J. Am. Chem. Soc. 1993, 115, 9824–9825

Effects of Symmetrical Diaryl Substitution on Intersystem Crossing in 1,3-Cyclopentanediyl Triplet Biradicals

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Received May 26, 1993

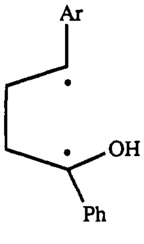
The lifetimes of triplet biradicals are often limited by their rate of intersystem crossing (ISC) to the singlet manifold; yet, experimental data that allow us to test the qualitative theoretical predictions given by Salem and Rowland[1a] and by Michl[1b] are still scarce. Whereas the geometrical requirements for effective ISC in biradicals have been extensively examined,[2] the effect of electronic factors has received little attention in experimental work. Both treatments[1a,b] predict that ISC from the triplet state will be accelerated in proportion to the zwitterionic contributions to the lowest singlet state wave function, and this is reproduced by *ab initio* MCSCF calculations on model systems.[1c] In this context, Caldwell[3] has examined substituent effects on the triplet lifetimes of Norrish type II biradicals of structure **1**. For such biradicals, the hydroxy-bearing radical site was considered as the donor, while the other radical site represented the acceptor whose electron affinity was varied. The results (Table I) were not in line with expectations based on the postulated zwitterionic effect, as substitution with stronger acceptors resulted in longer lifetimes for the triplet biradicals.

Besides the lifetimes of 1,4-biradicals, Caldwell has measured those of substituted 1,3-biradicals,[4] whereas Zimmt, Doubleday, and Turro have examined substituent effects on ISC in 1,5-biradicals.[5] The observed effects were either insignificant or they could not be reasonably accounted for on theoretical grounds. A definitive conclusion that could be drawn from these studies of substituent effects was that para bromine substitution causes faster ISC due to the well-established heavy atom effect.[3-5]

Table I. Substituent Effects on Triplet Lifetimes of Biradicals **1** and **2** and Calculated Energy Gaps between the Nonbonding Orbitals of Biradicals **4**

X	$^3\tau$ (**1**)/ns[a]	$^3\tau$ (**2**)/ns[b]	$\Delta\epsilon_{NBMO}$ (**4**)/cm^{-1}
MeO	38	690 ± 40	433
F		1150 ± 40	533
Me	44	1200 ± 20	543
H	53	1750 ± 20	586
Cl	69	1790 ± 60	588
Br	51	880 ± 40	628
COMe	76		652
NO_2		6000 ± 300	764

[a] Values taken from Caldwell.[3] [b] Errors are standard deviations of the mean (≥8 data points each).



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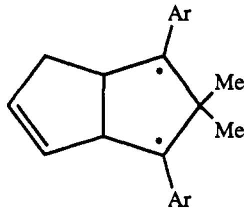

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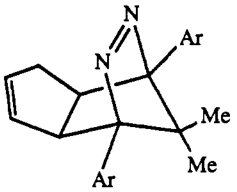

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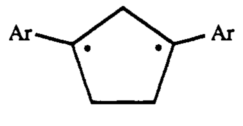

4

Ar = C_6H_4 - *p*X, where X = H, F, Cl, Br, Me, MeO, NO_2, COMe

The present study was done with the 1,3-cyclopentanediyls **2** which were obtained from the readily accessible azoalkane precursors **3**. A synthesis of the parent system **3** (X = H) has been described,[6] and the substituted derivatives were prepared accordingly. In conceptual variance with the earlier studies,[3-5] we substituted our compounds symmetrically to avoid dipolar effects. Our choice of the model compounds was guided by the fact that the exchange of hydrogen by phenyl at the radical sites of 1,3-cyclopentanediyls causes an increase in lifetime by 2 orders of magnitude.[7] The long lifetimes of 1,3-diphenyl-1,3-cyclopentanediyls should allow a sufficiently high accuracy of measurement that even small variations of triplet lifetimes, like those expected for substitution at the para positions, should become measurable. Moreover, the geometrical constraints of the cyclopentanediyls are advantageous for a theoretical analysis since conformational changes[8] need not be taken into account.

The triplet biradicals[9] were generated by direct (X = H, MeO, and NO_2) or benzophenone-sensitized photolysis of the corre-

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(1) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Michl, J. In *Theoretical and Computational Models for Organic Chemistry*; Formosinho, S. J., Csizmadia, I., G., Arnaut, L. G., Eds.; Kluwer: Dordrecht, 1991; p 207. See also: Bonačić-Koutecký, V.; Koutecký, J; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170. Michl, J.; Bonačić-Koutecký, V. In *Electronic Aspects of Organic Photochemistry*, Wiley: New York, 1990. Michl, J. *J. Mol. Struct. (THEOCHEM)* **1992**, *260*, 299. (c) Carlacci, L.; Doubleday, C.; Furlani, T. R.; King, H. F.; McIver, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 5323.

(2) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521.

(3) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1167.

(4) Caldwell, R. A. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 117. Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797.

(5) Zimmt, M. B.; Doubleday, C.; Turro, N. J. *Chem. Phys. Lett.* **1987**, *134*, 549.

(6) Beck, K.; Hünig, S. *Chem. Ber.* **1987**, *120*, 47.

(7) (a) Adam, W.; Grabowski, S.; Platsch, H.; Hannemann, K.; Wirz, J.; Wilson, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 751. (b) Adam, W.; Reinhard, G.; Platsch, H.; Wirz, J. *Ibid.* **1990**, *112*, 4570. The second sentence in the last paragraph of this paper should read: "Dimethyl substitution gives rise to *reduced* through-bond coupling"; this correction does not affect the subsequent arguments.

(8) Conformational flexibility complicates the analysis of ISC in biradicals: Doubleday, C.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199.

(9) The identification of the observed transients as the corresponding triplet biradicals is based on the similarity of their absorption spectra with those of the corresponding benzyl radicals,[10] product studies (housanes), EPR spectroscopy of the biradicals at low temperature,[11] the lack of quenching by *trans*-piperylene (up to 0.05 M), and scavenging by triplet molecular oxygen. In the case of the nitro derivative (X = NO_2), the same transient intermediate was generated by direct flash photolysis of the housane. The absorption maxima were located at 370 and 580 nm; the strong 580-nm absorption of **2** (X = NO_2) is unprecedented for *p*-nitrobenzyl radicals. Lemmetyinen has kindly generated the parent *p*-nitrobenzyl by his method[10d] and has confirmed the presence of a strong 560-nm absorption (H. Lemmetyinen, personal communication, May 1993).

(10) (a) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1980**, *102*, 4798. (b) Tokumura, K.; Nosaka, H.; Ozaki, T. *Chem. Phys. Lett.* **1990**, *169*, 321. (c) Tokumura, K.; Ozaki, T.; Nosaka, H.; Saigusa, Y.; Itoh, M. *J. Am. Chem. Soc.* **1991**, *113*, 4974. (d) Mayouf, A. M.; Lemmetyinen H.; Koskikallio, J. *J. Photochem. Photobiol. A: Chem.* **1993**, *70*, 215.

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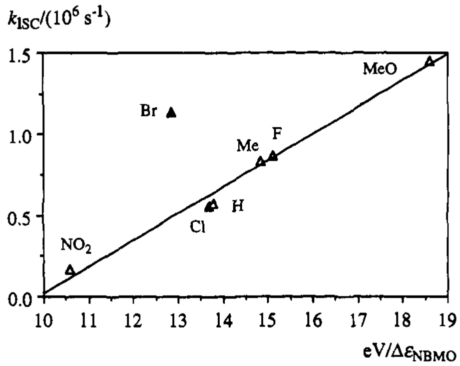

Figure 1. Correlation of ISC rate constants with calculated NBMO energy gaps.

sponding azoalkanes **3** in degassed benzene solution, and their transient absorption decay curves were monitored at 320 or 410 nm (or 580 nm for X = NO_2) by time-resolved laser flash spectroscopy.[7] The measured lifetimes (Table I) indicate that the donor substituents methoxy and methyl, but also fluorine, shorten the lifetimes of these biradicals, whereas the acceptor substituents chlorine and nitro prolong them; bromine substitution results in a shorter lifetime. Interestingly, the trend of the substituent effect in biradicals **2** is similar, though more pronounced, than that found for the asymmetrical biradicals **1** (Table I). This suggests that the dominant underlying effect may be the same in both series of substrates.

What is the origin of the presently reported substituent effects on ISC in the triplet 1,3-cyclopentanediyls **2**? The biradicals **2** are essentially of the homosymmetric[1] type; the slight asymmetry introduced by the fused cyclopentene ring remains the same in the whole series. The two-electron, two-orbital models[1a,b] predict that spin–orbit coupling, and hence the rate of ISC, should increase with the splitting between the two nonbonding molecular orbitals (NBMOs). Furthermore, the energy barrier for ISC is also expected to be reduced as the NBMO splitting increases, since this will tend to stabilize the lowest singlet state relative to the triplet ground state. The AM1 (3 × 3 CI) model[12] has performed adequately for the evaluation of the ground-state multiplicities of several biradicals,[13] and we have carried out such calculations for the *p*,*p*′-disubstituted series of 1,3-diaryl-1,3-cyclopentanediyls **4** as model systems for **2**.[14] The triplet state was calculated to be the ground state for all derivatives, in accord with the experimental observation of their EPR signals at low temperature.[11] The calculated singlet–triplet splittings (ΔE_{ST}) were all within 1.3 ± 0.1 kJ/mol.

Figure 1 shows that the NBMO energy gap ($\Delta\epsilon_{NBMO}$) calculated by the AM1 method is indeed correlated with the rates of ISC (k_{ISC}), the latter taken as the inverse of the observed triplet biradical lifetimes. As expected, the ISC rate of **2** (X = Br) lies well above the correlation line which was calculated by excluding **2** (X = Br). Surprising, however, is the fact that the observed trend of the other derivatives is *opposite* that predicted by qualitative theory![1a,b] The *inverse* of $\Delta\epsilon_{NBMO}$ was chosen as the independent parameter, which gave an essentially linear dependence: $k_{ISC}/(10^6\ s^{-1}) = -1.62 + 0.164\ eV/\Delta\epsilon_{NBMO}$; $r = 0.99$.

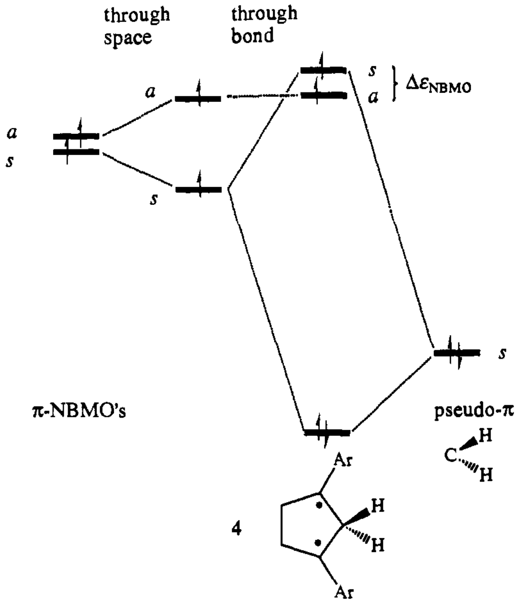

Figure 2. Through-space and through-bond coupling scheme for the NBMOs of 1,3-diaryl-1,3-cyclopentanediyls **4**. Symmetry labels *a* and *s* refer to the plane of symmetry lying vertical to the paper plane.

The remarkable quality of the correlation shown in Figure 1 leaves little doubt that the calculated NBMO splittings are picking up an essential quantity related to ISC. At this point, we offer the following (*ad hoc*) explanation for the apparent discrepancy with theoretical expectations.[1a,b] The near degeneracy of the NBMOs in cyclopentanediyl biradicals results from near-cancellation of the two opposing effects of through-space and through-bond coupling.[7b] The AM1 calculations for the model substances **4** place the *symmetric* (in-phase) NBMO at slightly higher energy than the *antisymmetric* NBMO, as shown in Figure 2. It may well be that the AM1 model slightly, but consistently, overestimates through-bond coupling. Another parametrization might place the *symmetric* orbital below the *antisymmetric* one. As shown below, this would *reverse* the trend along the series of substituents and bring the correlation with ISC rates in line with theoretical expectation. Acceptor substituents X will lower the basis energies of the NBMOs, and *vice versa*. As the NBMOs are lowered in energy, perturbation theory predicts that the importance of through-bond coupling will increase, and this will raise the energy of the *symmetric* NBMO relative to that of the *antisymmetric* one, because the latter is not affected by through-bond coupling (Figure 2). In other words, we believe that the trend in the absolute energies of the *symmetric* NBMO will be reproduced by any reasonable calculation but that the *relative* energies of the two NBMOs, and hence the sign of the trend in $\Delta\epsilon_{NBMO}$, may be rather coincidental.

Be this as it may, NBMO splittings calculated by the AM1 model prove to be a powerful and readily accessible empirical predictor for triplet biradical lifetimes. We are further exploring this concept, namely for alkylated and for asymmetrically substituted cyclopentanediyl biradicals.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Swiss National Science Foundation for support of this work. W.M.N. thanks the Fonds der Chemischen Industrie for a Kekulé doctoral fellowship.

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[13] Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3671.

[14] The parent biradicals **4** were chosen as model substances for higher computational accuracy. All geometries were optimized within C_{2v} symmetry. Similar calculations for **2** gave slightly smaller values for $\Delta\epsilon_{NBMO}$ with the same substituent ordering.