Properties of Stable Organic Bond-Stretched Non-Lewis Molecules[†]

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The conditions required for the existence of a stable bond-stretched singlet isomer of hetero derivatives of bicyclo[2.1.0]pentane (which is a cyclopentane-1,3-diyl derivative) are discussed. Such species are non-Lewis systems with a ruptured C−C bond (formally diradicals), in which two electrons occupy the nonbonding orbital. A high-level calculation shows that in contrast with the carbon substituted compounds, in which the open form is a transition state between two classical-bonded closed bicyclic forms, in the heterosubstituted molecules, the open form is calculated to be a stable minimum. The ionization potentials of the open forms are considerably lower than those of their bicyclic isomers and also of regular organic radicals/diradicals. Nitrogen atoms are found to be more effective than oxygen or sulfur in stabilizing the open isomer. In this case, the open isomer is calculated to be a little more stable than the bicyclic compound, and a barrier of ∼40 kcal/mol is computed for the ring closing reaction. Thus, the open isomer is both thermodynamically and kinetically stable. This result rationalizes some experimental observations that indicated the existence of non-Lewis singlet species.

I. Introduction

The quest for stable molecules having a singlet diradical structure led in recent years to the production, crystallization, and characterization of several inorganic species in crystalline form[1–3] and in solution.[4] As summarized in an extensive recent review,[5] these species turn out to have considerable charge-transfer character, leading to their designation as diradicaloids. Here, we discuss the properties of some formal organic diradicals that are calculated to be quite stable under ambient conditions. Their stability is due to polar structures that contribute significantly to the electronic wavefunction of the ground-state singlet. In the context of this paper, bond-stretched isomers are two isomers interconnected by a reaction in which a single bond is formed and separated by a large barrier from the open form side.

Figure 1 shows the structures of some cyclopentane-1,3-diyl diradicals that were examined as possible stable singlet diradicals. Buchwalter and Closs showed in 1975[6] that triplet diradicals of cyclopentane-1,3-diyl (Ia) can be prepared and observed by ESR. The triplet−singlet gap (ΔE_{ST}) was calculated to be a few kilocalories/mole, the triplet being more stable. The singlet diradical was taken as the transition state between the two closed forms of the bicyclic compound. Borden et al.[7] proposed that the singlet diradical can be stabilized by substituting the two geminal hydrogen atoms with fluorine ones (Ib). The idea was that the fluorine atoms will act as electron acceptors and help delocalize the electronic charge in the singlet state. Indeed, the singlet of 1b was calculated to lie well below the triplet at all geometries, but it turned out to be a transition state between the two classical closed structures.[7] Other modes of substitution were proposed theoretically and tested experimentally; Adam et al.[8] presented evidence for the existence of a reactive intermediate Ic, though it could not be observed directly. In an effort to stabilize carbon-based diradicals, the Z

= SiH$_3$ group was proposed[9] as a potent stabilizer of singlet diradicals with respect to the triplet one; the calculation showed that the singlet is indeed lower than the triplet, but only by about 2 kcal/mol. The singlet open form of Id was calculated to be 20.8 kcal/mol higher, with a barrier of 9.5 kcal/mol from the open form side.[9] The relatively large stabilization was assigned to strong hyperconjugation due to electron donation from the high lying C−Si sigma orbitals. Similar computational results were reported by Abe et al.[10]

We propose an approach that leads to substantially better stabilization of a singlet state of the open form in comparison to the corresponding triplet and more importantly, to the singlet of the closed form isomer in which the two atoms, C1 and C3, are covalently bonded. In other words, the system is shown to have two stable, iso-energetic bond-stretched singlet isomers, separated by a substantial barrier.

It was recently shown[11] that partial intramolecular charge transfer can lead to substantial stabilization of singlet ground-state diradicals and a corresponding increase of the singlet−triplet gap for molecules iso-electronic with the dianions of antiaromatic hydrocarbons. The formal diradicals 2,5-diheterosubstituted-pentalenes and 1,5-diheterosubstituted-cyclooctatetraenes were theoretically predicted to be stable persistent non-Kekulè molecules. In this communication, we further extend the idea and show that some non-Lewis heterosubstituted molecules are predicted to be as stable as their classical Lewis-type isomers. The relationship between these isomers is discussed within the concept of bond-stretched isomers as introduced by Stohrer and Hoffmann:[12] two stable conformations related by a simple bond stretching. These are the normal classical bonded form and a stabilized diradical form. Several bond-stretched isomer systems have been reported.[1–5] The stability of the novel bond-stretched isomers reported in this communication can be traced to the participation of at least four electrons in the bonding, which in VB language is explained by resonance stabilization of several diradical, zwitterion and ylide-type structures. Since the stability of some of the open forms of these systems is comparable to
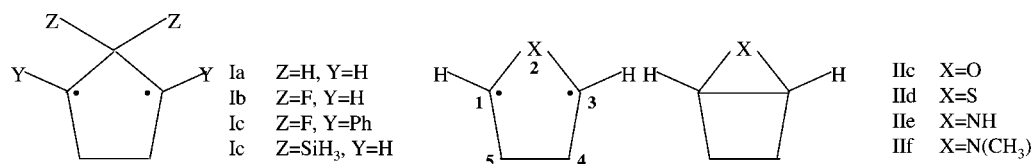
Figure 1. Left: structure of some previously studied cyclopentane-1,3-diyl diradicals; right: the open and closed forms of singlet heterosubstituted 2-cyclopentane-1,3-diyl diradicals.

those of the closed ones, the results strongly suggest that these open-form species can be observed experimentally.

II. Methodology and Computational Details

Initial calculations were made at the CASSCF(10e/8o)/cc-pVDZ level by using the GAMESS program suite.[13] All singlet minima and transition states were calculated, and a complete vibrational analysis was carried out. The energy of the critical points was then calculated by using CASMP2 (GAMESS). In addition, triplet minima were also calculated; they serve as a criterion for a pristine diradical character. In order to verify the existence of transition states, intramolecular reaction coordinate (IRC) calculations using the MOLPRO program suite[14] was also performed by using both CASSCF and MRCI, yielding the same results. The reaction leading from the classical bicyclic system to the bond-stretched open cyclic molecule was followed along the IRC. MOLPRO was also used for an MRCI calculation of all critical points.

III. Results

All stable bicyclic compounds considered in this work have C_s symmetry, the symmetry plane being perpendicular to the carbon frame. In contrast, all triplet states were found to have a minimum at C_2 symmetry because of the release of strain in the small rings. The ground states of open singlet species were also found to have a minimum at C_2 symmetry. It is noted that the heavy-atom frame is planar in the case of $X = CH_2$ or CF_2, as expected for C_{2v} symmetry[7] (Table 1), and the hydrogen atoms on atoms 4 and 5 are slightly out of this plane reducing the symmetry to C_2. Table 1 lists the calculated structures and energies of the singlet and triplet forms of all open species, as well as those of the bicyclic compounds. The data show that the $X-C_{1(3)}$ distance is shorter in the open isomer than that in the triplet, in which the distance is in turn shorter than that in the closed bicyclic isomer. The optimized C_1-C_3 distances in both the open isomer and the triplet are about 2.3 Å.

In all calculated species except for the parent cyclopentane-1,3-diyl, the open singlet form is more stable than the triplet. ΔE_{ST} increases in the sequence $X = CH_2 < CF_2 < O \approx S < NH \approx NCH_3$. The relative stabilities of the open singlet forms versus the closed ones are drastically changed upon substitution: whereas bicyclo[2.1.0]pentane (Ia) is >20 kcal/mol more stable than the open isomer, the aza-analogues show preference for the open isomer (−3.2 kcal/mol for $X = NH$ (IIe) and −6.5 kcal/mol for $X = NMe$, (IIf)). The energy difference between the closed form (S_0) and the open triplet 1,3-diradical (T_1) is much less sensitive to the nature of X: it is 21.9 kcal/mol for the parent hydrocarbon versus 31.5 kcal/mol for the aza-derivatives. These results hold also upon application of the MP2 correction. Evidently, the open singlet form is more strongly affected by the heteroatom substituent than the open triplet or closed form singlet. The nitrogen derivatives exhibit exceptional stabilization of their open form isomers.

Table 1 also reports some properties of the transition state for the cyclization reaction between the closed and open singlet

TABLE 1: Bond Lengths and Energies in Singlet (S_0) and Triplet (T_1) States of Some Cyclopentane-1,3-diyl Species (CASSCF(10/8)/cc-pVDZ)[a]
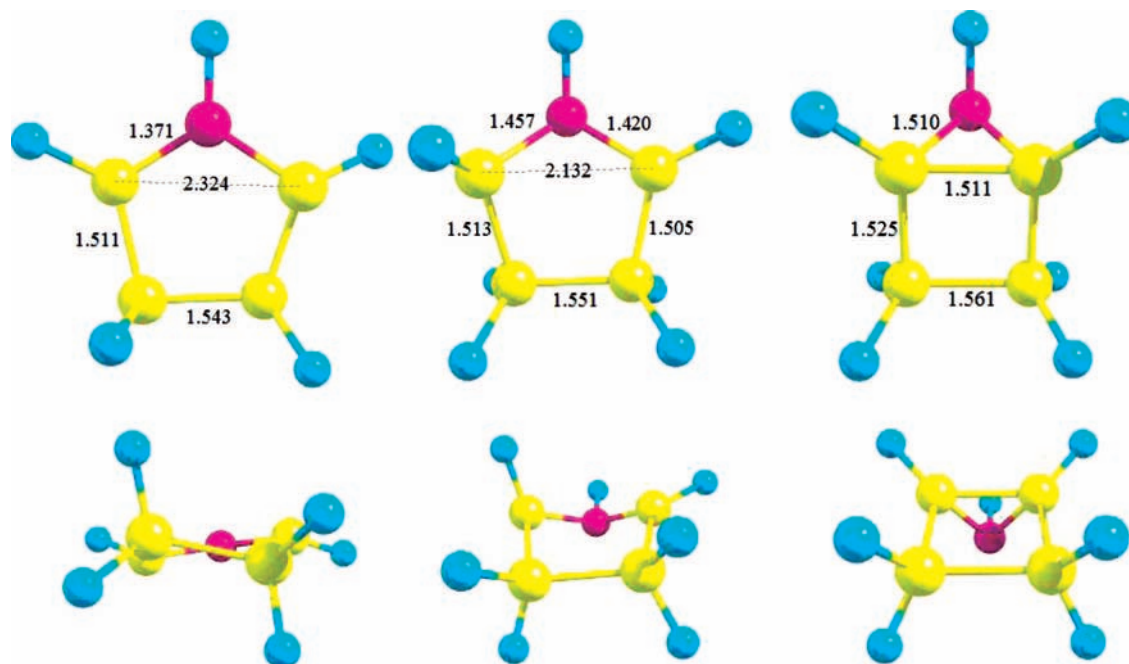
structure[b]	$R_{12(23)}$	R_{13}	$\Delta\Delta E$ kcal/mol (a.u.)
	X = CH₂		
Closed (S_0)	1.496	1.557	0.0 (−193.99196)
Open−TS (S_0)	1.537	2.395	22.7 {31.6}[d]
Open (T_1)	1.533	2.386	21.9
	X = CF₂		
Closed (S_0)	1.494	1.560	0.0 (−391.72874)
Open−TS (S_0)	1.474	2.314	12.3 {16.0}[d]
Open (T_1)	1.492	2.371	17.8
	X = O		
Closed (S_0)	1.455	1.455	0.0 (−229.85729)
Open (S_0)	1.365	2.256	18.1 {26.0}[d]
TS$_{OC}$[c] (S_0)	1.396 (1.446)	2.108	47.7
Open (T_1)	1.412	2.259	33.8
	X = S		
Closed (S_0)	1.864	1.534	0.0 (−552.50698)
Open (S_0)	1.717	2.443	12.8 {15.1}[d]
TS$_{OC}$[c] (S_0)	1.801 (1.803)	2.452	42.5
Open (T_1)	1.801	2.436	27.7
	X = NH		
Closed (S_0)	1.510	1.511	0.0 (−210.00437)
Open (S_0)	1.371	2.234	−3.2 {−3.7}[d]
TS$_{OC}$[c] (S_0)	1.420 (1.457)	2.132	38.5
Open (T_1)	1.426	2.235	31.4
	X = NCH₃		
Closed (S_0)	1.509	1.473	0.0 (−249.03280)
Open (S_0)	1.372	2.309	−6.5 {−8.7}[d]
Open (T_1)	1.423	2.283	31.5

[a] The relative energies of the different structures of a given species are with respect to the closed form. CASMP2 data are also given for of the energy difference ($\Delta\Delta E$) between the open and closed forms. [b] The open form is a transition state for $X = CH_2$ and $X = CF_2$, a minimum for all others. [c] TS$_{OC}$ is the transition state for the bond stretch reaction (Figure 2). In it, $R_{12} \neq R_{23}$. [d] CASMP2 calculation.

isomers (a single imaginary frequency was found in all cases). It is evident that the barrier for the reaction from both sides is substantial (∼40 kcal/mol in the case of $X = NH$)—the open form is consequently predicted to be both thermodynamically and kinetically stable. The singlet transition state between the open and closed (bicyclic) forms for all 2-heterosubstituted-cyclopentanes was found to transform as C_1, as expected because the point groups C_2 and C_s have no common symmetry element (Figure 2 shows the structures calculated for the case of IIe).

Further differences between the closed and open forms of the heterosubstituted cyclopentan-1,3-diyls are revealed in Table 2 which reports some electronic properties.

Table 2 shows that S_0-S_1 excitation energies for all open isomers are more or less equal (∼5 eV, CASSCF level and 3.5−4 eV, CASMP2 level) and similar to those in the case of ordinary unsaturated molecules. The ΔE_{ST} gap strongly depends on the type of heteroatom: for the parent hydrocarbons ($X = CH_2$), the singlet and triplet states are nearly degenerate, and X

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Figure 2. Calculated structures of the two isomers of the aza analogue of 2-cyclopentane-1,3-diyl diradical (IIe) in two projections: left, open form (C_2); right, closed (C_s) form; and middle, nonsymmetric (C_1) transition states between them.

TABLE 2: S_0-T_1 Gap, S_0-S_1 Excitation Energy, Ionization Potential, Energy of HOMO Cyclopentane-1,3-diyls (CAS(10/8)/cc-pVDZ), in ElectronVolts[a]

ΔE_{ST}[b]		$\Delta\Delta E$ (S_0-S_1; 1^1A-1^1B)[c]		IP ($D_{1,2}$)[d]		IP (D_1) Closed form		
CASSCF	CASMP2	CASSCF	CASMP2	CASSCF	CASMP2	CASSCF	CASMP2	HOMO (HF/cc-pVDZ)[e]
				X = CH$_2$				
−0.04	−0.05	5.28	3.41	6.98 (1^2A)	7.50 (1^2A)	8.28 (1^2A′)	9.15 (1^2A′)	
				7.34 (1^2B)	7.71 (1^2B)			
				X = CF$_2$				
0.24	0.44	6.49	4.16	7.77 (1^2B)	8.57 (1^2B)	9.08 (1^2A″)	9.99 (1^2A″)	7.76 (27b)
				9.61 (1^2A)	10.16 (1^2A)			
				X = O				
0.68	0.76	5.19	3.75	6.02 (1^2A)	7.20 (1^2A)	9.03 (1^2A′)	9.54 (1^2A′)	6.25 (19a)
				8.88 (1^2B)	9.36 (1^2B)			
				X = S				
0.65	0.73	4.34	3.29	6.03 (1^2A)	6.97 (1^2A)	7.76 (1^2A)	8.41 (1^2A)	6.64 (24a)
				8.33 (1^2B)	8.90 (1^2B)			
				X = NH				
1.50	1.37	5.31	3.99	5.16 (1^2A)	6.34 (1^2A)	7.91 (1^2A′)	8.69 (1^2A′)	5.87 (19a)
				8.45 (1^2B)	9.10 (1^2B)			
				X = NCH$_3$				
1.65	1.30	5.10	3.70	5.02	6.09	7.66 (1^2A′)	7.66 (1^2A′)	5.79 (23a)
				8.17	8.81			

[a] The relative energies of the different structures of a given species are with respect to the energy of S_0 (Open Form). In each column, the left value is calculated by using CASSCF(10/8)/cc-pVDZ, and the right value is calculated by using CASMP2(10/8)/cc-pVDZ. [b] $\Delta E_{ST} = \Delta E$ (S_0-T_1). [c] Vertical excitation energy. [d] $IP_{1,2} = E(S_0) - E(D_{1,2})$ is a difference between the energy of neutral molecule and that of the corresponding cation (vertical IP). [e] Energy of the HOMO of the open form, by Koopmans theorem, an estimate of the first ionization potential.
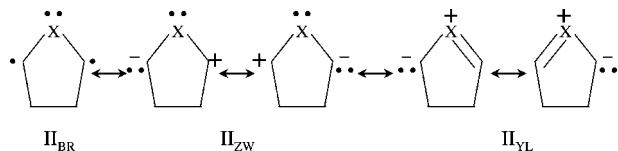
= CF$_2$ leads to the considerable stabilization of the singlet state[7]—T$_1$ is a 0.25 eV above the S$_0$. A modest gap is found for X = O or S ($\sim$0.6 eV). For the aza-derivatives, the gap is considerably larger ($\sim$1.3 eV), a typical value for heterosubstituted conjugated molecules. The trends found for the first ionization potentials (IPs) are also informative: the IPs of the parent cyclopenta-1,3-diyl and the fluoro-substituted analogue are typical of organic radicals, $\sim$8 eV (MP2 level). In contrast, the IPs of the aza-compounds are unusually low compared to stable organic molecules, only about 6 eV. The IPs of the closed isomers are 2−3 eV higher than those of the open ones. For

the parent molecule (Ia), the difference between the first two IPs are quite modest, indicating a strong biradical character. In the nitrogen substituted ones (IIe and IIf), the difference is much larger, about 2.5−3 eV. This result suggests that the first electron is held much less strongly than the second one. The estimation of the IPs by using Koopmans theorem shows reasonable agreement with the more sophisticated CASSCF method, in which the energies of the cation and the neutral molecule were compared.

Table 3 reports data relating to the electronic structure of the molecules; the second column shows that the principal two

TABLE 3: Contribution of the Two Leading Configurations of the Open Isomer and Changes in Charge Distribution in Electron Charge Units, Lowdin Charges (Δq, S_0 vs. T_1, CASSCF(10/8)/cc-pVDZ)

X	coefficients of the two leading configurations: (C_A:C_B)	Δq_X	$\Delta q_{HC1(3)}$
CH_2	0.70:0.69	−0.001	+0.000
CF_2	0.53:0.83	−0.054	+0.020
O	0.90:0.39	+0.147	−0.068
S	0.91:0.35	+0.208	−0.097
NH	0.93:0.31	+0.207	−0.092
NMe	0.94:0.30	+0.260	−0.117

Figure 3. VB structures of 2-heterosubstituted-cyclopenta-1,3-diyl: covalent diradical, II_{BR}; zwitterion, II_{ZW}; and ylide, II_{YL}.

Figure 4. Orbital interaction diagram between 1,3-diyl unit and donor (left) or acceptor (right) apical group. C_2 symmetry is assumed; the HOMO and LUMO orbitals are highlighted by a black solid and a gray dotted circle, respectively.

configurations account for over 95% of the electronic density population, justifying the use of a two-configuration approximation for further discussion. Column 3 reports the amount of charge transferred from X to rest of the molecule in units of electronic charge, and column 4 shows the charge transferred to each of the two neighboring carbon atoms (in fact, the CH group). (Lowdin charges are used, Mulliken charge distributions were also computed and lead to very similar results; they are reported in the Supporting Information).

Almost no charge is transferred for X = CH_2, in both the singlet and triplet states, and ΔE_{ST} is negligibly small (~1 kcal/mol). X = CF_2 is an electron acceptor, whereas O, S, and the nitrogen-based substituents are all donors. A measure for the diradical-zwitterion (II_{BR}-II_{ZW}) versus the ylide (II_{YL}) character of the open form may be correlated with the charge transfer. Complete one-electron charge transfer would result in a unit of positive charge on X and 0.5 units each on C1 and C3. However, the charge transfer, even in the case of the aza-derivatives, is limited to only about 0.2 e. The fact that even in the case of the most potent donor (NMe), only about a quarter of an electronic charge unit is transferred means that the contribution of the diradicaloid VB structures (II_{BR} and II_{ZW}) is more significant than that of the polar one (II_{YL}).

IV. Discussion

The open forms of the 1,3-diyls cannot be described by a single Lewis structure. A non-Lewis molecule with two equivalent radical centers is a diradical according to chemical intuition and simple VB description (II_{BR}, Figure 3). However, other VB structures may contribute: the zwitterion (II_{ZW}) and the ylide-type structure (II_{YL}), see Figure 3.

A diradical is defined in the MO approach as a structure with two unpaired electrons populating two degenerate or nearly degenerate MOs.[15-17] If the molecules under study were predominantly represented by structure II_{BR}, they could be classified as diradicals. However, it turns out that except for the carbon derivatives (Ia and Ib), they exhibit considerable zwitterion character, as expected for structure II_{ZW} and ylide-type charge transfer for II_{YL}. This is evident from the large singlet−triplet splitting and the large difference between the first and second IPs. An insight into their nature may be gained by considering a simple two-configuration model. The wave function of the parent 1,3-diyl is usually described in the FMO
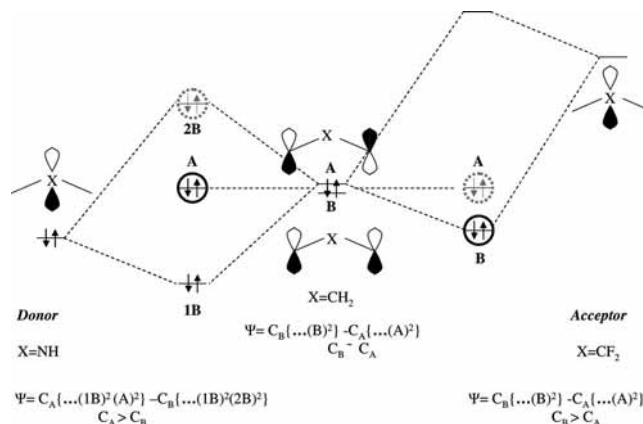
model by an anticombination of two configurations distinguished by highest occupied orbital−nonbonding MOs: $A = (\varphi_1 - \varphi_3)$ and $B = (\varphi_1 + \varphi_3)$, where φ_1 and φ_3 are the two atomic orbitals, localized on the C1 and C3 atoms. These two orbitals are degenerate, and the corresponding configurations contribute equivalently to the ground-state wave function. According to a classic model,[15] the anticombination of degenerate configurations ($C_A = C_B$) defines a purely covalent diradical without any ionic contributions:

$$\Psi(C_A = C_B = 1) = \bar{B}B - A\bar{A} = (\phi_1 + \phi_3)(\overline{\phi_1 + \phi_3}) - \\ (\overline{\phi_1 - \phi_3})(\phi_1 - \phi_3) = (\phi_1\overline{\phi_3}) - (\overline{\phi_1}\phi_3) \quad (1)$$

In contrast, when the two configurations are not equivalent, a nonzero ionic term appears:

$$\Psi(C_A \neq C_B) = C_B B\bar{B} - C_A A\bar{A} = C_B(\phi_1 + \phi_3)(\overline{\phi_1 + \phi_3}) - \\ C_A(\phi_1 - \phi_3)(\overline{\phi_1 - \phi_3}) = (C_A + C_B)\{\phi_1\overline{\phi_3} - \overline{\phi_1}\phi_3\} + (C_B - \\ C_A)\{\phi_1\overline{\phi_1} + \phi_3\overline{\phi_3}\} \quad (2)$$

Thus, the ratio $(C_B - C_A)/(C_B + C_A)$ can serve as an index for the relative contributions of an zwitterion form $-\{\varphi_1\overline{\varphi_1} + \varphi_3\overline{\varphi_3}\}$ and a diradical one $-\{\varphi_1\overline{\varphi_3} - \overline{\varphi_1}\varphi_3\}$ to the electronic wave function at the two-configuration approximation. The computational evidence of the diradical character, based on the ratio of the coefficients of leading configurations in a CI expansion, was discussed by Davidson.[18,19] Within the two-configuration approximation, the square of the ratio will be used as an estimate for the contribution of II_{ZW}.

Dewar[20] pointed out the importance of weak interaction between the radical centers for the pure diradical character. In the case of the heterosubstituted 1,3-diyls, the direct C1−C3 interaction is weak, but the three-centered C1−X−C3 one is quite strong. The interaction of the apical group with the 1,3-diradical moiety leads to the splitting of the degenerate nonbonding pair. Figure 4 shows two different ways leading to orbital splitting of the two degenerate orbitals (C_2 symmetry is used): an acceptor stabilizes the B-type orbital, which becomes the HOMO, whereas the LUMO is of A symmetry.[7] In contrast, a π-donor inverts this order: the A-type orbital becomes the HOMO, and the B-symmetry one is the LUMO.

In both of these cases, the increased HOMO−LUMO splitting means the increased contribution of one configuration over the other and a larger singlet−triplet splitting, reducing the diradical

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TABLE 4: Relative Weight (%) of the Three Main VB Structures (Figure 3), LUMO Occupation Numbers, and Percentage of Charge Transferred in Electron Charge Units (Lowdin Charges) Calculated for the Open Form of 2-X-cyclopentane-1,3-diyl Compounds (CASSCF(10/8)/cc-pVDZ)

X	II_{BR}	II_{ZW}	II_{YL}	LUMO occupation numbers	Δq_X
CH_2	100	0	0	0.947 (0.927[16])	−0.001
CF_2	91	4	5	0.562 (0.583[16])	−0.054
O	673	12	15	0.304	+0.147
S	65	14	21	0.245	+0.208
NH	64	15	21	0.192	+0.207
NMe	58	16	26	0.180	+0.260

character.[18,19] Figure 4 shows the order of the combined orbitals and, consequently, defines the dominant configuration. Although this is clearly an oversimplified picture in the case of the weak coupling, because the second configuration (of the occupied LUMO, marked by gray color) must also be taken into account, the basic characteristics are explained by the dominant configuration. The relative contribution of these two configurations: ...(HOMO)^2 versus...(LUMO)^2 determines the ratio between the covalent diradical contribution (II_{BR}) and the zwitterion one (II_{ZW}). This reasoning can be compared to Head−Gordon's suggestion to use the LUMO-occupation numbers as an indication of the extent diradical character.[17]

Table 4 summarizes the contribution of the three main VB structures for the different diyls. As a rough approximation, the fraction of charge transferred (Table 3) is used as an estimate for the contribution of the polar form II_{YL}; the balance is distributed between the dot−dot form (II_{BR}) and the zwitterion one (II_{ZW}) by using the ratio $[(C_B − C_A)/(C_B + C_A)]^2$

$$\% \text{ of } II_{ZW} = (1 − \Delta q_X)([(C_B − C_A)/(C_B + C_A)]^2 \quad (3)$$

$$\% \text{ of } II_{BR} = (1 − \Delta q_X)([1 − (C_B − C_A)/(C_B + C_A)]^2 \quad (4)$$

where Δq_X is the fraction of charge transferred (Table 3).

The fifth column of Table 4 reports the LUMO occupation numbers;[17] it is evident that the magnitude of charge transfer is closely correlated with these numbers.

In the case of the parent singlet cyclopentane-1,3-diyl IIa, which is a well-known perfect diradical,[7,16] the electronic wave function can be described adequately as the anticombination of two configurations with equivalent weights, which indicates, according to eq 2, a purely diradical character (II_{BR} contributes 100%). Almost no charge is transferred for X = CH_2, in both the singlet and triplet states, and ΔE_{ST} is negligibly small (~1 kcal/mol). In the heterosubstituted molecules, the contribution of the two configurations is not equal, leading to two different IPs as found computationally. This difference can be readily verified experimentally by photoelectron spectroscopy. In these molecules, the contribution of the polar structure is non-negligible.

Borden considered the case of 2,2-difluoro-cyclopentane-1,3-diyl as an acceptor hyperconjugation.[7] An analysis of the Lowdin charge distribution shows that in this case, only 0.054 electronic charges are transferred to the CF_2 group in the singlet state relative to a perfect diradical triplet. Among the systems considered, this molecule is the only case for which the dominant configuration is *B*-type (Figure 4, right); Here, $C_B > C_A$, and the contribution of the covalent configurations is dominant, leading to a relative small ionic contribution, only 4%. All other studied molecules show the domination of the *A*-type configuration ($C_A \geq 0.9$), indicating donor substitution (Figure 4, left). The contribution of the *B*-type configuration,

although small, increases in the sequence $CH_2 < CF_2 < O < S < NH$ (Table 3), indicating the decreasing importance of the pure diradical character. The open forms containing X = O and S show 3−4 times larger charge transfer compared to that for X = CF_2. The largest transfer (compared to the triplet) occurs with X = $NH(NCH_3)$, wherein about a quarter of an atomic unit charge is transferred. As in the case of the heterosubstituted pentalenes and cyclooctatetraenes,[11] nitrogen proves to be the most efficient atom for stabilizing diradicals. A possible explanation is that although oxygen and sulfur also transfer nonbonding electrons, the effect is smaller in oxygen because it is more electronegative and a weaker donor. Sulfur has an electron affinity comparable to that of nitrogen; however, its larger size leads to a smaller overlap with the orbitals of the neighboring carbon atoms, making it less efficient as an electron donor.

The calculated charge transfer indicates the importance of the ylide form II_{YL} (Figure 2). In a previous paper,[11] it was proposed that formal diradicals may be stabilized by charge transfer. The systems discussed there (heterosubstituted di-X-pentalenes and di-X-cyclooctatetraenes) were $4n + 2$ electron systems, so that the stabilization might be assigned to increased aromaticity. The systems studied in this work have four interacting electrons (one each on carbon atoms C1 and C3 and two on the heteroatom); yet, they are also remarkably stabilized.

The upshot of the analysis given above is that these non-Lewis systems are expected to exhibit normal properties of a species having partial polar and partial diradical character. Yet, the unusually low IP, especially in the case of aza-derivatives for which it is only ~6 eV, is surprising at first sight. It cannot be explained by the contribution of either the biradical structure (II_{BR}) or the ylide one (II_{YL}). We propose that it is due to the importance of the zwitterion structure II_{ZW} in which two electrons occupy a single nonbonding orbital centered on carbon atoms. The simultaneous occupation of an orbital by a half-electron pair on C1 and C3 increases the electrostatic repulsion compared to a single electron on C1 and C3 in the diradical II_{BR} structure. This accumulation of negative charge is equivalent to imparting these species with a quasi-anion character. Unlike a lone pair on a nitrogen atom, a lone pair on a carbon atom leads to excess charge and strong interelectron repulsion. An experimental method to probe this prediction is photoelectron spectroscopy—the open form is predicted to show a much smaller IP than the closed one.

Another important result of this work is the relatively high kinetic stability of the open form; at first sight, the high barrier (~40 kcal/mol for IIe) for ring closure is surprising. However, the nature of the reaction can be rationalized by considering the electronic properties of the transition state between the closed and open forms. A simplified MO correlation diagram obtained by using the dominant configuration is shown in Figure 5 for X = NH and CF_2. In this diagram, C_{2v} symmetry was assumed for both open and closed forms, allowing the use of symmetry. The real minima are somewhat distorted to C_2 and C_s symmetry, respectively, but the C_{2v} structure is only a few kilocalories higher in energy in both cases. The closure of the open to the bicyclic form must be disrotatory—the p orbitals of atoms 1 and 3 rotate in a disrotatory motion to form the new bond (the conrotatory motion leads to the nonrealistic trans-isomer of bicyclo-[2.1.0]-pentane). In the case of X = CF_2, the process is an allowed one (Figure 5, right). In fact, the species Ib was found to be a transition state and not a minimum, but the example serves to show that if a carbon-substituted molecule were found, it would transform easily to the closed form.
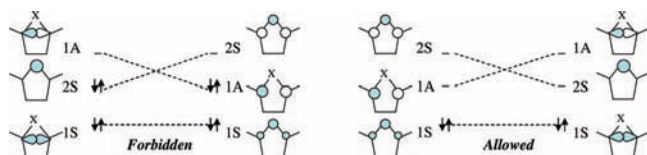
Figure 5. Simplified MO correlation diagram of the open-closed form isomerization reaction. Left: for donor-substituted molecules (e.g., X = NH); Right: for acceptor-substituted molecules (e.g., X = CF$_2$). The high barrier computed for the donor substituted system arises from the participation of four electrons in the process, leading to curve crossing. In this diagram, C$_{2v}$ symmetry was assumed for both open and closed forms to allow the use of symmetry, and a disrotatory motion of the two carbon atoms' p orbitals with respect to the plane of symmetry perpendicular to the molecules plane was assumed. The A and S labels denote symmetric and antisymmetric MOs with respect to this plane.

However, donor substitution exchanges the HOMO−LUMO pair, making the disrotatory reaction a symmetry forbidden process (Figure 5, left). The high barrier and the geometry of the transition state indicate that ring closure is not a simple two-electron process but involves four electrons. Thus, the addition of the two nonbonding electrons of the heteroatom changes the electronic nature of the C1−C3 bond rupture from that of a two-electron process (covalent bond) to a four-electron process.

Bond-stretched isomerism was first proposed for metal complexes that differ only by the length of one or more bonds.[12] Stohrer and Hoffmann[12] discussed several possible candidates for observing this phenomenon in organic molecules, concentrating on CC bonds and proposing that singlet diradicals may be stabilized sufficiently to form a minimum on the ground-state potential surface. Interestingly, work by Arnold et al.[22] on 5-oxabicyclo[2.1.0]pentanes (in which it was shown that the bicyclic compound can be converted thermally or photochemically to a five-membered carbonyl ylide structure) was overlooked by previous workers discussing bond-stretched isomerism, although it is an example of bond-stretched isomerism. Although Arnold et al. considered the open isomer as an ylide of primarily charge-transfer character (II$_{YL}$), disregarding the contribution of diradical character, we propose that the contribution of the two other forms (II$_{BR}$ and II$_{ZW}$) is essential. They found a color change indicating the presence of the open form only at elevated temperatures (100 °C), in agreement with our computational results predicting for the oxo-derivatives a larger stabilization of the closed form. Another early example of a stable five-membered non-Lewis molecule was reported by Grellman et al.,[23] as an intermediate in the photochemical ring closure of diphenylamine to carbazole. In this case, as in the former, the open isomer was considered as pure zwitterion specie, with no diradical contribution. This trend was endorsed by most workers in the field, as can be learned from an extensive discussion by Huisgen.[24] The present analysis implicates that these bond-stretched non-Lewis molecules have a considerable biradical character. It also predicts that the open form is a little more stable than the closed one in the aza derivatives; thus, the open forms of these molecules are predicted to be observable at room temperature.

V. Concluding Remarks

Open heterosubstituted cyclopentane-1,3-diyl derivatives are shown to be energetically and kinetically stable species because of a partial charge transfer character. The highest stabilization was obtained for X = NH or NCH$_3$, with one quarter of an electronic charge transferred from the nitrogen atom to the neighboring carbon atoms. The resulting open form species can

be considered as a non-Lewis molecule, in which two electrons occupy the nonbonding orbital. Depending on the HOMO−LUMO gap, the electronic character of these species varies from the pure diradical (HOMO degenerate or nearly degenerate with LUMO) to the 50:50 diradical and zwitterion composition for the molecules with a big HOMO−LUMO gap. The hetero-derivatives of cyclopentane-1,3-diyl show spectroscopic characteristics expected for stable heterocyclic molecules. The only exception is the low IP—about 2 eV below the typical IP for organic radicals or diradicals. This is a result of quasi-anion electronic distribution in the zwitterion, where one half of the electron pair populated at C1 and the second half populated at C3. An important aspect of these systems is that the open singlet is stable not only with respect to the triplet but also with respect to the closed form. Thus, it is predicted that the nitrogen derivatives can be prepared and isolated as the open form isomers. The photoelectron spectrum of the open form is expected to be very different from that of the closed one.

To summarize, the main features found for these interesting systems—the extra stability of the bond-stretched isomers, the high barrier to the 1,3 ring-closure, the large HOMO−LUMO gap, and at the same time, relatively small charge transfer—are attributed to the participation of at least four electrons in the bonding, which in VB language is explained by resonance stabilization of zwitterion and ylide-type structures in addition to the dominant diradical contribution.

Supporting Information Available: 1. Cartesian coordinates and absolute energies (in Hartree units) for the species in Table 1 with X = O, S, NH, and NCH$_3$ at the CASSCF(10/8)/cc-pVDZ level. 2. IRC energy calculation from the reactant to the product at HF, MP2, CASSCF, and MRCI levels. 3. Vibrational frequencies and normal modes for the transition state between the closed and open forms of the specie with X = NH (CASSCF(10/8)/cc-pVDZ). 4. Mulliken and Lowdin charges. 5. Configurations used in the CASSCF and in the MRCI calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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