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Limits of Delocalization in Through-Conjugated Dinitrenes: Aromatization or Bond Formation?

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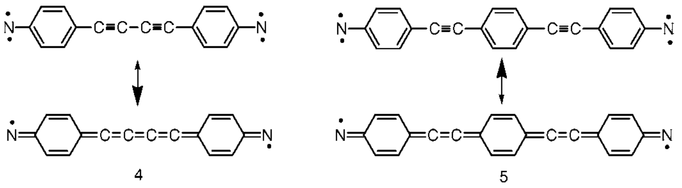
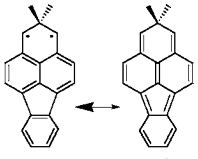
ABSTRACT



Dinitrenes 4 and 5 both can form quinonoidal structures by conjugative bond formation. However, ESR spectroscopy detects a thermally populated, excited-state, triplet quinonoidal structure only for 4, with a zero-field splitting of $|D/hc| = 0.0822$ cm^{-1}, $|E/hc| \cong 0.0$ cm^{-1}. The tendency to maintain aromaticity in the additional ring of 5 favors a dinitrene structure (with one less formal π-bond) over a quinonoidal structure. The thermally populated quintet state of 5 has a zero-field splitting of $|D/hc| = 0.287$ cm^{-1}, $|E/hc| \leq 0.002$ cm^{-1}.

The pairing of electrons to form a chemical bond has long been of interest to chemists. The relationship between structure and bonding in organic π-conjugated systems can be complex in systems with unpaired electrons (non-Kekulé molecules). *o*-Quinonoidal systems, for example, can have varying degrees of open-shell biradicaloid character by comparison to closed-shell olefinic character.[1] In an extreme case, McMasters, Wirz, and Snyder described[2] system **1** as a triplet biradical that is electron-spin resonance (ESR) active, although it can nominally have a closed-shell, quinonoidal Kekulé resonance structure with one more bond (**1Q**) at the cost of losing the aromaticity of three benzene rings. A number of systems with para-linked open-shell units do not undergo simple spin-pairing to a closed-shell state, especially for radical ions.[3] Understanding such systems increases our understanding of the limits of simplistic, inspection-based assignment of chemical bonds in covalent systems. As part of our ongoing studies of such molecules, we photolyzed diazides **2** and **3** under matrix isolation conditions to generate dinitrenes **4** and **5**, which can form either benzenoid dinitrenes or quinonoidal diiminediyls (biradicals).



1 1Q

Scheme 1 shows the synthesis of diazide precursors **2** and **3**.[4] Compound **2** was made by Sonogashira coupling of TMS-acetylene with 4-iodonitrobenzene to make **6**, deprotection to **7**, acetylene coupling to give **8**, reduction to diamine **9**, and Sandmeyer azidification to give the diazide, which was photolabile and best if purified immediately before use.

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[1] Borden, W. T., Ed. *Diradicals*; John Wiley and Sons: New York, 1982.

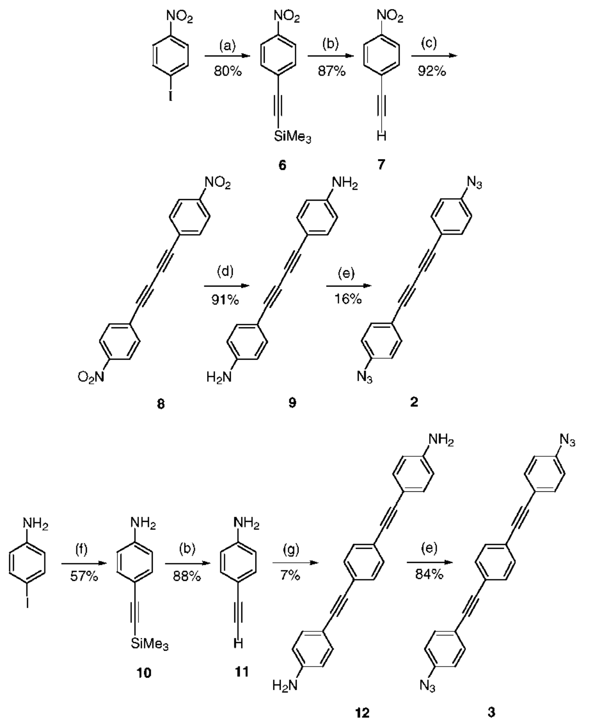
[2] McMasters, D. R.; Wirz, J.; Snyder, G. J. *J. Am. Chem. Soc.* **1997**, *119*, 8568.

[3] For some examples and guidelines, see: (a) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109. (b) Hrovat, D. A.; Borden, W. T. **1997**, *398*, 211. (c) Baumgarten, M. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel-Dekker: New York, 1999; p 147. (d) Blackstock, S. C.; Selby, T. D. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel-Dekker: New York, 1999; pp 165ff.

[4] Compound **2**: softens at 153−161 °C, 360 °C dec; HRMS(EI) theoretical for $C_{16}H_8N_6$ *m/z* 284.0810, found 284.0811; FTIR (cm^{-1}) 2130 (strong N_3 str); ^{1}HNMR (200 MHz, $CDCl_3$) δ 7.51 (d, 1 H, $J = 8.84$ Hz), 6.99 (d, 1 H, $J = 8.54$ Hz); UV−vis (CH_2Cl_2) 297 (29 100), 313 (40 300), 333 (49 400), 357 nm (41 800 L/mol-cm). Compound **3**: mp >360 °C; HRMS(EI) theoretical for $C_{22}H_{12}N_6$ *m/z* 360.1123, found 360.1125. FTIR (KBr, cm^{-1}) 2127 (strong N_3 str); ^{1}H NMR (200 MHz, THF-d_8) δ 7.54 (d, 4 H, $J = 8.46$ Hz), 7.51 (s, 4 H), 7.10 (d, 4 H, $J = 8.46$ Hz); UV−vis (CH_2Cl_2) 339 (46700), 360 nm (31000 L/mol-cm). Anal. Calcd for $C_{22}H_{12}N_6$: C, 73.32; H, 3.36; N, 23.32. Found: C, 73.18; H, 3.51; N, 23.34.

10.1021/ol034511c CCC: $25.00

Scheme 1. Synthesis of Diazide Precursors **2**−**3**[a]



[a] Key: (a) $Pd_2(dba)_3/PPh_3/CuI$, Et_3N, then TMS-acetylene; (b) K_2CO_3, $MeOH/CH_2Cl_2$; (c) CuI, TMEDA, acetone, O_2; (d) $SnCl_2{\cdot}2H_2O$, HOAc, 80 °C; (e) $NaNO_2$/aq HCl 0 °C, then NaN_3; (f) $PdCl_2(PPh_3)_2/CuI$, Et_3N, then TMS-acetylene; (g) $Pd_2(dba)_3/PPh_3/CuI$, Et_3N, *p*-diiodobenzene.

Compound **3** was made by a related strategy. TMS-acetylene was coupled with 4-iodoaniline to give **10**, which was deprotected to **11**, coupled by the Sonogashira method with 1,4-diiodobenzene to give diamine **12**, following the method of Hogarth et al.[5] The diamine was then azidified to give **3**. Diazides **2** and **3** are stable, but discolor easily if exposed to typical room lighting. Both are relatively soluble in organic solvents, despite their rigid geometries.

Precursors **2** and **3** were photolyzed at 20 K in 2-methyltetrahydrofuran (MTHF) matrix using an APD Cryogenics Displex CS-202 closed-cycle helium cryostat with optical spectroscopic attachments. The post-photolysis spectra are shown in Figure 1. Peaks associated with reactive intermediates are indicated in Figure 1, as determined by their disappearance upon warming of the matrix above its softening point at 110 K. By comparing our spectrum from **2** to those obtained from other[6] para-connectivity diazides, we assigned peaks at 475 (weak) and 492 nm to **4**. Broad peaks at 616 and 705 nm grow uncharacterized additional processes. The photolysate spectrum from **3** is much richer, with new intermediates during warming of the matrix above 90 K (at the expense of the peaks at 475 and 492 nm fade) due to peaks at 293, 316, 332, 346, 465, 490, and 532 nm that we assign to **5**. The peaks at 385 and 513 nm grow at the expense of the peaks assigned to **5** as the matrix is thawed. The dominating band at about 500 nm assigned to **4** is consistent with the appearance of UV−vis spectra assigned by Reiser et al.[6b] to para,para′-linked diiminediyls with extended conjugation. The spectrum assigned to **5** shows increased conjugation relative to the diazide but is significantly different from the spectrum for **4**.

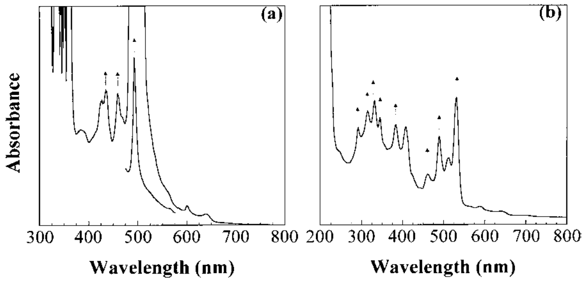


Figure 1. UV−vis spectra from photolyses of diazides **2** (a) and **3** (b) in frozen 2-methyltetrahydrofuran. The peaks assigned to **4** and **5** are indicated with growth arrows.

The electronpin resonance (ESR) spectra derived from photolysis of **2** and **3** are shown in Figures 2 and 3. The spectrum from **2** at 77 K showed a triplet mononitrene *xy*-transition corresponding to a zero-field splitting (zfs) of $|D/hc| = 0.856$ cm^{-1}, $|E/hc| \cong 0.003$ cm^{-1}. This is attributable to incomplete photolysis. The $\Delta m_s = 2$ and the four various turning point $\Delta m_s = 1$ peaks of a typical triplet biradical spectrum were observed at 1615 ($\Delta m_s = 2$ peak), 2480, 2915, 3790, and 4270 G. As shown by the simulation in Figure 1, these peaks can be fit to a triplet biradical spectrum of

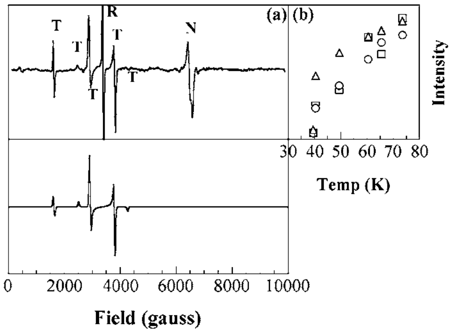


Figure 2. Baseline-corrected ESR spectrum from photolysis of diazides **2** ((a), $\nu_0 = 9.4925$ GHz) in 2-methyltetrahydrofuran at 77 K. (b) Intensity data for peaks at 1615 (△), 2915 (○), and 3790 G (□). R = radical, N = mononitrene, T = triplet **4**. A spectral simulation is shown below plot (a) for $S = 1$, $g = 2.003$, $D/hc = 0.0822$ cm^{-1}, $E/hc = 0.000$ cm^{-1}.

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(5) Hogarth, G.; Humphrey, D. G.; Kaltsoyannis, N.; Kim, W.-S.; Lee, M.-Y.; Norman, T.; Redmond, S. P. *J. Chem. Soc., Dalton Trans.* **1999**, *16*, 2705.

(6) (a) Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162. (b) Reiser, A.; Wagner, H. M.; Marley, R.; Bowes, G. *Trans. Faraday Soc.* **1967**, *63*, 2403. (c) Ohana, T.; Kaise, M.; Yabe, A. *Chem. Lett.* **1992**, 1397. (d) Harder, T.; Bendig, J.; Scholz, G.; Stösser, R. *J. Am. Chem. Soc.* **1996**, *118*, 2497.

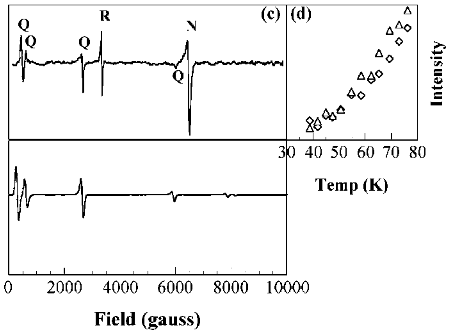


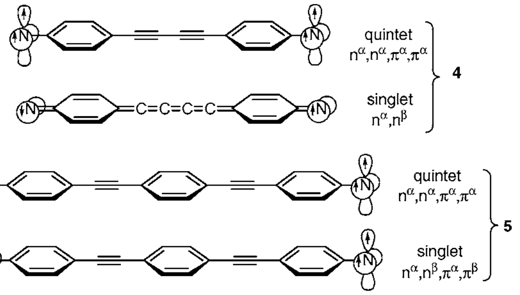
Figure 3. Baseline-corrected ESR spectrum from photolysis of diazide **3** in 2-methyltetrahydrofuran at 76 K, $\nu_0 = 9.3734$ GHz. (d) Intensity data for peaks at 320 (△) and 2640 G (◇). R = radical, N = mononitrene, Q = quintet **5**. A spectral simulation is shown below plot (c) for $S = 2$, $g = 2.003$, $D/hc = 0.287$ cm^{-1}, $E/hc = 0.000$ cm^{-1}.

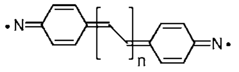
diiminediyl **4** with parameters $S = 1$, $g = 2.003$, $D/hc = 0.0822$ cm^{-1}, $E/hc \cong 0.0$ cm^{-1}. The intensities of the triplet biradical peaks all decreased with decreasing temperature and disappeared below 30 K, showing the triplet to be an excited state. The intensity versus temperature behavior is consistent with a singlet to triplet gap of 200−30 cal/mol.

The ESR spectrum derived from photolysis of **3** is substantially different. At 77 K, a triplet *xy*-transition attributable to the mononitrene of partially photolyzed **3** is observed that is consistent with $|D/hc| = 0.850$ cm^{-1}, $|E/hc| \leq 0.002$ cm^{-1}. Under no conditions did we observe a triplet biradical set of peaks analogous to those of **4**. Instead, we observed a set of peaks at 470, ~630, 2640, and 6000 G (weak), which all reversibly disappeared as the temperature was reduced below 30 K. The thermal behavior shows that the spectrum belongs to a thermally populated excited state. The observed spectrum fits very well to a quintet state spectrum simulated by the eignfield method[7] with parameters $S = 2$, $g = 2.003$, $D/hc = 0.287$ cm^{-1}, and $E/hc \leq 0.002$ cm^{-1}. We believe that this is quintet dinitrene **5**, which does *not* have a predominantly diiminediyl structure.

The difference between the ESR spectral behaviors of **4** and **5** is striking. Excited-state biradical triplet diiminediyl-type spectra such as that assigned to **4** have readily been observed in through-conjugated systems with substantial conjugation lengths,[4c−e,8,9] such as **6** and **7**. The zfs parameters in these systems are sizable due to[5] a dominant one-center contribution to the **D**-tensor at the hypovalent nitrogen, where the localized σ-electron and partial spin from a delocalized π-electron interact strongly. In accordance with valence bond and spin-parity[1,3a,10] models, a low-spin ground state was observed in **6** and **7**. Intermediate **4** follows analogous behavior, surrendering the aromaticity of its benzene rings to form an extra bond in a quinonoidal cumulated structure (Scheme 2).

Scheme 2. Electron Pairing in **4** To Give a Diiminediyl Structure with Bond Formation and Electron Pairing in **5** To Give Quintet and Singlet States by Weak Spin-Pairing Interaction





6 n = 2
7 n = 4

Intermediate **5** acts as if its nitrene centers interact only weakly, without sufficient pairing of nitrene π-electrons to form an extra π-bond and a cumulated, diiminediyl structure. The change does not appear to be due to inherent differences in the interacting mononitrenes—the zfs parameters of the mononitrenes from partial photolyses of **2** and **3** are remarkably similar. But, the energy of the extra bond formed in a quinonoidal form of **5** is apparently insufficient to make up for the de-aromatization of the central phenylene ring. Thus, **5** seems best described as a dinitrene, with individual nitrene sites weakly coupled by spin polarization effects to give an ESR silent singlet ground state lying below an ESR active quintet dinitrene state (Scheme 2). The exchange between the nitrene sites is insufficient to give an extra π-bond in a biradical structure.

Wasserman[11] and Itoh[12] have detailed a dipolar model describing the ESR zfs tensor behavior of high spin states that are comprised of individual carbene or nitrene sites that retain a large one-center interaction between localized σ-electrons and delocalized π-electrons. The basic relation between the zfs tensors of a quintet state ($\mathbf{D_Q}$) and two interacting triplet sites that comprise it ($\mathbf{D_T}$) is given[8] in eq 1.

$$\hat{\mathbf{D}}^{S=2} = \frac{1}{6}\left(\hat{\mathbf{D}}_a^{S=1} + \hat{\mathbf{D}}_b^{S=1}\right) + \frac{1}{3}\left(\hat{\mathbf{D}}_{ab}\right) \qquad (1)$$

If the one-center two-electron interaction in the triplet sites is large—as it is in nitrenes and (to a lesser extent) in

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[7] (a) Teki, Y. Ph.D. Thesis, Osaka City University, Osaka, Japan, 1985. (b) Teki, Y.; Takui, T.; Yagi, H.; Itoh, K.; Iwamura, H. *J. Chem. Phys.* **1985**, *83*, 539. (c) Sato, K., Ph.D. Thesis, Osaka City University, Osaka, Japan, 1994. (d) Takui, T. In *Molecular Magnetism in Organic-Based Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999.

[8] (a) Minato, M.; Lahti, P. M. *J. Phys. Org. Chem.* **1993**, *6*, 483. (b) Ling, C.; Lahti, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 8784. (c) Minato, M.; Lahti, P. M. *J. Am. Chem. Soc.* **1997**, *119*, 2187.

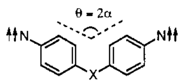
[9] Nimura, S.; Kikuchi, O.; Ohana, T.; Yabe, A.; Kaise, M. *Chem. Lett.* **1996**, 125.

[10] For more about parity models, see citations and an overview in: Lahti, P. M. In *Molecule-Based Magnetic Materials. Theory, Techniques, and Applications*; Turnbull, M. M., Sugimoto, T., Thompson, L. K., Eds.; American Chemical Society: Washington, DC, 1996; Vol. 644, pp 218ff.

carbenes—then the two-center term ($\mathbf{D_{ab}}$) governing interaction between the nitrene sites can be ignored. In this case, the vector angle formed between the interacting triplet zfs tensors will be the major contributor to the quintet zfs, which can be predicted by equations 2 and 3, where D and E are the zfs values for the quintet dinitrene (Q) and triplet mononitrene (T) and $\alpha = \theta/2$ is a measure of the vector angle between the C−N bonds in the dinitrene.

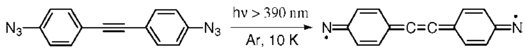
$$D_Q = \frac{3}{2}D_z^{S=2} = \frac{1}{2}\left[(D_T + E_T)\sin^2\alpha - \frac{1}{3}D_T - E_T\right] \qquad (2)$$

$$E_Q = \frac{1}{2}(D_s^{S=2} - D_y^{S=2}) = \frac{1}{6}\left[-(D_T + E_T)\sin^2\alpha + D_T - E_T\right] \qquad (3)$$

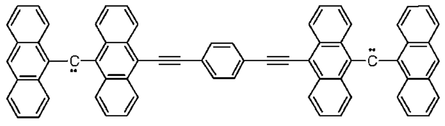


For dinitrene **5**, $\theta = 180°$, $|D_T/hc| = 0.850$ cm^{-1} and $|E_T/hc| \leq 0.002$ cm^{-1}. Applying eqs 2 and 3, the predicted $|D_Q/hc| = 0.283$ cm^{-1}, $|E_Q/hc| \sim 0.0$ cm^{-1}. These are quite close to the observed values of $|D_Q/hc| = 0.287$ cm^{-1}, $|E_Q/hc| \leq 0.002$ cm^{-1}. Given this and the fact that the ESR peaks assigned to **5** follow excited-state thermal behavior, the evidence supports formulating **5** as a weakly interacting singlet dinitrene, not a diiminediyl like **4**, **6**, and **7**. On the basis of the temperature versus intensity behavior for a thermally excited quintet state expected for the singlet-triplet-quintet equilibrium model of two weakly interacting triplet nitrenes,[13] the singlet to quintet energy gap is about 500−600 cal/mol, with the singlet state lowest in energy. Given the narrow range over which we have data, the precision of this estimate is limited but is reasonable for the observed spectral intensities.

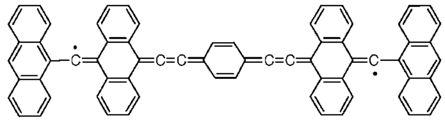
Tomioka and Sawai have found[14] that photolysis of diazide **8** gives spectroscopic evidence consistent with product **9**, a close analogue of **4**. Interestingly, dicarbene **10** shows an excited-state triplet biradical ESR spectrum like that of **4**, despite having a central phenyl ring and connectivity similar to **5**. Tanaka et al.[15] suggested strong delocalization of unpaired electron density from the carbene sites into the central diethynylbenzene portion of **10**. Qualitatively, the electronic nature of **10** is similar to that of **4** and **5**, since the spin centers are antiferromagnetically exchange coupled. The ESR spectrum of **10**, however, is quite different from that of **5**. The exchange interaction and tendency toward cumulated bond formation is apparently much weaker in **5**. Although this may be partly due to the fact that aryl nitrenes are inherently more localized that aryl carbenes, or to a greater degree of torsion between the aryl rings in **5**, we note that the cumulated resonance form of **10** has *more* aromatic sextets than the acetylenic form. Thus, the anthranyl rings help to compensate for the loss of central ring aromaticity in a biradical, cumulated form of **10**. Analogous compensation is lacking in **5**, which loses all benzenoid rings in a cumulated resonance structure.



8 **9**



10 (acetylenic)



10 (cumulated)

We have no direct evidence concerning whether **4** or **5** have coplanar or twisted phenylene rings, but it seems clear that the maximum number of double bonds expected by applying Kekulé criteria to the π-system is not formed in **5**. Whatever its geometry, compound **5** is a striking case where offsetting structural features—through-conjugation connectivity versus a tendency to maintain an aromatic sextet in the central ring—lead to an unusual electronic structure by comparison to typical notions of π-bond formation. Compound **5** is a case where the addition of a benzene ring actually inhibits cumulated bond formation with Kekulé-type behavior (by comparison to cumulated structural analogue **4**), allowing a high spin state with fewer formal bonds to be observed.

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Supporting Information Available: Synthetic procedures and characterization for precursors **2** and **3** and intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(12) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251.

(13) Itoh, K. In *Magnetic Molecular Materials, NATO ASI Series*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 67. In this model, the singlet to triplet energy gap is 2 J/*k*, the singlet to quintet energy gap is 6 J/*k*, where J/*k* is an interelectronic exchange constant. Unlike the case for the quintet state, we observe no clear evidence for a thermally populated triplet state formed by interaction of the two nitrene sites in **5**. However, any triplet state so formed is expected to have quite weak intensity bands and likely to overlap the mononitrene transition in a randomly oriented sample in the ESR X-band, so it is not surprising that it is not observed here. We thank Prof. Takeji Takui of Osaka City University for this insight (private communication, 2003).

(14) Tomioka, H.; Sawai, S. Unpublished results. We thank Prof. Hideo Tomioka of Mie University for communicating this to us in advance of publication.

(15) Tanaka, K.; Sato, K.; Shiomi, D.; Takui, T.; Nozaki, Y.; Hirai, K.; Tomioka, H. *Synth. Met.* **2001**, *121*, 1818.