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Approaches toward High-Spin Poly[*m*-(nitrenophenylene)ethynylenes]. Magnetic Interaction in the Oligomers Containing Two, Three, and Five Nitrene Units†

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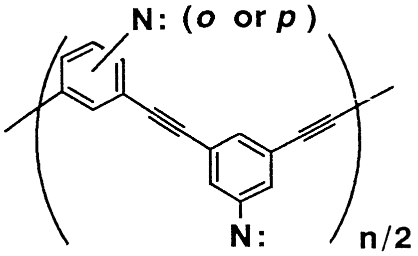
Oligonitrenes representing the various unit structures in poly[*m*-(nitrenophenylene)ethynylenes] (**1**) were prepared and studied by means of EPR and magnetization measurements which support our hypothesis that **1** will have a superhigh-spin ground state.

The ground state multiplicities of π-conjugated radicals can be designed to become high-spin by placing a second radical center in phase with the spin polarization of the intervening π-electrons due to the first radical center.1) On the basis of this theory on molecular topology,2) organic molecules with very high-spin ground states have been achieved in the oligomers of poly(*m*-phenylene-X)s where X is a carbene,3) an arylmethyl,4,5) a nitroxide,6) or a polaron.7) Modification of the skeletal structure where radical centers are placed in their main chains to conjugated linear polymers to which radical centers are attached as pendants has not been that successful.1,8) We propose that polynitrene **1** will have a superhigh-spin ground state and report here the intramolecular magnetic interactions between nitrenes in oligomers (**2a**, **2c** - **2g**, **3a**, **3b**, **5**) representing the various substructures in **1**.

The polymer skeleton itself is known9) and appears to have a number of merits over other conjugated polymers. The oligomers carrying azide groups were prepared similarly by means of Castro-type coupling reactions of the corresponding ethynylanilines with iodoaniline derivatives.10) The polyanilines were converted by Sandmeyer reactions to polyazides. The polynitrenes were then generated by photolysis with a Xenon or a



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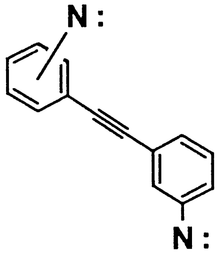
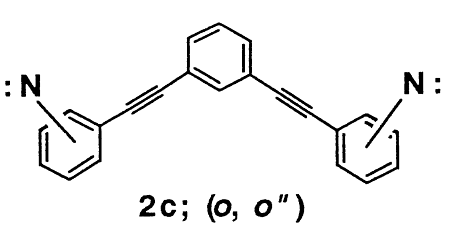


2a; (*o*, *m'*)
2b; (*p*, *m'*)



2c; (*o*, *o"*)
2d; (*p*, *p"*)
2e; (*o*, *p"*)
2f; (*m*, *p"*)
2g; (*m*, *m"*)

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† Dedicated to Professor Emeritus Osamu Simamura of The University of Tokyo on the occasion of his 80th birthday.

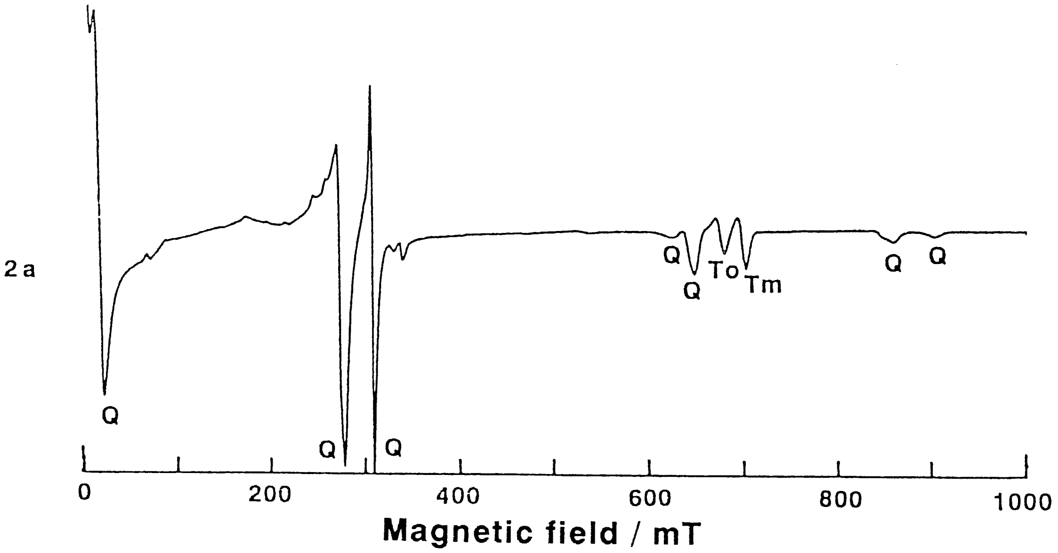


Fig. 1. X-Band EPR spectrum of dinitrene **2a**. Q, T_o, and T_m indicate signals due to quintet dinitrenes, *o*-, and *m*- substituted mononitrenes, respectively.

high-pressure mercury lamp (Pyrex filters, λ > 300 nm) at cryogenic temperatures and studied in situ.

X-Band EPR spectra were obtained for solutions (10^{-3} M) of the nitrenes in 2-methyltetrahydrofuran at 6 K. The EPR spectrum of **2a** shown in Figure 1 displays the characteristic fine structures of quintet dinitrenes.[11,12] Compounds **2c**, **2d**, and **2e** had similar spectra. From a set of the highest-field Z transition ($m_s = -2 \rightarrow -1$) and next highest-field Y transition ($m_s = 1 \rightarrow 2$), zero-field splitting (zfs) parameters were calculated on the basis of a third-order perturbation method proposed by Itoh:[13] **2a**: D = 0.1630, E = 0.0148 cm^{-1}; D = 0.1758, E = 0.0065 cm^{-1}. **2c**: D = 0.1620, E = 0.0077 cm^{-1}; D = 0.1577, E = 0.0137 cm^{-1}; or D = 0.1622, E = 0.0125 cm^{-1}; D = 0.1575, E = 0.0089 cm^{-1}. **2d**: D = 0.1488, E = 0.0055 cm^{-1}. **2e**: D = 0.1510, E = 0.0116 cm^{-1}. Two sets of the highest- and next highest-field transitions were observed in **2a** and **2c** corresponding presumably to the presence of two planar conformers.

Plots of the signal intensities vs. temperature for these quintet dinitrenes followed the Curie law in the range of 6 - 80 K, and no thermally populated signals were detected. The two triplet units in these dinitrenes are concluded to interact ferromagnetically. From these results, together with the reported quintet ground state of **2b**,[11] the ground state of polymer **1** is predicted to be high-spin. Since loss of a nitrene meta to the ethynylene bridges should not disrupt the exchange coupling between the two remote neighbors, such a chemical accident in **1** may be acceptable in retaining the intramolecular ferromagnetic exchange coupling along the chain.

On the other hand, when two terminal nitrenes were both meta (**2g**) to the respective ethynylene bridge, only a strong signal due to the X, Y transition of a triplet mononitrene was observed at 699 mT. The two nitrene units are concluded to be independent of each other; loss of the triplet center ortho or para to the ethynylene bridges should lead to the separation of the polymer molecule **1** into magnetically independent parts. In **2f**, signals due to a quintet state (**2f**: D = 0.1508, E = 0.0104 cm^{-1}) were observed as a thermally accessible excited state having a maximum intensity at 8 K. The quintet is estimated to be less stable than the ground singlet state by 27 cal/mol from a model of two weakly interacting triplets.[11,14]

The EPR results for trinitrenes **3a**, **3b**, and a pentanitrene **5** showed widely ranged fine structures that were too complex to analyze. The temperature dependence of the intensities of new signals (probably septet trinitrenes) other than the small signals due to lower spin multiplicities (quintet dinitrenes and triplet mononitrenes) followed the Curie law and no thermally excited signals were observed in the range 6 - 80 K. In order to confirm the high-spin ground states, some oligonitrenes have been studied on an Oxford Faraday balance installed with a quartz light guide through which the photolysis of the precursor azides diluted in poly(methyl methacrylate) (ca. 0.2 wt%) was performed. The plots of the magnetization vs. the applied magnetic field strength at several temperatures in the range 4.2 - 10.5 K were analyzed in terms of the Brillouin function to determine the effective total spin quantum number, S. Examples of such plots are shown in Figure 2. Both **3a** and **3b** gave best fits with $S = 2.9 \cong 3$. Similarly, **5** gave a result in which S is greater than 4 but not quite as high as theoretical value of **5**. Difficulty in effecting a complete photochemical reaction is responsible for the observed lower S value.

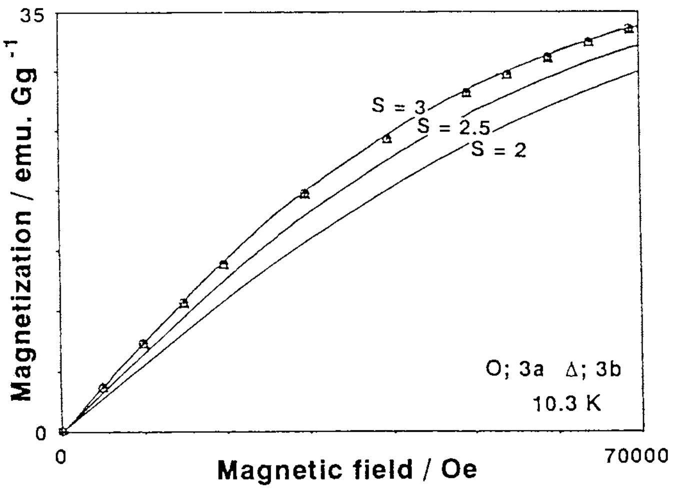
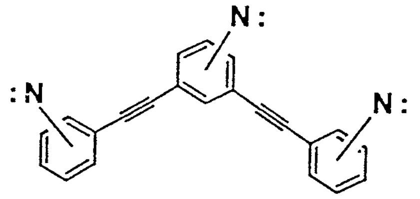
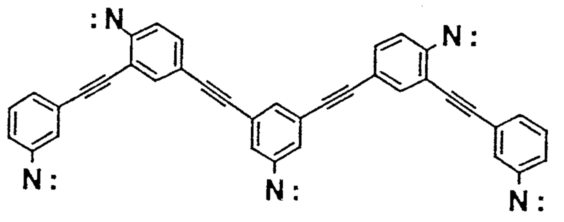


Fig. 2. Field dependence of the magnetization of trinitrenes **3a** (o) and **3b** (Δ) at 10.3 K. Theoretical curves were calculated from the Brillouin function for several S values



3a; (*p*, *m'*, *p"*)
3b; (*m*, *p'*, *m"*)



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It is concluded that **1** promises to be a super-high spin polymer. Masking of the phenyl azide chromophore by that of the polymer skeleton may become a practical obstacle.

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