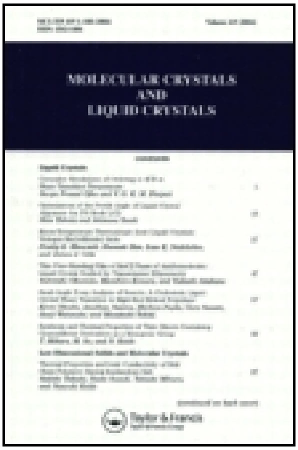


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Magnetic Coupling of Two Triplet Phenylnitrene Units Joined Through an Acetylenic or a Di-Acetylenic Linkage

Hiizu Iwamura [a] & Shigeru Murata [b]

[a] Department of Chemistry, The University of Tokyo, Hongo, Tokyo, 113, Japan

[b] Department of Industrial Chemistry, Mie University, Tsu, 514, Japan

Version of record first published: 22 Sep 2006.

To cite this article: Hiizu Iwamura & Shigeru Murata (1989): Magnetic Coupling of Two Triplet Phenylnitrene Units Joined Through an Acetylenic or a Di-Acetylenic Linkage, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 33-47

To link to this article: http://dx.doi.org/10.1080/00268948908037466

Mol. Cryst. Liq. Cryst., Vol. 176, pp. 33–48
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

MAGNETIC COUPLING OF TWO TRIPLET PHENYLNITRENE UNITS JOINED THROUGH AN ACETYLENIC OR A DIACETYLENIC LINKAGE

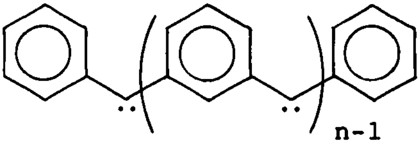
HIIZU IWAMURA
Department of Chemistry, The University of Tokyo, Hongo, Tokyo 113, Japan
SHIGERU MURATA
Department of Industrial Chemistry, Mie University, Tsu 514, Japan

Abstract Some polymer radicals have been proposed as potential organic magnetic materials. In order to determine where to place the doublet or triplet centers on the side chains of a conjugated polymer chain, we have studied model dimers, i.e., isomeric bis(nitrenophenyl)acetylenes and diacetylenes. They were generated by photolyses of the corresponding diazides in MTHF at 10 K in an ESR cavity. The m,p'-dinitrenes showed strong fine-structure signals characteristic of quintet states that obeyed Curie law in the range 12-85 K. The m,m'-dinitrenes showed fine-structure signals due to quintet states that had the maximum intensities at 50 and 28 K for the mono- and diacetylenes, respectively. It is concluded that the two triplet centers at the m,p'- and m,m'-positions interact, respectively, ferro- and antiferromagnetically. Efforts directed to the construction of ferromagnetic poly(acetylenes) are briefly discussed.

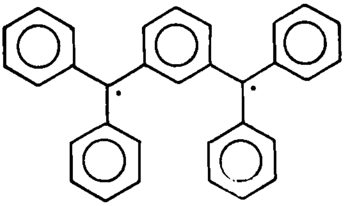
INTRODUCTION

Since the dicarbene 1(n = 2)[1] and the Schlenk hydrocarbon 2[2] were established to have a quintet and a triplet ground state in 1967 and 1970, respectively, they have served as the structural basis of further theoretical and experimental studies on organic high-spin molecules. Their structures are characterized by the 1,3-benzoquinodimethane moiety for which no stable Kekule structure can be drawn. As an extension of 1(n = 2), we have generated the tri-, tetra- and pentacarbenes 1(n = 3, 4, 5), and established by means of ESR spectroscopy and paramagnetic susceptibility measurements that these carbenes have a septet, nonet and undecet ground state, respectively.[3] In principle, further extension of this series might produce polycarbenes 1 with higher ground state spin multiplicities. The photolysis of the corresponding polydiazo compounds would be appropriate for generation of 1. Indeed some efforts in this direction are in progress in these laboratories. However, there are a number of disadvantages to these systems. First, the carbenic centers reside on the main chain of the cross-conjugated molecules in 1. Therefore only when all sites are intact, would the expected spin multiplicity be realized. If one diazo group remains unconverted to the carbene or one carbene site is lost by further chemical reactions, the coupling of the spins would be severed at this site, leading to the loss of the expected high spin multiplicity. Such possibility would increase as the chain length is elongated. Second, there are no straightforward polymerization or condensation reactions leading to this skeleton. Therefore synthesis becomes more and more difficult as the chain is lengthened. Third, carbenes are, after all, reactive intermediates. Since bulk ferromagnetic behavior of organic materials is of considerable interest, it is desirable to be able to use persistent radicals as open-shell centers. It may not be easy , however, to replace the carbene centers in 1 with stable radical centers.

In order to overcome these demerits, we turn our

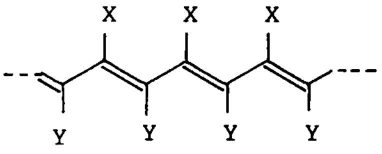


1

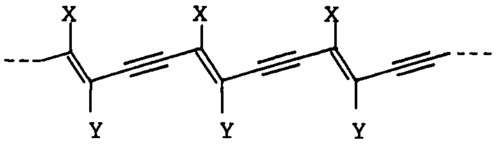


2

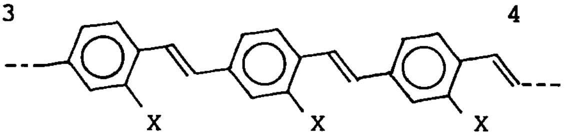
attention to another possibility of designing high-spin systems, in which the unpaired electrons reside on the side chains of a conjugated polymer main chain. Poly(acetylene) 3, poly(diacetylene) 4 and poly(phenylenevinylene) 5 are good candidates for the conjugated backbones. Even when one radical center fails to be generated or to survive, exchange coupling could possibly occur between the two intact radical centers on either side by bypassing the very site where the chemical accident took place.



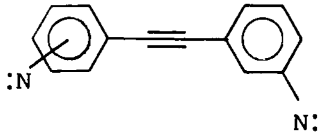
3



4

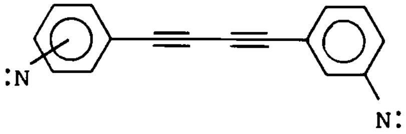


5



6 : p'

7 : m'



8 : p'

9 : m'

The spin multiplicities of these systems have been discussed theoretically. Ovchinnikov predicted that poly(p-oxyphenylacetylene) 3a would have a high-spin multiplicity in the ground state.[4] Recently Yamaguchi and his coworkers have pointed out the potential usefulness of 3 and 5 in the construction of high-spin organic molecules.[5] However, no experimental tests have appeared. Before getting involved in the synthesis of the polyradicals $3 \sim 5$, two problems should be solved experimentally; first, whether two remote triplet carbenes divided by such conjugated systems can interact sufficiently to form a high-spin state, and second, how the two open-shell centers should be placed regiochemically on the conjugated systems to realize ferromagnetic coupling.

In order to answer the above two questions, we have studied the magnetic interaction of two phenylnitrene units linked together through an acetylenic bond (6 and 7) and a diacetylenic linkage (8 and 9).

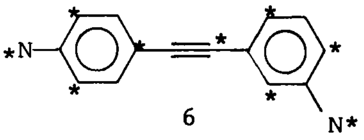
THEORETICAL PREDICTION

The spin multiplicity of conjugated alternant hydrocarbons have been discussed on the basis of molecular orbital (MO) theory and valence-bond (VB) theory. The non-bonding molecular orbitals (NBMO's) of more electronegative hetero atoms are lower in energy. Therefore the degeneracy of NBMO's of hydrocarbon polyradicals will be lifted by introduction of a heteroatom radical center. In this paper it is presumed that these theories can be applied to hetero-atom-perturbed conjugated alternant systems. This assumption is supported by the report that m-phenylenedinitrene 10 has a quintet ground state.[1] The validity of this assumption has been discussed by Berson and his coworkers theoretically and experimentally in oxygen perturbed systems.[7] Even unsymmetrical (m-nitrenophenyl)-methylene 11 has recently been shown to be a ground quintet species.[8] For the sake of simplicity, the dinitrenes 6 ~ 9 are assumed to have planar conformations, and let us take the π-conjugated systems spanning the whole molecules into account.

In 1950 Longuet-Higgins showed that an alternant hydrocarbon has N - 2T NBMO's, where N represents the number of carbon atoms in the conjugated system and T the maximum number of double bonds occurring in any resonance structure.[9] Both 6 and 7 have $N = 16$ and $T = 7$, and both

8 and 9 have N = 18 and T = 8. Accordingly, the number of NBMO's in their π-conjugated systems is two. He also noted that the neutral hydrocarbons have one electron in each NBMO with parallel spins by application of Hund's rule. Taking two additional non-bonding electrons in MO's localized on the nitrogen atoms into account, the Longuet-Higgins theory predicts quintet ground states for all dinitrenes 6 ~ 9.

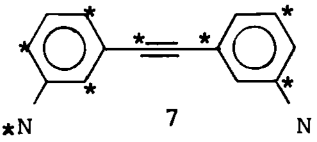
However, according to the advanced theory of Borden and Davidson,[10] meta, meta' isomers 7 and 9 are classified as disjoint, having their π-NBMO's confined to separate regions of the molecules with zero NBMO coefficients on the acetylenic carbon atoms. The non-bonding electrons do not appear simultaneously in the same atomic orbital, and therefore their Coulomb interactions do not necessarily stabilize a high-spin state. The meta, meta' isomers 7 and 9 are thus predicted to have singlet ground states. In meta, para' isomers 6 and 8, π-NBMO's cannot be localized to different sets of atoms. They are classified as nondisjoint, and are predicted to have quintet ground states.



6

$N - 2T = 2$

$(n^{*} - n)/2 = 1$



7

$N - 2T = 2$

$(n^{*} - n)/2 = 0$

The same prediction is obtained also by the VB theories of Ovchinnikov[4] and Klein.[11] According to them, the total spin of the ground state of an alternant hydrocarbon equals one half of the difference between the number of starred and unstarred carbon atoms. In meta, meta' isomers 7 and 9, the number of starred and unstarred atoms are equal, but in meta, para' isomers 6 and 8 they differ by two. Thus, including the spins localized on nitrogens, 6 and 8 are predicted to have quintet ground states by both the classical Longuet-Higgins' theory and the modern theories. On the other hand, in 7 and 9, where the number of the π-NBMO's are two as in 6 and 8, there are some discrepancies in the theoretical predictions. Thus the spin multiplicities in the ground states of these two regioisomeric dinitrenes warrant experimental determination as unit model compounds for the high-spin organic polymers.

Results

Syntheses of Precursors

All dinitrenes 6 ~ 9 were generated by photolysis of the corresponding diazide precursors 6a ~ 9a, respectively. Each diazide was synthesized by a Sandmeyer reaction of the corresponding diamine, which in turn was obtained by the reduction of the corresponding dinitro compound. The dinitro compounds with diphenylacetylene skeletons were prepared by Castro reactions of cuprous m-nitrophenylacetylide with m- and p-iodonitrobenzene. The 1,4-bis-(m,m'- and m,p'-nitrophenyl)buta-1,3-diynes were synthesized by the use of Eglinton and Cadiot-Chodkiewicz couplings, respectively.

All diazides 6a ~ 9a were obtained as fine needles and purified by repeated recrystallization from hexane.

ESR Spectroscopy

Photolysis of 6a ~ 9a produced signals in the region from 10 to 850 mT in the X-band ESR spectrum. The irradiations were carried out with a high-pressure mercury lamp through a Pyrex filter in 2-methyltetrahydrofuran (MTHF) glasses at 10 K. When the Pyrex filter was removed during the irradiation, the intensity of the signal at 332 mT due to radicals formed by side reactions increased relative to the other signals. All spectra were recorded in the dark after the photolysis.

(1) Meta, para' isomers. The spectra obtained by the irradiation of diazides 6a and 8a are reproduced in Figures 1. They resemble each other. From the relative intensities of the signals under various conditions and their thermal behavior, the peaks are classified into three groups: a signal at 332 mT, two signals with moderate intensities at 650 and 688 mT, and a set of a strong signal at 303 mT, weak and broad peaks at 90-150 mT and weak but clearly detectable signals at around 834 mT. As mentioned above, the first signal is for undefined doublet radical(s). A pair of signals at ca. 670 mT are assigned to the X,Y transitions of two triplet nitrenes.[12] They must have been produced by partial photolysis of the diazide or partial loss of the dinitrene sites via chemical reaction(s). The mononitrene at 650 mT, of which the zero-field splitting parameters are calculated to be D = 0.878 cm^{-1} and E = 0.000 cm^{-1}, is assigned to the nitrene with the acetylenic substituent at para position.

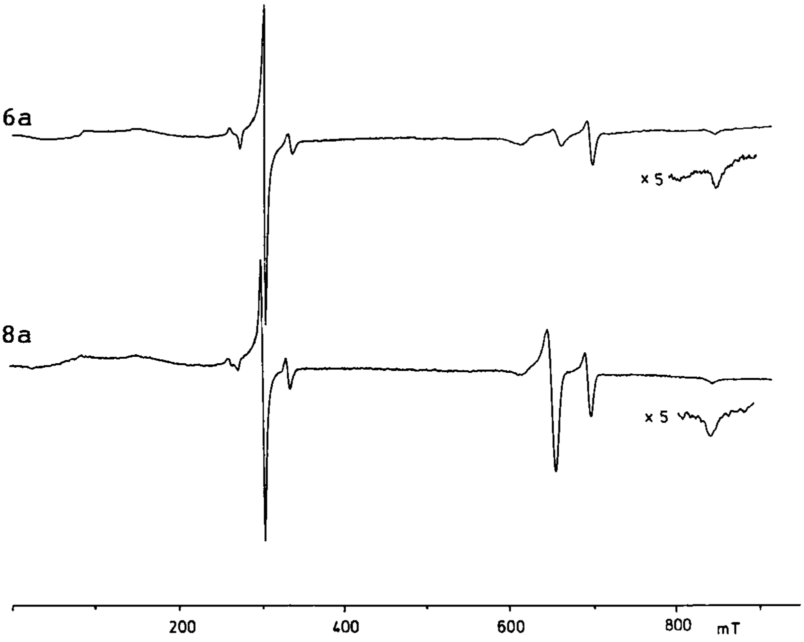


FIGURE 1. ESR spectra (ν_0 = 9.323 GHz) obtained by irradiation of m,p'-diazides 6a and 8a in MTHF at 10 K.

The other mononitrene with the X,Y transition at 688 mT, D = 1.025 cm^{-1} and E = 0.000 cm^{-1}, is assigned to the nitrene with the substituent group at meta position. Both the acetylenic and diacetylenic derivatives have the same D values within experimental error.

The remaining signals are very similar to those of 10 generated by photolysis of m-diazidobenzene and are assigned to the dinitrenes 6 and 8 in the quintet states. The zfs parameters of a quintet species consisting of two triplet units depend on the relative orientation of the two triplet units. Since the orientation of the two nitrene moieties is identical with an angle of 120 in these three quintet species, it is not surprising that the ESR spectra of the three are essentially identical, indicating that these species have similar zfs parameters. We tried to estimate the zfs values on the basis of the third-order perturbation theory by assuming that the highest-field transitions are the signal at 834 mT in 6 and 8 and 846 mT in 10 and that the next highest transition could not be observed because of overlapping with the intense X,Y transition of the triplet mononitrenes. Then the zfs parameters are roughly estimated to be D = 0.1575 cm^{-1} and E = 0.020 cm^{-1} for 6 and 8, and D = 0.1620 cm^{-1} and E = 0.025 cm^{-1} for 10.

In order to determine whether the observed quintet state is a ground state or a thermally excited one, the temperature dependence of the signal intensities was investigated. The intense signal at around 303 mT of 6 and 8 assigned to the quintet dinitrene was used for a study of its temperature dependence. As shown in Figure 2, the intensity of this signal followed Curie law in the temperature range of 12-80 K.

(2) Meta, meta' isomers. The spectra recorded after the irradiation of diazides 7a and 9a under conditions similar to the meta, para' isomers were quite different from those obtained from the latter regioisomers. At 10

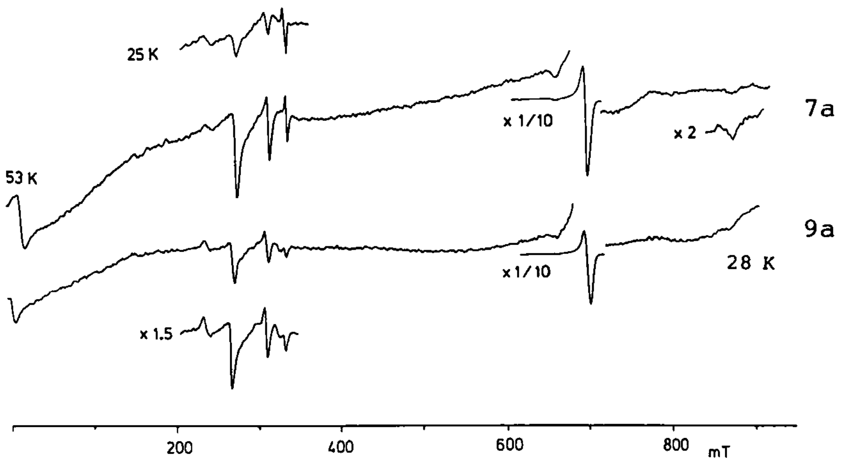


FIGURE 3. ESR spectra recorded at higher temperature after photolysis of m,m'-diazides 7a and 9a at 10 K.

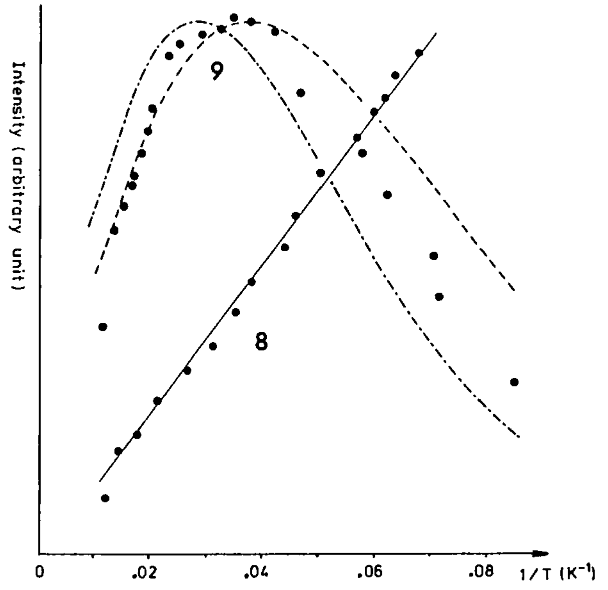


FIGURE 2. Plots of ESR signal intensities due to m,p'- and m,m'-dinitrenodiacetylenes 8 and 9 vs. 1/T.

K, the ESR spectra contained an intense signal at 692 mT, which was characteristic of the X,Y transitions of a triplet mononitrene (D = 1.031 cm^{-1} and E = 0.000 cm $^{-1}$) as mentioned before, with a weak signal due to a triplet species at 332 mT.

When the temperature was raised, the intensity of the signals assigned to the triplet mononitrene and the doublet radical simply decreased. Nonetheless, the spectra showed other interesting changes (Figure 3). At ca. 16 K, weak but significant peaks appeared at 15, 237, 272, 311 and 860 mT. The positions of the new peaks were practically identical for 7 and 9. The intensities of the signals at 272 and 311 mT were found to increase and reach a maximum and then decrease as we raised the temperature. It was noted that the temperature at which the intensities reached a maximum was quite different between the two compounds; the signals from the photolysis of the acetylenic diazide 7a showed maximum intensity at 50 K, while the signal from the diacetylenic diazide 9a at only 28 K. In Figure 2 are shown plots of the intensity vs. the reciprocal of temperature for the signals at 272 and 311 mT obtained from dinitrenodiacetylene 9.

DISCUSSION

Interaction of the Two Triplet Phenylnitrenes.

In both meta, meta' and meta, para' isomers, our results show that the interaction between the two triplet nitrene moieties is strong enough to form quintet states even when linked with a diacetylenic bridge. If the interaction of the two triplets were negligibly small, the dinitrenes would have shown ESR fine structures characteristic of two independent triplet mononitrenes. It is evident that the intramolecular interaction of the two nitrene moieties is "through bonds", since the rigid linear molecular structure does not permit approaches of the two nitrene moieties. On the basis of the results of temperature dependences, the spin multiplicity of the ground state could be determined and the energy gap between the ground and thermally excited states could be estimated semi-quantitatively.

The results that Curie law holds in the meta, para' dinitrenes 6 and 8 show that their ground states are quintet, although the possibility that the quintet state is degenerate with the singlet or lies at most 30 cal/mol above the latter state cannot be excluded logically. A similar situation holds also in 10. According to the theory on two weakly interacting triplet species,[13] the triplet and singlet states would be expected to lie above the quintet ground state by an energy of 4J and 6J, respectively, where J is the positive exchange integral of the two interacting triplet species. However, the strict applicability of this theory of weak coupling to these meta, para' dinitrenes is not necessarily guaranteed. For these reasons, we can predict neither the spin state populated thermally above the quintet ground state nor the energy gap between the two states.

As shown in Figure 2, plots of the signal intensities of the quintet states derived from the meta, meta' isomers 7 and 9 vs. the reciprocal of temperature display convex curves. It is apparent that these quintet states are populated thermally but lie close to the ground states. It is reasonable to assume that the theory on two triplet species interacting weakly with negative J values could be applied to the meta, meta' dinitrenes; the energy gaps of the triplet and quintet states from the singlet ground state are estimated to be 2J and 6J, respectively. Thus, within the approximations that the energy gaps between the states are much larger than those among the spin sub-levels within the triplet or quintet manifold, and that the Boltzman distribution among the spin sub-levels is neglected, Eq. (1) applies to the ESR signal intensities of the thermally populated quintet state, where C and R mean an arbitrary constant and the gas constant,

$$I = \frac{C}{T} \cdot \frac{5\ \exp(-6J/RT)}{5\ \exp(-6J/RT) + 3\ \exp(-2J/RT) + 1} \qquad (1)$$

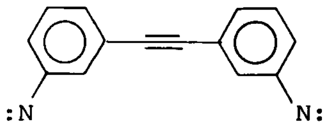
respectively. Using this equation, the theoretical intensity curves are given for $J = -15$ and -20 cal/mol in Figure 2. These curves are normalized so that the maxima fit the experimental data. In the dinitrene with the diphenylacetylene skeleton, the experimental data illustrated by the full circles in Figure 2 fall between the two curves. Therefore we roughly estimate the energy gap $6J$ between the singlet and the quintet states to be ca. 200 and 100 cal/mol for m,m'-dinetrenoacetylene and diacetylene, respectively. These results are the first example, to our knowledge, that showed the dependence of the magnitude of exchange coupling on the distance between two organic triplet moieties. The magnitude of the interaction of the two phenylnitrenes through the acetylenic bond is nearly identical to that of the two groups through the ethylenic double bond.[14]

Conformations of the Dinitrenes

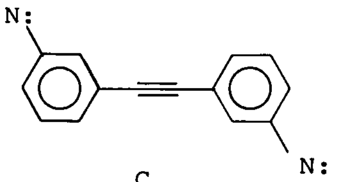
In the previous theoretical section, we assumed planar conformations in the dinitrenes with acetylenic and diacetylenic linkages. Crystalline diphenylacetylene is reported to be planar indeed.[15] The photoelectron spectra of the two molecules suggest that these molecules are present as conformational mixtures in the gas phase. Moreover, also in the gas phase, the ground state molecular geometry of diphenylacetylene is reported to be planar with a low barrier to rotation of ca. 575 cal/mol. In the meta, meta' dinitrenes, even if their structures are predominantly planar in solid solutions, conformational isomers are still present, one of which is of C_{2v} symmetry and the other has C_{2h} symmetry. As mentioned before, the zfs parameters of the quintet state formed from the two weakly interacting triplet species are strongly dependent upon the orientation of the two triplets. In the case of our nitrenes, the orientation can be described by the dihedral angle θ made by the two carbon-nitrogen bonds, because of the cylindrical symmetry of the electrons on the nitrene center. Therefore the zfs parameters can be estimated for the given structures of the dinitrenes by the sum of the dipolar coupling tensor $\mathbb{D}_T$ of each triplet species (Eq. (2)).

$$\mathbb{D}_Q = (\mathbb{D}_T{}^1 + \mathbb{D}_T{}^2)/6 \qquad (2)$$

$\mathbb{D}_Q$ stands for the dipolar coupling tensor of the quintet. The zfs parameters D and E are calculated from its Z and X,Y diagonal elements, respectively. Using the zfs parameters of the mononitrene triplet observed in the spectra for the calculation of $\mathbb{D}_T{}^i$, we could estimate the parameters of the quintet with the structure C_{2v} ($\theta = 60°$) and C_{2h} ($\theta = 180°$) to be D = 0.215 cm^{-1}, E = 0.043 cm^{-1} and D = 0.344 cm^{-1}, E = 0.000 cm^{-1}, respectively. The observed parameters (D = 0.169 cm^{-1}, E = 0.040 cm^{-1}) are moderately close to those of the C_{2v} structure. However, the presence of the C_{2h} form is not excluded. From the estimated zfs parameters of the C_{2h} structure, the highest-field transition of the quintet would be calculated to appear at above 1200 mT, and the thermally populated triplet signal would be expected to overlap with that of the mononitrene triplet signal completely. Thus it is quite possible that the signals derived from the C_{2h} structure might have eluded our ESR detection. In the meta, para' isomers 6 and 8, the method for the estimation of the zfs parameters could not be adopted, because the theory on two weakly interacting triplets is not likely to be applicable in these more strongly coupled isomers.



C_{2v}



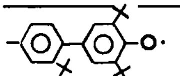
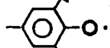
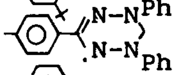
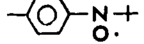
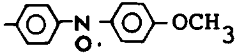
C_{2h}

HIGH-SPIN POLYRADICALS

Having completed the model experiments to show where to place the radical centers on the side chains of a conjugated polymer chain, we set out to synthesize high-spin polymers. Phenylacetylenes are known to polymerize in the presence of WCl_6/Ph_4Sn in hydrocarbon solvents or $[Rh(COD)Cl]_2$ in alcoholic solvents to give colored amorphous solids that are very often soluble in organic solvents. By taking advantage of the last property,[16] the polymers in Table 1 have been prepared. While the spin concentrations are not satisfactorily high, some of the products are attracted to a magnet at ambient temperature due probably to local macroscopic alignment of the spins.

A limited number of 1-phenyl-1,3-butadiyne derivatives undergo topochemically controlled polymerization in crystals. The polymers have metallic luster and usually insoluble in solvents. Efforts are in progress to polymerize the diacetylene derivatives carrying a stable radical on the phenyl ring.

Table 1. Poly(phenylacetylenes) 3(X = H, Y = ϕ) carrying radical centers in the side chains[6]

ϕ	$\overline{M}_W/10^4$	spin concentration/10^{19}g
	4	4.4
		8[17]
	7	23
	3	130
	14	190

CONCLUSION

It should be emphasized that the interaction of two remote triplet phenylnitrenes connected through an acetylenic or a diacetylenic bond is sufficient for forming quintet states. These high spin states are apt to be ground states in the meta, para' isomers, while the meta, meta' isomers have singlet ground states. These experimental results are thoroughly consistent with the predictions of the valence-bond theories of Ovchinnikov and Klein and also the MO theory of Borden and Davidson. Thus we obtained experimental results to resolve the regiochemical problems of where to place open-shell centers on the side-chains of high-spin organic polymers.

Attempts at constructing real high-spin poly(acetylenes) and poly(diacetylenes) are in progress.

REFERENCES

1. K. Itoh, Chem. Phys. Lett., 1, 235 (1967); E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, G. Smolinsky, J. Am. Chem. Soc., 89, 5076 (1967).
2. G. Kothe, K. H. Denkel, and W. Summermann, Angew. Chem., Int. Ed. Engl., 9, 906 (1970).
3. Y. Teki, T. Takui, H. Yagi, K. Itoh, and H. Iwamura, J. Chem. Phys., 83, 539 (1985); Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, J. Am. Chem. Soc., 108, 2147 (1986); I. Fujita, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, F. Miko, Y. Sawaki, A. Izuoka, and H. Iwamura, Symposium on ESR Spectroscopy, Abstract of Papers, p. 101, Sendai, October 27-29, 1988.
4. A. A. Ovchinnikov, Theor. Chim. Acta, 47, 297, (1978).
5. K. Yamaguchi, Y. Toyoda, and T. Fueno, Synth. Metals, 19, 81 (1987).
6. To be published elsewhere.
7. J. A. Berson, Pure Appl. Chem., 59, 1 (1987).
8. H. Tukada, K. Mutai, and H. Iwamura, J. Chem. Soc., Chem. Commun., 1159 (1987).
9. H. C. Longuet-Higgins, J. Chem. Phys., 18, 265 (1950).
10. W. T. Borden and E. R. Davidson, J. Am. Chem. Soc., 99, 4587 (1977).
11. D. J. Klein, C. J. Nelin, S. Alexander, .F. A. Matsen, J. Chem. Phys., 77, 3101 (1982).
12. E. Wasserman, Prog. Phys. Org. Chem., 8, 319 (1971).
13. K. Itoh, Pure Appl. Chem., 50, 1251 (1978).
14. S. Murata, T. Sugawara, and H. Iwamura, J. Am. Chem. Soc., 109, 1266 (1987).
15. F. H. Wiebenga, Z. Krist., 102, 193 (1940).
16. H. Iwamura and R. D. McKelvey, Macromolecules, 21, 3386 (1988)
17. H. Nishide, N. Yoshioka, K. Inagaki, E. Tsuchida, Macromolecules, 21, 3119 (1988).