Direct Observation and Characterization of *p*-Phenylenebisnitrene. A Labile Quinoidal Diradical

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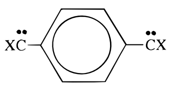
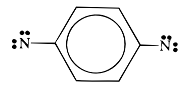
Carbenes coupled via *m*-phenylene linkers have received a lot of attention due to their high-spin properties, which make this type of compound a promising candidate for the preparation of organic materials with novel ferromagnetic properties.[1] Thus, connecting the divalent subunits in a conjugative manner (ortho or para topology) has been often intentionally avoided. As a result, little is known about the low-spin topologies, even though such reactive intermediates are interesting in other less technologically oriented aspects.[2] Earlier studies on conjugated carbenes and nitrenes were based mainly on product analysis.[3] More recently, the direct observation of these species by using elaborate spectroscopical techniques has started to unfold information about their structures and properties.[4−6]

Direct observations of halogen-substituted *p*-phenylenebiscarbenes (**1**, X = F,Cl) were reported just a few years ago,[5] and it is only recently that the parent biscarbene (**1**, X = H) has been clearly identified.[6] In this connection we report our results on the heteroanalogue phenylene-1,4-dinitrene (**2**). Efforts to generate **2** have been reported previously,[7,8] but this is the first IR spectroscopic observation of **2**.



1, X = H, F, Cl



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p-Diazidobenzene (**3a**) matrix-isolated in Ar at 12 K was irradiated ($\lambda > 300$ nm),[9] and the progress of the reaction was carefully monitored by IR as a function of time (Figure 1). The new (relatively weak) absorption bands, which appear initially are assigned to **A** (Figure 1a). The concentration of **A** reached a maximum *before* complete consumption of the precursor **1**, as was evident from the decrease in the bands ascribable to **A** and the rise of new absorption bands (**B** and **C**, Figure 1c). Upon switching to shorter wavelength irradiation ($\lambda > 250$ nm), some of these bands decreased at the expense of the others, indicating that these absorptions are due to two different components, **B** and **C**, the latter being the only component detected at the end of the irradiation.

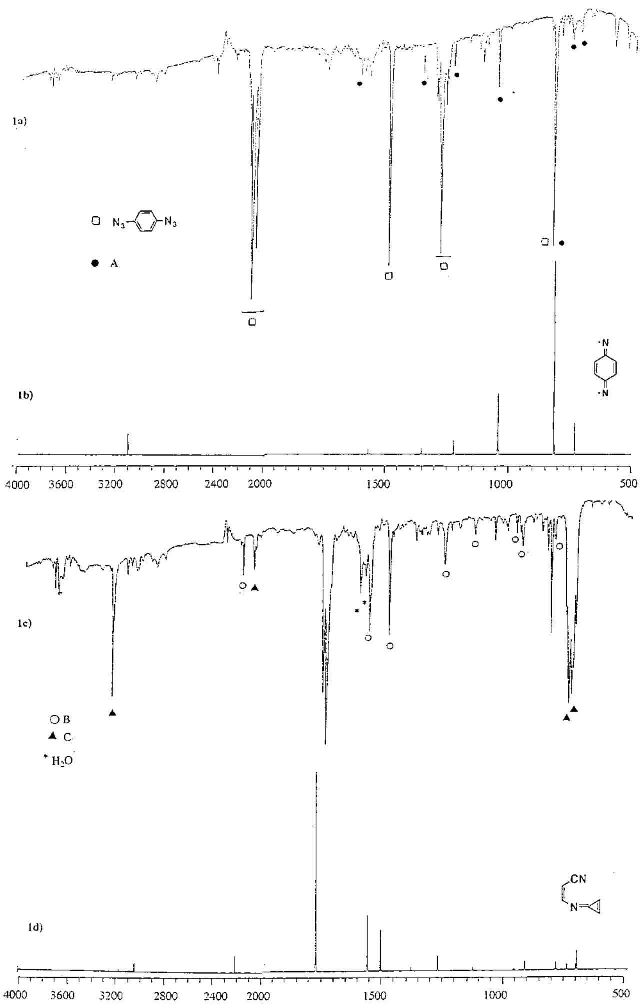
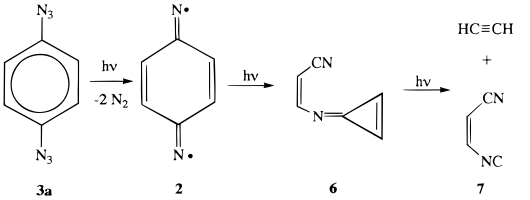


Figure 1. Products of the photolysis of bisazido **3a** in Ar matrix at 12 K and related computational data. (a) IR spectrum (500−4000 cm^{-1}) of primary photoproduct **A** in the presence of **3a** ($\lambda > 300$ nm). (b) Calculated (UB3LYP/6-31G(d)) IR of ^{1}**2**. (c) IR of secondary photoproducts **B** and **C** ($\lambda > 300$ nm). (d) Calculated spectrum for *s-cisoid*-(*Z*)-**6**.

Scheme 1



The strong C−H bond stretch and the intense signals at 744 and 755 cm^{-1} in **C** provide strong support for the presence of acetylene,[10] although the presence of the 2120 and 2126 cm^{-1} absorptions suggests the concomitant formation of another product

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[1] Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179 and references therein.

[2] (a) *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982. (b) Nicolau, K. C.; Smith, A. C. *Acc. Chem. Res.* **1992**, *25*, 497.

[3] For example, see: (a) Hall, J. H.; Patterson, E. *J. Am. Chem. Soc.* **1967**, *89*, 5856. (b) Peek, M. E.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1260. (c) Rees, C. W.; Storr, R. C.; Whittle, P. *J. Chem. Soc., Chem. Commun.* **1976**, 411. (d) Yabe, A. *Bull. Chem. Soc. Jpn.* **1979**, *51*, 789. (e) Baum, M. W.; Font, J. L.; Meislich, M. E.; Wentrup, C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2534.

[4] For example, see: (a) Ohana, T.; Kaise, M.; Mimura, S.; Kikuchi, O.; Yabe, A. *Chem. Lett.* **1993**, 765. (b) Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1993**, *115*, 4532. (c) Harder, T.; Bendig, J.; Scholz, G.; Stösser, R. *J. Am. Chem. Soc.* **1996**, *118*, 2497.

[5] (a) Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788. (b) Tomioka, H.; Komatsu, K.; Nakayama, T.; Shmizu, M. *Chem. Lett.* **1993**, 1291. (c) Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 9381.

[6] Subhan, W.; Rempala, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 11528.

[7] Ohana, T.; Ouchi, A.; Moriyama, H.; Yabe, A. *J. Photochem. Photobiol., A* **1993**, *72*, 83.

[8] For ESR and UV/vis studies of **2** see: (a) Trozzolo, A. M.; Murray, R. W.; Smolinsky, g,; Yager, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 2526. (b) Nimura, S.; Kikuchi, O.; Ohana, T.; Yabe, A.; Kaise, M. *Chem. Lett.* **1996**, 125. (c) Minato, M.; Lahti, P. M. *J. Am. Chem. Soc.* **1997**, *119*, 2187. (d) Reser, A.; Wagner, H. M.; Marley, R.; Bowes, G. *Trans. Faraday Soc.* **1967**, *63*, 3162.

[9] Decomposition of **3a** with longer wavelength irradiation ($\lambda > 350$ nm) gives essentially the same results, but proceeds much slower.

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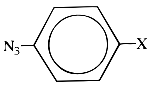
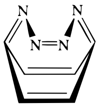
(vide infra). The "splitting" of the observed peaks is most likely due to a matrix site effect[11] as confirmed by the somewhat simplified spectrum obtained when the matrix was warmed to 35 K. This implies that the primary and/or secondary photoproducts are quite labile under our experimental conditions, since, despite the low temperature, they decompose, partially forming acetylene, even at the very early stages of the irradiation.

The previously reported IR spectrum[7] of the irradiation of **1** is essentially identical to our recorded **B**. At that time the strong absorption bands near 1750 cm^{-1} were assigned to the C=N bonds in **2**. If this is correct, what is the structure of the initial photoproduct **A**, which is likely to be some type of a precursor for **2**? An obvious possibility is the monoazidonitrene **3b**, resulting from the elimination of a single N_2 molecule from **1**. However, no new bands attributable to a monoazido species appear in the spectrum, and in addition, the calculated[12] spectrum for **3b** is in poor agreement with that observed for species **A**. Two other possible structures lacking azido groups are **4** and **5**. It was proposed recently by Davidson[19] that *p*-phenylenebiscarbene (**1**, X = H) may exist as its tricyclic isomer 2.2.2-propellatriene, which was actually reported to be lower in energy than the singlet biradical form $^{\bullet}HC{=}C_6H_4{=}CH^{\bullet}$. By analogy, we considered structures **4** and **5**, which is the diazo analogue of 2.2.2-propellatriene, as possible precursors for **2**. However, neither of these structures is calculated to correspond to **A**. The best agreement, and actually an excellent one, between experimental and computational data is found if **A** is assumed to be the desired biradical **2** (Figure 1b).



3a, X = N_3
3b, X = N



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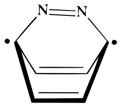

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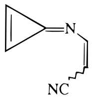

6

2 is predicted to have a singlet ground state, with a small S−T splitting (Table 1),[20] in agreement with the experiment.[8] Singlet **2** has a quinoidal structure and can be best described as a bisiminyl diradical. Due to its high symmetry (D_{2h}), only one C=N bond stretch is IR-active (1576 cm^{-1}, with a very weak absolute intensity of 1.7 km mol^{-1}).

Having assigned **2** as the species giving rise to spectrum **A**, the next question to answer is the identity of the species responsible for spectrum **B**. Typical C=N bonds absorb below 1690 cm^{-1} and are usually rather weak. "Strained" C=N bonds, as in 1-azirene rings, absorb at higher frequencies, and several possible structures containing this subunit were screened computationally. While such systems are indeed found to have higher C=N frequencies, the corresponding intensities were not particularly strong and additionally the rest of the peaks did not match the experimental data in a satisfactory way. A hint as to the possible structure of **B** was provided by the weak absorption observed at 2210 cm^{-1}. It is reasonable to assign this to the presence of a CN group, and with this in mind, the vibrational frequencies of several isomers of **2** were calculated. These efforts lead us to propose **6** as the secondary photoproduct (**B**) (Figure 1d).

Table 1. UB3LYP, MCSCF, and CASPT2 Total (hartree) and Relative (kcal mol^{-1}) Energies of 1,4-Dinitrenobenzenes (**2**) at Various Electronic States and Calculated Spin-Squared Expectation Values ($\langle S^2\rangle$) for UB3LYP[a]

	UB3LYP	$\langle S^2\rangle$	MCSCF	CASPT2
^{5}**2**	32.8 (33.8)[b]	6.02	35.7	32.3
^{3}**2**	1.2 (2.2)[b,c]	2.02	1.3[c]	1.9[c]
^{1}**2**	−340.31730	1.05	−338.37477	-339.31740

[a] At the UB3LYP/6-31G(d) optimized geometry, of the respective electronic state and including ZPE corrections. [b] "Corrected" values based on the assumption that the UB3LYP energy of ^{1}**2** is overestimated by an amount equal to the UB3LYP S−T gap before ZPE corrections (1.0 kcal mol^{-1}). [c] Experimental value of S−T gap: 0.72[8b] and 0.58[8c] (in MTHF) and 0.82 (in *p*-dinitrobenezene) kcal/mol.[8c]

Structure **6** accommodates both the presence of a CN group and strong C=N bond stretches associated with unusually high intensities. The C=N stretch in **6** is calculated to absorb in the range of 1779−1795 cm^{-1} (depending on the geometrical/rotational isomer) and is actually the most intense IR band predicted. Its absolute intensity is between 562 and 862 km mol^{-1}, 2−3 orders of magnitude stronger than that of the C=N absorption in biradical **2**.

Finally, from the interpretation of spectrum **B**, the second component present in **C** (besides acetylene) follows easily. According to calculations, it is 1-cyano-2-isocyanoethylene quite likely in its *Z* form ((*Z*)-**6**). If, under our experimental conditions, *Z* to *E* isomerization of **7** takes place, then it is reasonable to expect that isomerization to dicyanoethylene is also possible. While from the computational data the presence of *cis*-dicyanoethylene cannot be entirely excluded, the *trans* isomer is shown to have its strongest absorption at 944 cm^{-1}, and if it was formed in significant amounts, we should have observed it. So, on the basis of the current data, we prefer to assign both 2120 and 2126 cm^{-1} peaks to (*Z*)-**7**, attributing this "splitting" to matrix-site effects.

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Supporting Information Available: Selected geometrical parameters for ^{1}**2**, ^{3}**2**, and ^{5}**2** (Figure S1), archive entries for optimized B3LYP/6-31G(d) geometries for **2** and **6** (Table S1), computed vibrational analysis data for **2**−**7** and dicyanoethylene (Table S2), and relative energies of the geometrical isomers/rotamers of **6** (Table S3) (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[10] Corresponding calculated[12] values for frequencies (cm^{-1}) and absolute intensities (km mol^{-1}) in parentheses are 3309 (76.5) and 745 (81.1, π_u). An authentic sample shows bands at 3288 and 743 cm^{-1} in Ar at 12 K.

[11] Meyer, B. *Low-Temperature Spectroscopy*; American Elsevier Publishing Company, Inc.: New York, 1971; Chapters 4 and 6.

[12] For an excellent review on how to deal computationally with open-shell species see: Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*; Lipowitz, K. B., Boyd, D. B., Eds.; Wiley: New York, 1998.

[13] B3LYP[14,15] calculations were carried out with Gaussian94[16] and MCSCF calculations with MOLCAS.[17] All geometry optimizations and vibrational analyses were carried out at the B3LYP/6-31G(d) level of theory. Frequencies were scaled by 0.961 and ZPEs by 0.981.[18] For the MCSCF calculations the active space consisted of 10 electrons and 10 orbitals (8 π electrons and the 2 "odd" electrons of the N centers).

[14] For **2**, **3b**, and **5** unrestricted (UB3LYP) wave functions were used. In the case of ^{1}**2** (and ^{1}**5**) the "singlet" corresponds to a broken symmetry but stable wave function. Additionally this "singlet" is actually a (almost equal) mixture of singlet and triplet states as also suggested by the high-spin contamination (Table 1, ^{1}**2**). However, since multireference DFT calculations are currently not available, we consider this singlet wave function as the best UB3LYP approximation for ^{1}**2** (and ^{1}**5**). The extension of this approach to other triplet−singlet computational problems is however unclear yet.

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

[16] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

[17] Molcas Version 4: K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, and P.-O. Widmark, Lund University, Sweden, 1997.

[18] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

[19] Davidson, E. R. *J. Am. Chem. Soc.* **1997**, *119*, 1449.

[20] Calculations at the 6-31G*/CASSCF (8 × 8) level give a singlet−triplet gap of 890 cal/mol.[8c]