O_4$ in Table I) the formerly $8b_2$ orbital is strongly stabilized because its C_2O_1 and C_3O_4 bonding character compensates for its antibonding C_2C_3 nature. Now, from these results it becomes clear that when a closed-shell RHF calculation is performed for *p*-dioxyne at the C_2 molecular geometry, during the iteration to self-consistency, the variational principle will enforce the occupation of the 10b orbital rather than 11b one. Consequently, *within the framework of the conventional RHF single-configuration wave function approach it is not possible to locate a ^1A singlet state for p-dioxyne possessing the acetylenic structure **5**.*

Triplet *p*-Dioxyne. The C_2 symmetry constrained geometry reoptimization of the MNDO predicted equilibrium geometry for the lowest triplet state of *p*-dioxyne led to a structure which was shown to be a ^3B state. Although such structure was computed using an UHF wave function, the calculatd expectation value of the total spin angular momentum operator S^2 (2.0047) indicated that the contamination by higher spin states was unimportant. The relevant geometrical details of the optimized structure are summarized in column 3 of Table I and the calculated total energy is given in row 4 of Table II. The force constant analysis revealed that the latter structure is a true energy minimum on the corresponding potential-energy hypersurface. The harmonic vibrational frequencies calculated for this triplet state of *p*-dioxyne are listed in column 2 of Table III.

From the relative energies shown in Table II, the calculated ^3B triplet state is found to lie 18.8 kcal/mol *below* the ^1A singlet state. Thus, at the single-configuration SCF/3-21G level of theory the ^3B triplet is predicted to be the ground state of *p*-dioxyne.

In comparing the optimized structures obtained for the ^1A and ^3B states (Table I), it is readily noticeable that the C_2C_3 bond distance is notably shorter (by 0.097 Å) in the case of the triplet. In the latter state, this distance is nearly identical with the RHF/3-21G optimized carbon–carbon double-bond distance (1.315 Å) in ethylene.[21] Furthermore, the harmonic vibrational frequency assigned to the C_2C_3 stretching (normal mode ν_{20} in Table III) is calculated to be 1864 cm^{-1}, which is nearly identical with the value (1869 cm^{-1}) calculated for the lowest triplet state of cyclohexyne at the same level of theory.[22] These results suggest, unexpectedly, that the *calculated lowest triplet state of p-dioxyne is structurally related to a triplet state (**5c**) arising from the acetylenic structure **5** rather than from the "nonacetylenic" Lewis structure **5b**.* This assertion is strongly supported by the electronic configuration obtained for the triplet state (^3B). Thus, in terms of the MOs used to define the electronic configuration (2) found for the ^1A state, the predicted electronic configuration for the ^3B state can be written in short form as:



5c

$$\ldots\ 12a^1\ 10b^1\ 11b^2 \qquad {}^3B \tag{4}$$

On the grounds of the arguments given above in discussing the electronic configuration of the singlet states ^1A and $^1A_1$, the latter ^3B state formally correlates with another triplet state of B_2 symmetry which has a planar-ring structure (C_{2v} molecular symmetry). In terms of the MOs used to define electronic configuration 1, this hypothetical triplet state will arise from the electronic configuration:

$$\ldots\ 10a_1{}^1\ 8b_2{}^1\ 3b_1{}^2 \qquad {}^3B_2 \tag{5}$$

This electronic state ($^3B_2$) is just the normal triplet state (**5c**) that might have been expected to arise from the planar acetylenic singlet state ($^1A_1$) by excitation, relative to configuration 1, of a $10a_1$ electron to the $8b_2$ orbital. In order to verify the latter hypothesis, a C_{2v} symmetry-constrained geometry reoptimization of the structure obtained for the ^3B state was carried out. This reoptimization led to a $^3B_2$ triplet state lying 10.3 kcal/mol above the ^3B state and 20.4 kcal/mol below the planar acetylenic singlet

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(22) Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Org. Chem.*, in press.

state ($^1A_1$). The total energy calculated for this $^3B_2$ state is given in row 5 of Table II. As expected, its electronic configuration is just that shown in (5), and the calculated C_2C_3 bond distance (1.306 Å) again is nearly identical with the RHF/3-21G optimized carbon–carbon double-bond distance in ethylene.

We conclude, therefore, that the calculated lowest triplet state ^3B of *p*-dioxyne does *not* arise from the singlet state ^1A by excitation (relative to configuration 2) of one 12a electron to the 11b orbital but from an hypothetical singlet state of acetylenic nature with the electronic configuration 3, by promotion of one electron from the doubly occupied 12a orbital to the empty 10b orbital. As previously mentioned, this acetylenic singlet state (^1A) cannot be calculated at the conventional SCF level of theory.

At this point it is worth noting that, at variance with the lowest energy singlet state, in lowering the molecular symmetry from C_{2v} to the C_2 point group the electronic configuration of the lowest triplet state is maintained; namely, the formerly $3b_1$ MO (11b in C_2 symmetry) remains doubly occupied in both molecular geometries. This is illustrated in the MO correlation diagram in Figure 2b. Since the single-configuration SCF treatment of a triplet state (e.g., ^3B) allows for some electron corelation between the electrons of the singly occupied MOs (e.g., 12a and 10b in ^3B), due to the exchange correlation, the above results suggest that if in some way one allows for electron correlation between these two electrons in the corresponding closed-shell singlet state (e.g., the electrons occupying the 12a MO in the ^1A singlet 3, the electronic configuration of this state would also be maintained during the above-mentioned molecular geometry changes.

III. Generalized Valence-Bond Approach to the Electronic Structure of Singlet *p*-Dioxyne

The conclusion reached at the end of section II seems to suggest rather strongly that for singlet *p*-dioxyne it may exist an acetylenic C_2 structure which has electronic configuration 3. As a consequence of the deviation of the O—C≡C—O moiety from the linear geometry in this strained structure, it is likely that one of the two formally equivalent acetylenic carbon–carbon π bonds might be partially broken (i.e., the π bond lying in the plane containing the four atoms of the ynedioxy group). Therefore, such a structure is expected to have some diradical character and cannot be adequately described by a single-configuration wave function because it is necessary to include the electron correlation between the two electrons forming the partially broken in-plane π bond. A proper description requires a two-configuration SCF (TCSCF) wave function composed of configuration 3 plus the 12a → 10b double excitation or the equivalent GVB treatment.[23] Consequently, the equilibrium geometry of the hypothetical acetylenic singlet state (^1A) of *p*-dioxyne was searched at the GVB/3-21G level by using a one-pair function to represent the above-mentioned in-plane π-type bond. This calculation and all those reported in this section were carried out employing the GAMESS program package[24] with suitable modifications.[25] Geometry optimizations used analytically calculated atomic forces in a Murtagh–Sargent multiparameter search routine,[19] and the Cartesian force constant matrices were evaluated by numerical differentiation of the analytic energy gradient.[20]

The most important geometric parameters of the resulting GVB/3-21G optimized structure for the singlet state ^1A of *p*-dioxyne are summarized in column 2 of Table I and its total energy in row 6 of Table II. Although the predicted C_2C_3 bond distance is slightly (0.026 Å) larger than the prototype C≡C distance in acetylene (1.203 Å) and the distance of the two C—O bonds adjacent to the C_2C_3 bond are somewhat short for a normal carbon–oxygen single bond, the optimized geometry is consistent with the acetylenic structure **5**. Moreover, it is worth mentioning that at the same level of theory (GVB/3-21G) the C≡C bond distance in singlet cyclohexyne is predicted to be 1.219 Å.[22]

The force constant analysis of the optimized structure for the above acetylenic state (^1A) proved that it is a true equlibrium geometry. The calculated harmonic vibrational frequencies are listed in column 1 of Table III. It is noteworthy that the vibrational frequency assigned to the C_2C_3 stretching (normal mode ν_{20} in Table III) is calculated to be 2132 cm^{-1}, which is somewhat closer to the value (2051 cm^{-1}) calculated for the singlet cyclopentyne than to the value (2251 cm^{-1}) calculated for singlet cyclohexyne at the same level of theory.[22] Moreover, the occupation number of the acetylenic in-plane π and π^* natural orbitals in the GVB calculation are found to be 1.71 and 0.29, respectively, which are identical with those calculated for the lowest singlet state of cyclopentyne.[5] From the latter natural orbital occupation number a 29% of diradical character is evaluated for both species. Interestingly, this diradical character is substantially higher than the value (16%) calculated for singlet cyclohexyne at the same level of theory.[22] These results indicate that the main effect of the oxygen atoms upon the alkyne fragment of the singlet state of the prototype six-membered ring cycloalkyne is a small weakening of the C≡C bond strength along with an augmentation of its diradical character. In other words, the lowest singlet state of *p*-dioxyne resembles more singlet cyclopentyne than singlet cyclohexyne.

In light of the total energies shown in Table II, the acetylenic singlet state ^1A calculated at the GVB/3-21G level of theory is predicted to be the lowest electronic state of *p*-dioxyne. Consequently, *only when the diradical character of the strained structure **5** is properly taken into account, does it become clear that the acetylenic singlet state ^1A is the ground state of p-dioxyne.*

The ^1A–^3B energy separation calculated at the GVB/UHF level is 12.7 kcal/mol. One must be cautious here, however, since the level of theory employed, although comparable for both electronic states, is by no means complete. In particular, it would be desirable to calculate the influence of both polarization functions and electron corelation 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 nonhydrogen 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.[5] Nonetheless, it is worth noting that in the latter cycloalkyne the single–triplet energy gap calculated at the GVB/ROHF level with the 3-21G basis set is 20.6 kcal/mol while that at the CISD/6-31G* level was estimated to be 25 kcal/mol.[5] Therefore, although it is likely that at higher levels of theory the above calculated ^1A–^3B energy separation may change somewhat, we believe with some degree of confidence that the relative energy ordering of these states in *p*-dioxyne is not going to be reversed.

Finally, we thought it would be interesting to evaluate at the same level of theory the energy difference between the planar (C_{2v}) and nonplanar (C_2) arrangement of the six-membered ring atoms in the lowest singlet state of *p*-dioxyne. Enforcing C_{2v} molecular symmetry, a geometry optimization was carried out, starting at the RHF/3-21G calculated geometry for the $^1A_1$ state using a GVB one-pair function to represent the in-plane acetylenic π-type bond. The resulting structure showed a C_2C_3 bond distance of 1.220 Å. As expected, the harmonic vibrational analysis indicated that this structure has an imaginary frequency that coresponds to a vibrational mode of a_2 symmetry which leads to the singlet ground state (^1A); thus, it is the transition state for the interconversion of the two C_2 conformations of the latter state. From the calculated total energy for this $^1A_1$ state (given in row 7 of Table II), an energy difference of 8.4 kcal/mol is predicted between the planar and nonplanar arrangement of the six-membered

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[23] Goddard, W. A.; Dunning, T. H.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.

[24] Dupuis, M.; Spangler, D.; Wendoloski, J. J. *National Resource for Computation in Chemistry*, Software Catalog Program QG01, 1980 (extended by N. W. Schmidt and S. T. Elbert, 1983).

[25] Solé, A., unpublished. Most of the modifications made in the original GAMESS code concern its implementation on IBM computers running under the VM/CMS operating system. Other changes are related with new restart options concerning large CI calculations and the computation of the Cartesian force constant matrix.

[26] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

ring atoms in the singlet ground state of *p*-dioxyne. This value is substantially larger than the calculated (0.04 kcal/mol) energy difference between the planar (C_{2v}) and folded (C_s) structures of singlet cyclopentyne. Interestingly, from the relative energies given in Table II, it is found that at the GVB/3-21G level the $^1A_1$ singlet state, which is the planar form of the singlet ground state of *p*-dioxyne, lies 14.6 kcal/mol *below* the corresponding planar triplet state ($^3B_2$). This prediction is consistent with the relative singlet–triplet energy ordering found for the equilibrium structures (C_2) of these states.

Since it is plausible that the most promising technique for the identification of singlet *p*-dioxyne in the near future will be the infrared matrix spectroscopy, we turn our attention to the calculated C≡C stretching frequency for this species. 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.[27] Therefore, an empirical correction of 11% would reduce the calculated C≡C stretching frequency in singlet *p*-dioxyne to 1897 cm^{-1}. Analogously, for the lowest triplet state (^3B) of *p*-dioxyne, a corrected C_2C_3 bond stretching frequency of 1659 cm^{-1} can be predicted. For comparison, the observed C=C stretching frequency[28] in the structurally related *p*-dioxene molecule is 1654 cm^{-1}. Consequently, strictly on the basis of these carbon–carbon bond stretching frequencies, we would conclude that the triplet *p*-dioxyne should be considered as a cycloalkene rather than a cycloalkyne. We hope that these frequencies will prove to be helpful in aiding the identification of these species.

IV. Conclusions

The following conclusions can be drawn from the calculations presented here. (1) The electronic ground state of *p*-dioxyne is a singlet state (^1A) which has a nonplanar (C_2) acetylenic structure. (2) Because of the considerable amount of diradical character exhibited by the ground-state singlet, the single configuration RHF approach predicts an artificial nonacetylenic Lewis structure for this state. (3) The lowest energy triplet state of *p*-dioxyne (^3B) is predicted to lie about 13 kcal/mol above the ground-state singlet and also has a nonplanar (C_2) structure with a normal carbon–carbon double bond in the ynedioxy moiety. (4) The triple-bond stretching frequency for singlet *p*-dioxyne is predicted to be 1897 cm^{-1}, while the double-bond stretching frequency for the triplet state is 1659 cm^{-1}.

Acknowledgment. The authors have benefited from several discussions with Professor Roald Hoffman during his visit to Barcelona. The calculations were carried out using the IBM 4341 computer at the "Centre d'Informàtica de la Universitat de Barcelona" and a DEC VAX 11-750 computer purchased with funds provided by the CAICYT (Grant No. 657/81). The GAMESS program was kindly made available by Dr. Michael L. Mckee. We are indebted to the referees for their useful remarks, which served to clarify various points in the initial manuscript.

Registry No. *p*-Dioxyne, 68997-21-7.

Supplementary Material Available: Cartesian coordinates of the optimized molecular structures (C_2 and C_{2v} symmetries) and harmonic frequencies and normal modes (in internal valence coordinates) for the ground-state singlet (at GVB/3-21G level of theory) and triplet (at UHF/3-21G level of theory) electronic states of *p*-dioxyne (16 pages). Ordering information is given on any current masthead page.

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

(28) Measured by the authors (liquid film, NaCl) on a Perkin-Elmer 681 spectrophotometer.

Insertion of Carbon Monoxide into the Sc–H Bond of Cl_2ScH

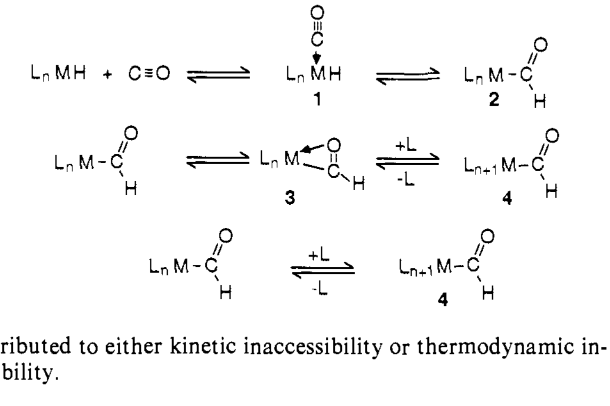
A. K. Rappé

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received February 5, 1987*

Abstract: Correlated ab initio theoretical calculations at the valence double-ζ plus polarization level are used to study the insertion of carbon monoxide into a scandium–hydrogen σ bond. We find a Lewis acid–Lewis base interaction between scandium and the carbon monoxide of 16.4 kcal/mol. The reaction occurs with a relatively small activation energy ($\Delta E^* = 23.7$ kcal/mol with respect to the Lewis acid–base complex) leading to an η^2-formyl complex. The reaction is moderately exothermic ($\Delta E = -6.1$ kcal/mol with respect to the Lewis acid–base complex). The explanation for the small barrier is precisely the same as for previously studied metallo 2 + 2 reactions. The effect of polarization functions and electron correlation on the position of the transition state and the exothermicity of the reaction were also studied.

Metalloformyl and acyl species are frequently invoked as key intermediates in the metal-catalyzed reduction of CO and the synthetically useful carbonylation reactions.[1] Despite η^1-acyls being rather common[1,2] there are relatively few examples of η^1-formyl complexes[3] and even fewer examples of direct insertion of CO into M–H bonds.[4] There are also few examples of η^2-formyl or -acyl species.[5] The rarity of these species has been attributed to either kinetic inaccessibility or thermodynamic instability.

Scheme I



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(3) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1 and references therein.

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