to ours. Their rate constant for 1-hexyl radical trapping by MNP in methanol is 1.16×10^7. This rate constant agrees well with those of the present study, as Maeda et al. showed that spin trapping with nitroso and nitrone spin traps becomes faster as solvent polarity increases. Ingold and co-workers[21,23] also measured trapping of 1-hexyl and 2-hexyl radicals by MNP in benzene, finding a rate constant of 8.8×10^6 for the primary alkyl radical vs 6.1×10^6 M^{-1} s^{-1} for the secondary species. The ratio of these rates, 0.69, closely matches the 0.67 ratio we observed between 1-propyl and 2-propyl radical trapping by MNP in aqueous solution.

The present results show that rate constants for spin trapping can vary by over 2 orders of magnitude in a series of small carbon-centered radicals. Electronic factors primarily control trapping rates, as reducing hydroxyalkyl radicals and substituted alkyl radicals capable of electron release show the fastest rates. Steric effects can greatly retard trapping reactions with parent radicals of marginal electron-releasing capability. Our results show that reaction of hydroxyalkyl radicals with MNP in neutral aqueous media leads only to formation of the hydroxyalkyl–MNP spin adduct. In basic media, however, we have seen formation of net hydrogen atom–MNP adduct, as well as hydroxyalkyl–MNP spin adduct during reaction of 2-hydroxy-2-propyl radical with MNP; the trapping rate constant of hydroxyalkyl radicals was pH dependent.[60] In biological systems, where spin trapping has found its greatest utility, radicals may be located in regions of greatly varying polarity and effective pH, which potentially could cause site-specific trapping rate variation for a given radical. Experiments in progress are extending trapping rate studies to acidic and basic aqueous solutions to determine the cause of the pH-dependent trapping rate variations. We believe that the time-resolved ESR pulse radiolysis method is uniquely suited to measure the selectivity and efficiency of spin trapping reactions.

Acknowledgment. We gratefully acknowledge helpful discussions with Professor R. W. Fessenden, Professor Paul Percival, and Dr. John Bentley. We thank anonymous reviewer II for pointing out to us the electron-withdrawing nature of the carboxylate anion.

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Magnetic Interaction between the Triplet Centers in Ethynylenebis(phenylnitrenes) and 1,3-Butadiyne-1,4-diylbis(phenylnitrenes)

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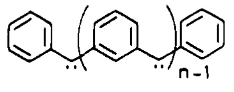
Abstract: The magnetic interaction of the two triplet phenylnitrene units linked together through an acetylene or a diacetylene linkage has been investigated by ESR spectroscopy. Two regioisomeric (meta,para' and meta, meta') diazides of 1,2-diphenylacetylene **12a** and 1,4-diphenyl-1,3-butadiyne **13a** were prepared and photolyzed in a 2-methyltetrahydrofuran glass at 10 K to give the corresponding dinitrenes **12n** and **13n**. The *m,p'*-dinitrenes of **12n** and **13n** showed intense quintet signals which obeyed a Curie law in the temperature range 12–85 K. The *m,m'*-dinitrenes of **12n** and **13n** showed signals due to the thermally populated quintet states, the intensities of which reached a maximum at 50 and 28 K for **12n** and **13n**, respectively. It is concluded that the two remote phenylnitrene units in **12n** and **13n** interact sufficiently strongly through bonds to form quintet states that are concluded to be the ground state in the meta,para' isomers as predicted by theory. In the meta,meta' isomers, the quintet states are thermally populated from ground singlet states, the energy gaps between the two states (ca. 200 and 100 cal/mol for $—C{\equiv}C—$ and $—C{\equiv}C—C{\equiv}C—$, respectively) being dependent reasonably upon the distance between the two moieties. The results serve as good guiding principles for designing high-spin conjugated polymers with pendant radical centers.



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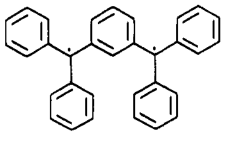

2

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.[3] Their structures have in common the π-moiety of 1,3-benzoquinodimethane, for which no stable Kekulé structure can be drawn. In contrast, the *p*-dicarbene **3**[4] and the Chichibabin and Thiele hydrocarbons (**4** and **5**)[5] are in lower spin

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[†] Mie University.

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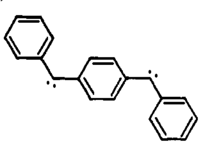
ground states. As an extension of **1** ($n = 2$), we have generated the tricarbene **1** ($n = 3$),[6] the tetracarbene **1** ($n = 4$),[7,8] and the pentacarbene **1** ($n = 5$)[9] and established by means of ESR spectroscopy and paramagnetic susceptibility measurements that these carbenes have a septet, a nonet, and an undecet ground state, respectively. 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.[3i,10] More recently the non-Kekulé polyradicals of the type **2** have been stabilized by perchlorination[11] or extended to the higher analogues.[12]



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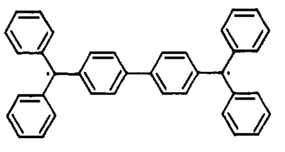

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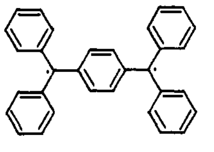
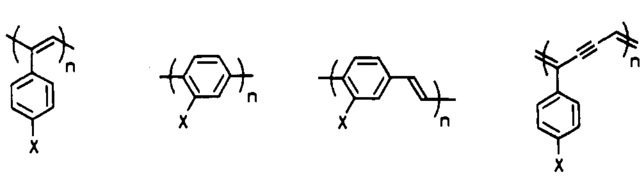


5

However, there are some disadvantages to these systems. First, the polycarbene **1** has the origin of spins in the main framework of the molecule. Therefore only when all carbene 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 chemical reactions with the surroundings or through dimerization, the coupling of the spins would be severed at this site, leading to the loss of the expected high-spin multiplicity. Such a possibility would increase as the chain length is elongated. Second, there are no straightforward polymerization or condensation reactions leading to the skeleton of the higher series of **1**. Therefore synthesis becomes more and more difficult as the chain is lengthened. The corresponding polyradicals would encounter similar situations as long as the radical centers reside on the cross-conjugated main chain. In order to overcome these demerits, we turn our attention to another possibility of designing high-spin systems in which the origin of the spins resides on the side chain of a conjugated polymer chain. Poly(phenylacetylenes) **6**, polyphenylenes **7**, poly(phenylenevinylenes) **8**, and poly(phenyldiacetylenes) **9** are good candidates for the conjugated backbones.

The spin multiplicities of these systems have been discussed theoretically. Ovchinnikov predicted that poly(*p*-ethynylphenoxyl) **6p** would have a high-spin multiplicity in the ground state.[13] Recently Yamaguchi and his co-workers have pointed out the potential usefulness of polyacetylene **6** and poly(phenylenevinylene) **8** systems in the construction of high-spin organic molecules.[14]



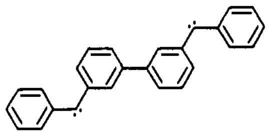
6 **7** **8** **9**

(X = substituents carring open-shell centers)

c, X = -$\ddot{C}$Ph ; **p**, X = -O·

However, few experimental tests have appeared. Before getting involved in the synthesis of these polycarbenes **6c**–**9c**, two questions should be answered experimentally. The first question would be if two remote triplet carbenes separated by the conjugated systems can interact strongly enough to form the expected high-spin state. If the interaction is not strong, lower spin states would also be degenerate with the high-spin state. The second question is concerned with how the two open-shell centers should be placed regiochemically on the conjugated system to realize a high ground-state multiplicity. It is evident from the comparison of the ground spin states between **1** ($n = 2$) and **2** on the one hand and **3**, **4**, and **5** on the other that topology of the π-framework is important in determining the ground spin states.

Recently we reported that the interaction of two diphenylcarbene moieties linked with an ethylenic double bond leads to a quintet ground state only when the carbene centers are placed at the meta,para′ positions as in **10**.[15] Itoh et al. studied in detail the spin multiplicities of a pair of isomeric biphenyldicarbenes and concluded that the meta,meta′ isomer **11** is in a singlet ground state.[16] These two works may be considered as two prototypes for two carbene centers on **6** and **7**.



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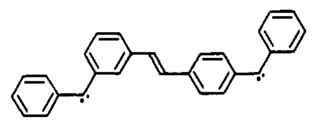
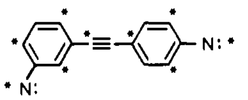
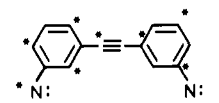


10

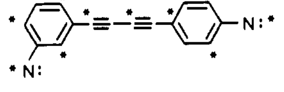
In this paper we have studied the magnetic interaction of two phenylnitrene units linked together through an acetylene bond (**12n**) and a diacetylene linkage (**13n**) to supply answers to the above two questions.[17] The diacetylenic compounds **13n** are thought to be an important prototype for polydiacetylene skeleton **9a**.



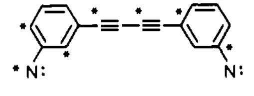
m,p′-**12n**



m,m′-**12n**



m,p′-**13n**



m,m′-**13n**

There are few precedents for high-spin polynitrenes: quintet dinitrene **14**[1b] and septet trinitrene **15**[18] are the only examples. In this study we have chosen triplet phenylnitrene as the origin

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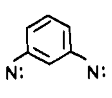
of spins in place of phenylcarbenes for the following reasons. First, aromatic nitrenes are chemically more stable than phenylcarbenes in frozen matrices, although possible ring expansion to azacycloheptatetraene may not be neglected.[19] Once generated, experiments can be performed over a wider temperature range. Secondly, the nitrene unit has a local axial symmetry and therefore it has a single conformation as compared with phenylcarbenes in which there are rotational degrees of freedom around the C–C(carbene) bonds. Third, azides, precursors of nitrenes, are chemically and thermally more stable than diazo compounds, making the precursor more easily purified and handled. Lastly, since the diphenyldiacetylene skeleton is known to react with hydrazine monohydrate, a reagent used during the preparation of diazo compounds, to give a diazole derivative,[20] the diazo precursor to carbenes is not readily compatible with the diacetylene skeleton.

Theoretical Background

Since high-spin **1** ($n = 2$) and **2** on the one hand and low-spin molecules **3**, **4**, and **5** on the other have similar π-frameworks, respectively, it is clear that topology of the molecular structure and, in other words, connectivity or periodicity of the π-framework is crucial in determining the ground spin state.

The spin multiplicity of alternant hydrocarbons (AH) has been discussed on the basis of molecular orbital theory[21] and valence bond theory.[13,22] Since the Coulomb integral of more electronegative heteroatoms is larger in absolute value, the degeneracy of nonbonding molecular orbitals (NBMOs) of hydrocarbon polyradicals will be lifted to some extent by the introduction of a heteroatom radical center. In this paper it is presumed that the perturbation due to the introduction of heteroatoms is small and that the above theories appropriate for AH can be applied to heteroatom-perturbed conjugated alternant systems. This assumption is supported by the report that *m*-phenylenedinitrene (**14**) has a quintet ground state.[1b] Even unsymmetrical (*m*-nitrenophenyl)methylene is a ground-state quintet species.[23]



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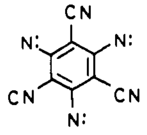


15

Furthermore the validity of this assumption has been discussed by Berson and his co-workers theoretically and experimentally in the oxygen-perturbed systems:[24] the topology appears to be more important than the Coulomb integral of the constituent atoms in determining the ground-state spin multiplicity. For the sake of simplicity, the dinitrenes **12n** and **13n** 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 AH has ($N - 2T$) Hückel NBMOs, where N represents the number of carbon atoms in the conjugated system and T is the maximum number of double bonds occurring in any resonance structure.[21a] The π-skeletons corresponding to *m,m′*- and *m,p′*-**12n** have $N = 16$ and $T = 7$, and both isomers of **13n** have $N = 18$ and $T = 8$. Accordingly the number of π-NBMOs is always two. The second part of the theory employs Hund's rule, placing one electron in each NBMO with parallel spins. There are two additional unpaired electrons, one on each σ-nonbonding orbital of the nitrogen atom. They are expected to interact strongly with the π-spins through one-center exchange coupling, aligning their spins in parallel. Taking these into account, the Longuet-Higgins' theory predicts quintet ground states for all dinitrenes **12n** and **13n**.

However, according to the advanced theory of Borden and Davidson,[21b] meta,meta′ isomers of **12n** and **13n** are classified as disjoint, having their Huckel NBMOs confined to separate regions of the molecules with zero NBMO coefficients on the acetylenic carbon atoms. The nonbonding electrons do not appear simultaneously in the same atomic orbital, and therefore their Coulomb interactions do not necessarily stabilize a high-spin state. The singlet and triplet states should be nearly degenerate; higher order effects lead to meta,meta′ isomers of **12n** and **13n** in singlet ground states. In meta,para′ isomers of **12n** and **13n**, NBMOs cannot be localized to different sets of atoms. They are classified as nondisjoint and are predicted to have high-spin ground states.

A similar prediction is also obtained by the valence bond theory of Ovchinnikov.[13] According to the latter theory, the total spin (S) of the ground state of an AH equals one-half of the difference between the numbers of starred (n^*) and unstarred (n) carbon atoms (eq 1).

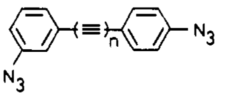
$$S = (n^* - n)/2 \qquad (1)$$

In meta,meta′ isomers, n^* and n are both 8 in **12n** and 9 in **13n**. The numbers n^* and n are 9 and 7 in *m,p′*-**12n** and 10 and 8 in *m,p′*-**13n**; they differ by two and therefore $S = 1$. Thus including the unpaired electrons localized on nitrogens, the meta,para′ isomers are predicted to have quintet ground states by both the classical Longuet-Higgins' theory and the modern theories. On the other hand, in the meta,meta′ isomers, where the number of the NBMOs are two, there are some discrepancies in the theoretical predictions. Thus the spin multiplicities in the ground states of these two regioisomeric dinitrenes, meta,para′ and meta,meta′ isomers, warrant experimental determination as unit model compounds for the high-spin organic polymers.

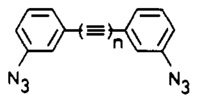
We have excluded another regioisomer, para,para′ isomers of **12n** and **13n**, from our discussion, since the π-framework can have quinoidal Kekulé structure as in **3**,[4] **4**, and **5**[5] and every theory predicts these isomers to have singlet ground states, unless two halves each containing one pen-shell center are held in a perpendicular conformation.

Results

(A) Syntheses of Precursors. All four dinitrenes *m,p′*-**12n**–*m,m′*-**13n** were generated by photolysis of the corresponding diazide precursors *m,p′*-**12a**–*m,m′*-**13a**, respectively. Each diazide was synthesized by the diazotization followed by reaction with



m,p′-**12a** ($n = 1$)
m,p′-**13a** ($n = 2$)



m,m′-**12a** ($n = 1$)
m,m′-**13a** ($n = 2$)

sodium azide of the corresponding diamine, which in turn was obtained by the iron–acetic acid reduction of the corresponding dinitro compound. The dinitro compounds with diphenylacetylene skeleton were prepared by Castro reactions of cuprous *m*-nitrophenylacetylide with *m*- or *p*-iodonitrobenzene. The *m,m′*- and *m,p′*-dinitrodiphenyldiacetylenes were synthesized by the use of the Eglinton coupling and the Cadiot–Chodkiewicz coupling, respectively. The synthetic route used to prepare the dinitro precursors is summarized in Scheme I. All diazides *m,p′*-**12a**–*m,m′*-**13a** were obtained as fine needles and purified by repeated crystallization from *n*-hexane.

(B) ESR Spectroscopy. Photolysis of the diazides *m,p′*-**12a**–*m,m′*-**13a** produced signals in the region from 10 to 850 mT in the X-band ESR spectra. 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

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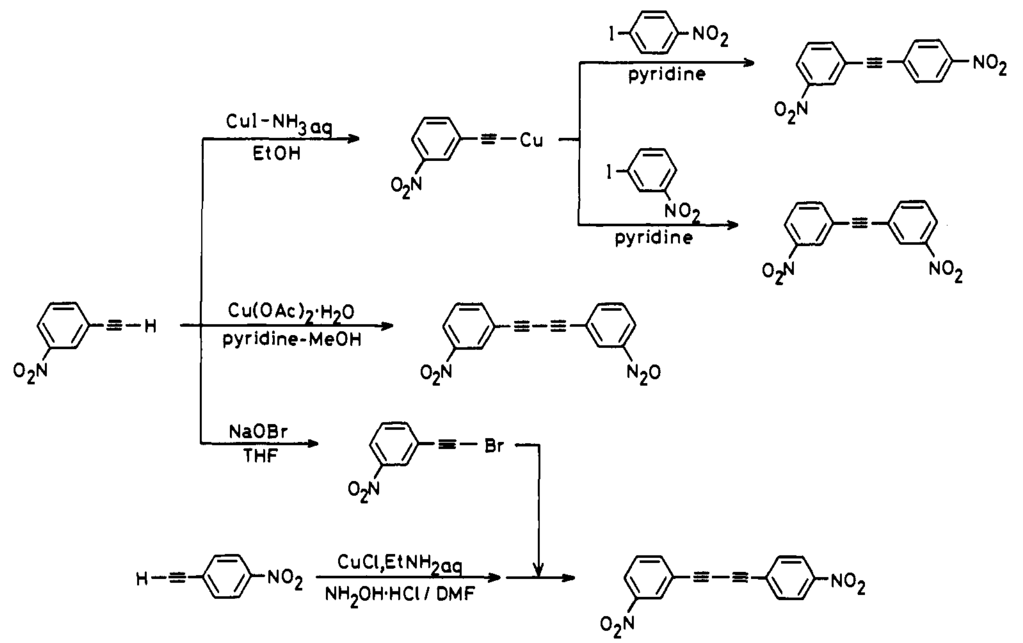
Scheme I



filter was removed during the irradiation, the intensity of the signal at 332 mT due to free radicals formed fortuitously increased relative to the other signals. All spectra were recorded in the dark after the photolysis.

The spectra obtained by the irradiation of the *m,p'*-diazides of **12a** and **13a** resemble each other, as do the spectra obtained from the meta,meta' isomers. Assignment of the signals derived from the dinitrenes *m,p'*-**12n**–*m,m'*-**13n** has been made as described below. The spin multiplicities of their ground states have been investigated by the temperature dependencies of the signal intensities.

***m,p'*-Dinitrenes.** The spectra obtained by the photolysis of *m,p'*-diazides with diphenylacetylene skeleton **12a** and with diphenyldiacetylene skeleton **13a** are shown in Figures 1 and 2, respectively. As mentioned above, a signal at 332 mT in each spectrum is assigned to doublet free radicals which are thought to be formed by undefined photoreactions in matrices. Apart from this signal, the spectra are characterized by an extremely intense signal at 303 mT, weak and broad peaks at 90–150 mT, two signals with moderate intensities at 650 and 688 mT, and weak but significant signals at around 834 mT. During the irradiation of the diazides, the rates of increase of the signal intensities were significantly different between the signals at 650 and 688 mT and the others. At 85 K the intense signal at 303 mT and the weak signals decreased irreversibly, but the signals at 650 and 688 mT remained strong at this temperature. Therefore it is evident that the two signals at 650 and 688 mT were derived from a chemical species different from the others.

The signals at 650 and 688 mT are assigned to the X, Y transitions of triplet mononitrenes. Since an ESR spectral observation of parent triplet phenylnitrene was made by Smolinsky and Wasserman in 1962,[25] an intense signal at ca. 680 mT in the X-band is safely attributed to triplet phenylnitrenes. It is not unreasonable to assume that, upon irradiation of the diazides **12a** and **13a**, the triplet mononitrenes were formed by the extrusion of one nitrogen molecule from the two azide groups, generating monoazidomononitrene species, or by the loss of one nitrene site of the dinitrene via rearrangement to azacycloheptatetraene[19] or chemical reaction with the surroundings. In **12n** and **13n** the two nitrene groups are not equivalent; one is attached to the meta and the other to the para position with respect to the acetylenic bond. It is well-known that the substitution at the para position of phenylnitrene results in the delocalization of the spin density to decrease the zero-field splitting (zfs) parameter D.[26] Thus, two triplet mononitrenes were observed by the irradiation of diazides **12a** and **13a**. The mononitrene with the signal at 650 mT was calculated[25] (see eq 7 in Experimental Section) to have the zfs parameters $D = 0.878$ cm^{-1} and $E = 0.000$ cm^{-1} and is assigned to the nitrene with the ethynyl substituent at para position **16**, where Y stands for the azide group or the group formed by the reaction of nitrene with the media. The other mononitrene with the signal 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

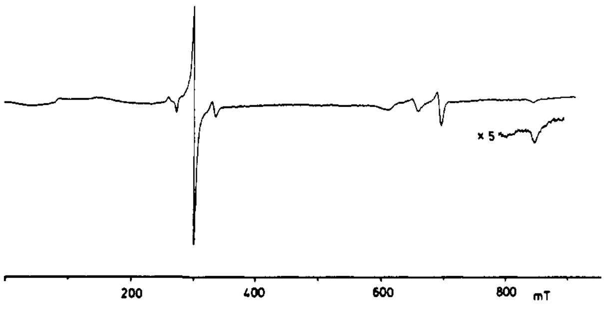


Figure 1. ESR spectrum obtained after irradiation of diazide *m,p'*-**12a** in MTHF at 10 K. The Klystron frequency was 9.30 GHz. See text for the signal assignment.

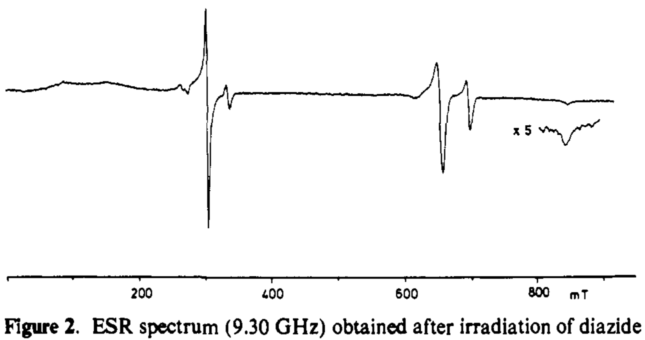


Figure 2. ESR spectrum (9.30 GHz) obtained after irradiation of diazide *m,p'*-**13a** in MTHF at 10 K.

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(24) (a) Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5144. (b) Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251. (c) Berson, J. A. *Pure Appl. Chem.* **1987**, *59*, 1.

(25) Smolinsky, G.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3220.

(26) Hall, J. H.; Fargher, J. M.; Gisler, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 2029.

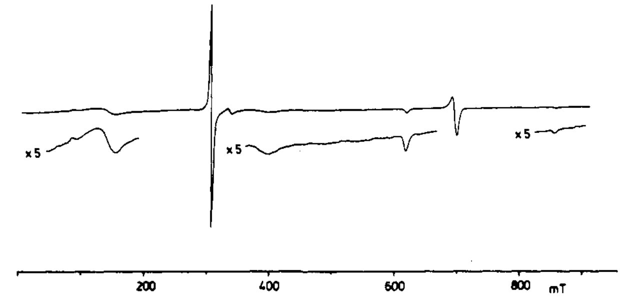
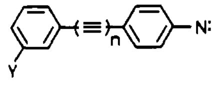


Figure 3. ESR spectrum (9.30 GHz) obtained after irradiation of diazide **14** in MTHF at 10 K.

17. Both the acetylene and the diacetylene derivatives **16** and **17** have the same D values within experimental error.



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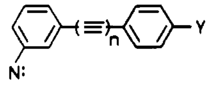

17

The remaining signals, an intense signal at around 303 mT and weak signals at 90–150 mT and around 834 mT, are assigned to the dinitrenes *m,p′*-**12n** and *m,p′*-**13n** in quintet states. The only known example of a dinitrene in the quintet state is *m*-phenylenedinitrene (**14**) which is reported to show signals in the range of 10–840 mT in the X-band ESR spectrometer.[1b] In order to compare the spectra of the dinitrenes obtained here with that of dinitrene **14**, we repeated its generation by the irradiation of *m*-diazidobenzene under conditions similar to those mentioned before. The spectrum (Figure 3) is very similar to those obtained by the photolysis of the acetylenic **12a** and diacetylenic diazides **13a**, except that the signal due to the X, Y transition of triplet mononitrene was only one at 688 mT (D = 1.023 cm^{-1} and E = 0.000 cm^{-1}). The similarity of the observed spectra strongly suggests that the intense signal at around 303 mT and some of the weak signals are derived from the dinitrenes *m,p′*-**12n** and *m,p′*-**13n** in their quintet states.

The zfs parameters of a quintet species consisting of two triplet carbenes or nitrenes that have large one-center interactions depend on the relative orientation of the two triplet units (vide infra, eqs 4 and 4′).[1b,4a,b] Therefore it is not surprising that the ESR spectra of the quintet species, **12n**, **13n**, and **14**, are essentially identical, indicating that these species have similar zfs parameters; in these three quintet species the orientation of the two nitrene moieties is identical in that the angle between the two C–N bonds is 120°.

$$\mathcal{H} = \beta\cdot\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S} = \beta\cdot\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2) \quad (2)$$

The zero-field tensor is defined and solved by the spin Hamiltonian consisting of the Zeeman and fine structure terms as given by eq 2. However, it is difficult to estimate the zfs parameters of the quintet dinitrenes unambiguously from the above spectra. Instead of diagonalizing a full matrix, we relied on third-order perturbation theory[27] and tried to estimate the zfs parameters on the assumption that the highest field transitions are the signals at 834 mT in *m,p′*-**12n** and -**13n** and 846 mT in **14** and that the next highest energy transition may not be observed because of overlapping with the intense signals at around 680 mT of the triplet mononitrenes (see eqs 5 and 6 in Experimental Section). Thus the zfs parameters were roughly estimated to be D = 0.1575 cm^{-1} and E = 0.020 cm^{-1} for *m,p′*-**12n** and -**13n** and D = 0.1620 cm^{-1} and E = 0.025 cm^{-1} for **14**. Since the third-order perturbation treatment assumes a high-field approximation, lower field signals cannot be taken into account. The acetylenic *m,p′*-**12n** and the diacetylenic dinitrenes **13n** have the same parameters within experimental error.

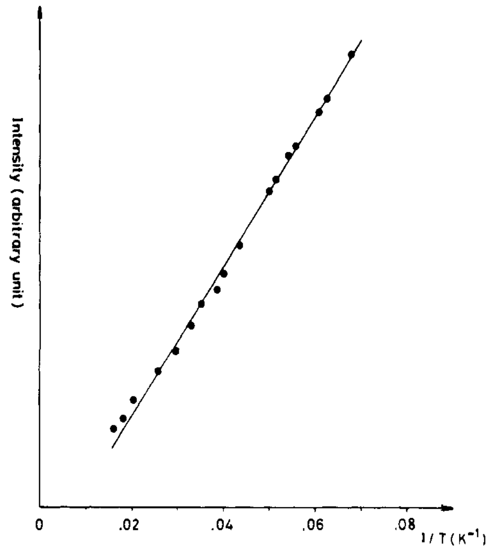

Figure 4. Plots of the intensities of the ESR signal at 303 mT due to quintet *m,p′*-**12n** vs the reciprocal of temperature after annealing at 65 K for ca. 30 min.

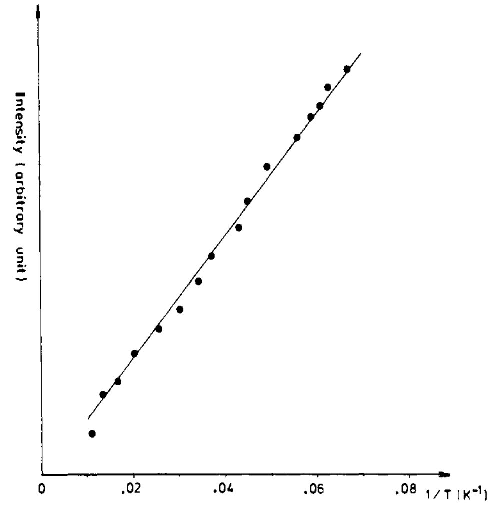

Figure 5. Plots of the intensities of the ESR signal at 303 mT due to quintet *m,p′*-**13n** vs the reciprocal of temperature after annealing at 65 K for ca. 30 min.

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 near 303 mT of *m,p′*-**12n** or -**13n** assigned to the quintet dinitrene was used for the study of its temperature dependence. The intensity of this signal decreased as the temperature was raised. The signal intensity was completely reproducible in the temperature range 12–65 K. However when the temperature was raised about 65 K and lowered again to the previous temperature, a slight enhancement of the intensity was observed. There was little change in the whole spectrum above 65 K, except that the intensity of the signal at 303 mT increased slightly and the intensity of the weak signal around 250 mT decreased. This irreversible enhancement of the signal at 303 mT was observed in both **12n** and **13n**. Therefore the study of the temperature dependence of the quintet species was eventually carried out as follows: after photolysis of the diazide at 10 K the temperature was raised, and the sample was allowed to stand at ca. 65 K for about half an hour for annealing the matrices in the dark. The intensity was recorded after the temperature had been lowered to 10 K and raised again. Reproducible signal intensities were then obtained in the temperature range 12–80 K. The signal intensities decreased irreversibly above 85 K, presumably due to chemical reactions of the dinitrenes with their surroundings. In Figures 4 and 5 are shown plots of the signal intensity vs the reciprocal of temperature

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(27) Itoh, K. *Abstract of Papers*, 6th ESR Symposium of the Chemical Society of Japan, Kyoto, October 1967; p 117. See, also: ref 6.

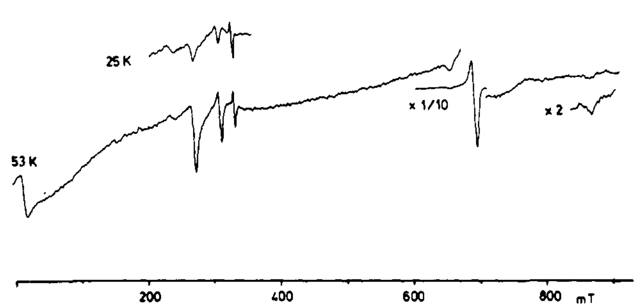


Figure 6. ESR spectrum (9.30 GHz) recorded at 53 K after photolysis of diazide *m,m'*-**12a** in MTHF at 10 K. A part of the spectrum was recorded also at 25 K.

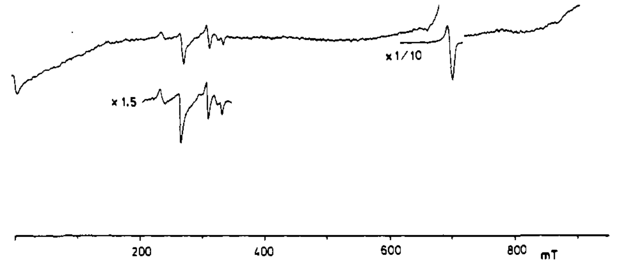
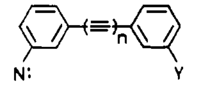


Figure 7. ESR spectrum (9.30 GHz) recorded at 28 K after photolysis of diazide *m,m'*-**13a** in MTHF at 10 K.

for dinitrenes **12n** and **13n**, respectively. The ESR intensity of these quintet species varies linearly with T^{-1} in accord with a Curie law.

***m,m'*-Dinitrenes.** The spectra recorded by the irradiation of the *m,m'*-diazides of **12a** and **13a** under conditions similar to the meta,para' isomers were quite different from those obtained from the latter regioisomers. It should be noted that the spectra were recorded at a concentration of ca. 4×10^{-3} M in MTHF. At 10 K, the ESR spectra contained an intense signal at 692 mT, which was characteristic of the X, Y transitions of a triplet mononitrene as mentioned before, with a weak signal due to a doublet species at 332 mT. In these *m,m'*-**12a** and -**13a**, the two azide groups are identical so that a single signal of the triplet species was observed with the structure **18**. The zfs parameters are estimated to be $D = 1.031$ cm^{-1} and $E = 0.000$ cm^{-1}, the values being almost equal to those of the mononitrene **17**.



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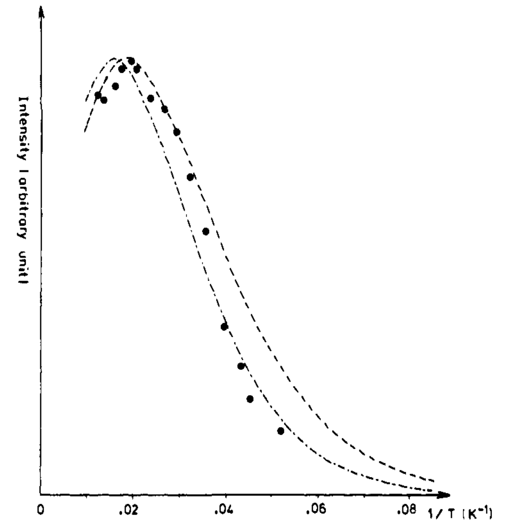

Figure 8. Plots of the intensities of the ESR signal at 272 mT due to thermally populated quintet *m,m'*-**12n** vs the reciprocal of temperature after annealing at 65 K for ca. 30 min. The signal at 311 mT behaved similarly. Two theoretical curves for $J = -30$ (--) and -35 (-•-) cal/mol in eq 3 are shown.

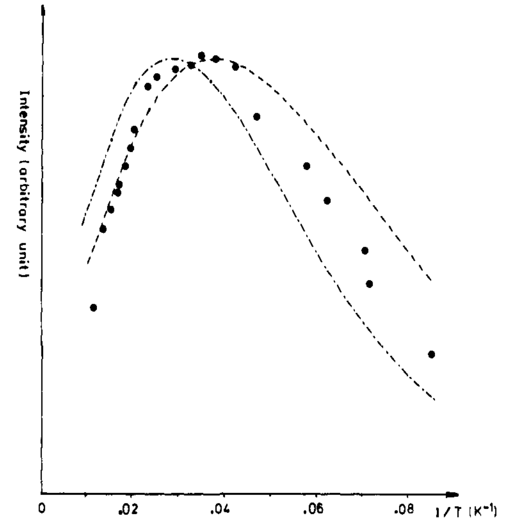

Figure 9. Plots of the intensities of the ESR signal at 272 mT due to thermally populated quintet *m,m'*-**13n** vs the reciprocal of temperature after annealing at 65 K for ca. 30 min. The signal at 311 mT behaved similarly. Two theoretical curves for $J = -15$ (--) and -20 (-•-) cal/mol in eq 3 are given for comparison.

When the temperature was raised, the intensity of the signals assigned to the triplet mononitrene and the doublet radical simply decreased. However, the spectra showed other interesting changes. 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 the acetylenic **12a** and diacetylenic **13a** compounds. The intensities of the signals at 272 and 311 mT were found to increase and reach a maximum and then decrease as the temperature was raised. It should be mentioned, however, that the temperature at which the intensities reached a maximum was quite different between the two compounds; the signals at 272 and 311 mT obtained from the photolysis of the acetylenic diazide *m,m'*-**12a** showed maximum intensity at 50 K, while the signal from the diacetylenic diazide *m,m'*-**13a** was at 28 K. In Figure 6 is shown the spectrum recorded at 53 K after photolysis of *m,m'*-**12a** at 10 K, with a part of the figure recorded at 25 K. The spectrum shown in Figure 7 is that obtained at 28 K after irradiation of *m,m'*-**13a** at 10 K. The temperature dependencies of the signals at 272 and 311 mT were studied as described for the meta,para' isomers, since an irreversible enhancement of the signals in question occurred at around 65 K in the meta,meta' isomers as well. After annealing the solid solutions, reproducible signal intensities were recorded in the temperature range 12–80 K. These signals started to disappear irreversibly above 85 K. In Figures 8 and 9 are shown plots of the intensity vs the reciprocal of temperature for the signals at 272 or 311 mT obtained from *m,m'*-**12a** and -**13a**, respectively. The experimental data are illustrated by full circles.

When the temperature dependence of the signal intensities was studied in detail, it was revealed that the signals at 15, 272, 311, and 860 mT obeyed the temperature dependence indicated in Figures 8 and 9, but the intensity of the signal at 237 mT varied differently with temperature. Although the signal at 237 mT was too weak to accurately study its temperature dependence, it was evident that at temperatures below 10 K there was no meaningful signal observed at this field; the signal appeared and reached maximum intensity in the temperature range 10–20 K and decreased as the temperature was raised above 20 K. Unfortunately we could not see if there was a difference between the acetylenic and diacetylenic derivatives in the temperature dependencies of the signal at 237 mT because of its weakness. It should be noted that the signal at 237 mT and the other signals with the temperature dependence shown in Figure 8 and 9 appeared to derive from the same species, since both kinds of signals disappeared at the same time above 85 K, whereas the signals due to doublet radicals and the triplet mononitrenes remained intact. ESR signals saturate easily at cryogenic temperatures. This could have distorted the intensity vs temperature plots. Therefore the microwave power was minimized to avoid the saturation, and the linearity of the intensity vs power relation was confirmed under the experimental conditions.

The most reasonable explanation for these experimental results is that the signals at 15, 272, 311, and 860 mT are derived from the dinitrenes *m,m′*-**12n** and -**13n** in quintet states and the signal at 237 mT is from the same species in a triplet state. The reasons for the assignment to the quintet states are as follows: first, the signals appeared at the characteristic region around 300 and 850 mT, where the quintet dinitrenes, *m,p′*-**12n**, **13n**, and **14** showed signals. Secondly, the thermal instability of the species at >85 K was very similar to that of *m,p*-**12n** and -**13n**. On the basis of the temperature dependence data, it is quite evident that the quintet states of the dinitrenes *m,m′*-**12n** and -**13n** are populated thermally. So it is not surprising to detect thermally populated triplet states of the dinitrenes, because the triplet state is expected to lie between the quintet and the ground singlet states according to the theory of two weakly interacting triplet species.[1b,4]

This theory also states that the zfs parameters of the quintet state are equal to one-third of those of the thermally populated triplet state. If the highest field transition of the quintet state is assigned to the signal at 860 mT, the zfs parameters of *m,m′*-**12n** and -**13n** are estimated to be $D = 0.169$ cm^{-1} and $E = 0.040$ cm^{-1} within the framework of third-order perturbation theory.[27] Moreover the peculiar signal at 237 mT is not inconsistent with the X transition of the thermally populated triplet dinitrenes with $D = 0.507$ cm^{-1} and $E = 0.120$ cm^{-1}, although the corresponding Y and Z transitions expected at 768 and 869 mT could not be detected above the signal to noise level (see eq 8 in Experimental Section).

An additional feature of the ESR spectra of the meta,meta′ isomers is their dependence on the concentrations of the precursors. When the concentration of the diazide *m,m′*-**12a** and -**13a** in MTHF is on the order of 10^{-2} M, the irradiation at 10 K produced an additional peak at around 300 mT. The intensity of this signal simply decreased as the temperature was raised. Presently, the origin of the signal which appeared only at high concentration is not fully explained, but it is tentatively interpreted in terms of the quintet state produced by the intermolecular interaction of two triplet mononitrenes. In solutions of high concentration, the diazides might probably associate to form aggregates, so that the triplet mononitrenes which were predominant species generated upon irradiation would lie close together to allow them to interact intermolecularly. Precedents for such ferromagnetic intermolecular interactions are found in some carbenes in host crystals of their parent diazo compounds.[28]

Discussion

(A) Interaction of the Two Triplet Phenylnitrenes. In both meta,para′ and meta,meta′ isomers, the present results show that the two triplet nitrene moieties interact sufficiently strongly to form quintet states when linked together through the ethynylene and even 1,3-butadiyne-1,4-diyl linkages. 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 derived from the interaction through bond, since the rigid linear molecular structure does not permit approach of the two nitrene moieties. On the basis of the temperature dependence, the spin multiplicity of the ground state could be determined, and the energy gap between the ground and thermally excited states could be estimated semiquantitatively.

As shown in Figures 4 and 5, the intensity of the quintet signals derived from diazide *m,p′*-**12a** and -**13a** decreased linearly with the reciprocal of the temperature in good agreement with a Curie law. This temperature dependence shows that dinitrenes *m,p′*-**12n** and -**13n** have quintet ground states. Strictly speaking, a possibility that the quintet state might be degenerate with the singlet or lies very closely with the latter state cannot be excluded. The same is true for *m*-phenylenedinitrene (**14**). If the quintet states were thermally populated, the signal intensities should have deviated from Curie laws and showed a maxima where thermal populations between the states and between spin sublevels balanced (vide infra: the *m,m′*-dinitrenes and eq 3). If the maxima of the signal intensity vs reciprocal of temperature plots appear at 8 K or lower, the limit of our experiments, the energy gap is estimated to be 30 cal/mol or lower. In dinitrenes *m,p′*-**12n** and -**13n**, no thermally populated signals could be observed within the temperature range 10–90 K. Moreover we have neither theoretical nor experimental grounds to expect thermally excited electronic states lying closely above the quintet ground state. According to the theory on two weakly interacting triplet species, the triplet and singlet states would be expected to lie above the quintet state by an energy of $4J$ and $6J$, respectively, where J is the positive exchange integral of the two interacting triplet species.[4,28b] However, there appears to be a rather strong interaction in these *m,p′*-dinitrenes and the strict applicability of this theory to them is not necessarily guaranteed. For these reasons, we cannot predict the spin state populated thermally above the quintet ground state nor the energy gap between the two states. As expected in a quintet state consisting of two triplets attached to the meta positions of a benzene ring such as **1** and **14**, we feel that the through-bond interaction between the two remote nitrene moieties is large enough to produce "stable" quintet ground states.

As shown in Figures 8 and 9, plots of the signal intensities of the quintet states derived from *m,m′*-**12a** and -**13** vs the reciprocal of temperature display convex curves. It is apparent that these quintet states are populated thermally but lie very close to the ground states. Moreover, since we could detect signals assigned to the thermally populated triplet states from both *m,m′*-**12n** and -**13n**, it is reasonable to think that the theory on two triplet species interacting weakly with negative J values could be applied to these *m,m′*-dinitrenes. Thus *m,m′*-**12n** and -**13n** are considered to have singlet ground states with thermally populated triplet and quintet states above the ground state. According to the theory, the energy gaps of the triplet and quintet states from the singlet 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 sublevels within the triplet or quintet state and that the Boltzmann distribution among the spin sublevels is neglected, eq 3 applies to the ESR signal intensities of the thermally populated quintet state, where C and R mean an arbitrary constant and the gas constant, respectively.[29] With

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

this equation, the theoretical intensity curves are given for $J = -30$ and -35 cal/mol in Figure 8 and for $J = -15$ and -20 cal/mol in Figure 9, respectively. These curves are normalized so that the maximal intensities fit the experimental data. In the dinitrene with the diphenylacetylene skeleton **12n**, the experimental data illustrated by the full circles in Figure 8 fall approximately between the two curves. Therefore the energy gap, $6J$, between the singlet and the quintet states is estimated to be ca. 200 cal/mol. On the other hand, as shown in Figure 9 the energy gap in the dinitrene with the diphenyldiacetylene skeleton **13n** is estimated to be ca. 100 cal/mol.

This is the first example, to our knowledge, that showed the dependence of the magnitude of magnetic coupling on the distance

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(28) (a) Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1980**, *102*, 5104, 7391. (b) Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H.; Sugawara, Y.; Iwasaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293. (c) Sugawara, T.; Tukada, H.; Izuoka, A.; Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1986**, *108*, 4272. (d) Murai, H.; Safarik, I.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 1025.

(29) A similar treatment is reported: (a) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786. (b) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

Table I. Relative State Energy Gaps (in kcal/mol) for the Dinitrenes

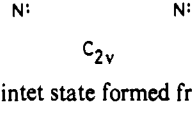
compd	AM1-CI[30b]	this work (6*J*)
m,m'-acetylene **12**	1.2	−0.2
m,p'-acetylene **12**	2.7	≫0
m,m'-diacetylene **13**	0.0	−0.1
m,p'-diacetylene **13**	2.0	≫0

between two organic triplet moieties. The magnitude of the interaction of the two polynitrenes through the acetylenic bond is nearly identical with that (200 cal/mol) of the two diphenylcarbenes through the ethylenic double bond in **10**.[15]

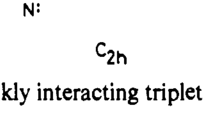
It should be noted that, whereas the magnitude of the interaction of the two phenylnitrene triplets in the meta,para' isomers is considerable, the interaction in the meta,meta' isomers is so small that the excited triplet and quintet states are readily accessible and depend strongly upon the distance between the two moieties. This striking contrast may be understood when the nonbonding molecular orbitals (NBMOs) of the isomers are studied by means of the simple Hückel molecular orbital method. In the meta,para' isomers, the atoms having nonzero NBMO coefficients are the starred atoms described in the section on the theoretical predictions. Since, to a first approximation, the spin densities are thought to be generated on the atoms with such nonzero coefficients, the interactions of the spins are transmitted effectively through the atoms of the bridging groups in the meta,para' isomers. On the other hand, in the meta,meta' isomers the NBMOs are completely localized in the two phenylnitrene moieties with zero coefficients in the NBMOs for the atoms of the bridging groups. Therefore for the interaction of the two phenylnitrene moieties to occur, the spin interactions would have to take place through the atoms with the zero spin densities. The magnitude of these spin interactions is expected to be small and to be reduced each time they pass through the bonds.

It will be worthwhile to compare the above results with a recent AM1 calculation (Table I).[30] The computation at this level of approximation predicts the highest spin ground states for all the dinitrenes except for *m,m'*-**13n** for which high-spin and low-spin states are nearly degenerate. Higher level computation would be necessary to obtain quantitative results.

(B) Conformations of the Dinitrenes. In the section of the theoretical predictions, we assumed planar conformations for **12n** and **13n**. Some information on the conformations of diphenylacetylene and diphenyldiacetylene is available in the literature. In the crystalline state, diphenylacetylene is reported to be planar.[31] The photoelectron spectra of diphenylacetylene and diphenyldiacetylene suggest that these molecules are present as conformational mixtures in the gas phase.[32] Moreover, also in the gas phase, the ground-state molecular geometry of diphenylacetylene is reported to be planar with a low barrier of ca. 575 cal/mol for the torsional motion.[33]



C_{2v}



C_{2h}

Even when their structures are predominantly planar in the solid solutions, two conformational isomers are still possible for *m,m'*-**12n** and -**13n**: one with the C_{2v} symmetry and the other having the C_{2h} symmetry. As mentioned before, the zfs parameters of the quintet state formed from two weakly interacting triplet species depend more on the relative orientation of the two triplets rather than the distance separating them. This is explained in terms of the spin Hamiltonian for the system consisting of weakly interacting units a and b as written in eq 4. The dipolar coupling tensor

$$\mathcal{H} = \mathcal{H}^{a}(1) + \mathcal{H}^{b}(2) + \mathcal{H}^{ab}(1,2) \tag{4}$$

$\mathbf{D}_Q$ of the quintet is then given by eq 4'.[4b] When the component

$$\mathbf{D}_Q = \frac{1}{6}(\mathbf{D}_T^a + \mathbf{D}_T^b) + \frac{1}{3}\mathbf{D}_T^{ab} \tag{4'}$$

triplets a and b have strong one-center interaction as in carbenes and nitrenes, their dipolar coupling tensors, $\mathbf{D}_T^a$ and $\mathbf{D}_T^b$, are much larger than $\mathbf{D}_T^{ab}$. When the last term in eq 4' thus drops out, $\mathbf{D}_Q$ becomes independent of the distance between the two triplets a and b but depends only on their relative orientation.[1b,4a,b,29]

Therefore the zfs parameters can be estimated for given structures of the dinitrenes by the sum of the dipolar coupling tensors $\mathbf{D}_T$ of each triplet species (the first two terms in eq 4'). The zfs parameters *D* and *E* of the quintet are calculated from the Z and X, Y diagonal elements, respectively, of the tensor $\mathbf{D}_Q$. In the case of *m,m'*-**12n** and -**13n**, the orientation can be defined by the angle θ made by the two carbon–nitrogen bonds, because of the local cylindrical symmetry of the electrons on the nitrenic centers. With the zfs parameters of the mononitrene triplet observed in the spectra for the calculation of $\mathbf{D}_T$, we could estimate the parameters of the quintet with the structure C_{2v} ($\theta = 60$) and C_{2h} ($\theta = 180$) to be $D = 0.215$, $E = 0.043$ cm^{-1} and $D = 0.344$, $E = 0.000$ cm^{-1}, respectively. The observed zfs parameters ($D = 0.169$, $E = 0.040$ cm^{-1}) are moderately close to those of the C_{2v} structure. However the presence of the C_{2h} structure is not necessarily 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 (see eq 5 in Experimental Section),[27] 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 *m,p'*-**12n** and -**13n**, the method for the estimation of the zfs parameters could not be employed, since the theory of two weakly interacting triplet species is unlikely to be applicable in these more strongly coupled isomers.

In any event, it would be reasonable to assume that the dinitrenes are present in matrices as a mixture of various conformational isomers, though the predominant structure would be planar. However, it has been confirmed that the multiplicities of the ground state of all these dinitrenes are independent of their conformations. Itoh and his co-workers reported previously that tetracarbene **1** ($n = 4$) has nonet ground states irrespective of its conformation.[7b] We showed that, in the meta,meta' dicarbene of **10**, both the cis and trans structures have singlet ground states and that both geometric isomers have nearly the same energy gap between the quintet and singlet states.[15] It is the regiochemistry or topology which really matters.

In the previous section, we mentioned the irreversible enhancement of the intensities of some quintet signals at 65 K. At present these phenomena are thought to be due to the relaxation of the conformations of these dinitrenes in the softened matrices at 65 K. Although the details of the relaxation cannot be discussed, it would be likely that the population of the conformers could be changed irreversibly at the temperature where the torsional motion of molecules becomes possible in softened matrices.[34] Note that these molecules are flexible with the very low torsional barriers.[33]

(C) Origin of the Triplet Mononitrenes. The ESR signals due to the triplet mononitrenes, which were observed after irradiation of all the diazides discussed here, are especially intense in the

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meta,meta′ isomers. Since these signals appeared immediately after the irradiation at 10 K, it is reasonable to assume that the signals are derived from the monoazidomononitrene species, at least in the early stages of the photolysis. It was pointed out that only one photon was consumed for the extrusion of dinitrogen in the photolysis of bis(diazo) precursor to generate dicarbene **1** (n = 2) in the solid states at cryogenic temperature.[35] In the *m,m′*-**12a** and -**13a**, the efficiency of one photon to cleave both azide groups is thought to be rather low because of the weak interaction of the two moieties. Furthermore, once one azide group decomposes to form the monoazidomononitrene triplet, the second azide group is thought to become more difficult to cleave. Phenylnitrenes have much intense absorptions in the range 300–420 nm than precursor azides,[36] and therefore it would be the nitrene moiety that absorbed light when the monoazidomononitrene species are irradiated. This seems to be the reason for the observed extremely intense signals of the triplet species for the meta,meta′ isomers. The presence of such an amount of undesirable triplet species is not appropriate for investigation of the spin–spin interactions in these systems by means of magnetic susceptibility.

Conclusions

Two regioisomeric dinitrenes of the diphenylacetylene **12n** and diphenyldiacetylene **13n** series have been generated and studied by X-band ESR spectroscopy. It was necessary to anneal the photochemically generated samples in MTHF at 65 K for half an hour in order to obtain the reproducible temperature dependencies of the signal intensities at cryogenic temperature (10–85 K). It should be emphasized again that the interaction of two remote triplet phenylnitrene units connected through an acetylenic or a diacetylenic bond is sufficiently strong to form the quintet states. These high-spin states are apt to be ground states in the *m,p′*-**12n** and -**13n**, while they are the thermally accessible (by ca. 200 and 100 cal/mol, respectively) excited states for the meta,meta′ isomers. These experimental results are thoroughly consistent with the topology of the π-framework as predicted by the valence bond theory of Ovchinnikov[13] and also the molecular orbital theory of Borden and Davidson.[21b] Thus we have obtained experimental evidence for solving the regiochemical problems of where to place open-shell centers on the side chains of conjugated polymers **6**–**9**. The conclusion can be paraphrased as follows. The radical, carbene, or nitrene centers X must be introduced at the equivalent positions on the phenyl or phenylene rings, all para, all meta, or all ortho. These situations can be realized by head-to-tail homopolymerizations.

Phenylacetylenes are known to undergo such a type of polymerization with metal complex catalysts containing tungsten or rhodium.[37a,b,38b] Some poly(phenylacetylenes) carrying persistent radicals as pendants have been obtained. Such samples are still at the embryonic stage of super high-spin organic materials in that either the radical contents are lower than stoichiometry[37c] or radical centers are not fully in conjugation with the main chain.[38] In principle, *m,p′*-**13a** could also give high-spin poly(diphenyldiacetylene) by stereoregular polymerization followed by photolysis. Whereas similar 1,4-bis-(3-acetamidophenyl)-1,3-butadiyne is known to undergo solid-state polymerization,[39] none of the diphenyldiacetylene derivatives described in this paper showed any sign of polymerization in the solid state. In order to realize the high-spin polymers with backbone structure **9**, the synthesis of polymerizable crystals of diacetylenes carrying radical centers or precursors at the positions delineated in this study remains to be accomplished.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer (90 MHz) and a JEOL JNM-GX-400 spectrometer. IR spectra were recorded on a Hitachi 295 spectrometer. 2-Methyltetrahydrofuran was purchased from Aldrich Chemical Company, Inc. and distilled from sodium. ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100-kHz field modulation) equipped with an optical transmission cavity and an Air Products LTD-3-110 liquid helium transfer system at the Instrument Center of the Institute for Molecular Science in Okazaki. The diazide compound (ca. 0.5 mg) was dissolved in 2-methyltetrahydrofuran (0.5 mL). The solution was placed in a quartz tube (5-mm o.d.) and degassed by 3 freeze–thaw cycles. The sample was cooled in a precooled ESR cavity and irradiated with a high-pressure mercury lamp (500 W) through a Pyrex filter at 10 K. The microwave frequency was measured with a Takeda Riken 5210 M frequency counter, and the resonance magnetic field values of the signals were measured with the aid of a Varian E-500 NMR gaussmeter. The dependence of the signal intensities on temperatures was measured by the use of an Air Products APD-E temperature-controlling accessory. The microwave power employed at cryogenic temperatures was in the range 100 μW–1 mW to avoid saturation of ESR signals.

Analysis of ESR Spectra. The third-order perturbation theory[27] was employed to estimate the zfs parameters in eq 2. The highest field transition of a quintet species is assigned to the transition parallel to the z principal axis from $m = -2$ to $m = -1$ sublevels. The resonance field of this transition is estimated by eq 5 where $\gamma = D$, $\delta = 3E^2/2$, and $\lambda = 4\gamma\delta$. The next highest transition is assigned to the Y transition from

$$H = H_0 + 3\gamma + \delta/(H_0 + 3\gamma) - \lambda/H_0^2 \qquad (5)$$

$m = 1$ to $m = 2$ sublevels, the resonance field of which is estimated by eq 6 where $\gamma = -(D + 3E)/2$, $\delta = 3(D - E)^2/8$, and $\lambda = 4\gamma\delta$.

$$H = H_0 - 3\gamma + \delta/(H_0 - 3\gamma) + \lambda/H_0^2 \qquad (6)$$

In the case of phenylnitrenes in which there is local axial symmetry, the X and Y transitions coincide at $H_{x,y}$ and the D and E parameters are given by eq 7. The microwave frequency for obtaining these numerical values was 9.2996 GHz.

$$D = (g\beta H_{x,y})^2/H_0 - H_0 \qquad (7)$$

$$E = 0$$

The resonance field of the X transition of a thermally populated triplet from the interaction of two triplets is given by eq 8.

$$(g\beta H_x)^2 = (H_0 + D - E)(H_0 - 2E) \qquad (8)$$

Materials. 1-(3-Nitrophenyl)-2-(4-nitrophenyl)acetylene. To a solution of 500 mg (3.40 mmol) of (3-nitrophenyl)acetylene[40] in 17 mL of ethanol was added with stirring a solution of 650 mg (3.41 mmol) of copper(I) iodide in 10 mL of aqueous ammonia. The reaction mixture was allowed to stand for 15 min. The precipitate was collected by filtration, washed successively with water, ethanol, and ether, and dried at 50 °C (20 mm) to give 380 mg (53%) of copper(I) (3-nitrophenyl)-acetylide as orange granules. To a solution of 450 mg (1.81 mmol) of 4-iodonitrobenzene in 8 mL of dry pyridine was added 380 mg (1.81 mmol) of copper(I) (3-nitrophenyl)acetylide with stirring under the nitrogen flush. The reaction mixture was refluxed gently with stirring for 3.5 h, cooled, and diluted with water. The organic material was extracted with ether, and the extract was washed successively with dilute hydrochloric acid, 5% aqueous sodium bicarbonate and water, and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was developed on a silica gel column with hexane–dichloromethane (3:1) to afford 430 mg (88%) of 1-(3-nitrophenyl)-2-(4-nitrophenyl)acetylene. The material was purified by recrystallization from hexane–dichloromethane: light yellow granules; mp 161–162 °C (ethanol); ^{1}H NMR (CDCl$_3$) δ 7.60 (1 H, dd, J = 8, 8 Hz), 7.72 (2 H, d, J

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= 9 Hz), 7.87 (1 H, d, *J* = 8 Hz), 8.25–8.28 (3 H, m), 8.43 (1 H, s). Found: C, 62.53; H, 3.24; N, 10.40. Calcd for $C_{14}H_8N_2O_4$: C, 62.69; H, 3.01; N, 10.45.

1-(3-Azidophenyl)-2-(4-azidophenyl)acetylene (*m,p'*-12a). To a solution of 140 mg (0.52 mmol) of 1-(3-nitrophenyl)-2-(4-nitrophenyl)acetylene in 2.5 mL of acetic acid at 60–70 °C was added 250 mg of iron powder in small portions with vigorous stirring. The color of the reaction mixture changed to a dark brown after warming for 5 min. An additional iron (120 mg) was added in small portions to the reaction mixture, which gradually changed to a gray slurry. After warming for 30 min, the reaction mixture was cooled, diluted with water, and made basic with 20% aqueous sodium hydroxide. The organic material was extracted with ether, and the extract was dried over sodium sulfate. The solvent was removed under reduced pressure to give the crude diamine. The diamine was dissolved in 6 mL of dioxane, and 6 mL of 6 N sulfuric acid was added to the solution. The mixture was cooled to 0–5 °C, and a solution of 80 mg (1.2 mmol) of sodium nitrite in 2 mL of water was added dropwise to the solution. The reaction mixture was stirred for 30 min at this temperature. After removing excess nitrous acid by addition of urea, the cooled solution was filtered and added dropwise to a solution of 1.1 g of sodium azide in 7 mL of water with stirring at room temperature. After the addition, the reaction mixture was stirred for 30 min. The organic material was extracted with dichloromethane, and the extract was dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was developed on a silica gel column with hexane to give 50 mg (37%) of *m,p'*-**12a**. The solid was further purified by recrystallization from hexane: light yellow needles; mp 81–82 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 6.98–7.04 (3 H, m), 7.18 (1 H, s), 7.27–7.35 (2 H, m), 7.52 (2 H, d, *J* = 9 Hz); IR (KBr) 2120, 1592, 1500, 1295, 890, 831, 790 cm^{-1}. Found: C, 64.44; H, 3.23; N, 32.32. Calcd for $C_{14}H_8N_6$: C, 64.60; H, 3.10; N, 32.30.

1,2-Bis(3-nitrophenyl)acetylene. In the manner described for meta,-para' isomer, 360 mg (1.44 mmol) of 3-iodonitrobenzene was allowed to react with 300 mg (1.43 mmol) of copper(I) (3-nitrophenyl)acetylide in 6 mL of pyridine. The crude product was chromatographed on silica gel with hexane–dichloromethane (3:1) to afford 310 mg (81%) of 1,2-bis-(3-nitrophenyl)acetylene. The material was purified by recrystallization from hexane–dichloromethane: light yellow needles; mp 179–180 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 7.60 (2 H, dd, *J* = 8, 8 Hz), 7.86 (2 H, d, *J* = 8 Hz), 8.24 (2 H, d, *J* = 8 Hz), 8.41 (2 H, s). Found: C, 62.45; H, 3.11; N, 10.36. Calcd for $C_{14}H_8N_2O_4$: C, 62.69; H, 3.01; N, 10.45.

1,2-Bis(3-azidophenyl)acetylene (*m,m'*-12a). In the manner described for *m,p'*-**12a**, the dinitro compound was converted to the corresponding diamine,[41] and the Sandmeyer reaction of this diamine gave *m,m'*-**12a** in 81% yield: light yellow needles; mp 85–86 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.02 (2 H, d, *J* = 8 Hz), 7.20 (1 H, s), 7.29–7.36 (4 H, m); IR (KBr) 2100, 1600, 1290, 1250, 880, 782 cm^{-1}. Found: C, 64.53; H, 3.26; N, 32.53. Calcd for $C_{14}H_8N_6$: C, 64.60; H, 3.10; N, 32.30.

1-Bromo-2-(3-nitrophenyl)acetylene. To a mixture of 1.7 g of crushed ice, 0.9 mL of 10 N sodium hydroxide, and 0.2 mL bromine was added a solution of 500 mg (3.40 mmol) of (3-nitrophenyl)acetylene[40] in 0.2 mL of tetrahydrofuran, and the mixture was stirred vigorously for 5 h. After the addition of aqueous ammonium chloride solution, the mixture was extracted with ether. The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated under reduced pressure to afford 730 mg (95%) of 1-bromo-2-(3-nitrophenyl)acetylene as light yellow needles, which melted at 62–64 °C (lit. 65–67 °C[42]). This bromoacetylene was used without further purification.

1-(3-Nitrophenyl)-4-(4-nitrophenyl)-1,3-butadiyne. To a solution of 140 mg (0.95 mmol) of (4-nitrophenyl)acetylene[43] in 1 mL of *N,N*-dimethylformamide (DMF) was added under nitrogen atmosphere 20 mg of hydroxylamine hydrochloride. To the mixture were added a solution of 2 mg of copper(I) chloride in 1 mL of 33% aqueous ethylamine and then a solution of 230 mg (1.02 mmol) of 1-bromo-2-(3-nitrophenyl)acetylene in 0.5 mL of DMF with stirring under a nitrogen atmosphere. The contents were warmed at 40 °C for 2 h with stirring. The solution was cooled and diluted with water. The organic material was extracted with dichloromethane, and the extract was dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was developed on a silica gel column with hexane–dichloromethane (3:1) to afford 130 mg (47%) of *m,p'*-dinitrodiacetylene: white granules; mp 155–156 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 7.57 (1 H, dd, *J* = 8, 8 Hz), 7.71 (2 H, d, *J* = 9 Hz), 7.84 (1 H, d, *J* = 8 Hz), 8.21–8.27 (3 H, m), 8.39 (1 H, s). Found: C, 65.47; H, 2.90; N, 9.42. Calcd for $C_{16}H_8N_2O_4$: C, 65.75; H, 2.76; N, 9.59.

1-(3-Azidophenyl)-4-(4-azidophenyl)-1,3-butadiyne (*m,p'*-13a). 1-(3-Nitrophenyl)-4-(4-nitrophenyl)-1,3-butadiyne (150 mg (0.51 mmol)) in 2.5 mL of acetic acid was warmed to 60–70 °C. To the suspension was added in small portions 250 mg of iron powder with vigorous stirring. The color changed to a dark brown after warming for 5 min, and an additional iron (120 mg) was then added in small portions. After warming for 30 min, the reaction mixture was worked up in the manner described for *m,p'*-**12a** to afford the crude diamine. The diamine was dissolved in 6 mL of dioxane, and 6 mL of 6 N sulfuric acid was then added to the solution. The resulting suspension was diazotized by addition of sodium nitrite (80 mg, 1.2 mmol) in 2 mL of water at 0–5 °C. After stirring for 30 min, the filtered solution was treated with a solution of 1.1 g of sodium azide in 7 mL of water as described before. The crude product was separated by a silica gel column chromatography with hexane elution to give 114 mg (78%) of *m,p'*-**13a**. The material was further purified by recrystallization from hexane: light yellow needles; mp 133–134 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 6.99 (2 H, d, *J* = 8.4 Hz), 7.02 (1 H, dt, *J* = 7.8, 1.7 Hz), 7.16 (1 H, t, *J* = 1.24 Hz), 7.28 (1 H, d, *J* = 7.6 Hz), 7.31 (1 H, t, *J* = 7.7 Hz), 7.50 (2 H, d, *J* = 8.59 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 74.0, 74.8, 80.6, 81.5, 118.0, 119.2, 120.0, 122.6, 123.5, 129.0, 130.0, 134.1, 140.5; IR (KBr) 2100, 1590, 1281, 825, 778 cm^{-1}. Found: C, 67.36; H, 3.03; N, 29.64. Calcd for $C_{16}H_8N_6$: C, 67.59; H, 2.84; N, 29.57.

1,4-Bis(3-nitrophenyl)-1,3-butadiyne. To a solution of 2.44 g (12.2 mmol) of copper(II) acetate monohydrate in 40 mL of a 1:1 mixture by volume of pyridine and methanol was added dropwise with stirring 900 mg (6.12 mmol) of (3-nitrophenyl)acetylene[40] in 8 mL of methanol. The reaction mixture was stirred for 3.5 h and then poured with stirring onto 200 mL of ice-cooled 1 M sulfuric acid. The resulting suspension was extracted with dichloromethane, and the extract was washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed over silica gel with hexane–dichloromethane (3:1) to give 870 mg (97%) of 1,4-bis(3-nitrophenyl)-1,3-butadiyne: white needles; mp 155–156 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 7.56 (2 H, dd, *J* = 8, 8 Hz), 7.85 (2 H, d, *J* = 8 Hz), 8.26 (2 H, d, *J* = 8 Hz), 8.38 (2 H, s). Found: C, 65.58; H, 2.85; N, 9.52. Calcd for $C_{16}H_8N_2O_4$: C, 65.75; H, 2.76; N, 9.59.

1,4-Bis(3-azidophenyl)-1,3-butadiyne (*m,m'*-13a). In the manner described for *m,p'*-**13a**, the dinitro compound was converted to the corresponding diamine, and the Sandmeyer reaction of this diamine gave *m,m'*-**13a** in 78% yield: light yellow needles; mp 133–134 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.04 (2 H, d, *J* = 8 Hz), 7.18 (1 H, s), 7.27–7.36 (4 H, m); IR (KBr) 2120, 1596, 1318, 878, 780 cm^{-1}. Found: C, 67.36; H, 3.03; N, 29.64. Calcd for $C_{16}H_8N_6$: C, 67.59; H, 2.84; N, 29.57.

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