Cyclopropenyl Anions: Carbon Tunneling or Diradical Formation? A Contest between Jahn−Teller and Hund

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S *Supporting Information*

ABSTRACT: The π bond shifting (automerization) by carbon tunneling of cyclopropenyl anions was computationally analyzed by the small curvature tunneling methodology. Similar to other antiaromatic cases, the process is hindered by substituents departing from planarity, since these groups must be realigned along with the π bond shifting. With hydrogens as substituents the tunneling is extremely fast, in a case of both heavy and light atom tunneling. But, with more massive substituents (such as Me and F), and especially with longer groups (such as CN), the tunneling probability is reduced or even virtually canceled. The automerization of triphenylcyclopropyl anion by tunneling was supposed to be impossible due to the high mass of the phenyl groups. However, it was found that the ground state of this species is actually a D_{3h} aromatic triplet, a single-well system that cannot undergo automerization. For this and other systems with π acceptor groups, the superposition of states that generates the second-order Jahn−Teller distortion is diminished, and by Hund's rule, the triplet results in the ground state.
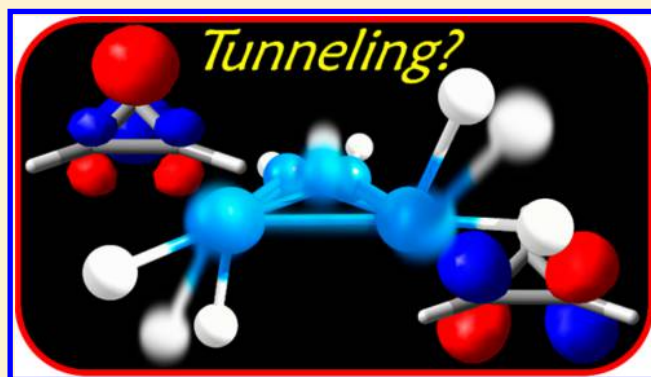
INTRODUCTION

Cyclopropenyl anion (**CPA**) is the smallest member of the family of "antiaromatic" molecules,[1−3] complying with the $4n$ Hückel rule (although it has been argued that its behavior is closer to a nonaromatic system,[4] since a ring that breaks the symmetry by a Jahn−Teller distortion technically loses its antiaromatic character). As other antiaromatic molecules, it can rearrange through π bond shifting (i.e., automerization reaction),[5] moving the shorter bond around the triangle, as exemplified by the valence bond structures of Scheme 1.

Scheme 1

Cyclopropenyl Anion (**CPA**)
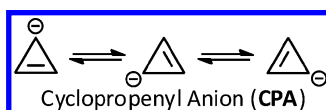
CPA has a two close energy isomers, according to its HOMO occupation (orbitals b_1 or a_2; see Scheme 2). In a perfect D_{3h} geometry both orbitals are degenerate, giving rise by Hund's rule to a triplet as the lowest state.

The distortion from a D_{3h} to a C_{2v} geometry is caused by a pseudo-Jahn−Teller effect.[6−9] However, having an imaginary out-of the plane vibrational mode, the planar C_{2v} is still not stable, and in a second distortion the molecule loses its planarity to end in a C_s symmetry,[8,10,11] as shown in Figure 1.
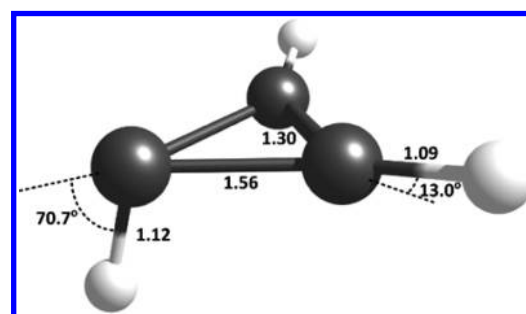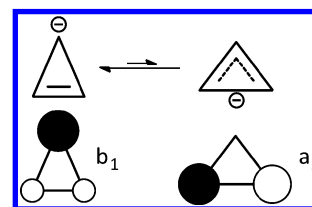
Scheme 2

Figure 1. Ground state geometry of **CPA**, calculated with M06-2X/6-31+G(d), including angles and bond distances (Å).

Quantum mechanical tunneling (QMT) on the π bond shifting of cyclobutadiene (**CBD**) has been observed over 30 years ago,[12−14] with subsequent experimental and theoretical confirmations of the carbon tunneling as the main factor for this reaction.[15−19] Due to the moderate activation energies, but mostly due to the narrow barriers,[20−22] QMT is a significant factor in the automerization of **CBD** and several other antiaromatic molecules, especially for pentalene.[23] However, some antiaromatic systems have a slow or inexistent tunneling for the π bond shifting. These cases have an out-of plane movement of the atoms through the automerization reaction, a fact that widens the barriers and hinders the tunneling probability. Such systems include heptalene and *tert*-butyl pentalene, which cannot tunnel from the ground state but require some thermal energy to proceed by QMT (i.e., thermally activated tunneling).[23]

CPA in its π bond shifting has a wide out-of plane bending of the hydrogens, as shown in Figure 2. This large trajectory may
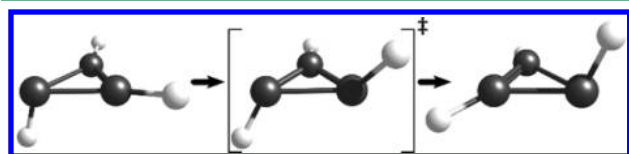

Figure 2. Automerization of **CPA**, illustrating the out-of plane movement of the hydrogens: the H on the right goes from an "equatorial" position to an "axial" one, while the opposite happens to the H on the left. The double bond shifts from right to left.

hinder the possibility of having QMT on this system. On the other hand, the mass of the hydrogens is low, and therefore, the carbon tunneling may be the determining factor.

Therefore, we will analyze the possibility of QMT on the automerization of **CPA**, and the factors that shape the kinetics of the reaction. This was already proposed by Dewar and Merz.[24] These results will be compared to other cyclopropenyl anions, including F, Me, CN, and Ph substituted systems. It must be noted that carbon QMT in three-member rings has also been observed and computed for ring opening and ring expansion reactions (see for instance refs 25−29).

CPA with phenyl substituents showed a different behavior compared to the other cyclopropenyl anion cases. Its ground state is not a singlet, but a diradical aromatic triplet with both b_1 and a_2 orbitals semioccupied. We will analyze the reasons for the stabilization of this spin state that produces a one-well potential canceling the possibility of QMT.

■ COMPUTATIONAL METHODOLOGY

Rate constants for passage over the reaction barriers were computed using canonical variational transition state theory (CVT)[30] and the contributions of multidimensional tunneling were incorporated using the small curvature tunneling (SCT) approximation[31] with step size of 0.001 Bohr and quantized reactant state tunneling (QRST) for the reaction coordinate mode. This approach has proven to be successful in previous theoretical studies.[32,33] The rate constants were computed with Polyrate,[34] using Gaussrate[35] as the interface between Polyrate and Gaussian09.[36] Unless specified, SCT values include the CVT rate constant and the tunneling correction.

SCT calculations require calculation of energies, energy gradients, and second derivatives, not only at the reactant and TS geometries but also at many points along the reaction

pathway. High quality, wave function based SCT calculations are not practical for this method. In our previous paper on the automerization of antiaromatic molecules it was found that, for these reactions, M06-2X[37] is an accurate functional, even with a small basis set, 6-31G(d).[23] We decided to use 6-31+G(d), since the diffuse function improve the accuracy of anionic molecules. Therefore, M06-2X/6-31+G(d) was selected for all the rate constant calculations presented here.

M06-2X is adequate for kinetic and tunneling calculations, but has a strong bias in favor of diradicals. Therefore, for accurate singlet−triplet excitations, (u)CCSD(T)-F12b single point energy calculations were carried out[38] with cc-pVDZ-F12 basis set[39] (unless specifically noted) with Molpro 10.[40]

An important and confusing conceptual point (that luckily does not significantly affect the rate constants) is the symmetry numbers of the reaction.[41] The reactant symmetry is C_s, with a symmetry number of $\sigma_R = 1$, while the TS is a C_2 with $\sigma_{TS} = 2$, and therefore $\sigma = \sigma_R/\sigma_{TS} = 1/2$ (i.e., the rate should, in principle, be divided by two). However, as long as all the C and H atoms are indistinguishable, the reaction is symmetric (reactant to product is identical to the reaction in the opposite direction), and therefore, the rate must be doubled, resulting in a cancellation of the symmetry number effect.[42]

■ RESULTS AND DISCUSSION

Cyclopropenyl Anion (CPA). The internal energy barrier for the automerization reaction of **CPA** is small, only 3.9 kcal/mol at the M06-2X/6-31+G(d) level (3.8 kcal/mol with CCSD(T)-F12b/cc-pVTZ-F12). At room temperature, the bond shifting is so fast that the rate with (SCT) or without (CVT) tunneling are virtually identical (1.6×10^{10} 1/s; see Table 1 and Figure 3). However, at cryogenic temperatures the thermal reaction is negligible, while the calculated tunneling corrected rate is significant (2.5×10^6 1/s). In other words, similar to other antiaromatic molecules,[23] the π bond shifting on **CPA** is so fast that any experimental measure of this rate will show an apparent one well system instead of the three wells corresponding to the three isomers (Scheme 1).

From Table 1 and Figure 3 we can conclude that below 50 K, where a plateau is reached, tunneling proceeds exclusively from the ground state. At 100 K approximately half of the automerization proceeds by tunneling from the ground state, half by thermally activated tunneling, and only 1% occurs by a classical over the barrier mechanism. At 175 K the tunneling probability equals the thermal crossing probability, while above 250 K QMT is insignificant.

As mentioned before, a factor that hinders the automerization of antiaromatic molecules is their nonplanarity. For instance in heptalene, the π bond shifting requires an almost planar transition state, but the displacement of the atoms to achieve that planarity is significant. Therefore, in spite of the fact that the planarization barrier of heptalene is low,[23] its automerization by QMT is improbable from the ground state. Nevertheless, with a small amount of thermal energy it is possible for heptalene to reach the flat geometry, and therefore a thermally activated tunneling is possible.

CPA has a planar carbon structure, but the hydrogens are not in the plane (see Figure 1). The automerization involves the out-of plane bending of the hydrogens, a significant movement. Can this nonplanarity cause a drastic lowering in the tunneling probability from the ground state (as in the heptalene case) in spite of the low mass of the H atoms? Clearly the automerization of **CPA** is fast even at 0 K (see Table 1), but

Table 1. CVT and SCT Rate Constants (1/s), Half-life (s), and Computed Internal Energies of Activation ($\Delta E^{\ddagger}$, kcal/mol) for the Automerization of CPA, FCPA, MeCPA, and CNCPA

|	CPA			FCPA			MeCPA			CNCPA		
$\Delta E^{\ddagger}$	3.9			6.0			2.3			4.3		
T	CVT	SCT	$t_{1/2}$	CVT	SCT	$t_{1/2}$	CVT	SCT	$t_{1/2}$	CVT	SCT	$t_{1/2}$
10	1.7×10^{-64}	2.5×10^{6}	2.7×10^{-7}	4.5×10^{-114}	8.9×10^{-7}	7.8×10^{5}	5.8×10^{-35}	4.9	0.14	4.7×10^{-83}	2.6×10^{-20}	2.6×10^{19}
50	9.7×10^{-4}	2.6×10^{6}	2.7×10^{-7}	1.2×10^{-13}	4.3×10^{-6}	1.6×10^{5}	8.5×10^{2}	5.7×10^{3}	1.1×10^{-4}	1.9×10^{-7}	7.0×10^{-7}	1.0×10^{6}
100	6.2×10^{4}	6.2×10^{6}	1.1×10^{-7}	0.64	2.6	0.26	6.4×10^{7}	1.2×10^{8}	5.7×10^{-9}	7.1×10^{2}	8.1×10^{2}	8.6×10^{-4}
125	2.5×10^{6}	2.4×10^{7}	2.9×10^{-8}	2.4×10^{2}	5.1×10^{2}	1.4×10^{-3}	6.4×10^{8}	1.0×10^{9}	6.7×10^{-10}	6.0×10^{4}	6.3×10^{4}	1.1×10^{-5}
150	2.9×10^{7}	9.8×10^{7}	7.1×10^{-9}	1.2×10^{4}	2.0×10^{4}	3.5×10^{-5}	3.0×10^{9}	4.5×10^{9}	1.6×10^{-10}	1.2×10^{6}	1.2×10^{6}	5.9×10^{-7}
200	6.6×10^{9}	9.5×10^{8}	7.3×10^{-10}	1.8×10^{6}	2.2×10^{6}	3.1×10^{-7}	2.1×10^{10}	2.8×10^{10}	2.5×10^{-11}	4.8×10^{7}	4.7×10^{7}	1.5×10^{-8}
250	4.4×10^{9}	4.8×10^{9}	1.4×10^{-10}	3.5×10^{7}	4.0×10^{7}	1.8×10^{-8}	6.7×10^{10}	8.5×10^{10}	8.1×10^{-12}	4.5×10^{8}	4.4×10^{8}	1.6×10^{-9}
300	1.6×10^{10}	1.6×10^{10}	4.5×10^{-11}	2.5×10^{8}	2.8×10^{8}	2.5×10^{-9}	1.5×10^{11}	1.8×10^{11}	3.9×10^{-12}	2.0×10^{9}	2.0×10^{9}	3.6×10^{-10}
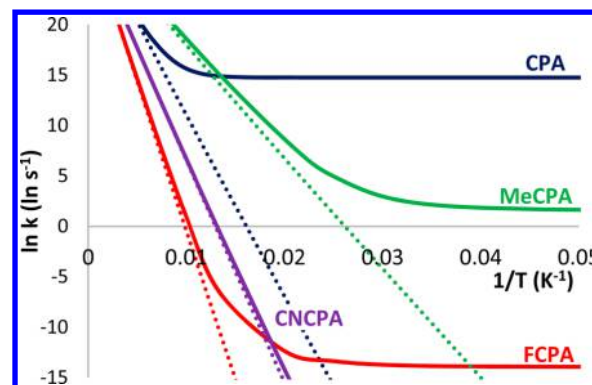
Figure 3. Arrhenius plot for the automerization of **CPA** (blue), **MeCPA** (green), **FCPA** (red), and **CNCPA** (purple). Solid lines include tunneling (SCT), while dotted lines are semiclassical CVT values.

it is possible that the out of plane hydrogens indeed are the "tunneling determining atoms".[33,43]

One way to test the importance of the hydrogens for the QMT probability is by calculating the deuterium kinetic isotope effect—KIE(H/D). The substitution of deuterium for all the hydrogens produces a KIE of 81 at 10 K and only 1.1 at room temperature, a clear indication of hydrogen tunneling from the ground state (see the SI for the full tables of KIE vs temperature).

A calculation of the KIE(^{12}C/^{13}C) of the substitution of the three inner carbon atoms provides a value of 1.47 at 10 K and 1.07 at room temperature, a clear indication of carbon tunneling. Therefore, *CPA is a particular case of both heavy and light atom QMT*. As a reviewer pointed out, there is a possibility of an *indirect* effect on the KIE by a change of the $\Delta ZPE^{\ddagger}$ in a secondary KIE on the H tunneling, caused by the added mass on the carbon atoms. However, the computed $\Delta ZPE^{\ddagger}$ for the ^{12}C/^{13}C substitution on the three carbon atoms is only 0.005 kcal/mol, a minuscule difference compared to the total barrier heights. Therefore, it is safe to say that the carbon KIE is a *direct* effect of the mass on the tunneling probability.

But, if the hydrogens are tunneling, what would happen with alternative, inevitably heavier substituents?

Fluoro, Ciano, and Methyl Cyclopropenyl Anion (FCPA, CNCPA, MeCPA). Gas phase **CPA** was calculated to be unstable to oxidation [IP of −8.4 kcal/mol at CCSD(T)-F12b level],[11,44−46] but electron-withdrawing groups can stabilize the ring. In particular, tricyanocyclopropenyl anion (**CNCPA**) is supposed to be a good candidate to the synthesis of a stable anionic ring (IP of 62.2 kcal/mol).[47] But from a QMT viewpoint, these substituents may strongly affect the possibility of tunneling. In addition to **CNCPA**, we considered in this section two other molecules, fluoro and methyl **CPA** (**FCPA** and **MeCPA**, with IP of 34.1 and −4.6 kcal/mol, respectively, being the latter unstable to oxidation). Their minimum energy geometries are shown in Figure 4.

In these three cases the substituents are affecting the planarity of the carbons in the ring (one carbon strongly pyramidalyzed, the other two only slightly distorted), and similar to **CPA** the ground state is a singlet with a distorted orbital b_1 as the HOMO (see Scheme 2). As a consequence, the π bond shifting must realign the outer groups (as in Figure 2), which requires them to cover a long trajectory. However, contrary to the simple **CPA**, now the mass of the substituents is high, producing a much slower tunneling.
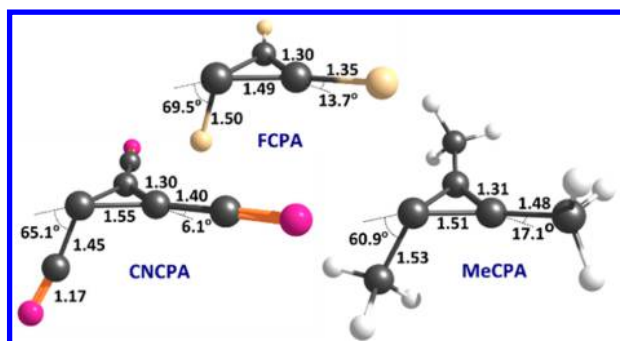
Figure 4. Minimum energy geometries of **FCPA**, **CNCPA**, and **MeCPA**, with selected bond distances (Å) and angles.

Indeed, as can be seen from Table 1 and Figure 3, **CNCPA** will be completely inert to the automerization at cryogenic conditions ($t_{1/2}$ = 2.6 × 10^{19} s at 10 K), in spite of the fact that its $\Delta E^{\ddagger}$ is similar to the $\Delta E^{\ddagger}$ of **CPA**. The CN groups are not only more massive, but also they must move through a much wider radius for the out of plane bending. This is especially prominent for the nitrogens, being at 2.6 Å from the ring (see Figure 4).

MeCPA has a much faster automerization than **CNCPA**, but still much slower than **CPA**, with a $t_{1/2}$ = 0.14 s. Not only the turning radius of the Me substituents is smaller than of CN, but they are also lighter and the barrier is significantly lower (2.3 kcal/mol vs 4.3 kcal/mol for **CNCPA**).

For **MeCPA** we can do a direct comparison between the influence of the ring atoms and the substituent atoms for the tunneling, by contrasting their KIE(^{12}C/^{13}C) (an analysis we could not do for **CPA**, since the H/D and ^{12}C/^{13}C KIEs are not comparable). At cryogenic temperatures, where the automerization occurs only by QMT from the ground state, the substitution of the three ring carbons for ^{13}C produces a KIE of 2.08, while the substitution at the three methyl carbons generates a KIE of 1.25. Therefore, despite the fact that all the carbons of **MeCPA** are affecting the QMT rate, the ring carbons are more "tunneling determining".

FCPA has a computed half-life of 7.8 × 10^5 s below 30 K, approximately 5 days. The mass of the substituents and their out of plane displacement through the automerization is not radically different than **MeCPA**, but its barrier is significantly higher (6.0 vs 2.3 kcal/mol; see Table 1). The cryogenic ^{18}F/^{19}F KIE is 1.39, a high value indicating tunneling of the fluorines, but significantly lower than the ^{12}C/^{13}C KIE of 4.85 (calculated by the substitution of the three F or C). This again points to a stronger tunneling dependency on the movement of the ring atoms (the π bond shifting) compared to the out of plane bending of the F substituents. We can predict that by doing isotopic substitutions to ^{13}C or ^{19}F, experimental NMR studies will show a broadening and latter coalescence of the peaks when heating over 50 K, due to thermally activated tunneling.

Phenyl Cyclopropenyl Anion (PhCPA). Phenyl-cyclopropenyl anion (**PhCPA**) is a known, stable molecule.[5,48,49] In the battery of substituents to test for the automerization reaction of different cyclopropenyl anions this molecule was included expecting that, due to the mass and volume of this heavy substituent, the possibility of π bond shifting by QMT will be impossible. Because of unexpected reasons, we were completely wrong.

The ground state of **CPA**, **FCPA**, **CNCPA**, and **MeCPA** is a closed shell singlet with the HOMO being a pyramidalyzed b_1 orbital (see Scheme 2). This produces a ring with two long single bonds and one short double bond, as can be seen in Figures 1 and 4. Conversely, in the closed-shell singlet of **PhCPA** the HOMO is a_2 (without out-of plane distortion), and therefore, it has two short and one long bond, as can be seen at the C_2 geometry in the left side of Figure 5 (interestingly,
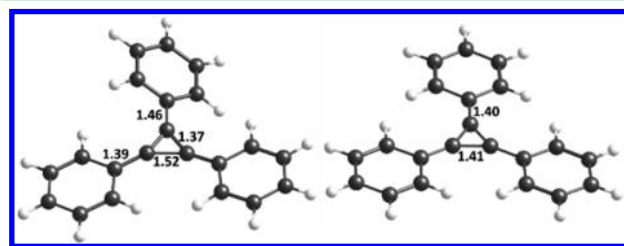

Figure 5. PhCPA geometries at the C_2 closed-shell singlet (left, with the a_2 orbital doubly occupied) and D_{3h} triplet (right) states.

MNDO geometry optimization provides similar results compared to M06-2X,[11] but HF is qualitatively different[50]). Due to the conjugation of the π antibonding HOMO orbital of the inner cyclopropenyl ring with the π benzenic systems, the two lower phenyls of Figure 5 are closer to the ring compared to the upper phenyl (1.39 vs 1.46 Å).

If this singlet was the global ground state, there would still be a possibility for an automerization reaction.[5] However, according to our calculations that is not the case. Both orbitals (b_1 and a_2)[51] are fairly close in energy for the closed-shell **PhCPA**; so, thanks to Hund's rule, we computed that actually a triplet with geometry D_{3h} is the ground state (see right side of Figure 5). Even in the singlet surface an open-shell state results more stable than the closed shell, being 8.8 kcal/mol lower in energy than the C_2 closed-shell singlet (calculated at the uM06-2X/6-31+G* level). Interestingly, by Baird's rule[52,53] the $4n$ open shell triplet species is aromatic, as suggested by a negative NICS(1)[54] value of −8.2.[55,56]

The triplet is 9.6 kcal/mol more stable than the closed-shell singlet at the CCSD(T)-F12b/cc-pVDZ level (−15.0 kcal/mol with M06-2X/6-31+G*). For comparison, in **CPA** the singlet is 10.7 kcal/mol lower than the triplet (see Table 2).[57] **PhCPA** is

Table 2. Average Atomic Contribution of the Three Carbon Ring Atoms for the Two SOMO Orbitals in the Triplet State [M06-2X/6-31+G(d)], Singlet-Triplet Excitation Energy (kcal/mol) [CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-31+G(d), Respective to the Closed-Shell Singlet], and the Symmetry Group of the Singlet and Triplet Optimized Structures, Specifying if They Are Planar (p) or Not (np)

substituent	cont	ΔE_{st}	S symm	T symm
F	0.94	23.1	C_s (np)	C_s (np)
CH$_3$	0.93	17.6	C_s (np)	C_s (np)
H	0.94	10.7	C_s (np)	C_s (np)
C≡N	0.60	3.2	C_s (np)	D_{3h} (p)
C≡CH	0.46	−0.8	C_s (np)	C_s (p)
BH$_2$	0.44	−4.6	C_{2v} (p^a)	D_{3h} (p)
Ph	0.35	−9.6^b	C_2 (p^a)	D_{3h} (p)
HC=NH	0.44	−11.5	C_s (p)	C_{3h} (p)
HC=CH$_2$	0.35	−13.0	C_s (p)	C_{3h} (p)

^{a}One of the substituents is rotated. ^{b}Calculated with cc-pVDZ.

one of the first theoretically documented cases of a diradical cyclopropenyl anion.[7] It must be noted that Breslow et al. estimated that a nitrophenyl substituted **CPA** will be a triplet as well.[58]

The two SOMO of **PhCPA** are shown in Figure 6. There is a clear electron delocalization from the π orbitals of the inner
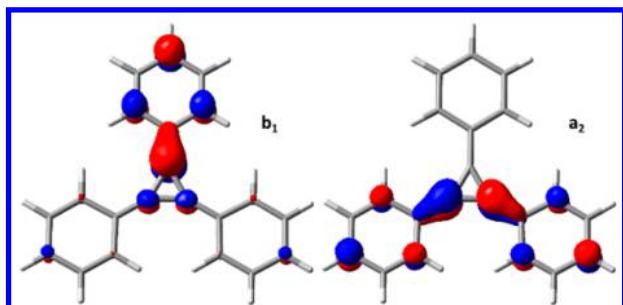

Figure 6. Two SOMO orbitals of the triplet **PhCPA**.

ring to the LUMO of the phenyl groups (this can be related to the singlet−triplet competition in carbenes[59,60]). Because of the lower electronic density in the cyclopropenyl ring, the superposition between states is smaller, causing a reduced second order Jahn−Teller effect. In other words, a lower electron density favors Hund over Jahn−Teller. If this is the case, then other π electron acceptors should also have a triplet ground state. As it is, BH_2, being a good π acceptor, generates a triplet 4.6 kcal/mol lower than the singlet, while for vynil substituents the triplet is lower by 13.0 kcal/mol (CCSD(T)-F12/cc-pVDZ-F12 values, see Table 2).

One question that should be addressed is why CN, also a π electron attractor, generates a singlet and not a triplet ground state in **CNCPA**. In Table 2 the singlet−triplet excitation energies vis-à-vis the atomic contribution of the three ring carbons in the SOMOs of selected cyclopropenyl anions is shown. There is a clear correlation between these two values ($R^2 = 0.90$), indicating that when the electron density of the a_2 and b_1 orbitals is spread out into the substituents, the pseudo Jahn−Teller effects are softened, whereas the Hund's rule is strengthened, favoring the triplet.

The cyano groups indeed are π electron withdrawing, but not enough to make the triplet the ground state (3.2 kcal/mol over the singlet). The ethynyl group is a slightly better electron attractor, making the singlet and triplet virtually degenerate (with the triplet 0.8 kcal/mol lower than the singlet). This is caused by the fact that the SOMOs can be considered antibonding between the ring atoms and the atom in the beta position of the substituent (see Figure 6); a more electronegative atom in that position—such as nitrogen in C≡N—will generate a higher orbital coefficient in the ring carbon compared to a more electropositive atom—such as in C≡CH.

However, the strongest effect is brought by changing the triple bonded substituents (cyano or ethylene groups) to double-bonded substituents (imino, vinyl, or phenyl groups). For instance, HC=NH has a triplet as the ground state (11.5 kcal/mol lower than the singlet), while C≡N is a singlet. The triple bond in the cyano causes a shorter C−N bond length compared to the imino, raising the LUMO of the CN group (the orbital that accepts the π electron density) and producing a worse charge transfer.

Therefore, to produce a diradical triplet cyclopropenyl anion the best strategy is to add substituents with double bonds, and,

secondary, to include electropositive atoms in the beta position. At the present time we are using the same strategy to design by computational means an open-shell singlet as the ground state of cyclobutadienes, the textbook molecules with a singlet ground state caused by a Jahn−Teller effect.

CONCLUSIONS

Two topics regarding the reactivity and structure of cyclopropenyl anions were tackled by computational means:

(I) the π bond shifting (automerization) of several substituted **CPAs**, driven by carbon quantum mechanical tunneling

(II) the stabilization of diradical triplet **CPA** systems, instead of the usual closed shell singlet as the electronic ground state

The automerization reaction, similar to other antiaromatic cases,[23] is hindered by substituents departing from the planarity of the **CPA** ring. A second order Jahn−Teller distortion causes the pyramidalyzation of the substituents, in such a way that the π bond shifting requires a long trajectory of those substituents to be realigned according to the new position of the double bond. Due to their low mass, with hydrogens as substituents the tunneling is still extremely fast, in a case of both heavy and light atom tunneling. But with more massive substituents (such as Me and F), and especially longer groups with a larger trajectory (such as CN), the tunneling probability strongly diminishes.

With triphenylcyclopropyl anion the tunneling process was originally supposed to be impossible due to the high mass of the phenyl groups. However, it was found that the ground state of this species is actually a D_{3h} aromatic triplet, with completely equivalent bonds in the ring, and therefore without the possibility of automerization. The phenyl groups act as π acceptors, diminishing the superposition of states that generate the second order Jahn−Teller distortion, and by Hund's rule the triplet results in a lower energy state. It was found that the atomic contribution of the ring carbons to the SOMOs of the triplet are a good indicator of the singlet−triplet excitation caused by the competition between Jahn−Teller and Hund.

It is hoped that these predictions of tunneling reactivity and singlet−triplet stability can be experimentally tested in the near future.

ASSOCIATED CONTENT

ⓢ Supporting Information

Complete Polyrate output (CVT/SCT) and KIEs and an example of a Polyrate input file. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00321.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

CBD, cyclobutadiene; **CNCPA**, tricyanocyclopropenyl anion; **CPA**, cyclopropenyl anion; CVT, canonical variational transition state theory; **FCPA**, trifluorocyclopropenyl anion; IP, ionization potential; KIE, kinetic isotope effect; **MeCPA**, trimethylcyclopropenyl anion; **PhCPA**, triphenylcyclopropenyl anion; QMT, quantum mechanical tunneling; SCT, small curvature tunneling; QRST, quantized reactant state tunneling; $t_{1/2}$, half-life

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