

Of Ortho-Conjugatively Linked Reactive Intermediates: The Cases of Ortho-Phenylene-(Bis)Nitrene, -Carbenonitrene, and -(Bis)Carbene

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Abstract: ortho-Phenylene-bisnitrene (**2**) and -carbenonitrene (**3**) were generated in an inert matrix at low temperature, characterized by IR spectroscopy, and identified with the help of DFT calculations. Their thermal and photochemical reactivity was examined in the matrix, and it was found that both **2** and **3** ring-open to 1,4-substituted butadienes. Calculations (DFT and MCSCF) on the lowest singlet, triplet, and quintet states of **2**, **3**, and the all-carbon analogue ortho-phenylene-biscarbene (**4**) are also reported. All three species are found to have singlet ground states. The S–T splitting is small (2–3 kcal mol⁻¹), but the quintet states lie significantly higher in energy (20–25 kcal mol⁻¹). The ring-opening reactions of **2–4** (to give 1,4-substituted butadienes) as well as the ring-closure reactions (to give benzocyclobutadiene derivatives) were also investigated computationally. The calculated barriers for the ring-opening reactions are in reasonable agreement with the experimentally obtained activation energies for **2** and **3**. Calculations also suggest that **4**, unlike its heteroanalogues **2** and **3**, has a stronger preference for the ring-closure reaction (to form benzocyclobutadiene) rather than for the ring-opening reaction.

Introduction

Since the dicarbene having the 1,3-benzoquinodimethane framework (meta topology) was established to have a quintet ground state,¹ research activities on polydivalent species have focused on systems with *m*-phenylene bridges, as this class of compounds is promising for the generation of organic high-spin molecules.² Connecting the divalent subunits in a conjugative manner (ortho or para topology) has been intentionally avoided, and consequently, not much is known about the resulting reactive species. These species are an equally important class of intermediates in many aspects,³ even though they are less attractive in terms of technical application such as organic magnetic materials. Research along this line has proceeded gradually by using modern elaborate techniques that reveal very interesting facets of these intermediates.^{4–7} It is only recently that the properties and structures of the parent bis(carbene) and bis(nitrene) connected with a *p*-phenylene linker have begun to unfold.^{5,6c} However, almost nothing is known about their

analogues connected with an *o*-phenylene linker, although product analysis studies have been reported.^{8–10}

The para and ortho topologies are expected to share the electronic effects mediated in a π conjugative sense via the phenylene linker. As exemplified for the ortho case below, the four “active” electrons (excluding any lone-pair electrons on

(6) For dinitrenes conjugatively connected through benzene ring, see: (a) Singh, B.; Brinen, J. *J. Am. Chem. Soc.* **1971**, *93*, 540. (b) Yabe, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2933. (c) Ohana, T.; Ouchi, A.; Moriyama, H.; Yabe, A. *J. Photochem. Photobiol., A* **1993**, *72*, 83. (d) Ohana, T.; Kaise, M.; Yabe, A. *Chem. Lett.* **1992**, 1397. (e) Ohana, T.; Kaise, M.; Mimura, S.; Kikuchi, O.; Yabe, A. *Chem. Lett.* **1993**, 765. (f) Ling, C.; Lahti, P. M. *Chem. Lett.* **1993**, 769. (g) Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1993**, *115*, 4532. (h) Ichimura, A. S.; Lahti, P. M. *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 33. (i) Minato, M.; Lahti, P. M. *J. Phys. Org. Chem.* **1993**, *6*, 483. (j) Harder, T.; Bendig, J.; Scholz, G.; Stösser, R. *J. Am. Chem. Soc.* **1996**, *118*, 2497. (k) Nimura, S.; Kikuchi, O.; Ohana, T.; Yabe, A.; Kaise, M. *Chem. Lett.* **1996**, 125.

(7) For analogous studies on dicarbenes, see: (a) Sixl, H.; Mathes, R.; Schaupp, A.; Ulrich, K. *Chem. Phys.* **1986**, *107*, 105. (b) Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788. (c) Tomioka, H.; Komatsu, K.; Nakayama, T.; Shmizu, M. *Chem. Lett.* **1993**, 1291. (d) Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 9381. (e) Ohana, T.; Yabe, A. *IUPAC Symposium on Photochemistry*; July 1994, Prague, Czeck, 1994; p 351.

(8) (a) Hall, J. H. *J. Am. Chem. Soc.* **1965**, *87*, 1147. (b) Hall, J. H.; Patterson, E. *J. Am. Chem. Soc.* **1967**, *89*, 5856. (c) Yabe, A. *Bull. Chem. Soc. Jpn.* **1979**, *51*, 789.

(9) (a) Campbell, C. D.; Rees, C. W. *J. Chem. Soc. C* **1969**, 742. (b) Adger, B. M.; Keating, M.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Chem. Commun.* **1973**, 19. (c) Peek, M. E.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1260. (d) Gilchrist, T. L.; Nunn, E. E.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1262. (e) Adger, B. M.; Bradbury, S.; Keating, M.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Perkin Trans. 1* **1975**, 31. (f) Adger, B. M.; Keating, M.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Perkin Trans. 1* **1975**, 41. (g) Adger, B. M.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Perkin Trans. 1* **1975**, 45. (h) Rees, C. W.; Storr, R. C.; Whittle, P. *J. Chem. Soc., Chem. Commun.* **1976**, 411.

(10) Baum, M. W.; Font, J. L.; Meislich, M. E.; Wentrup, C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2534.

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(1) (a) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. (b) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

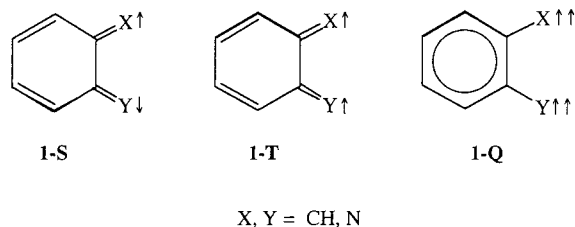
(2) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179 and references therein.

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

(4) (a) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G. J.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526. (b) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251.

(5) Subhan, W.; Rempala, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 11528. (b) Nicolaides, A.; Tomioka, H.; Murata, S. *J. Am. Chem. Soc.* **1998**, *120*, 11530.

nitrene centers) may be distributed in three different ways to give rise to the lowest states of three different multiplicities (singlet, triplet, and quintet, denoted by **1-S**, **1-T**, and **1-Q**, respectively). Similar valence bond depictions can be drawn for the corresponding para isomers. However, an important geometrical distinction between the ortho and para isomers is the closer proximity of the reactive centers in the former case, which offers the opportunity of intramolecular chemistry to take place. While this makes the study of the ortho isomers more complicated, it can provide valuable insight about the intrinsic chemical reactivity of such species.



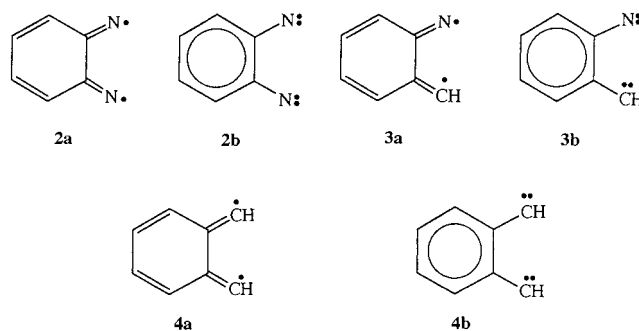
The detection and experimental characterization of such reactive species is a challenge in its own right, but their computational studies of these species is also far from trivial. Recent advances in computational chemistry have made the study of closed-shell species almost routine, providing the organic chemist with a variety of theoretical tools that are reasonably accurate and easy to use. On the other hand, open-shell species pose special problems in their computational treatment and fewer options are available. This is especially true for singlet biradicals, such as **1-S**, which formally requires two determinants for its proper description (unlike the corresponding triplet and quintet states, which, to a first approximation, are one-configuration problems).¹¹

A common practice in the study of such biradicals is the application of MCSCF methods, which can take into account static correlation. However, simple MCSCF methods recover only part of the dynamic correlation, and the computational effort increases rapidly with the size of the system and/or size of active space employed.¹² Furthermore these methods are not particularly "user-friendly" and are therefore less popular among experimental chemists who wish to use computational methods as an extra tool in their research.

An alternative method, which takes into account dynamic correlation, is density-functional theory (DFT). Some of these methods have become very popular for the prediction of molecular properties. In particular the B3LYP method (in the case of closed-shell species) has been found to give very good results in the prediction of IR spectra, which is one of our main concerns in this work.¹³ An attractive feature of B3LYP (and other DFT methods) is that it provides a computationally affordable way for the reliable study of medium- and large-size molecules. Although this method has not been fully tested for studying biradicals, it has been shown to perform in a satisfactory way for various types of radicals, provided that some

caution is exercised.^{11,14} Additionally, the application of such methods is quite straightforward, and undoubtedly, this has contributed to their popularity.

In this context, we report herein a systematic study on the conjugated carbenes and/or nitrenes connected by an ortho-phenylene linker. ortho-Phenylene-bisnitrene (**2**), -carbenonitrene (**3**), and -biscarbene (**4**) have been investigated in an integrated way combining experimental and computational techniques.¹⁵ We have been able to generate **2** and **3**, identify them by a combination of spectroscopic and computational methods, and examine their thermal and photochemical behavior. The good agreement between theory and experiment provides confidence that the different chemistry predicted for the analogous biscarbene system (**4**) is worth pursuing. Additionally the performance of B3LYP in the study of these systems has been evaluated against the more traditional MCSCF method and also directly with the experimental data and is found to be reasonably accurate and reliable.



1,2-Phenylene(bis)nitrene (2). Geometries of the singlet, triplet, and quintet states of **2** were optimized assuming C_{2v} symmetry. The stationary points were characterized by vibrational analyses (B3LYP/6-31G(d)) and found to be minima on the corresponding potential energy surfaces. In the case of ¹**2**, this was also verified by calculating the Hessian numerically at the MCSCF(10, 10)/6-31G(d) level. The active space for the MCSCF(10, 10) calculations consisted of 10 electrons (the 8 π electrons plus the 2 odd σ electrons).

Selected optimized geometrical parameters obtained at the B3LYP/6-31G(d) and MCSCF(10, 10)/6-31G(d) levels of theory for the lowest singlet, triplet, and quintet states of **2** are shown in Figure 1a. These two very different methods give quite similar results. The calculated bond lengths are generally within about 0.01 Å (or 1%) between the two methods. The only exception is the C—C bond between the carbons connected to the radical centers, where B3LYP/6-31G(d) predicts a longer bond by about 0.04 Å (or 3%) for ¹**2** and 0.02–0.03 Å for ³**2** and ⁵**2**.

The geometries of the singlet and triplet state display more bond localization in the benzene ring than in the geometry of the quintet (Figure 1a). This, along with the finding that the bond lengths between the radical centers and the benzene nucleus are shorter in the singlet and triplet states, as compared to the quintet state, implies that the π conjugation with the benzene ring is stronger in the former than in the latter. In other words, the geometries of the singlet and triplet states are

(11) An excellent review on calculations for open-shell species is: Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1.

(12) Methods using MCSCF wave functions and including dynamic correlation at the MP2 level of theory are available for single-point calculations, but not with analytic gradients, making their application to geometry optimizations quite limited.

(13) See for example: (a) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612. (b) Handy, N. C.; Murray, C. W.; Amos, R. D. *J. Phys. Chem.* **1993**, *97*, 4392. (c) Stephens, B. J.; Devlin, I. J.; Chabalowsky, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (d) Choi, C. H.; Kertesz, M. *J. Phys. Chem.* **1996**, *100*, 16530.

(14) For some examples of DFT calculations on open-shell singlets see: (a) Cramer, C. J.; Dulles, F. J.; Giesen, D. J.; Almlöf, J. *Chem. Phys. Lett.* **1995**, *245*, 165. (b) Schreiner, P. *J. Am. Chem. Soc.* **1998**, *120*, 4184. (c) Marquardt, R.; Balster, A.; Sander, W.; Kraka, E.; Cremer, D.; Radziszewski, J. G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 955.

(15) Preliminary MCSCF calculations on these systems have been reported previously, with similar results. (a) Koseki, S.; Tomioka, H.; Toyota, A. *J. Phys. Chem.* **1994**, *98*, 13203. (b) Koseki, S.; Tomioka, H.; Yamazaki, K.; Toyota, A. *J. Phys. Chem.* **1997**, *101*, 3377.

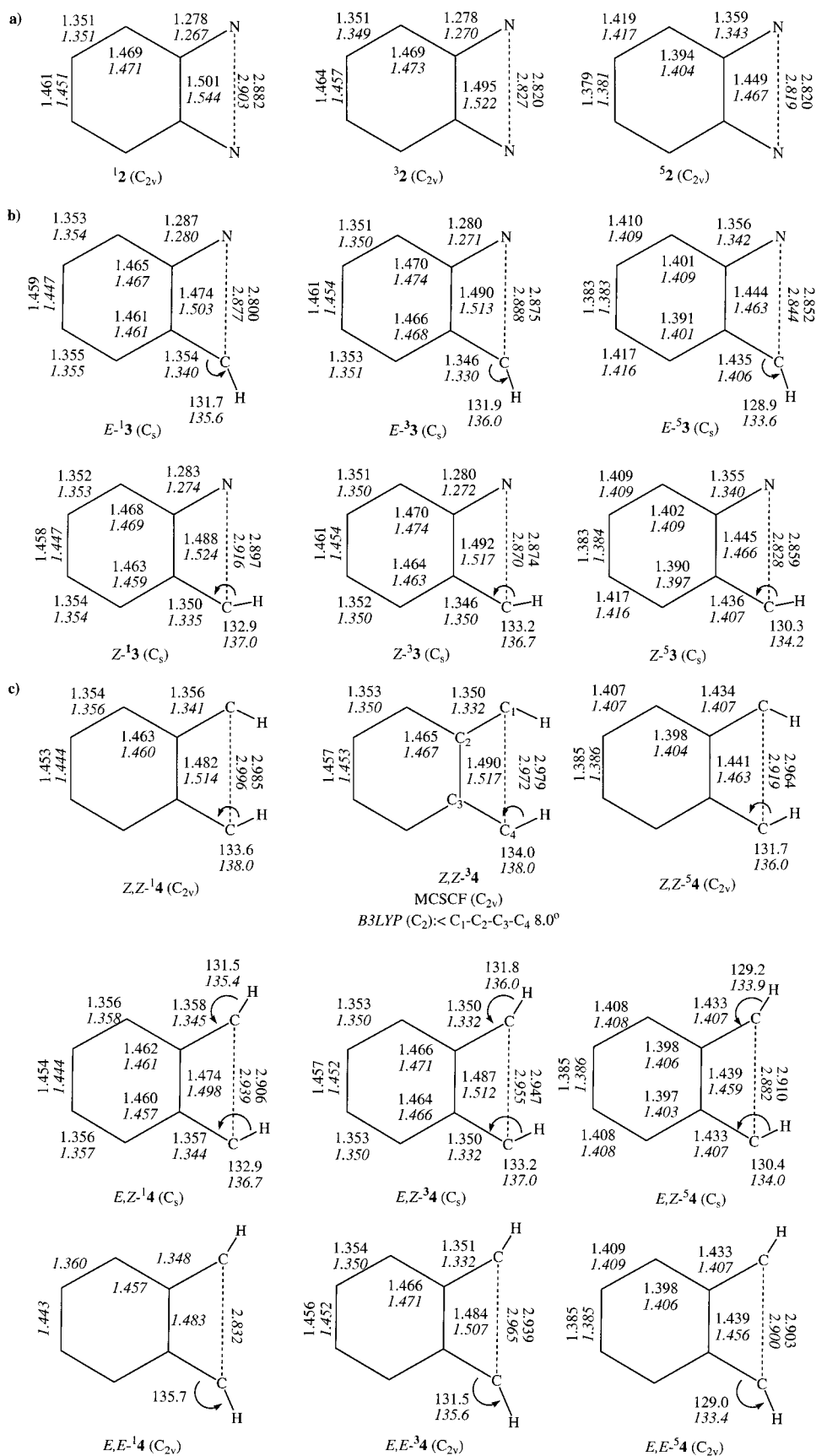


Figure 1. Selected geometrical parameters (distances in Å, angles in degrees) for **2–4** at the MCSCF and UB3LYP (shown in italics) levels of theory. Only important angles are indicated here for the sake of clarity. All other angles are normal ($121 \pm 2^\circ$).

consistent with that expected for *o*-quinodimide diradicals (**2a**), whereas that of the quintet looks more like a localized *o*-phenylbisnitrene (**2b**). The quintet is found to be significantly

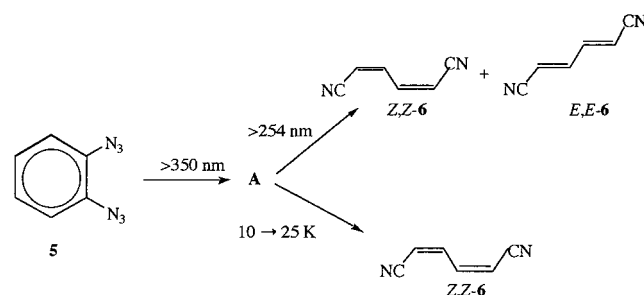
higher in energy (by 25.5 kcal mol⁻¹, Table 1) with respect to the ground state, which is predicted to be a singlet state, but with a small S–T gap of approximately 3 kcal mol⁻¹. It is note-

Table 1. Total (hartree) and Relative (kcal mol⁻¹) Energies of 1,2-Phenylene(bis)nitrene (**2**), 2-Nitrenophenylcarbenes (**3**), and 1,2-Phenylene(bis)methylenes (**4**) at the B3LYP/6-31G(d), MCSCF(10, 10)/6-31G(d), and CASPT2/6-31G(d) Levels of Theory and Calculated (B3LYP) Spin-Squared Expectation Values ($\langle S^2 \rangle$)^a

	B3LYP ^b	$\langle S^2 \rangle$	MCSCF ^c	CASPT2 ^c
⁵ 2	25.0	6.04	29.5	25.5
³ 2	2.7	2.02	1.5	2.7
¹ 2	-340.31041	1.10	-338.36713	-339.31035
<i>E</i> - ⁵ 3	23.2	6.03	25.8	23.0
<i>Z</i> - ⁵ 3	22.2	6.03	25.3	22.2
<i>E</i> - ³ 3	3.1	2.02	2.2	2.7
<i>Z</i> - ³ 3	2.2	2.02	1.5	1.9
<i>E</i> - ¹ 3	1.2	1.20	0.2	0.9
<i>Z</i> - ¹ 3	-324.22239	1.16	-322.31416	-323.23648
<i>E,E</i> - ⁵ 4	19.8	6.02	21.2	19.5
<i>Z,Z</i> - ¹ 4	19.2	6.02	21.5	19.3
<i>E,Z</i> - ⁵ 4	18.9	6.02	20.8	18.7
<i>E,E</i> - ³ 4	3.7	2.02	2.8	2.7
<i>Z,Z</i> - ³ 4	3.4	2.01	2.8	2.5
<i>E,Z</i> - ³ 4	3.0	2.02	2.4	2.1
<i>Z,Z</i> - ¹ 4	0.9	1.25	0.7	0.6
<i>E,Z</i> - ¹ 4	0.6	1.28	-306.25722	-307.15799
<i>E,E</i> - ¹ 4	-308.12897	1.28	<i>d</i>	<i>d</i>

^a With the 6-31G(d) basis set and including ZPE corrections based on the UB3LYP frequencies scaled by 0.981.⁴² The values of $\langle S^2 \rangle$ expected for pure singlet, triplet, and quintet are 0.0, 2.0, and 6.0, respectively. ^b At the UB3LYP/6-31G(d) optimized geometries. ^c At the MCSCF/6-31G(d) optimized geometries. ^d No minimum located at the MCSCF/6-31G(d) level of theory.

Scheme 1



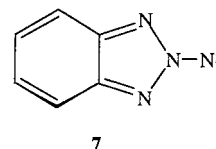
worthy and somewhat surprising that the UB3LYP/6-31G(d) relative energies of the different electronic states are within 0.5 kcal mol⁻¹ from the CASPT2/6-31G(d) values. While this may be fortuitous, at the same time it further demonstrates that B3LYP/6-31G(d) can treat the different states in a reasonably balanced fashion.¹⁶

Experimentally, 1,2-diazidobenzene (**5**) served as the potential precursor for **2**. Irradiation ($\lambda > 350$ nm) of **5** in Ar at 10 K resulted in the disappearance of all of the bands ascribable to the azido groups and concurrent formation of new bands in the IR (Scheme 1, Figure 2). Analysis of the product bands as a function of the irradiation time and wavelength of light suggested that all bands are ascribable to a single product (**A**). Product **A** quickly disappeared either upon annealing the matrix or upon irradiation with shorter-wavelength light. Thus, warming the matrix containing **A** from 10 to 25 K resulted in the formation of a product (Figure 2d), which was assigned as *Z,Z*-1,4-dicyano-1,3-butadiene (*Z,Z*-**6**) by direct comparison with the spectrum of an authentic sample. Irradiation of the matrix with

(16) As a word of caution, though, CASPT2 calculations tend to overestimate the stability of triplet states as compared to singlet ones, at least in the case where the electrons occupy different orbitals.¹⁷ In the present systems, since the singlet and triplet biradicals have the same molecular orbital occupancies, this may be less of a problem. However, the quintet states, which have a different number of electrons in the π space, may be favored energetically.

shorter-wavelength light ($\lambda > 254$ nm) also transformed **A** to **6** (as a mixture of *Z,Z*- and *E,E*- isomers (Figure 2e)). All attempts to trap **A** with O₂ or CO resulted in the formation of **6** without any signs for the formation of other products.¹⁸

Under our experimental conditions, an almost concerted elimination of two N₂ molecules from the precursor **5** is expected to take place (vide infra). This is compatible with the fact that no new azido bands ascribable to a monoazido species were observed. Nevertheless, a stepwise elimination of the N₂ molecules cannot be entirely excluded and so it is conceivable that nitrene **7** may be formed (presumably via capturing the monoazido species by the nearby nitrene center).¹⁹ However, the computed IR spectrum for **7** is quite different from the observed spectrum **A** (Table S2, Figure S1a in Supporting Information). In contrast, the calculations provide strong support that spectrum **A** is due to the desired singlet biradical ¹2 (Figure 2).²⁰



As mentioned above, the primary photoproduct, which we identify as the biradical ¹2, was found to be thermally reactive, even at this low temperature. Its thermal stability was examined by monitoring IR changes as a function of temperature. The useful temperature range of the matrix for the measurable disappearance of ¹2 and growth of **6** was 30–40 K. Thermal reactions in polycrystals usually follow nonexponential rate laws. This is attributed to a multiple-site problem.^{21,22} Therefore, in contrast to a first-order reaction in solution, the rate constant of a nonexponential process in the solid state is time-dependent; molecules located in a reactive site will have decayed during the warm-up procedure and/or the initial stage of the reaction at the given temperature.²³ Thus, increasing the temperature of a matrix of ¹2 from 10 to 35 K initially resulted in a fast decay of its IR signals (of about one-third of the overall change in intensity during the experiment), followed by a rather smooth

(17) As for example is the case with the S–T splitting of phenyl cation: Nicolaides, A.; Smith, D. M.; Jensen, F.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 8083.

(18) Decomposition of **5** has been investigated previously at much higher temperatures. Thus, Hall carried out the thermolysis of **5** in refluxing Decalin and found that *Z,Z*-**6** was produced exclusively.^{8a, b} Yabe et al. photolyzed **5** in an EPA matrix at 77 K and also obtained *Z,Z*-**6** quantitatively, no intermediates being detected even at this low temperature.^{8c}

(19) Generation of 2-nitrenobenzotriazole (**7**) by oxidation of the corresponding amine at high temperature also resulted in the isolation of *Z,Z*-**6** in high yield.^{8a}

(20) B3LYP calculations suggest that the three bands at 782, 815, and 866 cm⁻¹ (of Figure 2b) are due to the presence of the C₂ conformation of the final photoproduct *Z,Z*-**6**. The TS leading from the primary photoproduct (¹2) to the secondary one (*Z,Z*-**6**), has C₂ symmetry. It is reasonable then to expect that ring-opening of ¹2 forms initially the C₂ conformer, which relaxes slowly to the more stable C_s (*s-trans*) one. The formation of **6** at the early stages of the irradiation of **5** is compatible with the observed and calculated facile ring-opening isomerization of ¹2 (see text).

(21) (a) Sprague, E. D. *J. Phys. Chem.* **1973**, *77*, 2066. (b) Neiss, M. A.; Willard, J. E. *J. Phys. Chem.* **1975**, *79*, 283. (c) Hudson, R. L.; Shiotani, M.; Williams, F. *Chem. Phys. Lett.* **1977**, *48*, 193.

(22) (a) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240. (b) Siebrand, W.; Wildman, T. A. *Acc. Chem. Res.* **1986**, *19*, 238. (c) Platz, M. S. *Acc. Chem. Res.* **1988**, *21*, 236. (d) Tomioka, H.; Hayashi, N.; Izawa, Y.; Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5053.

(23) For kinetics of carbenes within noble gas matrixes, see: (a) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683. (b) Wierlacher, S.; Sander, W.; Liu, M. T. H. *J. Am. Chem. Soc.* **1993**, *115*, 8943.

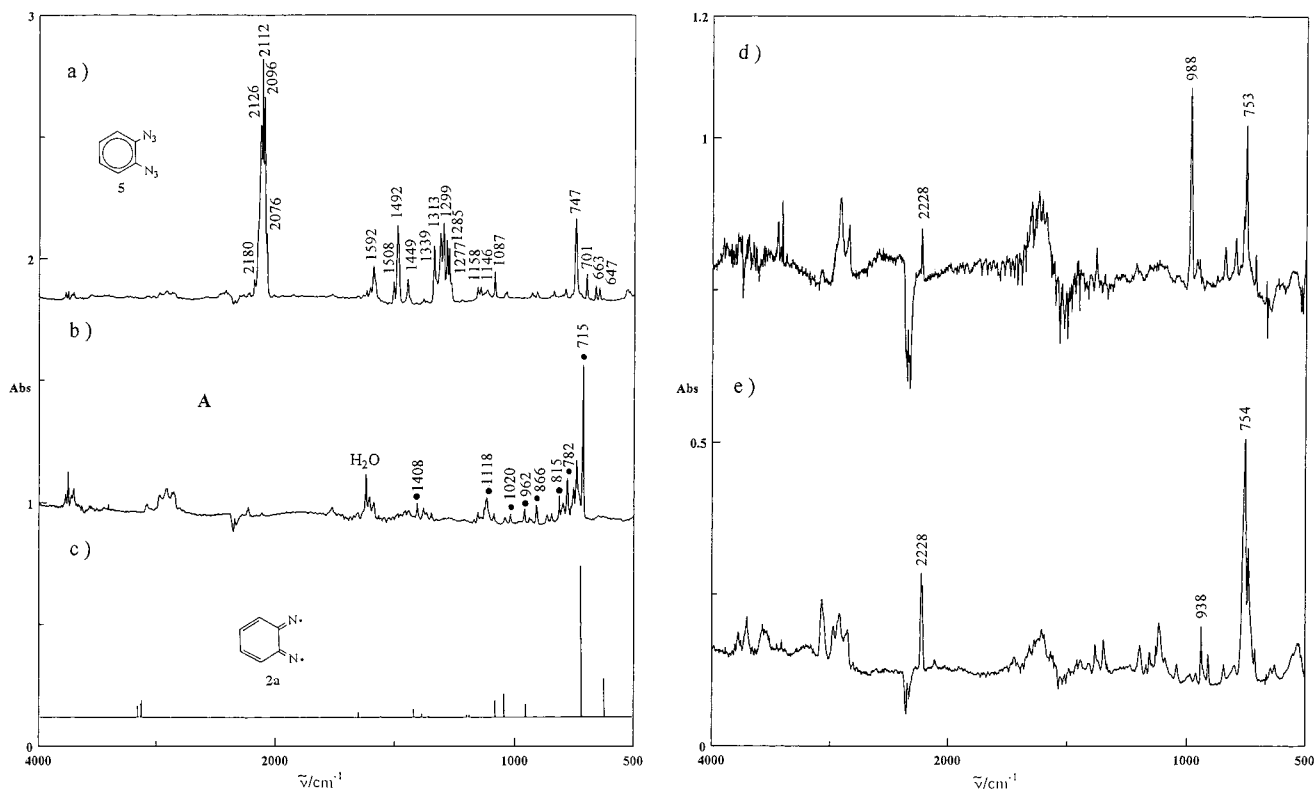


Figure 2. (a) IR spectrum of 1,2-diazidobenzene (**5**) matrix-isolated in Ar at 10 K. (b) IR spectrum obtained by irradiation ($\lambda > 350$ nm, 30 min) of **5** in Ar at 10 K. (c) Calculated (UB3LYP/6-31G(d)) IR spectrum of **2** scaled by 0.981. (d) Spectrum obtained after thawing (b) to 35 K. (e) Spectrum obtained after irradiation ($\lambda > 254$ nm, 155 min) of (b).

Table 2. Calculated Barriers of the Ring-Opening ($\Delta H_{\text{ro}}^{\ddagger}$, kcal mol⁻¹) and Ring-Closure ($\Delta H_{\text{rc}}^{\ddagger}$, kcal mol⁻¹) Reactions and Enthalpies of the Ring-Opening (ΔH_{ro} , kcal mol⁻¹) and Ring-Closure (ΔH_{rc} , kcal mol⁻¹) Reactions for **12**, **13**, and **14** at the B3LYP/6-31G(d) Level of Theory^a

	$\Delta H_{\text{ro}}^{\ddagger}$	ΔH_{ro}^b	$\Delta H_{\text{rc}}^{\ddagger}$	ΔH_{rc}
12	0.6	-55.2 ^c	18.9	-7.3
13	4.3	-44.4	6.8	-49.9
14	9.1	-36.1	~0	-77.8

^a Including ZPE corrections based on the B3LYP harmonic vibrational frequencies scaled by 0.981.⁴² ^b With respect to the Z,Z conformations of the resulting 1,4-X,Y butadienes (X, Y = CN, CCH). The more stable *s-trans* conformations of the butadienes were considered. ^c -47.8 kcal mol⁻¹, with respect to the "*s-cis*" (C_2 symmetry) of Z,Z-**6**.

disappearance of **12** and smooth growth of the diene **6**. Since the initial part of the decay is dependent on the time required to warm the matrix to the given temperature and to start the kinetic measurement, we considered only the residual part of the smooth decay curve. This was fit to a single exponential to yield an absolute pseudo-first-order rate constant of 2.7×10^{-5} s⁻¹ at 35 K. An Arrhenius plot of the decay kinetics was obtained by following the reaction at three temperatures between 33 and 37 K. From the plot, an activation energy of 2.8 kcal mol⁻¹ was derived.

In semiquantitative agreement with the experiment, **12** is predicted to ring-open to 1,4-dicyano-1,3-butadiene (**6**) with a very small barrier (0.6 kcal mol⁻¹ after ZPE corrections, Table 2) at the B3LYP/6-31G(d) level of theory.

1,2-Phenylencarbenonitrene (3). The CH radical center of this reactive intermediate introduces an extra degree of complexity, since the hydrogen can be directed either toward (*Z*-**3**) or away (*E*-**3**) from the nitrene center. The systems were assumed to be planar (C_s symmetry), and vibrational analyses

with DFT showed them to be minima. Selected optimized geometrical parameters for both isomers at different electronic states are shown in Figure 1b. Again the differences in the bond lengths are generally less than 0.01 Å (or <1%), with the exception of the C-C bond between the carbons of the ring that are adjacent to the reactive centers, where again B3LYP/6-31G(d) predicts somewhat longer bond lengths than MCSCF-(10, 10)/6-31G(d). It is interesting that these differences seem to be independent of the multiplicity of the system, which suggests that B3LYP/6-31G(d) is capable of describing the structures of the singlet biradicals with accuracy comparable to those of the triplet and quintet states.

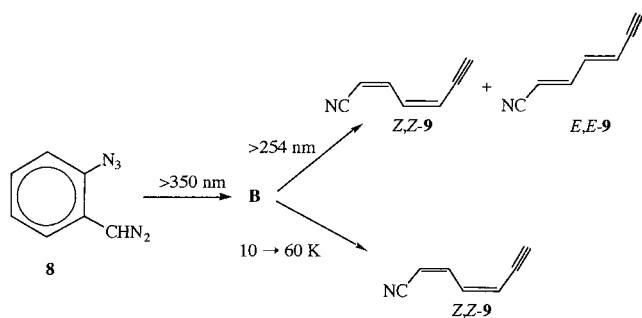
Not surprisingly, the geometries of the *E* and *Z* isomers are very similar (Figure 1b), and this is also reflected in their relative energies (Table 1). The only noteworthy difference is that, in the singlet state, the bond length between the carbons adjacent to the reactive centers is longer in the *Z* isomer by ~0.02 Å, presumably due to hyperconjugation (vide infra). By analogy to **2**, the singlet and triplet states display the structural characteristics expected of *o*-quinomethidemonoimine diradicals (**3a**), whereas the quintet states are best described as ("localized") 1,2-phenylencarbenonitrene (**3b**).

Energetically the *Z*- isomer is found to be favored over the *E*-isomer by approximately 1 kcal mol⁻¹ (Table 1), independent of the multiplicity. The interconversion of these two geometric isomers can be achieved via linearization of the vinyl group. The barrier for this process is calculated to be ~3 kcal mol⁻¹.²⁴ This is only slightly smaller than the barrier of 3.7 kcal mol⁻¹ predicted for the vinyl radical at the same level of theory.

The quintet states lie 22–23 kcal mol⁻¹ above the lowest singlet. While there is formally one more bond in structure **3a** as compared to **3b**, the latter benefits from the aromaticity of

(24) The *E*- to *Z*- isomerization of **3** requires 3.5 kcal mol⁻¹ on the singlet surface and 3.6 kcal mol⁻¹ on the triplet.

Scheme 2



the formally “intact” benzene nucleus. For both isomers, the lowest state is the singlet, with the triplet lying ~ 2 kcal mol⁻¹ higher in energy.

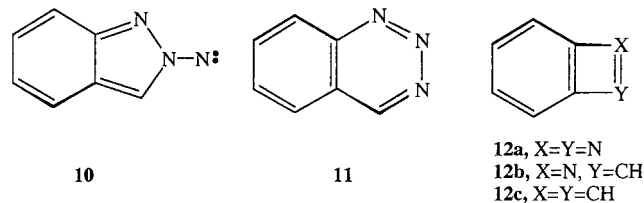
We sought to generate **3** by irradiation ($\lambda > 350$ nm) of 2-azidophenyldiazomethane (**8**) in Ar at 10 K (Scheme 2). As the bands ascribable to the diazo and azido groups of **8** disappeared, the matrix took on a faint yellow hue and new bands appeared in the IR (**B**, Figure 3b). Further irradiation of the initial product(s) **B** with shorter wavelength light ($\lambda > 254$ nm) afforded two new products, showing characteristic bands at 2224 and 2028 cm⁻¹ (Figure 3d). Comparison of their spectra with those of possible reaction products soon revealed that these products were an isomeric mixture of 1-cyano-1,3-dien-5-yne (**9**). One of the isomers is *Z,Z*-**9**, as judged by comparison with an authentic sample. Since the other isomers of **9** were not obtained at sufficiently pure forms to serve as standards, the vibrational frequencies of *Z,Z*-, *E,E*-, *E,Z*-, and *Z,E*-**9** were calculated (Supporting Information, Figure S2). Based on the comparison of computational and experimental IR data, the photoproducts are assigned to a mixture of *Z,Z*- and *E,E*-**9** (Figure 3d).

The same spectrum **B** was obtained when **8** was irradiated in a Xe matrix. Interestingly, warming the Xe matrix up to 60 K also resulted in the formation of 1-cyano-1,3-dien-5-yne, mainly in its *Z,Z* form (Scheme 2, Figure 3e). The spectrum shown in Figure 3b appears to be composed of at least two different components, since the peaks marked with \blacklozenge in Figure 3b did not disappear upon heating (Figure 3e). The peak at 3320 cm⁻¹ did not disappear on irradiation (Figure 3d). The thermal stability of the labile component of **B** was examined in more detail by monitoring IR changes as a function of temperature. The useful temperature range of the matrix for the measurable disappearance of **B** and growth of **9** was 40–50 K. Following a procedure similar to that above, we obtained an absolute pseudo-first-order rate constant of 3.85×10^{-6} s⁻¹ at 45 K, corresponding to an activation energy of 5.1 kcal mol⁻¹.

The similar chemistry observed between the bisazido **5** and the azidodiazole **8** suggests that irradiation of **8** is likely to have produced the desired biradical **3**. This is also supported by the calculated IR spectrum for **3** (Figure 3c), where the assumption that both *E* and *Z* conformers are present has been made. However, the other compound(s) present in the spectrum shown in Figure 3b have not yet been identified. In our efforts to do so, we have eliminated what appear to us as the most likely possibilities.

2-Nitrenoidazole (**10**) could in principle be formed by loss of a single N₂ molecule from **8**, followed by capture of the reactive center (carbene or nitrene) by the adjacent ortho group (azido or diazo, respectively). When Rees and co-workers generated **10** in solution at room temperature, they found that it underwent ring expansion to form 1,2,3-benzotriazine (**11**).^{9f} Cyanoacetylene **9** was formed only when **10** was generated at

a much higher temperature in the gas phase (450 °C/0.01 Torr).^{9f} Thus, it is highly unlikely that **B** (which leads to the formation of **9** at a temperature as low as 35 K) could be assigned to triazine **11** or nitrene **10**. In addition, no IR bands ascribable to **11** were observed, and the DFT vibrational frequencies (Table S2, Figure S1b) for **10** differ substantially from the recorded ones in spectrum **B** shown in Figure 3b.



Another possibility that we considered was the ring-closure reaction of **13** to form azabenzocyclobutadiene (**12b**). It was shown again by Rees and co-workers that 2-(phenyl)azabenzocyclobutadiene is formed by flash vacuum pyrolysis of 4-phenyl-1,2,3-benzotriazine,^{9b} while analogous pyrolysis of the triazine (**11**) results in the formation of biphenylene, most likely by way of benzyne as a result of loss of N₂ and HCN.^{9f} Thus, we photolyzed **11** under matrix conditions. Irradiation ($\lambda > 350$ nm) of **11** matrix-isolated in Ar at 10 K resulted in a clean disappearance of the original bands of the starting triazine to produce a single product (Figure 4a). The product bands did not fit with those observed for benzyne,²⁵ and no bands ascribable to HCN were detected, suggesting that complete fragmentation to benzyne did not take place. Since triazines eliminate N₂ upon irradiation^{9h} and also since the C–H deformation absorption of the aromatic ring changed very little during the photolysis, the spectral changes are best explained in terms of photodiazotization of **11** to generate **12b**. Furthermore, this assignment is supported by the good agreement between the experimental IR spectrum and that calculated for **12b** (Figure 4b). The spectrum of **12b**, however, cannot explain spectrum **B** shown in Figure 3b.

Several trapping experiments were also tried. When the irradiation of **8** was carried out in an Ar matrix doped with oxygen (0.5% and 19%), the same spectrum **B** (Figure 3b) was obtained. No oxidation products were formed, as judged from the complete absence of the bands in carbonyl and carbonyl oxide regions in the IR spectra. Similarly, doping the matrix with CO did not give rise to any new compounds at least to a detectable extent. When the doped (with O₂ or CO) Ar matrix was warmed to 35 K, the final product observed was the same as in the pure Ar matrix. Since “simple” phenylcarbenes and nitrenes can generally be trapped in one or more of the ways described, it is reasonable to conclude that the primary photoproduct is not likely to contain any carbene or nitrene centers. Further support for this was provided by the “silent” ESR spectrum obtained when 2-azidophenyldiazomethane (**8**) was subjected to long-wavelength photolysis ($\lambda > 571$ nm, > 497 nm, > 444 nm, > 399 nm, Ar, 12 K), which indicates the absence of species in triplet or quintet states.

To summarize, the available experimental and computational data, when considered in total, strongly suggest that the singlet biradical **3** is indeed formed upon irradiation of **8** (along with

(25) (a) Radziszewski, J. G.; Hess, B. A., Jr.; Zahrandnik, R. *J. Am. Chem. Soc.* **1992**, *114*, 52, and references therein. (b) Simon, J. G. G.; Schweig, A.; Xie, Y.; Shaefer, H. F., III. *Chem. Phys. Lett.* **1992**, *200*, 631.

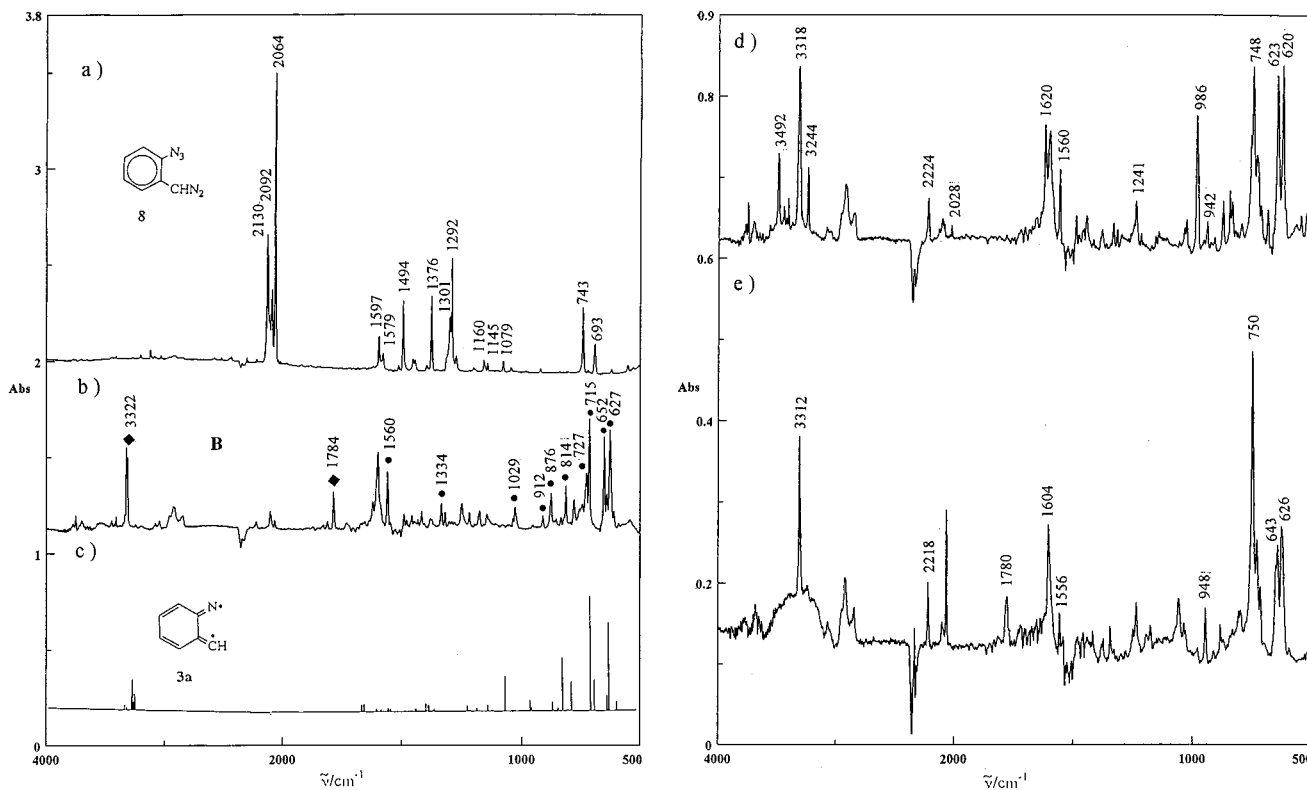


Figure 3. (a) IR spectrum of 1-azidophenyldiazomethane (**8**) matrix-isolated in Ar at 10 K. (b) IR spectrum obtained by irradiation ($\lambda > 350$ nm, 37 min) of **8** in Ar at 10 K. (c) Calculated (UB3LYP/6-31G(d)) IR spectrum of **13** scaled by 0.981 (equimolar mixture of *E*- and *Z*- forms). (d) Spectrum obtained after irradiation of (b) at $\lambda > 254$ nm for 240 min. (e) Spectrum obtained after irradiation of **8** in Xe matrix ($\lambda > 350$ nm, 37 min) and thawing to 60 K.

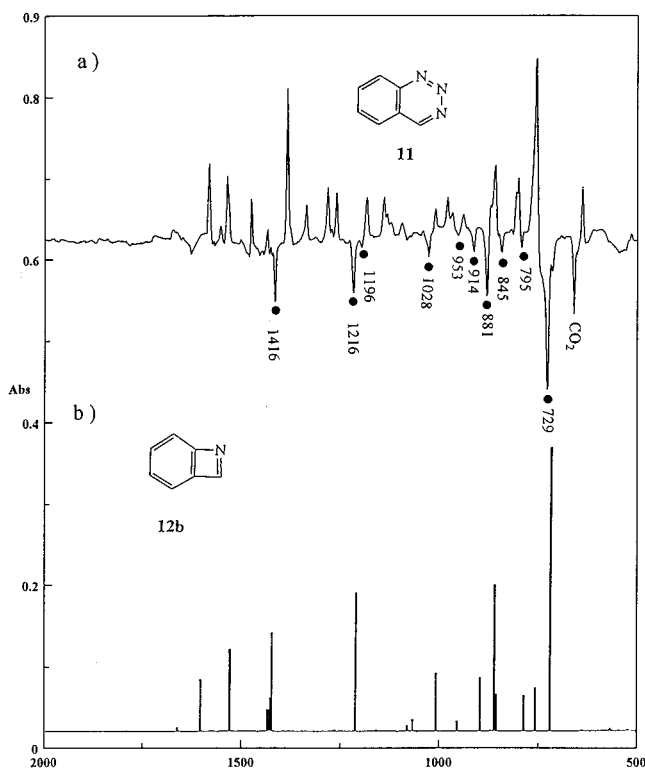


Figure 4. (a) Difference spectrum before and after irradiation ($\lambda > 350$ nm, 270 min) of benzotriazine (**11**) in Ar at 10 K. The positive and negative peaks are attributable to **11** and the photoproduct (●), respectively. (b) Theoretical (B3LYP/6-31G(d)) IR spectrum of **12b**.

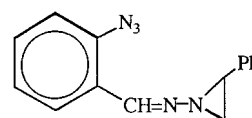
an unidentified component **X**).²⁶ Furthermore, this biradical has a sufficiently long lifetime to be observed experimentally but

is also quite labile thermally and sensitive photochemically, giving **9** via ring-opening of the benzene ring.

The ring-opening reaction of **13** to **9** was found to be less facile than that of its diaza-analogue **12**, requiring a somewhat higher activation energy (5.1 kcal mol⁻¹). In good agreement with the experimental data, B3LYP also predicts that the **13** → **9** barrier is 4.3 kcal mol⁻¹.

1,2-Phenylene(bis)carbene (4). In this case there are three possible geometrical isomers (*Z,Z*, *E,Z* and *E,E*), and their optimized bond lengths for the three different electronic states are shown in Figure 1c. As with **2** and **3**, **4** is also calculated to be essentially planar (*C_{2v}* for *Z,Z* and *E,E*-**4** and *C_s* symmetry for *E,Z*-**4**). One exception is *Z,Z*-**4**, which at the B3LYP/6-31G(d) level of theory is found to be nonplanar (*C₂* symmetry), with the *C_{2v}* geometry being a transition state (for the enantiomerization of the two *C₂* structures). However, the difference in energy between the two stationary points is minuscule (less than 0.01 kcal mol⁻¹), indicating a very shallow potential energy surface. Once more, B3LYP/6-31G(d) and MCSCF(10, 10)/6-31G(d) give similar results, except for the singlet *E,E* isomer

(26) To check whether the unknown component **X** is due to the presence of an impurity in our precursor **8**, we synthesized and carefully purified the more stable *N*-aziridinylimine **14** (>99% by ¹H NMR). During deposition of **14** into the Ar matrix, **8** was formed by loss of styrene. The photolysis gave exactly the same result as before (spectrum **B** in Figure 3b). This seems to suggest that component **X** does not originate from an impurity in the precursor and that it may be formed via a minor side reaction during the photolysis of **8**.

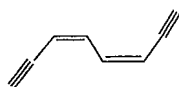


(*E,E*-**14**), which at the MCSCF(10, 10)/6-31G(d) level does not seem to exist as a stationary point on the potential energy surface. All attempts to optimize the MCSCF(10, 10)/6-31G(d) geometry of *E,E*-**14** led to benzocyclobutadiene (**12c**). However, this difference between the two methods does not need to be emphasized very much, since the B3LYP minimum is extremely shallow and the ring-closure of *E,E*-**14** to **12c** is essentially barrierless at the B3LYP/6-31G(d) level of theory (*vide infra*).

For a given electronic state, the geometries of the three isomers are quite similar, and so are their energies (Table 1). By analogy to **2** and **3**, the singlet and triplet states are characterized by *o*-quinonoid structures (**4a**), whereas the quintet states are best described as "localized" *o*-phenylene(bis)carbenes (**4b**). As with the case of **13**, the bond length between the carbons adjacent to the reactive centers displays some variation; for **14** it increases in steps of 0.15–0.16 Å (B3LYP/6-31G(d) values) on going from the *E,E* to the *E,Z* to the *Z,Z* isomer. The magnitude of this lengthening effect is very similar to that in the case of **13** and in the same direction (meaning that a *Z* CH group contributes more to the lengthening of the C–C bond than an *E* CH group does). It is likely that this is due to hyperconjugation of the odd electron of the CH group with the antibonding combination of the carbons adjacent to the reactive centers. The *Z* orientation of the CH group (which corresponds to a "trans" orientation between the orbital of the odd electron and the $\sigma^*(\text{C}-\text{C})$ in question) is better aligned for this hyperconjugative interaction than the *E* orientation (Scheme 3).

Energetically the *E,Z* isomer is the more stable one, but the differences between the isomers are small (~ 1 kcal mol⁻¹). Interconversion between the different isomers can be achieved via the linearization of one of the radical centers, a process with a barrier of ~ 4 kcal mol⁻¹.²⁷ The quintet states lie 19–20 kcal mol⁻¹ in energy above the lowest singlet, somewhat lower than in the case of **2** and **3**. Again the singlet is calculated to be the ground state, with the triplet lying 3–4 kcal mol⁻¹ higher in energy.

The ring-opening reaction of **4** to give octadien-diyne **13** is calculated to have a barrier of 9.1 kcal mol⁻¹ (Table 2), somewhat higher than in the two previous cases.



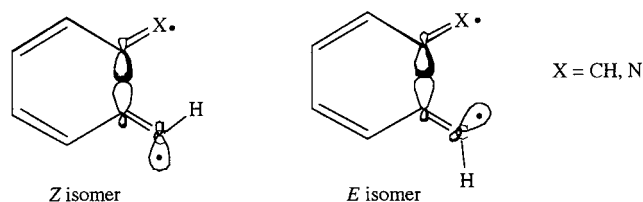
Z,Z-13

Discussion and Some Predictions

Both 1,2-diazidobenzene (**5**) and 2-azidophenyldiazomethane (**8**) give products as a result of double nitrogen-elimination upon excitation in an argon matrix at low temperature without showing any sign of formation of mono-carbene/nitrene intermediates, at least under the present conditions. It may be that such mono-carbene/nitrene species are highly photosensitive and therefore lose the remaining N₂ by subsequent photoexcitation before they accumulate to an extent detectable by our IR and ESR instruments. On the other hand, it is known that photochemical processes in noble gas matrixes sometimes result in the generation of reactive species in vibrationally excited states that undergo subsequent reactions faster than they dissipate energy to give thermally relaxed states. Therefore an intermediate thought to be involved is often elusive even under these

(27) *Z,Z* → *E,Z* isomerization requires 3.8 kcal mol⁻¹ (either on the singlet or on the triplet surface), whereas *E,Z* → *E,E* requires 4.5 kcal mol⁻¹ (triplet surface).

Scheme 3



conditions.²⁸ For instance, elimination of N₂ from diazomethane is estimated to require ~ 40 kcal/mol.²⁹ This means that an intermediate produced from the electronically excited state of **5** or **8** may still have enough excess energy for transfer to the appropriate vibrational mode for elimination of the remaining N₂.

The ortho-conjugatively linked compounds **1** can be predicted to have singlet ground states on the basis of simple spin-polarization arguments. This prediction is met by our calculations, which find that in bisnitrene **2**, carbenonitrene **3**, and biscarbene **4**, the singlet has the lowest energy, with the triplet lying 2–3 kcal mol⁻¹ higher in energy. At least in the case of **3**, this is compatible with the "silent" ESR results. Analogous para-conjugatively linked biscarbenes and nitrenes have also been reported to have singlet ground states with low-lying triplets.^{5–7}

Intramolecular reaction pathways available for the *o*-phenylene system are especially intriguing since they also provide insight into the nature of these exotic species. Bisnitrene **12**, carbenonitrene **13**, and biscarbene **14** are thermally quite labile,³⁰ and if we take into account the computational data as well, the reactivity pattern for the ring-opening reaction is **2** > **3** > **4**. This difference in reactivity can be considered in terms of the geometries of imino and vinyl radicals. ESR data and INDO calculations indicate that most of the spin density in imino radicals is concentrated in the p-orbital on nitrogen, while the free-spin value in the nitrogen 2s orbital is very low.³² On the other hand, ESR and product analysis data suggest that vinyl radicals have a nonlinear, sp²-like structure, where the spin density is in the sp² orbital of the carbon.³³ Thus, it is reasonable to think that in the *o*-quinone diradicals **2a**, **3a**, and **4a**, the p orbitals of the nitrogens (accommodating the "odd" electrons) are better aligned with the orbital of the breaking C–C bond than the sp² orbital of the vinyl radical, which is oriented somewhat away from the C–C bond. This better overlap is reflected also in the geometries of **14**, **13**, and **12**, where the length of the C–C σ bond in question generally increases as the vinyl radicals are gradually substituted by iminyl ones (the same trend but less pronounced is found also on the triplet surface). To the extent that these effects are present in the

(28) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 7250.

(29) (a) Laufer, A. H.; Okabe, H. *J. Am. Chem. Soc.* **1971**, *93*, 4137. (b) Papakondylis, A.; Mavridis, A. *J. Phys. Chem. A* **1999**, *103*, 1255.

(30) Despite the small S–T splitting, the spin–orbit coupling matrix elements between the two states are calculated to be smaller than 1 cm⁻¹, within a one-electron approximation.³¹ This suggests that intersystem crossing from the singlet to the triplet state should be very slow and therefore the latter state should not be an important factor in the thermal isomerization of the former.

(31) (a) Koseki, S.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem.* **1992**, *96*, 10768. (b) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga, N. *J. Phys. Chem.* **1995**, *99*, 12764. (c) Matsunaga, N.; Koseki, S.; Gordon, M. S. *J. Chem. Phys.* **1996**, *104*, 7988.

(32) Wood, D. E.; Lloyd, R. V.; Pratt, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 4115.

(33) (a) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1964**, *40*, 213. (b) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. (c) Shimamura, S. *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley: New York, 1969; Vol. IV, p 1.

corresponding transition state structures, the reactivity trend discussed above can be predicted. In addition, rehybridization of the carbon radical center from sp^2 to sp (as the vinyl group transforms to an acetylenic unit) during the course of isomerization may also contribute to an increasing reaction barrier in the same direction.

An alternative explanation for the faster ring-opening of **2** (as compared to **3** and **4**) can be provided in terms of simplistic thermodynamic arguments. According to the calculations, the exothermicity of the ring-opening isomerization increases with an increasing number of nitrogens ($4 < 3 < 2$) and by roughly 10 kcal mol⁻¹ for each CH unit substituted by N (Table 2). This is the same direction in which the barriers for the isomerization decrease, in accordance to what one may expect from Hammond's postulate.³⁴

Overall, both **12** and **13** ring-open quite fast, and the associated C–C bonds have very low BDEs (less than 3 kcal mol⁻¹ in the case of **12**). This is an unusual situation in organic chemistry but not unprecedented, as exemplified by the ring-opening reaction of the cyclopropylcarbinol radical, a well-studied isomerization.^{35,36}

To the extent that the previous thermodynamic argument can be applied to the ring-closure isomerization of **4**, **3**, and **2** (to form benzocyclobutadiene (**12c**), azabenzocyclobutadiene (**12b**), and diazabenzocyclobutadiene (**12a**), respectively), an interesting difference between **4** and its heteroatomic analogues is revealed. In this case, the exothermicity of the isomerization increases in a sense opposite to that of the ring-opening reaction (i.e., $4 < 3 < 2$). In addition, the exothermicity is increased by 30–40 kcal mol⁻¹ for each N substituted by a CH unit. The result is that, in the case of **4**, the ring-closure isomerization is heavily favored thermodynamically over the ring-opening one. According to Hammond's postulate, then, one expects that, on going from **12** to **13** to **14**, the preference for the ring-closure reaction will increase, and perhaps in the latter case ring-closure will be favored over ring-opening. Indeed this expectation is supported by the calculated barriers shown in Table 2.³⁷ Actually, the B3LYP/6-31G(d) barrier for the ring-closure of **14** is essentially zero, implying that *E,E*-**14** is not likely to be ever observed, since (if it exists) it would rapidly cyclize to **12c**. On the other hand, *Z,Z*- and *E,Z*-**14** require 4.5 kcal mol⁻¹ to isomerize to **12c** (via *E,E*-**14**). Thus, at low temperatures these isomers should be observable.

Experimental evidence that this prediction may be fulfilled is provided by the work of Jones et al.⁸ These workers provide strong arguments for the generation of *o*-phenylenebis(methylene) in the gas phase at high temperature (600 °C, 0.01 Torr) from the corresponding *p*-isomer (presumably via a carbene-carbene rearrangement) and propose that the dicarbene undergoes cyclization to produce benzocyclobutadiene (**12c**) based on the product analysis data. Obviously a better test of the validity of the theoretical prediction is the generation of **4** using

(34) The calculated transition state structures for the ring-opening of **12**, **13**, and **14** are characterized by increasing distances of the C••C breaking bonds (1.695, 1.774, and 1.842 Å, respectively), denoting increasingly later transition states.

(35) For a review on cyclopropylcarbinyl radical and several of its substituted derivatives (often used as "radical clocks"), see: Newcomb, M. *Tetrahedron* **1993**, *49*, 1150.

(36) Pasto, D. J. *J. Org. Chem.* **1996**, *61*, 252. (b) Martinez, F. N.; Schlegel, H. B.; Newcomb, M. *J. Org. Chem.* **1996**, *61*, 8457. (c) Smith, D. A.; Nicolaides, A.; Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1998**, *120*, 10223.

(37) The calculated distances of the C••C breaking bonds are 1.975, 2.249, and 2.574 Å for the ring-closure of **12**, **13**, and **14**, respectively, suggesting earlier TS in this direction.

matrix isolation techniques. However, due to the lack of a proper precursor, we have not been able to achieve this yet.

Conclusions

The available experimental and computational data suggest that bisnitrene **2** and carbenonitrene **3** can be generated photochemically in an inert matrix at low temperature. Both species are quite labile thermally and give ring-opening products (**6** and **9**, respectively) at temperatures around 35 K. Biscarbene **4** has not been generated yet, but it is predicted to be also labile thermally (like **2** and **3**). Unlike its analogues, it is expected to have a stronger preference for the ring-closure reaction (to form benzocyclobutadiene) than for the ring-opening reaction.

Experimental Section

Materials and General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer, and GC mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). ¹H NMR spectra were determined with a JEOL JNM-EX 270 spectrometer. UV/Vis spectra were determined with a Hitachi 200-S spectrometer. Column chromatography was carried out on Fuji Davison Silica gel BW-127ZH or ICN alumina (neutral). Thin-layer chromatography was done on Merck Kieselgel 60 PF254.

1-Azidophenyldiazomethane (8) was prepared according to a modified procedure of Rees.^{9c} Thus, a mixture of 2-azidobenzaldehyde (170 mg, 1.16 mmol) and *p*-tosylhydrazine (216 mg, 1.16 mmol) in anhydrous tetrahydrofuran (30 mL) was stirred overnight at room temperature in the dark. After evaporation of the solvent, 2-azidobenzaldehyde tosylhydrazone was obtained as yellowish solid (334 mg, 91.4%), which was used for the next step without further purification. To a stirred suspension of sodium hydride (60% oil suspension, 25.2 mg, 0.63 mmol) in anhydrous tetrahydrofuran (3 mL) was added the hydrazone (200 mg, 0.63 mmol), and the mixture was stirred for 15 min at room temperature. The precipitate was collected by filtration and washed thoroughly with anhydrous ether to give sodium 2-azidobenzaldehyde tosylhydrazone as a dark solid (282 mg, 98%). The sodium salt (50 mg, 0.15 mmol) was placed in a micro sublimation apparatus and heated at 120 °C under 5×10^{-4} Torr. The diazo azide **8** was collected from a coldfinger as a rather unstable red solid (18 mg, 75%) and was immediately used for the matrix photolysis experiments. ¹H NMR (CDCl₃) δ 5.15 (s, 1 H), 6.87–7.71 (m, 4 H); IR (Ar, 10 K), 2130 (vs), 2092 (vs), 2064 (vs), 1597 (m), 1579 (w), 1494 (s), 1376 (s), 1301 (s), 1292 (vs), 1160 (w), 1145 (w), 1079 (w), 743 (s), and 693 (m) cm⁻¹.

1-Cyanohexa-1,3-dien-5-yne (9) was prepared according to the modified procedure of Rees.^{9f} Thus, sodium 2-azidobenzaldehyde *p*-tosylhydrazone (50 mg, 0.15 mmol) was pyrolyzed at 280 °C under 5×10^{-4} Torr using a flash vacuum pyrolysis apparatus.³⁸ The pyrolysate was condensed on a coldfinger cooled with liquid nitrogen, collected, and purified by preparative TLC (*n*-hexane/ether 3:1) to afford **9** as a yellowish liquid (9.4 mg, 60%). ¹H NMR (CDCl₃) δ 3.48 (s, 1 H), 5.40 (d, *J* = 10.88 Hz, 1 H), 5.89 (d, *J* = 11.2 Hz, 1 H), 6.94 (dd, *J* = 10.88, 11.22 Hz, 1 H), 7.38 (dd, *J* = 10.56, 11.2 Hz, 1 H); IR (Ar, 10 K) 3244 (w), 2224 (w), 1241 (w), 986 (m), 748 (m), 626 (w) cm⁻¹; HRMS 103.0422 (C₇H₅N requires 103.0422).

1,2,3-Benzotriazine (11),^{9e} **1,2-diazidobenzene (5)**,^{8b} and **1,4-dicyano-1,3-butadiene (6)**^{8b} were prepared according to the literature procedures.

Computational Procedures. Ab initio molecular orbital calculations³⁹ were carried out using the GAUSSIAN 94,⁴⁰ GAMESS,⁴¹ and

(38) Tomioka, H.; Kobayashi, N.; Murata, S.; Ohtawa, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8771.

(39) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(40) 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.;

MOLCAS⁴² programs. Optimized geometries were obtained at the B3LYP/6-31G(d)^{40,43} and MCSCF(10,10)/6-31G(d) levels of theory. Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.⁴⁴

For the DFT calculations, UB3LYP functionals were used to describe the open-shell singlet biradicals (**12**, **13**, and **14**). As suggested by the high spin contamination (Table 1), these are not "pure" singlet states, but rather (roughly equal) mixtures of singlet and triplet states.¹¹ However, since multireference DFT methods are currently not available, we consider this to be the closest approximation to the singlet states (within the DFT approach). Some justification for this is also provided by the fact that the S–T gap in these systems is quite small (Table 1). The active space for the MCSCF(10,10) calculations consisted of 10 electrons (the 8 π electrons plus the two "odd" σ electrons). CASPT2/6-31G(d) calculations were carried out with MOLCAS at the MCSCF(10,10)/6-31G(d) optimized geometries using the MCSCF(10,10) wave functions as a reference basis.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by means of standard techniques^{45,46} 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 fit with KBr windows for spectroscopic viewing, and the remaining ports were fitted 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 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 500-W xenon high-pressure arc lamp or an Ushio 500-W mercury high-pressure arc lamp. For broad-band irradiation, Toshiba cutoff filters were used (50% transmittance at the wavelength specified).

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Supporting Information Available: Optimized UB3LYP geometries (Table S1), calculated frequencies and intensities (Table S2), and calculated IR spectra for **7** and **10** (Figure S1) and for isomers of **9** (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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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.

(41) Schmidt, M. W.; Baldridge, K. K.; Boats, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347.

(42) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. O.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O. *Molcas Version 4*; Lund University, Sweden 1997.

(43) (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.

(44) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(45) Tomioka, H.; Ichikawa, N.; Komatsu, K. *J. Am. Chem. Soc.* **1992**, *114*, 6045.

(46) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.