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On the Electronic Character of Localized Singlet 2,2-Dimethoxycyclopentane-1,3-diyl Diradicals: Substituent Effects on the Lifetime

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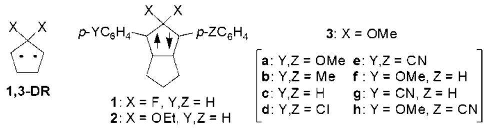
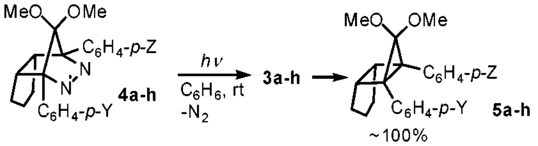
Our present day understanding of the electronic nature of localized *triplet* diradicals is well-documented by experimental as well as theoretical studies;[1] however, this is not the case for the corresponding *singlet* diradicals. The major reason resides in the fact that these species are quite short-lived and difficult to handle experimentally.[2] A breakthrough was the spectral detection and characterization of the first localized singlet diradical, namely the 2,2-difluoro-substituted 1,3-diradical **1** (X = F; Y, Z = H; λ_{max} 530 nm; $\tau_{293\ K}$ = 80 ns in *n*-pentane),[3] whose singlet ground state was predicted by Borden's computational work[4] for the parent cyclopentane-1,3-diyl (**1,3-DR**, X = F). More recently, we have found that an alkoxy group (X = OR in **1,3-DR**) stabilizes sufficiently such transient species to place the singlet below the triplet state, as confirmed by the long-lived singlet diradical **2** (X = OEt; Y, Z = H; λ_{max} 550 nm; τ_{293K} = 880 ns in benzene).[5]



In this study, we have examined the electronic substituent effects on the lifetime of the singlet diradicals **3a**−**h** (X = OMe), for which electron-donating (Y, Z = Me, OMe) and/or electron-withdrawing groups (Y, Z = Cl, CN) were introduced at the para position of the phenyl rings. The experimental results have provided valuable information on the electronic character of localized singlet diradicals.

For the generation of the diradicals **3**, we have chosen the photodenitrogenation of the azoalkanes **4a**−**h** (λ_{max} ~360 nm, ϵ ~ 100) by photolysis (>320 nm) in benzene, which afforded quantitatively the housanes **5a**−**h** (>95%, Scheme 1) by intramolecular cyclization of the singlet diradicals **3a**−**h**. The transient absorption spectra and decay traces of the intermediary singlet diradicals **3** were measured in benzene by means of laser-flash photolysis (λ_{exc} = 355 nm, 5 ns pulse). Strong absorption was observed in the visible region (ca. 600 nm), which decayed with clean first-order kinetics, as exemplified for the diazene **4a** (Y, Z = OMe) in Figure 1 (spectrum a and time profile d). A similar absorption band was observed in a methylcyclopentane (MCP) matrix at 77 K (Figure 1, spectrum b). The transient species were assigned to the diradicals **3a**−**h** on the following experimental evidence: (i) the absorption maxima (around 600 nm) are similar to those of the singlet diradicals **1** and **2**; (ii) the persisting species **3a**,**c** at 77 K are EPR silent; (iii) the lifetimes (Table 1) are not affected by the presence of molecular oxygen;[6] and (iv) the large (log *A* = 11.2) preexponential Arrhenius factor for **3c** (Y = H, E_a = 25.9 kJ/mol) suggests spin-allowed ring closure to housane **5**. Additionally, significant fluorescence (λ_{max} 740 nm at λ_{exc} 590 nm) was observed for the localized singlet diradical **3a** in the MCP matrix at 77 K (Figure 2c). As may be clearly seen from the lifetime (τ_{293K}) data of the singlet diradicals **3** in Table 1, both electron-donating and electron-withdrawing groups stabilize the singlet

Scheme 1



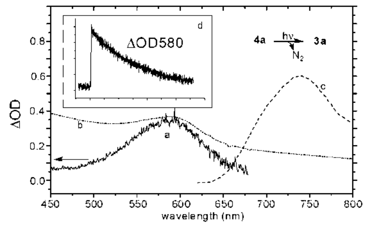


Figure 1. (a) Transient absorption spectrum for the singlet diradical **3a** measured immediately after the laser pulse (λ_{exc} 355 nm); (b) absorption spectrum in a MCP matrix at 77 K; (c) fluorescence spectrum (λ_{max} 740 nm) in the MCP matrix at 77 K (λ_{exc} 590 nm); (d) transient decay trace at 580 nm and 20 °C.

Table 1. Substituent Effects on the Lifetime of the Singlet Diradicals **3** (X = OMe)[a]

entry	3	τ_{293K} (ns)[b]
1	**3a** (Y, Z = OMe)	1050 ± 80
2	**3b** (Y, Z = Me)	460 ± 30
3	**3c** (Y, Z = H)	320 ± 15
4	**3d** (Y, Z = Cl)	490 ± 30
5	**3e** (Y, Z = CN)	625 ± 25
6	**3f** (Y = OMe, Z = H)	600 ± 35
7	**3g** (Y = CN, Z = H)	470 ± 30
8	**3h** (Y = OMe, Z = CN)	740 ± 60

[a] The diradicals **3a**−**h** were generated during laser flash photolysis (355 nm, 5-ns pulse width) of the diazenes **4a**−**h**. [b] In benzene solution at 20 °C; errors are standard deviations of the mean (5 data points).

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diradicals **3** relative to the parent case **3c** (Y, Z = H). From the symmetrical derivatives (entries 1−5) it is evident that a strong electron-donating group (**3a**: Y, Z = OMe, entry 1) increases significantly the lifetime; actually, derivative **3a** possesses the longest lifetime of all diradicals examined. In the unsymmetrical cases (entries 6−8), there is also a definite prolongation of the lifetime, but this is clearly less than that for the symmetrical **3a**.[7]

What electronic character of these singlet diradicals accounts for these unusual and unprecedented lifetime data? To rationalize the experimental substituent effects, we shall consider the possible mesomeric structures **A**−**D** depicted in Figure 2 for the singlet 2,2-dimethoxycyclopentane-1,3-diyls.

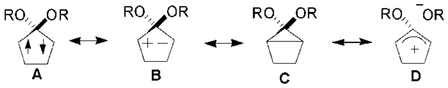
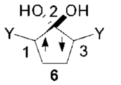


Figure 2. Possible mesomeric structures to express the electronic character in singlet 2,2-dimethoxycyclopentane-1,3-diyl diradicals.

(1) *Radical character*: Our previous study[5] disclosed that the singlet diradical **2** reacts with molecular oxygen at a significant rate, i.e., k is $\sim 10^5$ M^{-1} s^{-1}, which substantiates the radical character in such diradicals. Thus, the singlet-diradical structure **A** should significantly contribute in the stabilization of the radical site by the para-substituted phenyl group. For benzyl-type radicals, the stabilization power[8] of para substituents has the following order: CN ($\sigma_{\alpha}^{\bullet 8a} = 0.040$, $\sigma_{C}^{\bullet 8b} = 0.46$, $\Delta D^{8c} = 0.54$) $\gg$ Cl (0.011, 0.12, 0.04) $\sim$ Me (0.015, 0.11, 0.02) $\sim$ OMe (0.018, 0.24, −0.05) > H (0.00). Evidently, the prolonged lifetime of the dicyano derivative **3e** (Y, Z = CN) is well accounted for by such radical stabilization; however, it fails for the dimethoxy case **3a** (Y, Z = OMe), which is actually the longest lived singlet diradical in Table 1. Additionally, other electronic effects must operate to rationalize the observed substituent-dependent lifetimes of these singlet diradicals.

(2) *Zwitterionic character:* As suggested by Salem and Rowland,[9] the singlet structure **A** should have some dipolar contribution, as expected by the structure **B**. Our experimental work clearly manifests the importance of such dipolar character since the unsymmetrically substituted derivatives stabilize the singlet diradical in the order **3h** (Y = OMe; Z = CN) > **3f** (Y = OMe; Z = H) > **3g** (Y = CN; Z = H) > **3c** (Y, Z = H) (entries 3 and 6−8). Thus, in **3h** the electron-donating *p*-MeO group stabilizes the positive charge of the dipole and the electron-withdrawing *p*-CN group the negative one. However, this zwitterionic character does not explain why the symmetrical derivatives **3a** (Y, Z = OMe; 1050 ns) and **3e** (Y, Z = CN; 625 ns) possess longer lifetimes than the unsymmetrical ones **3e** (Y = OMe; Z = H; 600 ns) and **3f** (Y = CN; Z = H; 470 ns). In the case of **3a**, the methoxy group should destabilize the anionic center, while in the case of **3e** the cyano group should destabilize the cationic site. Thus, these symmetrical singlet diradicals should have shorter lifetimes than all the unsymmetrical ones. Again, still other factors must play a role.

(3) *π Bonding and hyperconjugation:* To understand the unexpected stabilization in the symmetrically disubstituted derivatives **3a** and **3e**, the Mulliken bond orders (BO) were computed for the model diradicals **6** at the UB3LYP/6-31G* level of theory (Figure 3).[10] The BO1 values reveal substantial π bonding [BO1 > 0; 0.35 (Y = OH), 0.58 (Y = H), 0.40 (Y = CN)] between the C1 and C3 radical sites, which implies that the mesomeric structure **C** is important. Thus, the stronger this π bonding in the singlet diradical, the more significantly structure **C** contributes and the shorter the lifetime. The calculated BO1 trend follows qualitatively very nicely the observed order (Table 1).



BO1 = C1-C3
BO2 = C1-C2
BO3 = C2-O

Figure 3. Pertinent bond orders (BO) in the model structure **6**.

Furthermore, also hyperconjugation operates through the mesomeric structure **D**, as expressed by the finding of BO2 > 1.0 [1.15 (Y = OH), 1.08 (Y = H), 1.00 (Y = CN)] and BO3 < 1.0 [0.82 (Y = OH), 0.90 (Y = H), 0.98 (Y = CN)]. Hyperconjugation accounts for the notable stabilization through electron donation to the allylic cation by the two terminal *p*-MeO substituents, which should prolong significantly the lifetime of the singlet diradical **3a**. Such electron donation through hyperconjugation also has been proposed in **1,3-DR** (X = F) by Borden et al.[11] Nevertheless, the electron-withdrawing substituents in the symmetrically disubstituted singlet diradical **3e** (Y, Z = CN) should destabilize the hyperconjugative structure **D** and lower the lifetime compared to unsymmetrically monosubstituted derivative **3g** (Y = CN; Z = H), which is contrary to our experimental results (compare entries 5 and 7). As already explained in point 1 (radical character), the radical-stabilizing effect of the *p*-CN group comes to bear.

In summary, the unprecedented substituent effects on the lifetime of the singlet diradicals reported herein provide valuable insight into the electronic character of these species. From the localized singlet 2,2-dimethoxycyclopentane-1,3-diyl diradicals **3** we have learned that the lifetime of such short-lived intermediates may be prolonged through the synergistic stabilization of radical zwitterionic, π-bonding and hyperconjugative structures.

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Supporting Information Available: Experimental and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The quenching rate constant for triplet states has been reported to be $k \sim 10^{10}$ M^{-1} s^{-1}; see ref 1e.

(7) Of note is the substantial geminal substituent effect on the lifetime of these singlet diradicals, namely **2** (X = EtO, 880 ns) > **3c** (X = MeO, 320 ns) > **1** (X = F, 80 ns). Presumably, steric effects operate in the cyclization step, which follow the order EtO > MeO > F.

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