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SHORT COMMUNICATION

ZERO-FIELD SPLITTING VERSUS INTERELECTRONIC DISTANCE IN TRIPLET ELECTRON SPIN RESONANCE SPECTRA OF LOCALIZED DINITRENES

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Triplet zero-field splitting parameters were obtained in 2-methyltetrahydrofuran glass at 77 K for phenylene-1,4-dinitrene (1), (biphenyl-4,4′-dinitrene (2), (*E*)-1,2-bis(4′-nitrenophenyl)ethene (3), 1,4-bis(4′-nitrenophenyl)buta-1,3-diene (4) and 1,8-bis(4′-nitrenophenyl)octa-1,3,5,7-tetraene (5). The results were (1) $|D/hc| = 0\cdot169\ \mathrm{cm}^{-1}$, $|E/hc| = 0\cdot004\ \mathrm{cm}^{-1}$, (2) $|D/hc| = 0\cdot189\ \mathrm{cm}^{-1}$, $|E/hc| = 0\cdot00\ \mathrm{cm}^{-1}$, (3) $|D/hc| = 0\cdot122\ \mathrm{cm}^{-1}$, $|E/hc| = 0\cdot00\ \mathrm{cm}^{-1}$, (4) $|D/hc| = 0\cdot0865\ \mathrm{cm}^{-1}$, $|E/hc| = 0\cdot00\ \mathrm{cm}^{-1}$ and (5) $|D/hc| = 0\cdot0442\ \mathrm{cm}^{-1}$, $|E/hc| = 0\cdot00\ \mathrm{cm}^{-1}$. All these biradicals are ground-state singlets. Based on the observed decrease in triplet signal intensities as temperature decreases. The substantial magnitudes of $|D/hc|$ for 3–5, despite the large distance between localized nitrene electrons, is much more than can be explained by a simple dipolar interaction between localized electrons, and is attributed at least partly to spin polarization effects on the π-electron clouds of these systems.

As part of our interest in investigating interelectronic exchange interaction in organic open-shell molecules, we have studied the triplet biradical electron spin resonance (ESR) spectroscopy of quinonoid, localized dinitrenes. Examples shown in Scheme 1 are phenylene-1,4-dinitrene (**1**), biphenyl-4,4′-dinitrene (**2**), 1,2-bis(4′-nitrenophenyl)ethene (**3**) 1,4-bis(4′-nitrenophenyl)buta-1,3-diene (**4**) and 1,8-bis(4′-nitrenophenyl)octa-1,3,5,7-tetraene (**5**). In these systems, unlike in conjugated biradicals and polyradicals, there is no direct conjugative exchange interaction between the unpaired electrons. Exchange is therefore weak, and mechanistically due to effects such as spin polarization through the π-network. We had theoretical reasons for believing that interelectronic interaction[1] in such systems would become negligible with extended length of the conjugated system. To probe this matter, we investigated zero-field splitting (zfs) parameters for the triplet ESR spectra of compounds **1**–**5**.

Diazide precursors **6**–**10** were synthesized by standard chemistry involving reduction of the corresponding dinitro compounds to diamines, double diazotization and treatment with sodium aside. Where multiple C=C bonds were present in a dinitro intermediate, the all-*E* geometry in the double bonds was generated by heating the compound overnight with a small amount of iodine in boiling acetone. All the diazides were stable for many months storage below room temperature in the dark and gave satisfactory spectral characteristics as follows. Compound **6**: m.p. 80–81 °C; IR (KBr, cm^{-1}), 2080, 2110 ($-\mathrm{N_3}$ str.); UV–visible ($\lambda_{\max}$/nm [ε]): 272 [12 400]; analysis: calculated for $C_6H_4N_6$, C 45·01, H 2·52, N 52·47; found, C 44·50, H 2·66, N 51·90%. Compound **7**: m.p. 80–81 °C; IR (KBr, cm^{-1}), 2120 ($-\mathrm{N_3}$ str.); UV–visible ($\lambda_{\max}$/nm [ε]), 297 [36 700]; analysis calculated for $C_{12}H_8N_6$, C 61·06, H 3·41, N 35·56; found, C 61·06, H 3·78, N 33·40%. Compound **8**: m.p. 154–155 °C; IR (KBr, cm^{-1}), 2140 ($-\mathrm{N_3}$ str.); 960 (*trans-CH*=CH); UV–visible ($\lambda_{\max}$/nm [ε]), 341 [34 400]; analysis calculated for $C_{14}H_{10}N_6$, C 64·12, H 3·84, N 32·03; found, C 63·19, H 3·72, N 31·42%. Compound **9**: m.p. 140 °C (decomp.); IR (KBr, cm^{-1}), 2130 ($-\mathrm{N_3}$ str.); UV–visible ($\lambda_{\max}$/nm [ε]), 361 [47 500], 381 [33 700], 384 [39 100]; analysis calculated for $C_{16}H_{12}N_6$, C 66·66, H 4·20, N 29·14; found, C 63·43, H 4·01, N 28·83%. Compound **10** decomposes above 250 °C; IR (KBr, cm^{-1}), 2130 ($-\mathrm{N_3}$ str.); UV–visible ($\lambda_{\max}$/nm [ε]), 379 [53 500], 397 [68 900],

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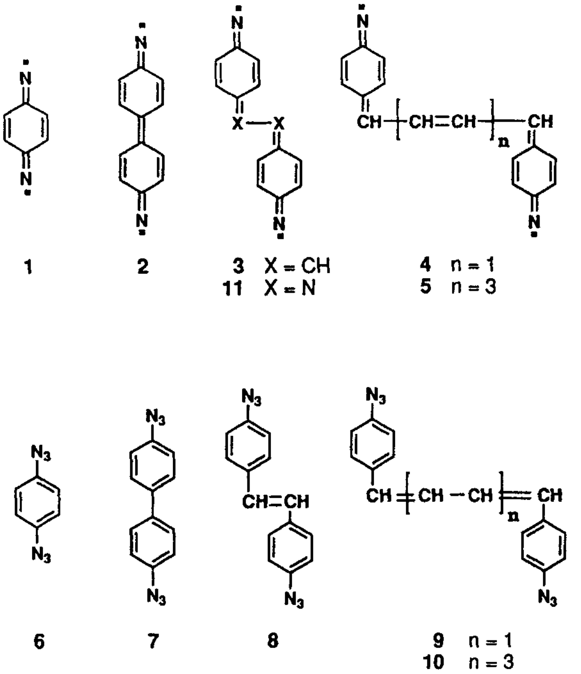

Scheme 1

423 [60 400]; the material was insufficiently stable to obtain consistent elemental analysis.

Dinitrene samples were prepared by dissolution of the appropriate diazide in dry 2-methyltetrahydrofuran, subjection to three freeze–pump–thaw vacuum degassing cycles, freezing at 77 K in a Suprasil liquid nitrogen finger Dewar and photolysis for ⩽5 min using a 1000 W xenon arc lamp with a Pyrex filter. The ESR spectra obtained at 9·57–9·58 GHz under these conditions are shown in Figure 1. All the spectra appear indefinitely stable at 77 K and disappear at once on thawing of the solvent matrix.

Strong peaks at about 3400 G are observed in all cases, due to radical impurities formed under the photochemical conditions used. These peaks have been omitted from Figure 1 for ease of representation. In the region of 5000–7000 G, all the spectra show peaks attributable to mononitrenes. The major mononitrene peak moves to progressively lower field in photolyses of **6–10**, showing that the π-electron of the mononitrene is increasingly delocalized by conjugation. In spectra derived from **8–10**, small peaks in the region of 6750–6850 G are also observed, a position consistent with non-conjugated aryl mononitrenes.[2] These peaks appear to be due to small amounts of terminal aryl mononitrenes which are generated in a twisted conformation that is deconjugated from the rest of the molecule, and so at higher field than the dominant, conjugated mononitrene peaks.

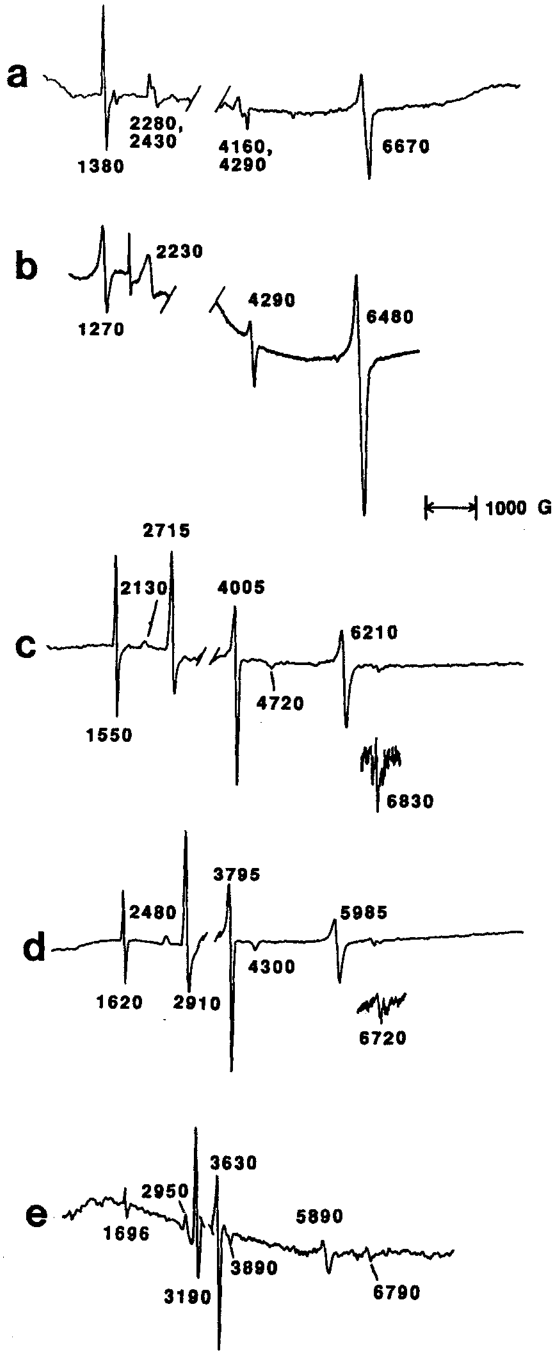

Figure 1. ESR spectra at 77 K and 9·57–9·58 GHz in 2-methyltetrahydrofuran from photolyses of (a) **6**, (b) **7**, (c) **8**, (d) **9** and (e) **10**. The $g \approx 2$ spectral region has strong radical impurity peaks in all spectra, and has been omitted for the sake of simplicity in presentation. Peak positions are given in units of gauss

All spectra show the resonances typical of biradical triplets in the region of 1000–5000 G, including triplet-definitive $\Delta M_s = 2$ half-field bands. The spectrum of dinitrene **1** has been reported previously.[3,4] and a description of '$|E/hc| \approx 0$' has been given;[4] we simulated the $|E/hc|$ value to be about equal to 0·004 cm^{-1}. In addition to work done by us on **2**,[5] Yabe and co-workers[6] have studied this species and found evidence for a highly twisted isomer of **2** formed on extended photolysis of diazide **7**, as is analogous to the minor, high-field mononitrene peaks described above. All biradical peak positions (including half-field band positions) were successfully simulated by the method of Kottis and Lefebvre[7]. (Our simulation program was adapted from that described by Jain *et al.*[8] The ESR triplet spectal simulation program described in the latter reference includes simulation of $\Delta M_s = 2$ transitions, the positions of which move to lower magnetic field as $|D/hc|$ grows larger. A good discussion and references can be found in ref. 9.) For **2**–**5**, $|E/hc|$ is essentially zero, consistent with the increasing elongation of the biradicals (assuming an extended conformation in **4** and **5**). Although many conformational isomers of **4** and **5** may be imagined, the modest linewidth and simplicity of these triplet spectra suggest that only one major ESR-active conformer is present. All the biradical spectral intensities decrease with increase in temperature, showing that the biradicals are ground-state singlets, with the ESR-active triplets being low-lying thermally excited states, in agreement with valence bond considerations [AM1-CI and PM3-CI computations using fixed geometries optimized with a PM3 OPEN(2, 2) C.I. = (5, 2) wavefunction find near-degenerate singlet and triplet states for the biradical bis(arylnitenes), typically with a small (200–600) cal mol^{-1}) (1 cal = 4·184 J) favoring of the singlet states. Calculations were carried out using MOPAC 6·0 (J. J. P. Stewart, QCPE Program 455)]. Table 1 summarizes zfs parameters for the triplet biradical portions of each spectrum, in addition to $|D/hc|$ values for mononitrenes[2] observed due to partial photolysis of each diazide.

As the distance between localized nitrene electrons increases in **1**–**5**, the zfs $|D/hc|$ value should decrease. This trend is observed (although the $|D/hc|$ value of **2** is anomalously large in the series for reasons still unclear to us), but the observed $|D/hc|$ values are fairly large. Large zfs $|D/hc|$ values are often associated with small distances between unpaired electrons, a relationship derived from the simple dipolar model of the triplet state (in the dipolar model, $|D/hc| = 1{\cdot}299\ g\ \mathrm{cm}^{-1}\ \mathrm{\AA}^3/r_{ij}^3$, where r_{ij} is the distance between interacting electrons in angstroms and g is the electron g-value; see citations in ref. 7). By this model, the zfs values of **1**–**5** should be much smaller than observed, as demonstrated by the data in Table 1 comparing observed $|D/hc|$ values with values predicted by assuming purely bipolar interaction of electrons completely localized at the nitrene nitrogen nuclear positions for reasonable molecular geometries.

Spin polarization of the π-electrons of these systems by the unpaired triplet electrons at the nitrene nitrogens could contribute to the magnitude of the observed zfs parameters.[3] The localized σ nitrene electrons of **1** can polarize the molecular π-spin density in the manner qualitatively shown in Scheme 2. The localized σ-electrons are shown as large arrows to signify approximately a full electron spin, and the small polarized π-spin densities are shown as small arrows, since the π-spin density on nitrogen is equivalent to about 2% of an electron spin[10] in **1**. Although the total π-spin density sums to zero, there can be non-zero spin density at each site, provided that sites of negative spin density exist. In this model, there could be considerable contributions to the zfs by *one-center* interactions between unpaired σ- and π-electron spin density at *each*

Table 1

Precursor photolyzed	Biradical zfs[a]	Mononitrene zfs[b]	N—N distance[c]	Dipolar zfs (predicted[d])
6	0·169 (0·004)	0·896	5·5	0·0156
7	0·189 (0·00)	0·830	9·7	0·0028
8	0·122 (0·00)	0·738 (0·96)	12·1	0·0015
9	0·8865 (0·00)	0·661 (0·92)	14·4	0·0009
10	0·0442 (0·00)	0·631 (0·94)		

[a] $|D/hc|$ ($|E/hc|$) in cm^{-1} for biradical dinitrenes produced from each precursor.

[b] $|D/hc|$ in cm^{-1} for the major mononitrene peak in each spectrum. Numbers in parentheses are for minor additional peaks assigned to less conjugated mononitrene byproducts.

[c] Distance in Å between terminal nitrene nitrogens, based on semi-empirically computed planar all-*E* geometries (see text).

[d] Zfs $|D/hc|$ in cm^{-1}; predictions based on the dipolar approximation (see text) and using the computed distance between nitrene nitrogens.

nitrene nitrogen. In addition, the triplet π-spin arrangement in the ring leads to a spin wave function mismatch, with sites of the same spin density adjacent to one another on the carbons of the phenylene ring, and also contributing to the zfs. *Ab initio* SCF-MO-CISD 6–31G* level computations on dinitrene **1** show[10] polarization of its π-spin density in essentially the manner shown in Scheme 2.

Although the polarized π-spin densities on the nitrogen atoms are small in **1**, they would contribute substantially to the magnitude of $|D/hc|$, since they are analogous to the one-center interactions that make monocarbene and mononitrene zfs so large. Because the π-spin density at each nitrogen of the dinitrene is small in **1–5**, the zfs values are nowhere near as large as that of a triplet aryl mononitrene, which has very large spin density populations for both the σ- and π-space. Extension of conjugation in **2–5** causes the π-spin density to be increasingly delocalized through the extended π-system (as demonstrated by the decreasing zfs for the analogous mononitrenes), so the π-spin density on each nitrene nitrogen will decrease. Since the nitrogen-centered σ-spin density of the unpaired electron will hardly change in **1–5**, the one-center interactions between the σ- and π-spin density at each nitrene nitrogen will decrease in **1–5**. The $|D/hc|$ value in the series **1–5** should therefore decrease (as observed, with the exception of the anomalous value for **2**), but much more slowly than expected by a model in which only σ-spin density interactions are considered.

Any perturbation to the above model that effects the amount of π-spin density on the nitrene nitrogens would strongly affect the observed $|D/hc|$ values. This would explain why dinitrene **3** has a zfs of $0{\cdot}122\ \mathrm{cm}^{-1}$, whereas the π-isoelectronic structural analog of **3**, 4,4′-azobenzenedinitrene (**11**), has a zfs of only $0.067\ \mathrm{cm}^{-1}$.[5] The electronegative azo linkage of **11** will withdraw π-spin density from the nitrene nitrogens toward the azo moiety, decreasing the one-center interactions on the nitrene nitrogens relative to the interactions present in **3**, and giving a smaller zfs for **11**. It is also plausible that some degree of non-planarity[6] in the nominally flat biphenyl dinitrene **2** forces some π-spin density on to the nitrene nitrogens relative to **1**, increasing the zfs for **2** in the observed anomalous fashion.

Recent ENDOR studies show spin polarization effects in quinonoidal dicarbenes[11] that are similar to the effects described above. We are currently endeavoring to obtain ENDOR data for quinonoidal dinitrenes, to allow us to probe directly the nature and degree of spin polarization along the framework of **1–5**. Such studies should shed light on whether the large zfs of these molecules is primarily due to spin polarization effects, or whether other spin-interactions are also important.

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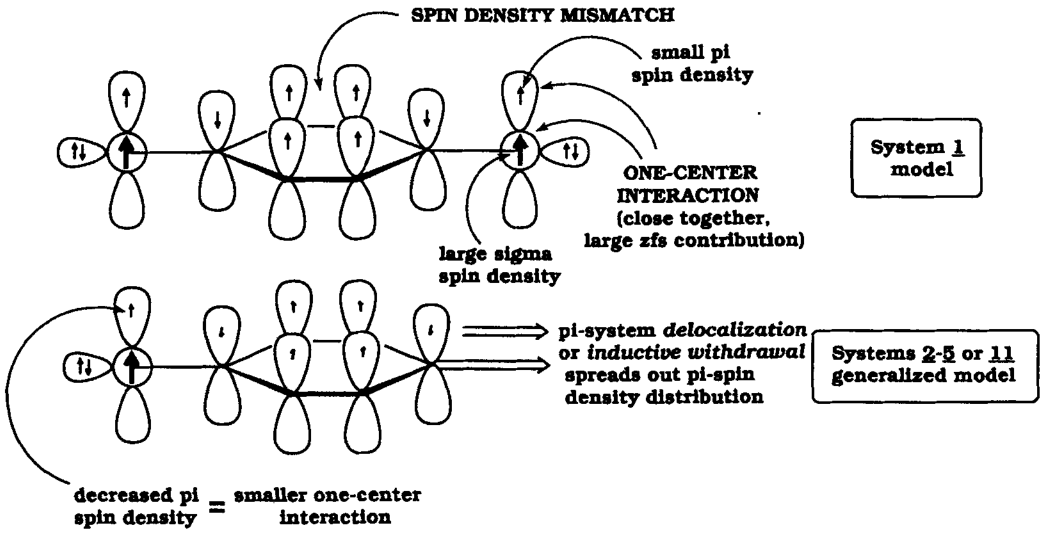

Scheme 2

Dougherty is thanked for providing a copy of the program described in Ref. 8. We also thank Professor T. Takui for a preprint of Ref. 11.

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