ARTICLE

OBC
www.rsc.org/obc

Photolysis of regioisomeric diazides of 1,2-diphenylacetylenes studied by matrix-isolation spectroscopy and DFT calculations†

Hideo Tomioka * and Shinji Sawai
Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan

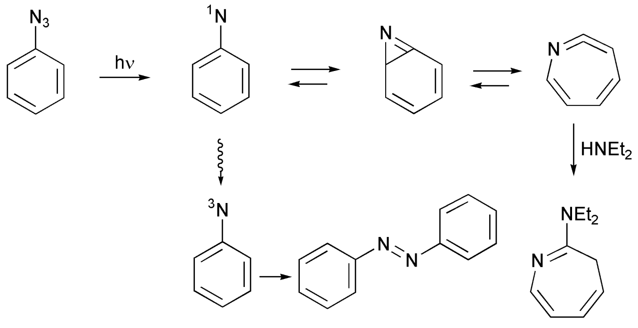
Received 18th July 2003, Accepted 7th October 2003
First published as an Advance Article on the web 30th October 2003

A series of diazides of 1,2-diphenylacetylenes was photolyzed in matrices at low temperature and transient photoproducts were characterized by using IR, UV/vis methods combined with ESR studies. Theoretical calculations were also used to understand the experimental findings. The introduction of phenylethynyl groups on phenyl azides has little effect on the photochemical pathway. Thus, upon photoexcitation, (phenylethynyl)phenyl azides afforded the corresponding triplet nitrene, which is in photoequilibrium with the corresponding azacycloheptatetraene. In marked contrast, azidophenylethynyl groups exhibited a dramatic effect not only on the photochemical pathway of phenyl azides but also on the electronic and molecular structure of the photoproducts. The patterns of the effect depended upon the relative position of azide groups in the diphenylacetylene unit. Whenever two azide groups were situated in a conjugating position with respect to each other, as in *p,p′*-, *o,o′*-, and *p,o′*-bis(azides), the azides always resulted in the formation of a quinoidal diimine diradical in which unpaired electrons were extensively delocalized in the π-conjugation. The situation changed rather dramatically when azide groups were introduced in the *meta* position. Thus, the formation of azacycloheptatetraene was noted in the photolysis of the *m,m′*-isomer. ESR studies indicated the generation of a quintet state that was shown to be a thermally populated state with a very small energy gap of *ca.* 100 cal mol^{-1}. The *m,p′*-isomer was shown to be an excellent precursor for the high-spin quintet dinitrene. The IR spectra of the photoproduct showed no bands ascribable to azacycloheptatetraene. The observed spectra were in good agreement with that calculated for the quintet state. Strong EPR signals assignable to the quintet state were observed, along with rather weak signals due to mononitrenes. Moreover, the quintet bis(nitrene) was rather photostable under these conditions.

Introduction

The photochemistry of phenyl azides has attracted interest in view of the useful applications of azides in heterocyclic syntheses,[1] photoresist techniques[1,2] and the biochemical method of photo-affinity labeling.[1,3,4]

The complete picture of the chemical reactions initiated by the elimination of molecular nitrogen has recently begun to unfold. A preparative study has revealed various chemical paths that require the involvement of different intermediates and matrix isolation,[5,6] and a flash-photolytic investigation[7] has provided direct evidence for the intermediates (Scheme 1). The photolysis of phenyl azide generates a singlet phenylnitrene, which isomerizes to benzazirine. Benzazirine can be intercepted with thiol before it opens to form azacycloheptatetraene.[8] This species can be intercepted with diethylamine to form an azepine adduct.[7a,c] In the absence of amine, the tetraene reverts slowly to a singlet phenylnitrene and relaxes to a triplet counterpart.[7g–j] The triplet nitrene within inert matrices at low temperature is shown to undergo ring expansion to give the tetraene upon photoexcitation.[5a,h]



Scheme 1

The photochemistry of phenyl polyazides has started to attract ever-increasing interest in view of the modern applications of polyazides in organo-ferromagnetic materials.[9] Since experimental studies found that *m*-phenylenedinitrene is a ground-state quintet,[10] many attempts have been made to generate and characterize polynitrenes, which are connected to appropriate linkers in a ferromagnetic fashion. For instance, two nitrene centers are introduced into a coupling linker group such as benzene,[11] biphenyl,[12] stilbene,[13] diphenylbutadiene,[13c,d] diphenyloctatetraene,[13c,d] diphenylacetylene,[14] diphenylbutadiyne,[14] tetraphenylallene,[15] benzophenone[16] and 1,1-diphenylethylene,[16] diphenyl sulfide,[17] azobenzene[17] and thiophene[18] to construct a π-conjugated system with the general structure of :N–Ph–X–Ph–N: and various possible connectivity types.

ESR measurements have been crucial in characterizing high-spin species, and they have been used successfully in many systems. However, the method has a serious disadvantage. Basically, it affords almost no information on the diamagnetic species that may be formed during irradiation. The fact that a triplet phenylnitrene easily undergoes ring-expansion upon photo-excitation, for example, clearly suggests that the high-spin species may not be photostable even at very low temperature. An independent investigation is thus desirable to reveal the overall reactions occurring upon photo-irradiation of polyazide compounds.

This paper is the report of an investigation in which aromatic diazides were photolyzed in matrices at low temperature and transient intermediates were characterized by using IR and UV/vis methods combined with ESR studies. Theoretical calculations were also used to understand the experimental findings.

---

† Electronic supplementary information (ESI) available: Tables S1–S7 (observed and calculated IR bands) and Figs. S1–3. See http://www.rsc.org/suppdata/ob/b3/b308138a/

DOI: 10.1039/b308138a

Two phenylazide units linked by an acetylene bond (**2**) were selected as the bisazides for this study. In order to learn the effect of the acetylene bond on the photochemistry of phenyl azide, the monoazide counterparts (**1**) were also investigated.

Results

Photolysis of ethynylphenyl azides (1)

The deposition of *m*-ethynylphenyl azide (*m*-**1a**-N_3) in Ar at 20 K gives an IR spectrum with absorptions at 2116 and 2098 cm^{-1} arising from the azide group and at 3318 cm^{-1} due to the acetylenic C–H bond. Broadband irradiation ($\lambda > 350$ nm) of the sample at 12 K resulted in a rapid decrease in the bands attributable to the starting material and the concurrent appearance of new bands in the IR (Fig. 1). Analysis of these product absorption bands by plotting their intensities as a function of the irradiation time and wavelength of light suggested that there were at least two photoproducts: **A** (3324 s, 1476 w, 972 w, 864 m, 720 m, 646 s, and 610 s cm^{-1}) and **B** (3318 s, 1888 s, 1380 m, 1230 m, 796 s, 752 m, 694 s, and 606 s cm^{-1}). Control experiments showed that those two products were interconvertible upon irradiation. Thus, irradiation of the initial photomixtures with light at $\lambda > 420$ nm resulted in the disappearance of the bands ascribable to **B** and in the concurrent growth of the bands due to **A**. Irradiation of the mixture with light of $\lambda > 300$ nm then reproduced the IR bands ascribable to **B** at the expense of those of **A**. The UV/vis spectral changes were not so prominent as those of IR, but they exhibited similar photo-interconversion (Fig. 2).

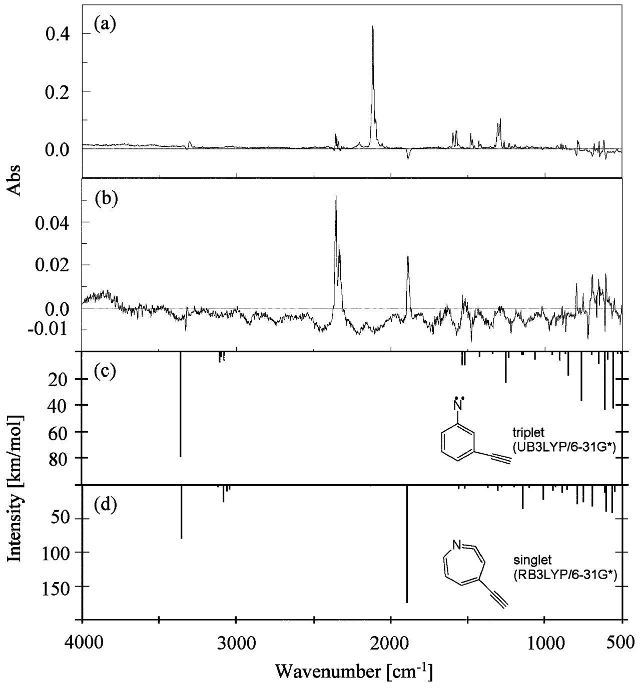


Fig. 1 Difference IR spectrum showing the photochemistry of 3-ethynylphenyl azide (*m*-**1a**-N_3) matrix-isolated in argon at 13 K. (a) Bands pointing upward are that of *m*-**1a**-N_3 and bands pointing downward are appearing upon irradiation at $\lambda > 300$nm. (b) Bands pointing downward are appearing upon subsequent irradiation at $\lambda > 420$ nm of the initial photoproduct from *m*-**1a**-N_3 upon irradiation at $\lambda > 300$ nm. (c) Calculated IR spectrum for triplet 3-ethynylphenylnitrene (*m*-**1a**-N). (d) Calculated IR spectrum for 4-ethynyl(aza)-cycloheptatetraene (*m*-**1a**-AZA).

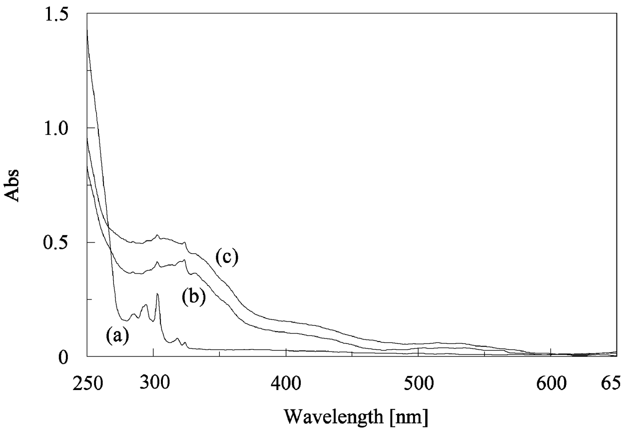
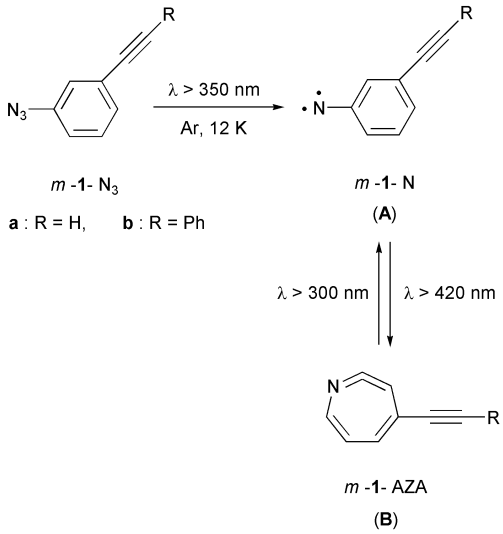


Fig. 2 (a) UV/vis spectrum of 3-ethynylphenyl azide (*m*-**1a**-N_3) matrix-isolated in argon at 13 K. (b) UV/vis spectrum obtained by irradiation of (a) at $\lambda > 420$ nm. (c) UV/vis spectrum obtained by irradiation of (b) at $\lambda > 300$ nm.

What are these photoproducts? Analysis of the major IR bands provided some insights into their structures. First, the appearance of an intense 1888 cm^{-1} band in **B** suggested the presence of a strained heterocumulene bond, indicating an aza-1,2,4,6-cycloheptatetraene structure for **B**. Only a slight shift of the acetylenic C–H absorption band in going from **1** to **B**, then, suggested that the ethynyl group was intact during this transformation. Thus, 4-ethynyl-1,2,4,6-azacycloheptatetraene (*m*-**1a**-AZA) was proposed as the most probable structure for **B**, which can be formed by loss of nitrogen from *m*-**1**-N_3, followed by ring expansion of the resulting nitrene (*m*-**1a**-N). The product **A**, which is interconvertible with **B** upon irradiation under these conditions, is then likely assignable to 3-ethynylphenylnitrene (*m*-**1a**-N) in its triplet state (Scheme 2).



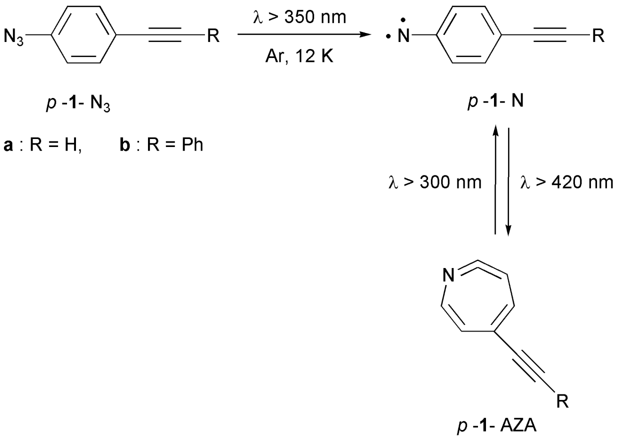
Scheme 2

Further assignment of the IR spectra of *m*-**1a**-AZA and *m*-**1a**-N was accomplished by comparison with the DFT calculation[19–21] at the UB3LYP/6-31G* level of theory (Table S1 and Fig. 1). The vibrational frequencies were calculated for those compounds and were compared with the experimental vibrational frequencies observed with *m*-**1a**-AZA and *m*-**1a**-N, which indicated that the calculated frequencies match the experimental data reasonably well.

Support is lent to this assignment by ESR studies. When the photolysis ($\lambda > 350$ nm) of *m*-**1**-N_3 in 2-methyltetrahydrofuran (2-MTHF) matrix at 77 K was monitored by ESR, a sharp signal appeared at around 700 mT. On the basis of the calculated zero-field splitting (ZFS) parameter ($|D/hc| = 1.15$ cm^{-1}) in comparison with that of triplet phenylnitrene,[22] this signal is assigned to triplet 3-ethynylphenylnitrene (*m*-**1a**-N). The intensity of the signal was decreased upon irradiation with light at $\lambda > 420$ nm but was recovered upon irradiation with light at $\lambda > 300$ nm. Thus, the interconversion between a triplet nitrene (*m*-**1a**-N) and the tetraene (*m*-**1a**-AZA) is suggested.

Essentially, the same chemistry was observed in the photolysis of 1-(3-azidophenyl)-2-phenylacetylene (*m*-**1b**-N_3), a phenylated derivative of **1a**. Thus, the irradiation generated triplet 4-(phenylethynyl)phenylnitrene (*m*-**1b**-N) and 4-(phenylethynyl)-1,2,4,6-azacycloheptatetraene (*m*-**1b**-AZA), which were again shown to be photointerconvertible under these conditions (Scheme 2, Fig. S1).

Irradiation of the *p*-isomers (*p*-**1**-N_3) afforded similar results. Thus, the irradiation resulted in the formation of triplet nitrene (*p*-**1**-N) and azacycloheptatetraene (*p*-**1**-AZA), which were interconvertible upon irradiation (Scheme 3). Again, the spectra calculated for *m*-**1b**-AZA and *m*-**1b**-N fit the experimental spectra (Fig. 3). An intriguing difference was observed, however, between the structures of the two nitrenes, *m*-**1**-N and *p*-**1**-N. The UV/vis spectra (Fig. 4) and ESR showed that spin delocalization into the ethynyl groups is more significant in the *p*-isomer than in the *m*-isomer. Thus, the ZFS parameters for *p*-**1a**-N and *p*-**1b**-N are estimated to be 1.01 and 0.93 cm^{-1}, respectively.[23] More prominently, the UV/vis spectra of *p*-**1**-N exhibited a series of sharp absorptions in the visible region, which are to be compared with that of the *m*-isomer. Thus, the smaller *D* values in ESR as well as the structured bands in the visible region both suggest that, in *p*-**1**-N, the contribution of the quinoidal structure as a result of the delocalization of the unpaired electrons is important.



Scheme 3

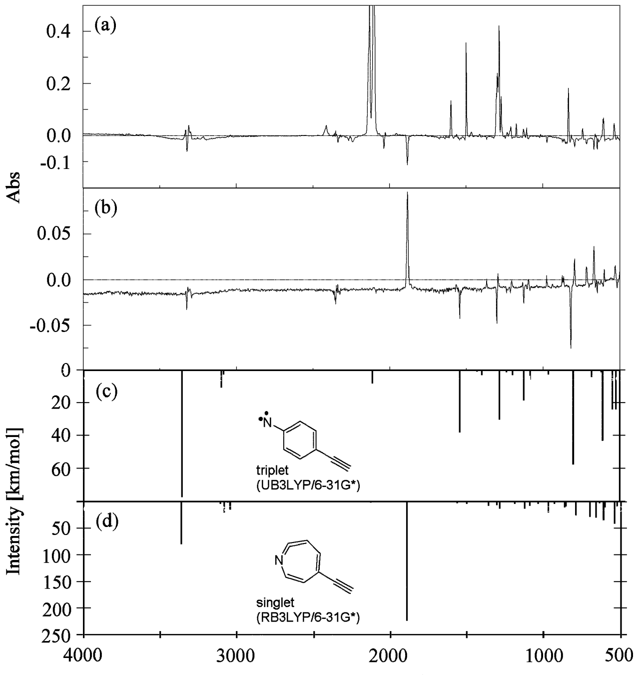


Fig. 3 Difference IR spectrum showing the photochemistry of 4-ethynylphenyl azide (*p*-**1a**-N_3) matrix-isolated in argon at 13 K. (a) Bands pointing upward are those of *p*-**1a**-N_3 and bands pointing downward are appearing upon irradiation at λ > 420nm. (b) Bands pointing downward are appearing upon subsequent irradiation at λ > 366 nm of the initial photoproduct from *p*-**1a**-N_3 upon irradiation at λ > 420nm. (c) Calculated IR spectrum for triplet 4-ethynylphenylnitrene (*p*-**1a**-N). (d) Calculated IR spectrum for 5-ethynyl(aza)cycloheptatetraene (*p*-**1a**-AZA).

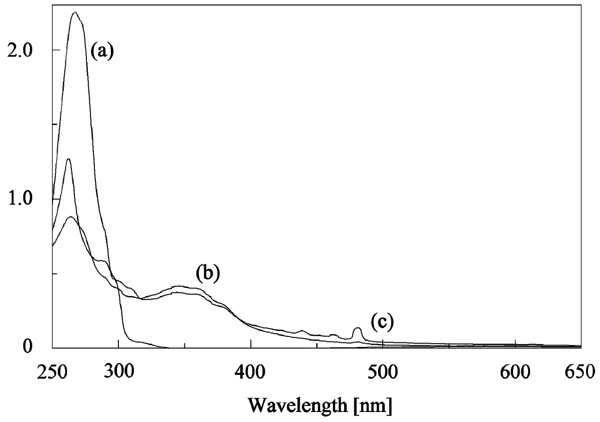


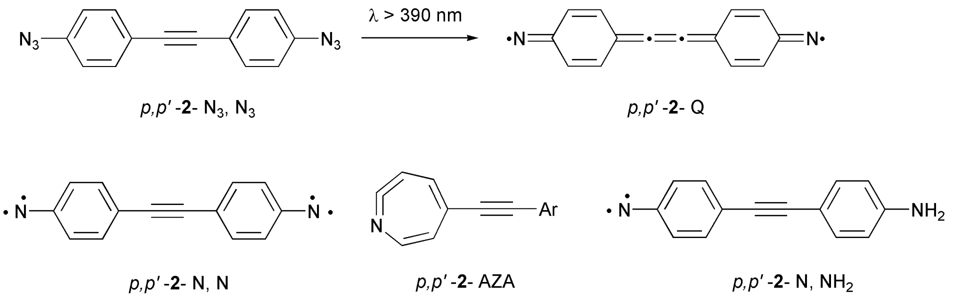
Fig. 4 (a) UV/vis spectrum of 4-ethynylphenyl azide (*p*-**1a**-N_3) matrix-isolated in argon at 13 K. (b) UV/vis spectrum obtained by irradiation of (a) at λ > 420 nm. (c) UV/vis spectrum obtained by irradiation of (b) at λ > 366 nm.

It is noteworthy that those sharp absorptions are red-shifted from 444, 468, and 487 to 506, 522, and 566 nm, respectively, on going from *p*-**1a**-N to *p*-**1b**-N. This can be interpreted to indicate that, in *p*-**1b**-N, the delocalization of the unpaired electrons onto the terminal phenyl ring is also important.

Photolysis of bis(azidophenyl)acetylenes (2)

***p,p′*-Isomer.** Irradiation (λ > 390 nm) of *p,p′*-**2**-N_3,N_3 matrix-isolated in Ar at 10 K resulted in the rapid and complete disappearance of strong bands characteristic of azide groups, indicating that both azide groups were destroyed to generate bis(nitrene). New bands formed upon irradiation showed a rather strong and sharp absorption band at 822 cm^{-1} along with small bands at 962, 1082, and 1230 cm^{-1}, but they exhibited no absorption in the region of 1780 to 1990 cm^{-1}, where bands ascribable to strained cumulenic bonds appeared (Fig. 5). The initial photoproduct was photostable under these conditions. This suggests that nitrene generated from *p,p′*-**2**-N_3,N_3 is photostable and does not undergo ring-enlargement to form azacycloheptatetraene, *e.g.*, *p,p′*-**2**-AZA, even upon photoexcitation. The matrix also took on a distinct pink color, and a series of sharp strong absorptions was observed at 333, 398, 401, 420, and 475 nm in the UV/vis spectrum. These strong absorptions in the visible region indicate the presence of the extended π-system (Fig. 6a). Therefore, bisnitrene exists as a delocalized bisquinoimine structure (*p,p′*-**2**-Q) rather than localized bis(nitrene) (*p,p′*-**2**-N,N) (Scheme 4). Similar structured absorptions were observed in the photolysis of 4,4′-diazidostilbene, in which the bisquinimine structure was also proposed.[13a] Actually, the vibrational frequencies calculated for the delocalized bis(iminoquinone) diradical (triplet) match the experimental vibrational frequencies observed for the photoproduct from *p,p′*-2-N_3,N_3 fairly well (Fig. 5).

In order to gain more insights into the structure of the bisnitrene, the photolysis was monitored by ESR in 2-MTHF at 77 K, which indicated a sharp signal at 642 mT ascribable to a triplet mononitrene ($|D/hc|$ = 0.92 cm^{-1}) along with weak signals at 472 and 63 mT and a signal in the g'= 2 region (Fig. 7a). When the photolysis of *p,p′*-**2**-N_3,N_3 was monitored by the UV/vis spectra in the same matrix at 77 K, strong absorptions in the region of 400 to 650 nm were observed (Fig. S2). Comparison of the absorptions with those observed in argon matrices at



Scheme 4

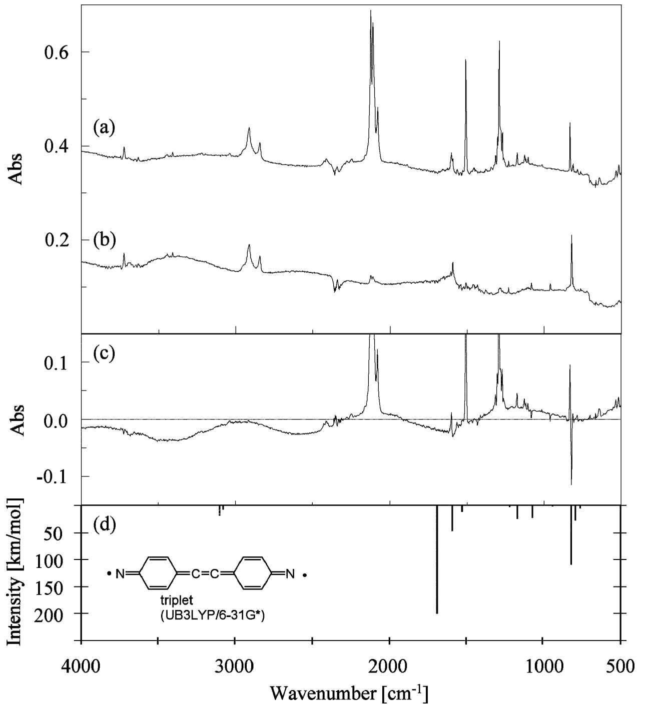


Fig. 5 (a) IR spectrum of 1,2-bis(4-azidophenyl)acetylene (*p,p′*-**2**-N_3,N_3) matrix-isolated in argon at 13 K. (b) IR spectrum obtained by irradiation of (a) at $\lambda > 390$ nm. (c) Changes in the IR bands upon irradiation (a − b). (d) Calculated (UB3LYP/6-31G*) IR spectrum for triplet quinoidal diradical (*p,p′*-**2**-Q).

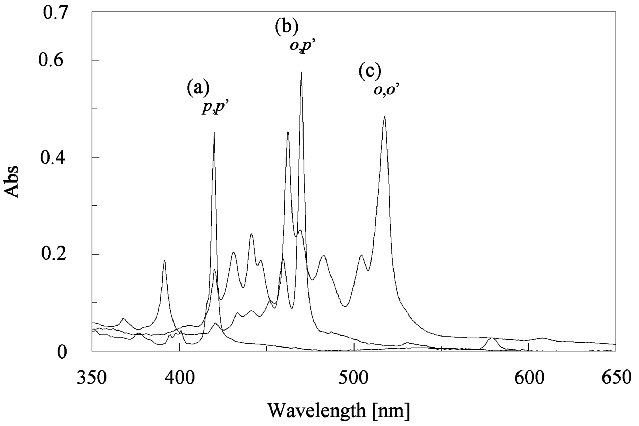


Fig. 6 UV/vis spectrum obtained by irradiation ($\lambda > 390$ nm) of (a) 1,2-bis(4-azidophenyl)acetylene (*p,p′*-**2**-N_3,N_3), (b) 1-(2-azidophenyl)-2-(4-azidophenyl)acetylene and (*p,o′*-**2**-N_3,N_3), and (c) 1,2-bis(2-azidophenyl)acetylene (*o,o′*-**2**-N_3,N_3) in argon at 13 K.

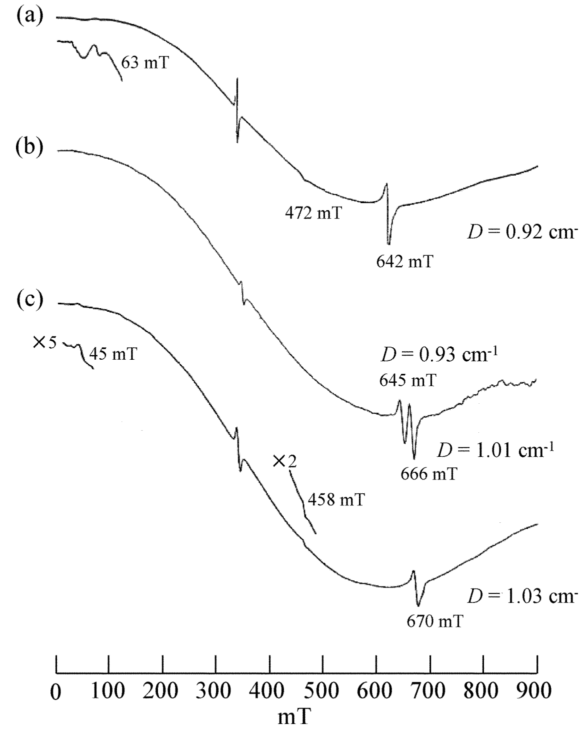
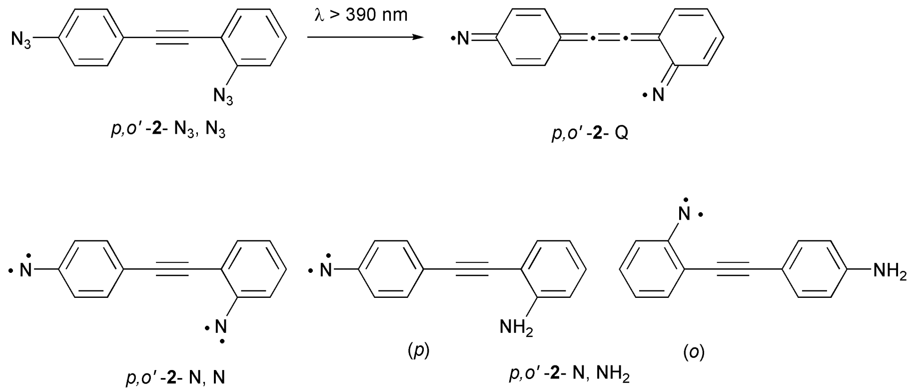


Fig. 7 ESR spectrum obtained by irradiation ($\lambda > 390$ nm) of (a) 1,2-bis(4-azidophenyl)acetylene (*p,p′*-**2**-N_3,N_3), (b) 1-(2-azidophenyl)-2-(4-azidophenyl)acetylene (*p,o′*-**2**-N_3,N_3) and (c) 1,2-bis(2-azidophenyl)acetylene (*o,o′*-**2**-N_3,N_3) in 2-methyltetrahydrofuran at 77 K.

10 K indicated that the bands at 389, 421, and 445 nm are similar to those generated in the noble gas matrix, although they are broad and red-shifted. However, bands at 492, 532, and 648 nm are not seen in the argon matrix, suggesting that new products are produced under these conditions. One of the probable reactions under these conditions is the hydrogen atom abstraction of nitrenes from matrices, which eventually results in the formation of the amino-nitreno compound *p,p′*-**2**-N,NH_2.[13,14] It has been shown that 4′-amino-4-nitrenostilbene exhibits weak absorptions around 500–700 nm.[13b] Thus, the species showing a sharp signal at 642 mT is assigned as 4′-amino-4-nitrenotolan (*p,p′*-**2**-N,NH_2). The peak at *ca.* 335 mT varies with the irradiation conditions and is due to radical impurities that are often observed in the irradiation of aryl azides.[14]

The origin of the weak signals at 472 and 63 mT is not clear at present. They may be some of the signals ascribable to the triplet state of the quinoidal diradical (*p,p′*-**2**-Q). It is to be noted here that the quinoidal triplet diradical form of 1,4-phenylene dinitrene,[11] 4,4-biphenyl dinitrene[12] and 4,4′-stilbene dinitrene[13a] show signals at 138, 243 and 416 mT ($|D/hc| = 0.169$ cm^{-1}), 116, 205 and 411 mT ($|D/hc| = 0.02$ cm^{-1}), and 148, 258 and 389 mT($|D/hc| = 0.122$ cm^{-1}), respectively.

***p,o′*-Isomer.** Similar results are observed in the irradiation of *p,o′*-isomer (*p,o′*-**2**-N_3,N_3). Thus, no absorptions ascribable to a strained cumulenic double bond were observed in the IR spectra of the photoproducts from those bisazide compounds. Again, the vibrational frequencies calculated for the quinoidal diradical (triplet state) fit the experimental spectrum nicely (Fig. 8). A series of sharp absorptions was observed in the region of 400 to 600 nm in the UV/vis spectra (Fig. 6b). These



Scheme 5

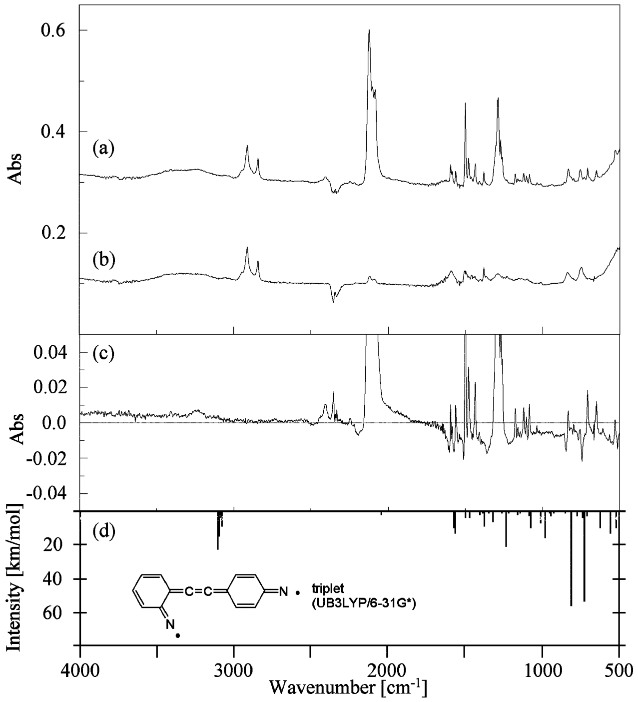


Fig. 8 (a) IR spectrum of 1-(4-azidophenyl)-2-(2-azidophenyl)acetylene (*p,o'*-**2**-N_3, N_3) matrix-isolated in argon at 13 K. (b) IR spectrum obtained by irradiation of (a) at $\lambda > 390$ nm. (c) Changes in the IR bands upon irradiation (a − b). (d) Calculated (UB3LYP/6-31G*) IR spectrum for triplet quinoidal diradical (*p,o'*-2-Q).

observations are consistent with the assumption that the species exist as quinoidal diradical structures (*p,o'*-**2**-Q) rather than as localized dinitrene species (*p,o'*-**2**-N,N) (Scheme 5).

ESR studies again showed the presence of signals attributable to triplet mononitrenes (Fig. 7b). Photolysis of the *p,o'*-isomer (*p,o'*-**2**-N_3,N_3) in 2-MTHF at 77 K, for instance, resulted in the formation of signals at 666 mT ($|D/hc| = 1.01$ cm^{-1}) and 645 mT ($|D/hc| = 0.93$ cm^{-1}), both attributable to triplet mononitrenes. Assuming again that triplet nitrenes undergo a hydrogen-abstraction reaction, these two mononitrenes are assigned to *o*- and *p*-amino(nitreno)tolans (*p,o'*-**2**-N,NH_2). The signals in a low-field region were too weak to be observable in this case.

***o,o'*-Isomer.** The irradiation *o,o'*-isomer (*o,o'*-**2**-N_3,N_3) gave similar results (Scheme 6). The experimental vibrational frequencies observed for photoproducts match those calculated for quinoidal diradicals (triplet) fairly well (Fig. 9).

A series of sharp absorptions is noted in the region of 400 to 600 nm (Fig. 6c). It is noteworthy that those bands in the visible region are notably shifted in going from the *p,p'*- to *p,o'*- to *o,o'*- isomer. This is in accord with the increasing length of the π-conjugation system.

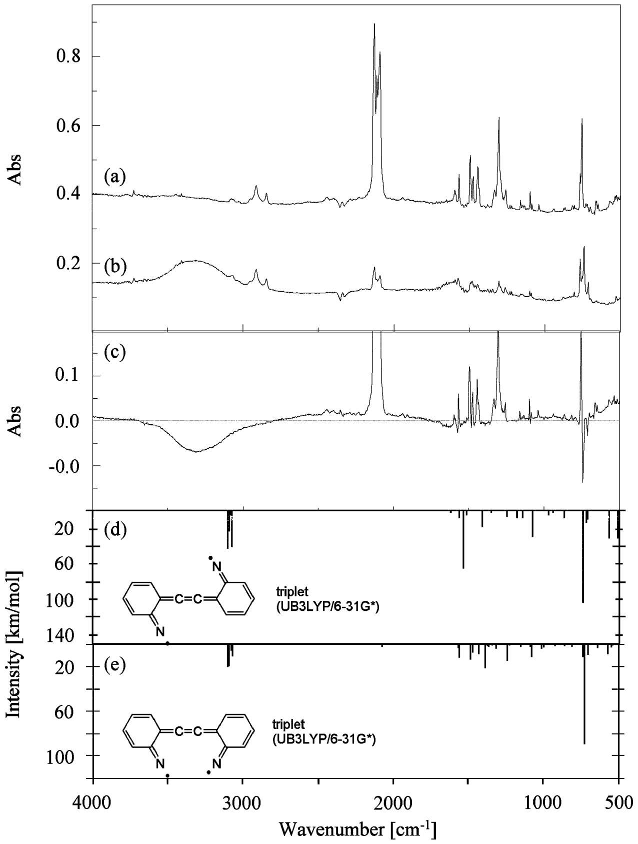
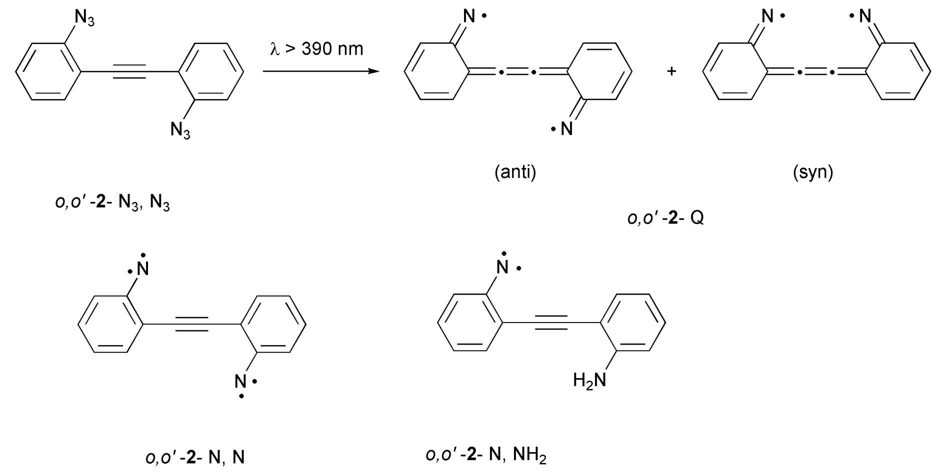


Fig. 9 (a) IR spectrum of 1,2-bis(2-azidophenyl)acetylene (*o,o'*-**2**-N_3,N_3) matrix-isolated in argon at 13 K.(b) IR spectrum obtained by irradiation of (a) at $\lambda > 390$ nm. (c) Changes in the IR bands upon irradiation (a − b). (d) and (d') Calculated (UB3LYP/6-31G*) IR spectrum for triplet quinoidal diradical (*o,o'*-**2**-Q).

Only one mononitrene signal (679 mT, $|D/hc| = 1.03$ cm^{-1}) was observed in this case, as expected from the structure. Very weak signals at 458 and 45 mT, presumably attributable to the triplet state of quinoidal diradicals, are also observable (Fig. 7c).

***m,m'*-Isomer.** Photolysis of the *m,m'*-isomer (*m,m'*-**2**-N_3,N_3) gave somewhat different results. Thus, irradiation ($\lambda > 350$ nm) of *m,m'*-**2**-N_3,N_3 matrix-isolated in Ar at 10 K gave a product exhibiting an absorption band at 1892 cm^{-1} in the IR spectra, as the strong bands due to azide groups disappeared (Fig. 10). These spectroscopic features suggest that the species formed as a result of the photodenitrogenation of *m,m'*-**2**-N_3,N_3 is mainly azacycloheptatetraene (*m,m'*-**2**-AZA) rather than bis(nitrene) (*m,m'*-**2**-N,N) (Scheme 7). Unlike its mononitrene analogue, *i.e.*, *m*-**1**-N, the species was photostable under these conditions. The UV/vis spectra of the photoproduct exhibited rather broad



Scheme 6

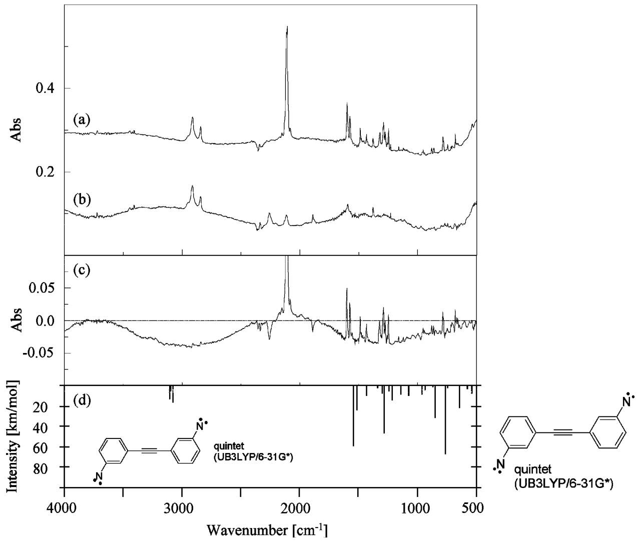
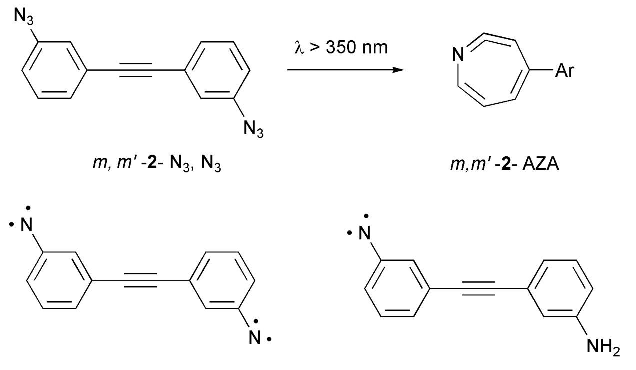


Fig. 10 (a) IR spectrum of 1,2-bis(3-azidophenyl)acetylene (*m,m'*-**2**-N_3,N_3) matrix-isolated in argon at 13 K.(b) IR spectrum obtained by irradiation of (a) at $\lambda > 390$ nm. (c) Changes in the IR bands upon irradiation (a − b). (d) Calculated (UB3LYP/6-31G*) IR spectrum for quintet bis(nitrene) (*m,m'*-**2**-N,N).



Scheme 7

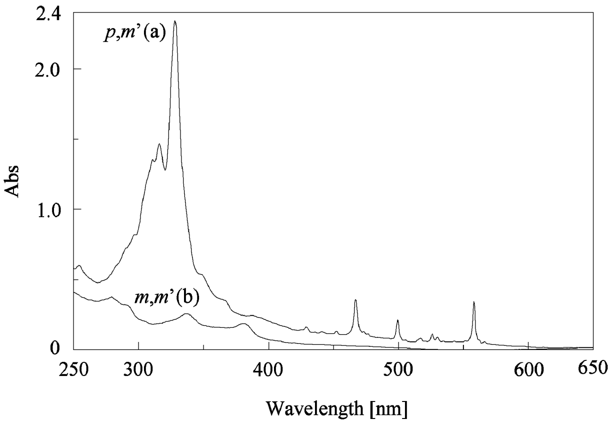


Fig. 11 UV/vis spectrum obtained by irradiation ($\lambda > 390$ nm) of (a) 1-(4-Azidophenyl)-2-(3-azidophenyl)acetylene (*p,m'*-**2**-N_3,N_3); (b) 1,2-bis(3-azidophenyl)acetylene (*m,m'*-**2**-N_3,N_3) in argon at 13 K.

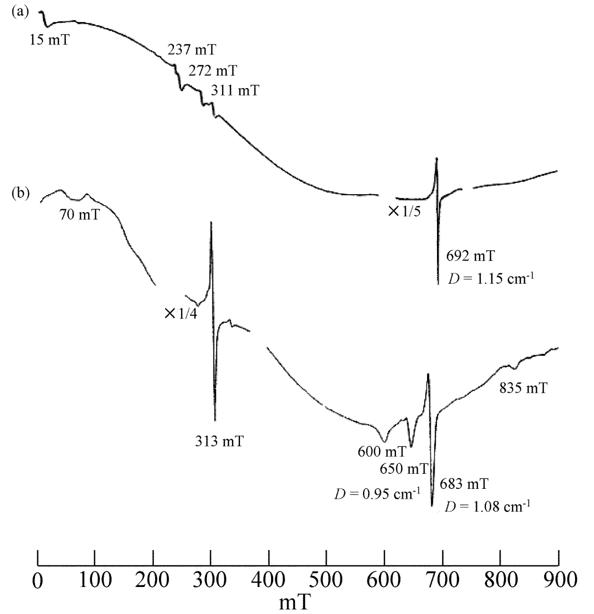


Fig. 12 ESR spetrum obtained by irradiation ($\lambda > 390$ nm) of (a) 1,2-bis(3-azidophenyl)acetylene (*m,m'*-**2**-N_3,N_3). (b) 1-(4-Azidophenyl)-2-(3-azidophenyl)acetylene (*p,m'*-**2**-N_3,N_3) in 2-methyltetrahydrofuran at 77 K.

bands at 382 and 336 nm without showing structured absorption bands in the visible region (Fig. 11a).

The ESR spectra obtained by the photolysis ($\lambda > 350$ nm) of *m,m'*-**2**-N_3,N_3 in 2-MTHF at 77 K were essentially similar to those observed in the same matrix at 10 K (Fig. 12a).[14] Thus, weak signals at 15, 272, 311, and 860 mT were assignable to the quintet states of bisnitrene *m,m'*-**2**-N,N. It has been demonstrated that bisnitrene (*m,m'*-**2**-N,N) has singlet ground states with thermally populated triplet and quintet states above the ground state.[14] A rather strong signal at 692 mT ($|D/hc| = 1.15$ cm^{-1}) can be assignable to a mononitrene. Since a signal assignable to a doublet free radical was not prominent in this case and since the formation of azacycloheptatetraene is clearly shown by IR experiments, aza-nitrene rather than amino-nitrene is suggested to be a product in this case.

***p, m′*-Isomer.** Irradiation of the *p,m′*-isomer (*p,m′*-**2**-N_3,N_3), on the other hand, led to different results from those observed in the photolysis of the *m,m′*-isomer. Thus, irradiation (λ > 350 nm) of *p,m′*-**2**-N_3,N_3 matrix-isolated in Ar gave a species showing no absorptions in 2000–1800 cm^{-1}, indicating that azacycloheptatetraene is not formed (Fig. 13). The spectra of the initial photoproduct changed very little upon continued irradiation under these conditions, indicating that the product is photostable. The observed IR bands fit those calculated for bis(nitrene) with the quintet state fairly well (Scheme 8).

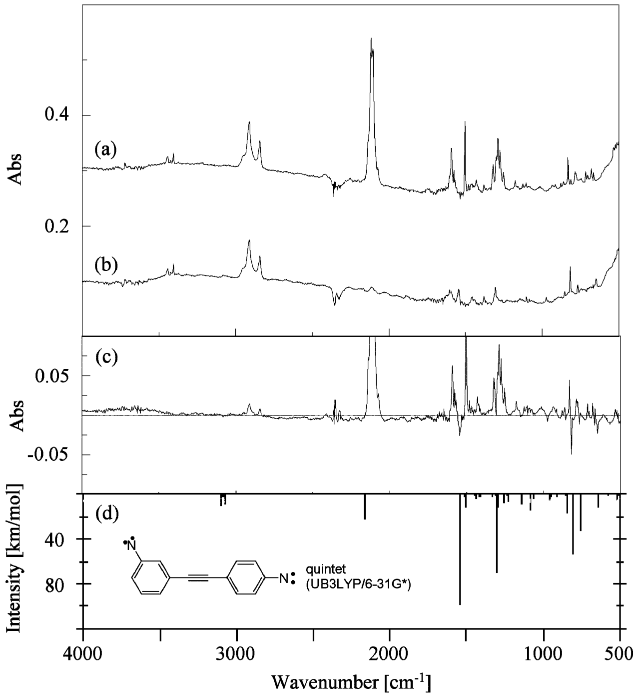


Fig. 13 (a) IR spectrum of 1-(4-azidophenyl)-2-(3-azidophenyl)-acetylene (*p,m′*-**2**-N_3,N_3) matrix-isolated in argon at 13 K. (b) IR spectrum obtained by irradiation of (a) at λ > 390 nm. (c) Changes in the IR bands upon irradiation (a − b). (d) Calculated (UB3LYP/6-31G*) IR spectrum for quintet bis(nitrene) (*p,m′*-**2**-N,N).

ESR spectra obtained by irradiation of the bisazide in 2-MTHF at 77 K are again essentially the same as those obtained in the photolysis at 10 K (Fig. 12b). Thus, they consisted of weak signals at 90–150 mT and around 834 mT and an intense signal at 303 mT, all ascribable to the dinitrene in quintet states. Two signals at 650 ($|D/hc|$ = 0.95 cm^{-1}) and 683 mT ($|D/hc|$ =1.08 cm^{-1}) ascribable to mononitrene are observed in this case. Since a signal due to a doublet free radical was also detected, these signals are assignable to amino-nitrenes, *i.e.*, (*p*-aminophenyl) (*m*-nitrenophenyl) and (*p*-nitrenophenyl) (*m*-aminophenyl) acetylenes. Again, taking into account the effect of *para* substituents on the *D* value, the mononitrene with the lower *D* value is assigned to the nitrene with the ethynyl substituent at the *para* position.

Discussion

The present investigation on the characterization of transient photoproducts from mono- and diazides employing versatile spectroscopic methods in combination with theoretical calculations revealed the nature of the photochemical process and the transient species in some detail.

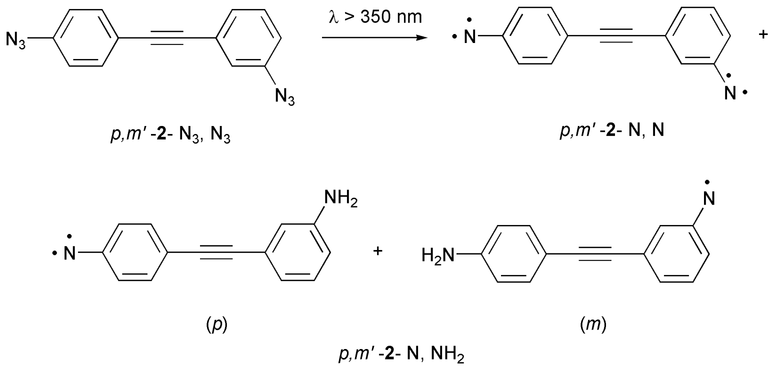
Due to the limitation of the experimental setup in this laboratory, it was impossible to obtain all the spectra in the same medium. Therefore the comparison of the IR and UV/vis data (obtained in argon matrix) with ESR data (observed in organic matrix) should be made with care by taking into account possible reactions with the solvents in the latter.

On the other hand, matching of calculated bands and experimental ones are not always very good. This is partly because some of the product IR bands were extremely weak which prevented us from obtaining apparent overall spectrum. Also, the limitation of DFT with open-shell diradicals and cumulenes should be taken into account.[24]

The introduction of phenylethynyl groups on phenyl azides shows little effect on the photochemical pathway. Thus, upon photoexcitation, (phenylethynyl)phenyl azides afforded the corresponding triplet nitrene, which is in photoequilibrium with the corresponding azacycloheptatetraene.

In marked contrast, azidophenylethynyl groups exhibited a dramatic effect not only on the photochemical pathway of phenyl azides but also on the electronic and molecular structure of the photoproducts. The patterns of the effect depend upon the relative position of the azide groups in the diphenylacetylene unit.

Whenever two azide groups were situated in the conjugating position with respect to each other, as in *p,p′*-, *o,o′*-, and *o,p′*-bis(azides), the azides always resulted in the formation of a quinoidal diimine diradical in which unpaired electrons were extensively delocalized in the π-conjugation framework. Geometries optimized by UB3LYP/6-31G(d) for the triplet biradical states clearly displayed bond alternation in the benzene ring and the ethynyl bond, suggesting the contribution of an extensively delocalized form. Even though quinoidal dinitrenes with triplet biradical states were detected, the ground state multiplicities of the diradical are not characterized in the present study. It has been shown that analogous quinoidal dinitrenes, such as 1,4-phenylenedinitrene,[11] 4,4-biphenyldinitrene,[12] 4,4′-stilbenedinitrene,[13] 1,4-bis(*p*-nitrenophenyl)-1,3-butadiene,[13c,d] and 1,8-bis(*p*-nitrenophenyl)-1,3,5,7-octatetraene,[13c,d] all have a singlet biradical ground state with a very small singlet-triplet energy gap of 150 to 600 cal mol^{-1}. Therefore, it is likely that the triplet biradical detected in the present system is in the thermally excited state.



Scheme 8

The situation changed rather dramatically when the azide groups were introduced in the *meta* position. Thus, the formation of azacycloheptatetraene was noted in the photolysis of the *m,m′*-isomer. ESR studies indicated the generation of the quintet state, which is shown to be a thermally populated state with a very small energy gap of *ca.* 100 cal mol^{-1}. It is interesting to note here that neither the quintet state nor the corresponding lower-lying singlet state of the dinitrene was characterized by the matrix-IR study. It is rather difficult to estimate the relative ratio of two species formed under two very different conditions. It is possible that nitrene generated in a rare-gas matrix at a very low temperature has more opportunities to undergo a ring-expansion reaction than nitrene in an organic matrix at 77 K. This is so because photochemical processes in noble gas matrices sometimes result in the generation of reactive intermediates in a vibrationally excited state and undergo subsequent reactions faster than when they cool off to thermally relaxed states.[25] However, in organic matrices, the intermediates can be easily relaxed by increasing the number of vibrational modes of the host molecules (see below, however). Strong EPR signals ascribable to mononitrene can be assigned to aza-nitrene rather than amino-nitrene. The intensity of this signal is stronger than those ascribable to the quintet state even though the population of this state is fairly high at this high temperature. The observation suggests that aza-nitrene formation is dominant even under these conditions.

The *p,m′*-isomer is shown to be an excellent precursor for high-spin quintet dinitrene. The IR spectra of the photoproduct showed no bands ascribable to azacycloheptatetraene, and the observed spectra are in good agreement with that calculated for the quintet state. Strong EPR signals assignable to the quintet state have been observed along with rather weak signals due to mononitrenes. Moreover, the quintet bis(nitrene) is rather photostable under these conditions; IR bands due to the quintet dinitrene showed no change even upon prolonged irradiation under these conditions.

Finally, monoazide derivatives to be formed by step-wise extrusion of a nitrogen molecule were not observed in the photolysis of bis(azides) in the Ar matrix. Only one photon was consumed for the extrusion of dinitrogen in the photolysis of the bis(diazo) precursor to generate dicarbene in the solid states at a cryogenic temperature.[26] Thus, the present observations suggest that similar one-photon processes took place in the photolysis of bis(diazides) at low temperature.

In 2-MTHF matrix at 77 K, on the other hand, the exact nature of the photo-deazetation process is not clear. However it is rather sensitive to the structure of the precursor bis(azides). For instance, in the case of the *m,m′* isomer, one photon double deazetation is probably a major process, while in the case of *p,m′* isomer, stepwise deazetation is the more likely process. It is to be noted here that, in the photolysis of polydiazo compounds in 2-MTHF matrix at low temperatures, photo-deazetation processes are sensitive to experimental conditions such as wavelength and intensities of the light and concentration of the precursor.[27] Further work is needed to make the process clearer.

Experimental section

General methods

^{1}H-NMR spectra were recorded on a JEOL JNM-AC300FT/NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured on a JASCO-Herschel FT/IR-600H spectrometer and UV/vis spectra were recorded on a JASCO CT-560 spectrophotometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO, Model HLC-01 instrument. The GPC column was a Shodex H-2001. Thin layer chromatography was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed on silica gel (Fuji Davidson) for column chromatography or ICN for dry column chromatography.

Materials

All the azides prepared below showed one spot in TLC.

4-Ethynylphenyl azide (*p*-1a-N_3). To a cooled solution of 4-iodoaniline (1.00 g, 4.57 mmol) and conc. HCl (8 ml) in H_2O (8 ml) was slowly added a solution of $NaNO_2$ (0.378 g, 5.36 mmol) in H_2O (5 ml) at 0 °C and the mixture was stirred for 1 h in the dark. The precipitate was filtered and the filtrate was then added to a cooled solution of NaN_3 (0.594 g, 9.14 mmol) in H_2O (5 ml) at 0 °C. After stirring for 1 h at 0 °C in the dark, the precipitate formed was filtered and purified by preparative TLC to afford **4-iodophenyl azide** (0.98 g, 81%) as a yellowish solid: mp 30.4–31.3 °C; ^{1}H-NMR ($CDCl_3$) δ 7.62 (d, J = 8.91 Hz, 2 H), 6.77 (d, J = 8.91 Hz, 2 H); IR (KBr) ν 2128 cm^{-1}. A solution of the azide (200 mg, 0.81 mmol) and trimethylsilylacetylene (0.113 ml, 0.81 mmol) in anhydrous NEt_3 (3 ml) was carefully degassed by repeated cycles of evacuation and purge with argon. To the mixture was added $(Ph_3P)_2PdCl_2$ (5 mg) and CuI (4 mg) and the resulting mixture was stirred for 24 h at room temp. Solvent was evaporated to leave the residue which was purified by TLC to give **4-trimethylsilylethynylphenyl azide** (55 mg, 31%) as a reddish liquid: ^{1}H-NMR ($CDCl_3$) δ 7.44 (d, J = 8.58 Hz, 2 H), 6.94 (d, J = 8.58 Hz, 2 H), 0.25 (s, 9 H); IR (KBr) ν 2112 cm^{-1}. The azide (40 mg, 0.196 mmol) was added to a solution of 1 M NaOH aq (1 ml) in MeOH (3 ml) and stirred for 3 h at room temp. The mixture was evaporated and extracted with Et_2O (20 ml × 3). The organic layer was dried and evaporated. The residue which was purified by preparative TLC (*n*-hexane) to give **4-ethynylphenyl azide** (20 mg, 71%) as a yellow solid: mp 23–24 °C; ^{1}H-NMR ($CDCl_3$) δ 7.47 (d, J = 8.58 Hz, 2 H), 6.98 (d, J = 8.58 Hz, 2 H), 3.08 (s, 1 H); IR (KBr) ν 2104 cm^{-1}.

3-Ethynylphenyl azide (*m*-1a-N_3). To a degassed solution of 3-iodonitrobenzene (160 mg, 0.65 mmol) and trimethylsilylacetylene (90 µl, 0.65 mmol) in anhydrous NEt_3 (2 ml) was added a catalytic amount of $(Ph_3P)_2PdCl_2$ and CuI. The mixture was worked up as described above to give **3-trimethylsilylnitrobenzene** (129 mg, 89%) as a yellow solid: mp 52.3–53.1 °C; ^{1}H-NMR ($CDCl_3$) δ 8.30 (s, 1 H), 8.15 (d, J = 8.25 Hz, 1 H), 7.95 (d, J = 7.91 Hz, 1 H), 7.48 (dd, J = 7.91, 8.25 Hz, 1 H), 0.25 (s, 9 H). To a solution of the nitrobenzene (206 mg, 0.92 mmol) in AcOH (3 ml) was slowly added Fe (250 mg) under vigorous stirring at 60–70 °C and the mixture was vigorously stirred for 5 min. After adding Fe (125 mg), the mixture was stirred for 12 h. After cooling to room temp, the mixture was made alkaline with 20% NaOH aq and extracted with Et_2O (3 × 20 ml). The organic layer was washed with H_2O, dried (Na_2SO_4) and evaporated to dryness. The crude 3-trimethylsilyllethynylaniline (162 mg) was diazotized, followed by addition of NaN_3 as described above. After usual work-up, followed by preparative TLC (*n*-hexane) **3-(trimethylsily)lethynylphenyl azide** was obtained as a yellow liquid (67 mg, 40%): ^{1}H-NMR ($CDCl_3$) δ 7.33–7.23 (m, 2 H), 7.12 (d, J = 1.66 Hz, 1 H), 6.96 (dd, J = 7.26, 1.66 Hz, 1 H), 0.25 (s, 9 H); IR (KBr) ν 2112 cm^{-1}. The azide (67 mg, 0.34 mmol) was desilylated as described above to give **3-ethynylphenyl azide** (*m*-**1a**-N_3) as a yellow liquid (27 mg, 54%): ^{1}H-NMR ($CDCl_3$) δ 7.38–7.25 (m, 2 H), 7.15 (d, J = 1.65 Hz, 1 H), 7.00 (dd, J = 7.26, 1.65 Hz, 1 H), 3.08 (s, 1 H); IR (KBr) ν 2112 cm^{-1}.

2-Ethynylphenyl azide (*o*-1a-N_3). In the manner described for *p*-**1a**-N_3, 2-iodoaniline was converted to 2-iodophenyl azide (60%, orange liquid, ^{1}H-NMR ($CDCl_3$) δ 788 (dd, J = 1.32, 7.98 Hz, 1 H), 7.42–7.36 (m, 1 H), 7.13 (dd, J = 1.32, 7.92 Hz, 1 H), 6.89–6.83 (m, 1 H); IR (KBr) ν 2128cm^{-1}). The azide was then coupled with trimethylsilylacetylene, followed by desilylation with base to give **2-ethynylphenyl azide** as a white solid in 60% yield: mp 25.3–27.1 °C; ^{1}H-NMR ($CDCl_3$) δ 7.32 (dd, J = 1.32, 7.79 Hz, 1 H); 7.23–7.18 (m, 1 H), 6.99–6.90 (m, 2 H), 3.24 (s, 1 H); IR (KBr) ν 2112 cm^{-1}.

1-(4-Azidophenyl)-2-phenylacetylene (*p*-1b-N$_3$). To a degassed solution of 4-ethynylphenyl azide (100 mg, 0.41 mmol) and phenylacetylene (45 µl, 0.41 mmol) in NEt_3 (2 ml) was added a catalytic amount of $(Ph_3P)_2PdCl_2$ and CuI. The mixture was worked up as described above to give the desired acetylene (*p*-**1b**-N$_3$) as a yellow solid (78 mg, 85%): mp 60.3–61.1 °C; ^{1}H-NMR ($CDCl_3$) δ 7.53–7.50 (m, 5 H), 7.35–7.33 (m, 2 H), 7.01 (d, J = 8.58 Hz, 2 H); IR (KBr) ν 2118 cm^{-1}.

1-(3-Azidophenyl)-2-phenylacetylene(*m*-1b-N$_3$). **1-(3-Nitrophenyl)-2-phenylacetylene** was prepared by Sonogashira coupling of 3-iodonitrobenzene (100 mg, 0.41 mmol) with phenylacetylene (45 µl, 0.41 mmol) as a pale yellow solid (63 mg, 69%): mp 102.5–104.0 °C; ^{1}H-NMR ($CDCl_3$) δ 8.36 (s, 1 H), 8.17 (d, J = 8.58 Hz, 1 H), 7.81 (d, J = 7.59 Hz, 1 H), 7.57–7.35 (m, 6 H). The nitro compound (63 mg, 0.28 mmol) was treated with Fe in AcOH to give **1-(3-aminophenyl)-2-phenylacetylene**, which was diazotized followed by NaN_3 treatment. The crude product was purified by preparative TLC to give **1-(3-azidophenyl)-2-phenylacetylene** (*m*-**1b**-N$_3$, 29 mg, 47%) as a yellow liquid: ^{1}H-NMR ($CDCl_3$) δ 7.56–7.52 (m, 2 H), 7.36–7.23 (m, 6 H), 6.99 (dd, J = 7.58, 1.32 Hz, 1 H); IR (KBr) ν 2118 cm^{-1}.

1,2-Bis(4-azidophenyl)acetylene (*p,p′*-2-N$_3$,N$_3$). **1,2-Bis(4-azidophenyl)acetylene** was prepared by coupling 4-iodophenyl azide with 4-ethynylphenyl azide in the presence of $(Ph_3P)_2$-$PdCl_2$/CuI in NEt_3 in 21% yield after GPC purification as an orange solid: mp 101.2–102.6 °C; ^{1}H-NMR ($CDCl_3$) δ 7.50 (d, J = 8.58 Hz), 7.01 (d, J = 8.58 Hz); IR (KBr) ν 2124 cm^{-1}.

1,2-Bis(2-azidophenyl)acetylene (*o,o′*-2-N$_3$,N$_3$). **1,2-Bis(2-azidophenyl)acetylene** was prepared by coupling 2-idophenylazide with 2-ethynylphenyl azide in 33% yield as a pale yellow solid: mp 90.4–91.8 °C; ^{1}H-NMR ($CDCl_3$) δ 7.55 (dd, J = 1.32, 7.98 Hz, 2 H), 7.40–7.34 (m, 2 H), 7.16–7.10 (m, 4 H); IR (KBr) ν 2112 cm^{-1}.

1-(2-Azidophenyl)-2-(4-azidophenyl)acetylene (*p,o′*-2-N$_3$,N$_3$). **1-(2-Azidophenyl)-2-(4-azidophenyl)acetylene** was prepared by coupling 4-iodophenyl azide with 2-ethynylphenyl azide in 47% yield as a yellowish solid: mp 95.5–96.9 °C; ^{1}H-NMR ($CDCl_3$) δ 7.56–7.47 (m, 3 H), 7.38–7.32 (m, 1 H), 7.15–7.09 (m, 2 H), 7.02 (d, J = 8.91 Hz, 2 H); IR (KBr) ν 2124 cm^{-1}.

1,2-Bis(azidophenyl)acetylene (*m,m′*-**2**-N$_3$,N$_3$) and **1-(4-azidophenyl)-2-(3-azidophenyl)acetylene** (*p,m′*-**2**-N$_3$,N$_3$) were prepared according to the literature procedures.[14]

Matrix-isolation spectroscopy. Matrix experiments were performed by means of standard techniques[28,29] using an Iwatani Cryo Mini closed-cycle helium cryostat. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing ports of a vacuum shroud surrounding the cold head were fitted with KBr with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For UV experiments, a sapphire cold window and a quartz outer window were used. The temperature of the matrix was controlled by an Iwatani TCU-1 controller (gold *vs.* chromel thermocouple).

Irradiations were carried out with a Wacom 500W xenon high-pressure arc lamp. For broad-band irradiation Toshiba cutoff filters were used (50% transmittance at the specified wavelength).

ESR measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (2-MTHF) (5×10^{-4} M), and the solution was degassed in a quartz cell by four freeze-degas-thaw cycles. The sample was cooled in a optical transmission ESR cavity at 77 K and irradiated with a Wacom 500 W Xe lamp using a Pyrex filter. ESR spectra were measured on a JEOL JES TE200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter.

Low-temperature UV/vis spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 2704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1 mm path length, and degassed by four freeze-degas-thaw cycles at pressure near 10^{-5} Torr. The cuvette was flame-sealed, under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 500 W high-pressure mercury lamp using a Pyrex filter and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

Acknowledgements

The authors are grateful to the Ministry of Education, Science, Sports and Culture of Japan for support of this work through a Grant-in-Aid for Scientific Research for Specially Promoted Research (NO. 12002007), and, Nagase Science and Technology Foundation and Mitsubishi Foundation for partial support.

Notes and References

1 (*a*) *Azides and Nitrenes, Reactivity and Utility*, ed. E. F. V. Scriven, Academic Press, New York, 1984; (*b*) *Nitrenes*, ed. W. Lwowski, Interscience, New York, 1970; (*c*) B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Suschitzky and P. T. Gallagher, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 900; (*d*) E. F. V. Scriven, in *Reactive Intermediates*, ed. R. A. Abramovitch, Plenum, New York, 1981, Vol. 2, Chapter 1; (*e*) W. Lwowski, in *Reactive Intermediates*, ed. M. Jones, and R. A. Moss, Wiley, New York, 1981, Chapter 8; (*f*) W. T. Borden, N. P. Gristan, C. M. Hadad, W. L. Karney, C. R. Kemnitz and M. S. Platz, *Acc. Chem. Res.*, 2000, **33**, 765.

2 (*a*) E. W. Meijer, S. Nijhuis and F. C. B. M. van Vroonhoven, *J. Am. Chem. Soc.*, 1988, **110**, 7209; (*b*) M. Yan, S. X. Cai, M. N. Wybourne and J. F. W. Keana, *J. Am. Chem. Soc.*, 1993, **115**, 814.

3 (*a*) K. Kanakarajan, R. Goodrich, M. J. T. Young, S. Soundararajan and M. S. Platz, *J. Am. Chem. Soc.*, 1988, **110**, 6536; (*b*) N. W. Shaffer and M. S. Platz, *Tetrahedron Lett.*, 1989, **30**, 6465; (*c*) N. Soundararajan and M. S. Platz, *J. Org. Chem.*, 1990, **55**, 2034; (*d*) M. S. Platz and D. S. Watt, *Photochem. Photobiol.*, 1991, **54**, 329; (*e*) S. X. Cai and J. F. W. Keana, *Tetrahedron Lett.*, 1989, **30**, 5409; (*f*) J. F. W. Keana and S. X. Cai, *J. Org. Chem.*, 1990, **55**, 3640.

4 V. Chowdhry and F. H. Westheimer, *Annu. Rev. Biochem.*, 1979, **48**, 293.

5 (*a*) O. L. Chapman and J. P. Le Roux, *J. Am. Chem. Soc.*, 1978, **100**, 282; (*b*) O. L. Chapman and R. S. Sheridan, *J. Am. Chem. Soc.*, 1979, **101**, 3690; (*c*) I. R. Dunkin and P. C. P. Tompson, *J. Chem. Soc., Chem. Commun.*, 1980, 499; (*d*) I. R. Dunkin and P. C. P. Thompson, *J. Chem. Soc., Chem. Commun.*, 1982, 1192; (*e*) I. R. Dunkin, T. Donelly and T. S. Lockhart, *Tetrahedron Lett.*, 1985, 359; (*f*) C. Wentrup and H. W. Winter, *J. Am. Chem. Soc.*, 1980, **102**, 6159; (*g*) C. Wentrup, C. Thètaz, E. Tagliaferri, H. J. Linder, B. Kitscke, H. W. Winter and H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 566; (*h*) J. C. Hayes and R. S. Sheridan, *J. Am. Chem. Soc.*, 1990, **112**, 5879.

6 (*a*) R. S. Sheridan, in *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker Inc, New York, 1987, Vol. 8, pp. 159–248; (*b*) I. R. Dunkin, *Chem. Soc. Rev.*, 1980, **9**, 1.

7 (*a*) W. v. E. Doering and R. A. Odum, *Tetrahedron*, 1966, **22**, 81; (*b*) R. J. Sundberg and R. W. Heintzelman, *J. Org. Chem.*, 1974, **39**,

2546; (*c*) B. A. DeGraff, D. W. Gillespie and R. J. Sundberg, *J. Am. Chem. Soc.*, 1974, **95**, 7491; (*d*) M. Sumitani, S. Nagakura and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2995; (*e*) P. E. Nielsen and O. Buchard, *Photochem. Photobiol.*, 1982, **35**, 317; (*f*) C. J. Shields, D. R. Chrisope, G. B. Schuster, A. J. Dixon, M. Poliakoff and J. J. Turner, *J. Am. Chem. Soc.*, 1987, **109**, 4723; (*g*) Y. Z. Li, J. P. Kirby, M. W. George, M. Poliakoff and G. B. Schuster, *J. Am. Chem. Soc.*, 1988, **110**, 8092; (*h*) A. K. Schrock and G. B. Schuster, *J. Am. Chem. Soc.*, 1984, **106**, 5234–5229; (*i*) C. G. Younger and R. A. Bell, *J. Chem. Soc., Chem. Commun.*, 1982, 1359; (*j*) T. -Y. Liang and G. B. Schuster, *J. Chem. Soc., Chem. Commun.*, 1987, **109**, 7803; (*k*) A. Albini, G. Bettinetti and G. Minoli, *J. Chem. Soc., Chem. Commun.*, 1991, **113**, 6928.

8 S. E. Carroll, B. Nay, F. F. v. Scriven, H. Saschitzky and D. R. Thomas, *Tetrahedron Lett.*, 1977, 175.

9 See for review: (*a*) A. Rajca, *Chem. Rev.*, 1994, **94**, 871; (*b*) H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179; (*c*) *Magnetic Properties of Organic Materials*, ed. P. M. Lahti, Marcel Dekker, New York, 1999.

10 E. Wassermann, R. W. Murray, W. A. Yager, A. M. Trozzolo and G. Smolinsky, *J. Am. Chem. Soc.*, 1967, **89**, 5076.

11 (*a*) A. Nicolaides, H. Tomioka and S. Murata, *J. Am. Chem. Soc.*, 1998, **120**, 11530; (*b*) A. Singh and J. S. Brinen, *J. Am. Chem. Soc.*, 1971, **93**, 540.

12 (*a*) C. Ling and P. M. Lahti, *Chem. Lett.*, 1993, 769; (*b*) T. Ohana, M. Kaise, S. Nimura, O. Kikuchi and A. Yabe, *Chem. Lett.*, 1993, 765; (*c*) T. Ohana, M. Kaise and A. Yabe, *Chem. Lett.*, 1992, 1397; (*d*) T. Ohana, A. Ouchi, H. Moriyama and A. Yabe, *J. Photochem. Photobiol. A, Chem.*, 1993, **72**, 83; (*e*) M. Minato, P. M. Lahti and H. van Willigen, *J. Am. Chem. Soc.*, 1993, **115**, 4532.

13 (*a*) T. Harder, J. Bendig, G. Scholz and R. Stösser, *J. Am. Chem. Soc.*, 1996, **118**, 2497; (*b*) T. Harder, R. Stößer, P. Wessig and J. Bendig, *J. Photochem. Photobiol. A, Chem.*, 1997, **103**, 105; (*c*) M. Minato and P. M. Lahti, *J. Phys. Org. Chem.*, 1993, **6**, 483; (*d*) M. Minato and P. M. Lahti, *J. Am. Chem. Soc.*, 1997, **119**, 2187; (*e*) S. Mimura, O. Kikuchi, T. Ohana, A. Yabe and M. Kaise, *Chem. Lett.*, 1996, 125.

14 S. Murata and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 5547.

15 T. Yamagata, H. Tukada and K. Kobayashi, *Chem. Lett.*, 1998, 129.

16 C. Ling, M. Minato, P. M. Lahti and H. van Willigen, *J. Am. Chem. Soc.*, 1992, **114**, 9959.

17 S. Mimura, O. Kikuchi, T. Ohana, A. Yabe and M. Kaise, *Chem. Lett.*, 1994, 1679.

18 A. Ling and P. M. Lahti, *J. Am. Chem. Soc.*, 1994, **116**, 8784.

19 B3LYP/6-31G(d)[20] optimized geometries and vibrational frequencies were obtained with GAUSSIAN 98[21].

20 (*a*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (*b*) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200; (*c*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, J. B. Raghavachari, K. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. W. M. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, GAUSSIAN 98, Gaussian Inc.: Pittsburgh, PA, 1998.

22 G. Smolinsky, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, 1962, **84**, 3220.

23 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 parameter *D*: J. H. Hall, J. M. Fargher and M. R. Gisler, *J. Am. Chem. Soc.*, 1978, **100**, 2029.

24 It has been pointed out that DFT calculations have problems with cumulenes. For instance, Schreiner and Schaefer mentioned that comparison of geometries obtained using various DFT approaches showed good agreement with MP2/cc-pVTZ, CCSD(T)/cc-pVTZ, and the experiment, but that DFT energetics displayed significant differences when compared to the explicitly correlated theoretical and experimental results. See: H. Lee, H. F. Schaefer, III and P. R. Schreiner, *J. Phys. Chem. A*, 2002, **106**, 11923 . Also, concerning the limitations of DFT on open-shell singlet diradicals, see: T. Bally and W. T. Borden, Reviews in Computational Chemistry, ed. K. B. Lipkowitz and D. B. Boyd, VCH-Wiley, New York, 1999, vol. 13, p. 1.

25 B. F. LeBlanc and R. S. Sheridan, *J. Am. Chem. Soc.*, 1988, **110**, 7250.

26 W. Subhan, P. Rempala and R. S. Sheridan, *J. Am. Chem. Soc.*, 1998, **120**, 11528.

27 Y. Teki, T. Takui, H. Yagi, K. Katoh and H. Iwamura, *J. Chem. Phys.*, 1985, **83**, 539. See also: K. Matsuda, N. Nakamura, K. Inoue, N. Koga and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1483; N. Nakamura, K. Inoue and H. Iwamura, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 872; T. Sugawara, M. Inada and H. Iwamura, *Tetrahedron Lett.*, 1983, **24**, 1723.

28 H. Tomioka, N. Ichikawa and K. Komatsu, *J. Am. Chem. Soc.*, 1992, **114**, 6045.

29 R. J. McMahon, O. L. Chapman, R. A. Hayes, T. C. Hess and H. P. Krimmer, *J. Am. Chem. Soc.*, 1985, **107**, 7597.