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Spin Delocalization by Triple-Bonded Functionalities in Propargyl and Heteropropargyl Radicals, Assessed from the EPR-Spectral *D* Parameter of 1,3-Cyclopentanediyl Triplet Diradicals

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The cyclopentane-1,3-diyl triplet diradicals **T** and **T′** with the triplet-bonded acetylene, cyano, and isocyano functionalities at one of the radical sites are readily prepared from the corresponding azoalkanes by photodenitrogenation in a 2-methyltetrahydrofuran (2-MTHF) matrix at 77 K. The EPR-spectral *D* values of these triplet diradicals show that the spin delocalizing ability of the triple-bonded π substituent follows the order $-C\equiv CH > -NC \approx -CN$. Good correlations of the *D* values have been obtained with the hyperfine coupling constants (a_H) and with the calculated spin densities (PM3/AUHF-CI method) of the corresponding monoradicals **M**. The propargyl-type mesomeric structure is favored over the allenyl-type contributor for all three triple-bonded functionalities; spin delocalization is less pronounced in the heteropropargyl derivatives due to the electronegativity effect of the nitrogen atom.

Introduction

The spin delocalization in allyl[1] and heteroallyl[2] radicals has been extensively studied during the past few years, whereas less is known about the electronic stabilization by triple-bonded radical systems. Consequently, the incentive of the present study was to assess the extent of spin delocalization in the propargyl radical systems and its nitrogen analogues, namely the cyanomethyl (NC-CH$_2$•) and isocyanomethyl (CN-CH$_2$•) radicals.

Early EPR-spectral work on the propargylic radical was carried out by Collin and Lossing,[3] who generated it by hydrogen abstraction from methylacetylene. Subsequent more detailed EPR studies by Kochi and Krusic[4] concluded from the hyperfine coupling constants (see structures below) that the propargyl mesomeric structure
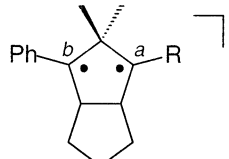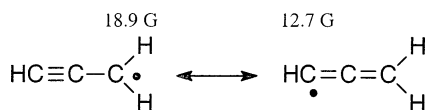

is favored over the allenylic one. The hyperfine coupling constants (a_H) calculated by Benson's[5] group (INDO method) confirmed the preference for spin localization in the propargylic (a_H = 19.2 G) versus the allenic (a_H = 10.9 G) structure.

For the cyanomethyl radical, the observed coupling constant was measured to be a_H = 20.8 G (the INDO

calculated value is a_H = 20.0 G),[5] which clearly indicates a higher spin localization at the methylene carbon atom than in the propargyl case. This is expected since the electronegative nitrogen atom will resist spin delocalization to populate the heteroallenic structure.[5]

The EPR-spectral work on the isocyanomethyl radical was conducted by Williams and Wang,[6] but strong anisotropic effects precluded the determination of a precise a_H coupling constant, such that the extent of spin delocalization by the isocyano group is not accurately accessible. These EPR-spectral results manifest the difficulties in acquiring information on the spin delocalization for unconventional groups such as the isocyano functionality by means of hyperfine coupling constants.

Low-temperature persistent 1,3-cyclopentanediyl triplet diradicals may be readily generated through the photochemical deazetation of diazabyciclo[2.2.1]heptene (DBH) derivatives.[7] These triplet diradicals have been characterized by the zero-field-splitting (zfs) parameters *D* and *E*. For such localized triplet 1,3-diradicals, the *D* parameter depends on the interspin distance d_{ab} and the spin densities ρ_a and ρ_b at the respective radical sites *a* and *b*, as displayed in eq 1. The spin density as well as

$$D = \frac{3 \cdot \mu_0 \cdot g_e^2 \cdot \mu_B^2}{16\pi}\left(\frac{\rho_a \cdot \rho_b}{d_{ab}^3}\right) \tag{1}$$

the distance dependences have been confirmed experi-

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mentally and theoretically,[8] which provide valuable structural and electronic information on spin delocalization and radical stabilization in triplet diradicals. When one radical site is kept electronically constant (e.g., phenyl substitution at the radical site *b*), and a set of triplet diradicals is considered for which d_{ab} is the same (1,3-cyclopentanediyl triplet diradicals), the D parameter is a sensitive probe of the electronic effects exerted by the substituents at the radical center *a* through the spin density ρ_a. This provides an accurate measure of radical stabilization in terms of the efficacy of spin delocalization in the monoradical fragments **M**.

In view of the conspicuous lack of information in most radical scales[9–13] on the ability of triple-bonded functionalities to delocalize an unpaired electron, we have measured the D values of the 1,3-cyclopentanediyl triplet diradicals **T1**−**3** and **T′1**−**3**, generated photochemically from the respective azoalkanes **A1**−**3** and **A′1**−**3** (Table 1). From the spin densities (ρ) accessible through the D values, we have determined the electronic stabilization in the propargylic versus the heteropropargylic radical fragments. The present results demonstrate unequivocally that the D parameter provides valuable data on the efficacy of radical stabilization by the triple-bonded functionalities −C≡CH, −C≡N, and −N≡C.

Results and Discussion

The known[14] azoaldehyde **A** was prepared in an overall yield of 24% from the commercially available benzoylacetone according to the Hünig route.[15] The azoaldehyde **A** was employed for the synthesis of the various functionalized azoalkanes **A1**, **A3**, **A′2**, and **A′3** as summarized in Scheme 1.

The cyano-substituted **A1** azoalkane was obtained from the corresponding oxime[2a] through dehydration with

TABLE 1. D Values of the Tripet Diradicals T and T′ and the PM3(AUHF/CI)-Calculated Spin Densities of the Corresponding Monoradical Fragments M and M′

X	T^a	ID/hcl[b]	T'^a	ID/hcl[b]	spin density $(\rho)^c$	
-CN	T1	0.0573[d]	T′1	0.0400	M1 0.755	M′1 0.474
-NC	T2	(0.0569)[e]	T′2	0.0397	M2 0.739	M′2 0.461
-C≡CH	T3	0.0537	T′3	0.0370	M3 0.698	M′3 0.447

[a] The triplet diradicals **T** and **T′** generated from the respective azoalkanes **A** and **A′** by irradiation with the 364-nm laser line of the argon-ion laser for 3 min in a 2-methyltetrahydrofuran (2-MTHF) matrix at 77 K. [b] The D values were measured by EPR spectroscopy (see Supporting Information) and are given in cm^{-1}, accuracy ±0.0001 cm^{-1}. [c] The spin densities were computed for the monoradical fragments **M** and **M′** with the semiempirical PM3(AUHF/CI) method. [d] D value taken from ref 21. [e] The D value was extrapolated from the correlation in Figure 3.

trichloromethyl chloroformate[16] in acetonitrile. The isonitrile- and acetylene-functionalized azoalkanes **A′2** and **A′3** were synthesized by Horner−Emmons olefination of the azoaldehyde **A** with the respective known phosphonates in THF.[17,18] The acetylene-substituted azoalkane **A3** was prepared by Peterson olefination of the azoaldehyde **A** with trimethylsilyldiazomethane at −78 °C, followed by thermal denitrogenation on warm-up of the Peterson product through the intermediary methylidene carbene.

The triplet diradicals **T** and **T′** were generated in a 2-methyltetrahydrofuran (MTHF) glass matrix at 77 K by means of irradiation with the 364-nm line of an argon-ion laser. In all cases, the characteristic half-field signal ($\Delta_{ms}= \pm2$) for the triplet state is located at 1650−1680 G; the relevant diradical z signals ($\Delta_{ms}= \pm1$) are $B_{min}= 1650 \pm 60$ and $B_{max}= 3924 \pm 60$ G at a microwave frequency of 9.43 GHz. The symmetry parameter (E) of the triplet diradical is very small and, thus, the upper limit was estimated to be ±0.0001 cm^{-1}. All triplet diradicals were persistent for hours at this temperature, as evidenced by the constant EPR signals.

In Table 1 are listed the experimental D values of the triplet diradicals **T1**−**3** and **T′1**−**3**, calculated from the EPR-spectral data, together with the theoretical spin densities (ρ) of the monoradicals **M** and **M′**. The theoretical spin densities (ρ) were computed for the model radical fragments **M** and **M′** in the corresponding triplet diradicals **T** versus **T′**. The geometry optimization of the model monoradical fragments **M** and **M′** was carried out by using the semiempirical PM3 method with annihilated

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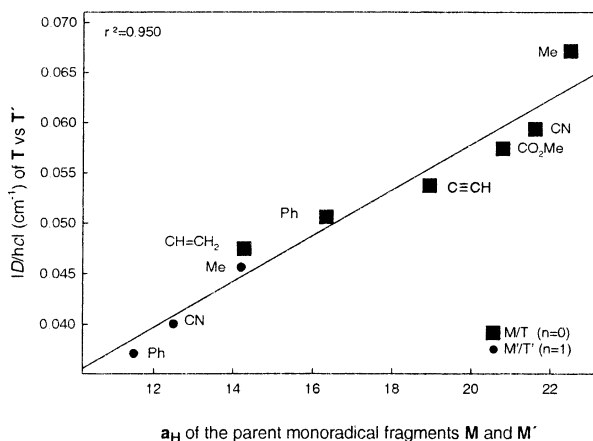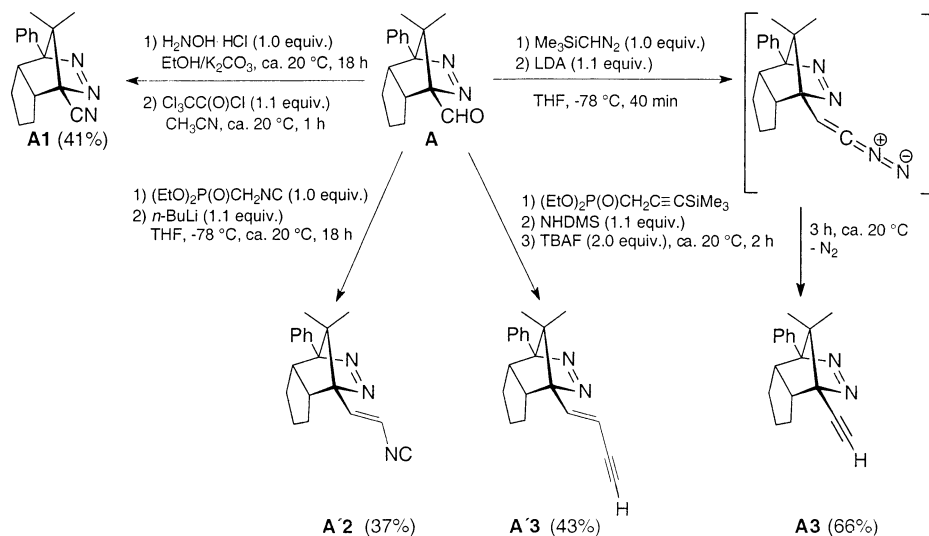**SCHEME 1. Synthesis of the Functionalized Azoalkanes A1, A′2, A3, and A′3 from the Azoaldehyde A**

FIGURE 1. Correlation of the D parameter for the triplet diradicals **T** and **T′** with the hyperfine coupling contants (a_H) for the **M** and **M′** radicals.

UHF wave functions, and the spin densities (Table 1) were obtained by means of a CI calculation.[19,20]

The D values in Table 1 have been arranged in decending order, i.e., in increasing degree of spin delocalization. Both sets of **T** and **T′** triplet diradicals reveal that the efficiency of radical stabilization, as displayed by the D values and the spin densities of the **M** and **M′** monoradicals fragments (see eq 1), follows qualitatively the order $-C\equiv CH > -N\equiv C \approx -C\equiv N$. This sequence is also displayed by the a_H coupling constants of the parent **M** and **M′** radicals, determined by EPR spectroscopy.[4,22] This is confirmed in Figure 1 by the good ($r^2 = 0.950$) linear plot of the D values for the triplet diradicals **T** and

T′ against the a_H values for the parent **M** and **M′** radicals. Although the EPR spectrum of the isocyanomethyl radical has been measured, its a_H value could not be determined precisely due to severe anisotropy effects,[6] but from Figure 1 it may be estimated to be about 20 G. Be this as it may, the correlation in Figure 1 conveys clearly that the efficacy of spin delocalization is higher for the propargyl than for the heteropropargyl radicals.

To determine quantitatively the efficiency of spin delocalization by these triple-bonded substituents, we assign a planar geometry to the diradicals, on the basis of previous MO calculations (PM3 method),[20] which yielded an energy minimum for the planar 1,3-cyclopentanediyl ring with coplanar substituents at the radical sites. The planarity of the 1,3-cyclopentanediyl ring is in line with earlier ab initio calculations for the 1,3-cyclobutanediyl[27] and the parent 1,3-cyclopentanediyl[23] triplet diradicals.

According to semiempirical computations (AM1 method), the rotation of the substituents about the radical centers in the triplet diradicals **T** and **T′** requires an appreciable (7 kcal/mol) activation barrier on account of deconjugation.[24] Therefore, the observed changes in the D values reflect the electronic effects exerted by the substituents on the spin delocalization in the planar triplet diradicals **T** and **T′**. Since in all of these triplet diradicals one radical center is kept electronically constant (phenyl substitution), the experimentally assessed changes in the D parameter provide a measure of the efficacy of delocalization by the substituent at the other radical site. According to eq 1, the D value depends on the spin densities (ρ) at this radical site and relates the experimental D values of the triplet diradicals **T** and **T′** to the

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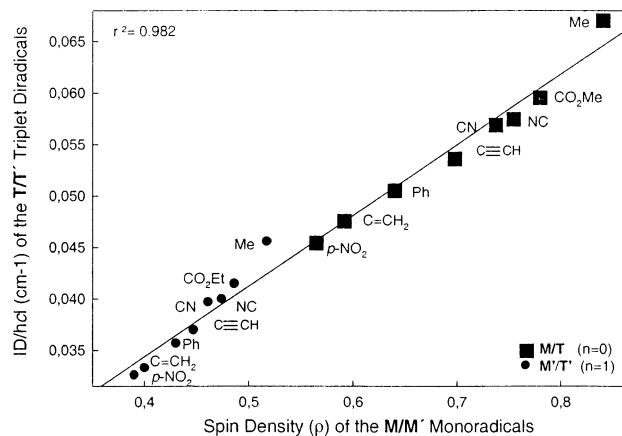
FIGURE 2. Correlation between the semiempirical PM3 (AUHF/CI) spin densities of the monoradicals **M/M′** and the D values of the triplet diradicals **T/T′**; the value of the isocyanide **M/T** set has been assessed by extrapolation (see Table 1, value in parantheses).

FIGURE 3. Correlation of the D values for the **T′** versus the **T** triplet diradicals.

theoretical spin densities of the monoradicals **M** and **M′**, which allows the quantitative evaluation of the observed electronic substituent effects. Indeed, as displayed in Figure 2, the D values of the triplet diradicals **T** and **T′** correlate impressively well ($r^2 = 0.981$, $n = 15$) with the spin densities (ρ) of the monoradical fragments **M** and **M′**. This confirms once again that the PM3(AUHF/CI) semiempirical method is reliable to assess the spin distribution in radicals. Included in this correlation are the data for the previously reported substituents, together with the CO_2Me functionality. The latter had hitherto not been examined and was presently prepared for comparison purposes and its D value measured (see Supporting Information).

Closer inspection of Figure 2 reveals that the directly bonded substituents in the triplet diradicals **T** ($n = 0$) and the extendedly bonded (alkenyl spacer) ones in **T′** ($n = 1$) fall into two well-defined sets without overlap: The directly bonded substituents (codified by the solid square) occupy the upper end and the extended ones (codified by the solid circle) the lower end of the correlation; note that in Table 1 the D values of the triplet diradicals, as well as the spin densities (ρ) of the monoradicals, are about 50% larger for the directly bonded **T/M** compared to the extendedly bonded **T′/M′** species.[13] This is due to the spin dilution by the allylic resonance in the alkenyl spacer of the **T′/M′** entities. Nonetheless, the correlation in Figure 2 covers perfectly the directly (**T**) as well as the extendedly (**T′**) bonded sets of triplet diradicals, which implies that the electronic effects of these substituents in the two series are the same and the extent of spin delocalization identical. That this is the case is most convincingly demonstrated by the essentially perfect straight line ($r^2 = 0.995$), when the D values of the directly bonded **T** set are plotted against those of the extendedly bonded **T′** set (Figure 3). Again, in this plot the previously reported derivatives of **T** and **T′** have been included, as well as the newly prepared CO_2Me functionality (see Supporting Information). Conspicuous in this plot is the omission of the isonitrile substituent in the directly bonded **T2** derivative, due to the fact that the corresponding azoalkane **A2** could not be prepared. However, since the D value for the extend-
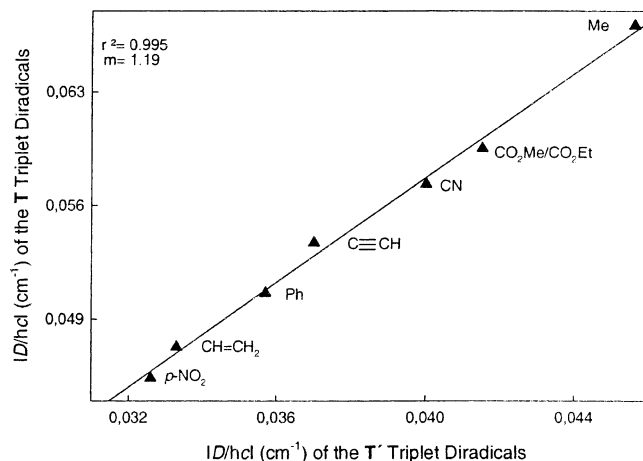
edly bonded isonitrile-substituted triplet diradical **T′2** is available (Table 1), with the help of the excellent correlation in Figure 3 we may extrapolate a reliable D value for the unknown directly bonded isonitrile-substituted triplet diradical **T2**; this D value is given in parentheses in Table 1. Clearly, the advantage of the correlation in Figure 3 should be evident, since once the D value for a particular substituent in the **T′** set has been experimentally determined, the unknown D value in the **T** set may be obtained by extrapolation, and vice versa.

The excellent correlation in Figure 3 between the two sets of triplet diradicals **T** and **T′** signifies that the electronic effects of the corresponding substituents in delocalizing spin and thereby the radical species are stabilized identically, except that in the **T** set, with the substituent directly bonded to the radical center, the electronic effects are more pronounced. Consequently, to analyze the efficacy of spin delocalization by the triple-bonded functionalities examined herein, we shall consider the directly bonded **T** set, especially since now the D value for the isocyanide functionality has become available through extrapolation (Table 1, value in parentheses).

Figure 2 reveals that the unsaturated functionalities follow the sequence $-CO_2Me < -CN \approx -NC < -C\equiv CH < -Ph < -C=CH_2$ in increasing order of spin delocalization. Evidently, the triplet-bonded substituents fall between the least stabilizing ester group and the most stabilizing phenyl and vinyl groups. We have shown previously that the spin delocalization in allyl and heteroallyl radicals follows the order $CH_2=CH-CH_2{}^{\bullet} > RN=CH-CH_2{}^{\bullet} > O=CH-CH_2{}^{\bullet}$, for which the reluctance of spin localization on the more electronegative heteroatom is responsible. Thus, comparison with the above sequence, which contains the triple-bonded substituents, shows the acetylenic group and its heteroatom congeners are all more effective in stabilizing the unpaired electron than the ester functionality, but not as effective as the vinyl group. That in the $CH_2=CH-CH_2{}^{\bullet}$ radical the unpaired electron is better stabilized than in $HC\equiv C-CH_2{}^{\bullet}$ is readily explained in terms of the more efficient allylic versus propargylic resonance. In the allyl radical, the odd electron is equally distributed between the equivalent methylene terminals through conjugation.
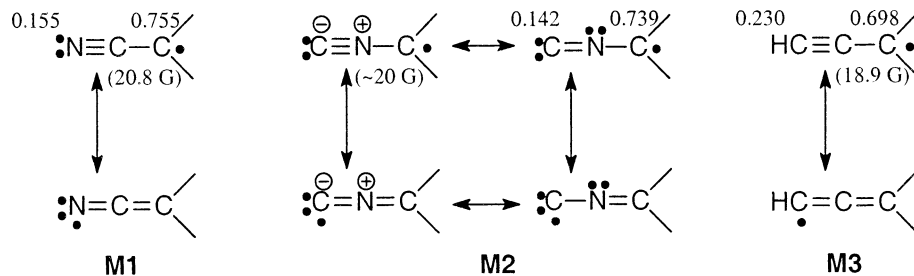
FIGURE 4. Mesomeric structures of the heteropropargyl (**M2-3**) and the propargyl **M3** monoradical fragments and their calculated spin densities (ρ) and EPR-spectral hyperfine coupling constants (a_H, in parentheses).

In contrast, in the propargyl-allenyl mesomerism (Figure 4), the unpaired electron prefers to populate the propargyl rather than the allenic structure, because in the latter the spin would have to reside at the less favored vinyl-type radical site.[5] This is also manifested by the hyperfine coupling constants (a_H) in Figure 1, which are 14.2 G for the allyl[22c] and 18.9 G for the propargyl[4] radicals. Clearly, in the unsymmetrical propargyl radicals, delocalization is less pronounced than in the symmetrical allylic radical, as displayed by the correlation of Figure 2.

When in the propargyl radical the CH terminal is replaced by a N atom, the resulting isoelectronic cyanomethyl radical is further destabilized, as evidenced by the higher spin density of the **M1** versus the **M3** monoradical at the methylene site and the higher D values of the corresponding triplet diradical **T1** versus **T3** (Table 1). Also the a_H values in Figure 1 expose this trend, since they are 18.9 G for the propargyl[4] but 20.8 G for the cyanomethyl[18] radical and, hence, the spin is not as well delocalized in the heteroatom analogues. Here operates again the electronegativity effect, since in the corresponding heteroatom-substituted propargyl-allenyl resonance (Figure 4), the unpaired electron would occupy the nitrogen terminal, which is unfavorable.[2a,4,26] Thus, the spin-delocalizing ability of the cyano group in the **M1** monoradical is markedly lower than that of the acetylene group in the **M3** species (Table 1).

A remarkable case constitutes the heteropropargyl radical **M2**, which results on replacement of the central carbon atom in the propargyl radical **M3** by a nitrogen atom (Figure 4). Although the EPR spectroscopy on the parent isocyanomethyl radical **M2** has been documented, only the nitrogen hyperfine coupling constant (a_N 6.5 G) is available, because anisotropy effects precluded the precise determination of the hydrogen coupling constant (a_H).[6] Also it should be emphasized that such heteropropargyl radicals are difficult to generate by the usual chemical means. Consequently, the photodenitrogenation of the azoalkane **A1** and **A2** to afford the corresponding triplet diradical **T1** and **T2**, which contains the desired heteropropargyl radical fragment **M**, constitutes a defi-nite advantage of the present methodology to assess the electronic radical-stabilizing ability of such complex functionalities as the isocyano substituent. In fact, from the D versus a_H plot (Figure 1) we have extrapolated an a_H value of about 20 G, which is close to the estimated value of ca. 21 G from the EPR spectrum of the parent isocyanomethyl radical.[6] Clearly, it should be apparent from the semiempirically calculated [PM3(AUHF/CI) method] spin densities of the radical fragments **M** (numbers above the structures at the two radical terminals), as well as the a_H values (numbers in parentheses below the structures) determined from the parent radicals **M** by EPR spectroscopy (Figure 4), that the isocyanomethyl radical is about as effective as the cyanomethyl radical in stabilizing the unpaired electron, but both are definitely worse than the propargyl radical.

On the basis of these spin-density data, we speculate on the radical-stabilizing ability of the isocyanomethyl radical (Figure 4) in terms of the various mesomeric structures. Although in all resonance structures the unpaired electron resides on the carbon-atom terminals, evidently neither the heteroallenic nor the iminic forms stabilize the spin effectively. Thus, the strong electron-withdrawing effect of the positively charged nitrogen atom oppossess such delocalization in the heteroallenic structure, whereas a rather electron-deficient carbon atom is generated in the iminic form, such that stabilization of the heteropropargyl species **M2** is ineffective compared to that of the propargyl species **M3** (Table 1). It hardly could have been anticipated that the isocyano group in the **M2** radical is about as efficient in stabilizing an unpaired electron as a cyano group in **M1**.

Supporting Information Available: Synthetic details and characteristic spectral data of the azoalkanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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