Structure and Rearrangements of 1,3-Diphenylpropynylidene

Jeffrey T. DePinto and Robert J. McMahon*

Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706-1396

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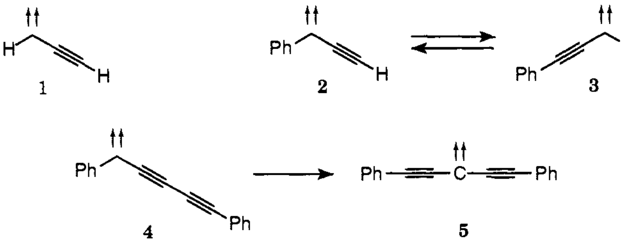
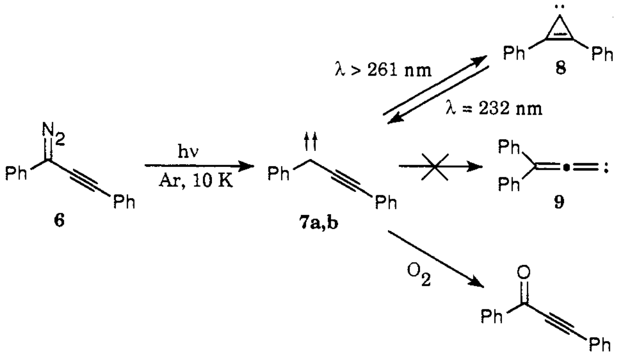
We seek a better understanding of the factors that influence electronic delocalization in open-shell, conjugated π-electron systems. Unsaturated organic carbenes serve as model systems in which these factors can be probed in detail. Propynylidene (**1**),[1-8] the simplest acetylenic carbene, can be viewed as the prototypical example of a conjugated polyyne chain containing a "defect" in the form of the carbene center. We are interested in determining whether this defect remains localized in the chain, propagates through the chain, or delocalizes over a substantial portion of the chain. If the defect remains localized, bond-shift isomerism is possible in both unsymmetrically-substituted propynylidenes (e.g., phenylpropynylidenes **2** and **3**)[1,8-10] and symmetrically-substituted carbenes consisting of two or more alkyne units (e.g., diphenylpentadiynylidenes **4** and **5**).[1,11] The chemical rearrangements of acetylenic carbenes are fundamentally interesting in their own right[1-11] and have recently been exploited in synthetic chemistry.[12] In addition, these carbenes serve as simple models for (i) defects in other conjugated systems, such as conducting polymers, and (ii) reactive intermediates involved in formation of new allotropes of carbon. In this study, we describe our preliminary findings concerning the structure and rearrangements of 1,3-diphenylpropynylidene (**7a,b**). Our experiments reveal a type of isomerism which, by virtue of the symmetric disubstitution, cannot be attributed to bond-shift isomerism. This observation raises questions concerning recent reports of bond-shift isomerism in acetylenic carbenes.[9,11]



Photolysis ($\lambda > 571$ nm) of 1,3-diphenyldiazopropyne (**6**),[13] matrix-isolated in argon at 10 K,[14] gives rise to a ca. 4:1 mixture of *two* species, as monitored by ESR, IR, and UV/vis spectroscopy.[15,16] We assign these two species as conformational isomers of triplet 1,3-diphenylpropynylidene (**7a** and **7b**) (Scheme I) on the basis of the following chemical and spectroscopic information. The ESR spectrum yields zero-field splitting parameters[17] (**7a**, $|D/hc| = 0.484$, $|E/hc| = 0.004\ 23$ cm^{-1}; **7b**, $|D/hc| = 0.468$, $|E/hc| < 0.0002$ cm^{-1}) that are in good accord with those expected for triplet arylcarbenes.[2,18] The IR spectra of **7a** and **7b** show strong absorptions characteristic of a monosubstituted phenyl ring (**7a**, 748, 680 cm^{-1}; **7b**, 745, 678 cm^{-1}), and a weak absorption characteristic of an acetylenic C≡C stretch in conjugation with the carbene center (**7a**, 1649 cm^{-1}; **7b**, 1645 cm^{-1}).[5c,8,15,16] The UV/vis spectrum of **7a** shows the long-wavelength π–π^* transitions (456–541 nm) characteristic of triplet arylcarbenes.[19] Warming an argon matrix containing the 4:1 mixture of **7a** and **7b** to 39 K and recooling to 10 K results in a decrease of the IR, UV/vis, and ESR signals of **7a**, and an increase in those of **7b**, to give a ca. 2:1 mixture of **7a** and **7b**.

Scheme I



ESR spectra obtained in two additional matrices are very similar to those described for argon, enabling us to rule out matrix effects

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(1) For reviews of the chemistry of acetylenic carbenes, see: (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971. (b) Jones, M., Moss, R. A., Eds. *Carbenes*; Wiley: New York, 1973; Vol. I and II. (c) Regitz, M., Ed. *Methoden der Organischen Chemie* (Houben-Weyl); G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 769–774. (d) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583–1621.

(2) (a) Skell, P. S.; Klebe, J. *J. Am. Chem. Soc.* **1960**, *82*, 247–248. (b) Gramas, J. V. Ph.D. Dissertation, The Pennsylvania State University, 1965. (c) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196–200. (d) Bernheim, R. A.; Kempf, R. J.; Reichenbecher, E. F. *J. Magn. Reson.* **1970**, *3*, 5–9.

(3) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378–4383.

(4) DeFrees, D. J.; McLean, A. D. *Astrophys. J.* **1986**, *308*, L31–L35.

(5) (a) Čársky, P.; Špirko, V.; Hess, B. A.; Schaad, L. J. *J. Phys. Chem.* **1990**, *94*, 5493–5496. (b) Maier, G.; Reisenauer, H. P.; Schwab, W.; Čársky, P.; Špirko, V.; Hess, B. A.; Schaad, L. J. *J. Chem. Phys.* **1989**, *91*, 4763–4773. (c) Maier, G.; Reisenauer, H. P.; Schwab, W.; Čársky, P.; Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 5183–5188.

(6) Jonas, V.; Böhme, M.; Frenking, G. *J. Phys. Chem.* **1992**, *96*, 1640–1648.

(7) Blush, J. A.; Clauberg, H.; Kohn, D. W.; Minsek, D. W.; Zhang, X.; Chen, P. *Acc. Chem. Res.* **1992**, *25*, 385–392.

(8) DePinto, J. T. Ph.D. Dissertation, University of Wisconsin, 1993.

(9) Koga, N.; Matsumura, M.; Noro, M.; Iwamura, H. *Chem. Lett.* **1991**, 1357–1360.

(10) (a) DePinto, J. T.; McMahon, R. J. *Abstracts of Papers*, 201st National Meeting of the American Chemical Society, Atlanta, GA; American Chemical Society: Washington, DC, 1991; ORGN 354. (b) DePinto, J. T.; McMahon, R. J., *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, DC, 1992; ORGN 555. (c) DePinto, J. T.; McMahon, R. J. 11th IUPAC Conference on Physical-Organic Chemistry, Ithaca, NY, 1992.

(11) Noro, M.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 4916.

(12) (a) Franck-Neumann, M.; Geoffroy, P.; Miesch, M.; Zaragoza Dörwald, F. *Tetrahedron Lett.* **1990**, *31*, 4121–4124. (b) Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637–2647.

(13) 1,3-Diphenyldiazopropyne (**6**) was prepared from the corresponding 2,4,6-triisopropylbenzenesulfonyl hydrazone. Experimental details are available as supplementary material.

(14) The apparatus and experimental technique for matrix isolation spectroscopy have been described elsewhere: Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183–7189 and references therein. In ESR warming experiments with argon, the argon matrices were capped with xenon in order to better maintain the integrity of the matrix at elevated temperatures: Swanson, B. I.; Jones, L. H. *J. Mol. Spectrosc.* **1981**, *89*, 566–568.

(15) 1,3-Diphenylpropynylidene (**7a**): IR (Ar, 10 K) 1649 w, 1556 m, 1478 m, 1461 m, 1438 m, 748 s, 680 s cm^{-1}; UV/vis (Ar, 10 K) λ_{max} 217.2, 266.4, 279.2, 287.2, 297.2, 307.6, 314.4, 324.8, 332.4, 335.6, 343.2, 456.4, 459.6, 463.3, 472.3, 494.9, 498.1, 498.7, 507.6, 508.5, 510.9, 511.8, 512.8, 513.9, 520.8, 522.1, 539.5, 540.8 nm; ESR (Ar, 10 K) $|D/hc| = 0.484$, $|E/hc| = 0.004\ 23$ cm^{-1}; Z_1 1778, X_2 5316, Y_2 5490, Z_2 8571 G; frequency = 9.5304 GHz; ESR (MTHF, 4 K) $|D/hc| = 0.457$, $|E/hc| = 0.0113$ cm^{-1}; Z_1 1542, X_2 5017, Y_2 5477, Z_2 8220 G; frequency = 9.3516 GHz; ESR (MCH, 4 K) $|D/hc| = 0.457$, $|E/hc| = 0.0102$ cm^{-1}; Z_1 1547, X_2 5053, Y_2 5465, Z_2 8218 G; frequency = 9.3515 GHz.

(16) 1,3-Diphenylpropynylidene (**7b**): IR (Ar, 10 K) 1645 w, 1553 m, 1472 m, 1458 m, 1435 m, 745 s, 678 s cm^{-1}; UV/vis (Ar, 10 K) 273.2, 278.4, 294.4 nm; ESR (Ar, 10 K) $|D/hc| = 0.468$, $|E/hc| < 0.0002$ cm^{-1}; Z_1 1612, XY 5306, Z_2 8404 G; frequency = 9.5313 GHz; ESR (MTHF, 4 K) $|D/hc| = 0.458$, $|E/hc| < 0.0002$ cm^{-1}; Z_1 1562, XY 5219, Z_2 8226 G; frequency = 9.3507 GHz; ESR (MCH, 4 K) $|D/hc| = 0.460$, $|E/hc| < 0.0002$ cm^{-1}; Z_1 1580, XY 5226, Z_2 8252 G; frequency = 9.3515 GHz.

(17) Zero-field splitting parameters were determined from the best fit of the observed ESR spectra to the spin Hamiltonian (assuming $g_x = g_y = g_z = g_e$): Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772. The upper limit for $|E/hc|$ was determined by assuming that we could resolve X_2 and Y_2 transitions separated by >10 G. Thus, the upper limit for $|E/hc|$ was calculated using $X_2 = XY - 5$ G, $Y_2 = XY + 5$ G.

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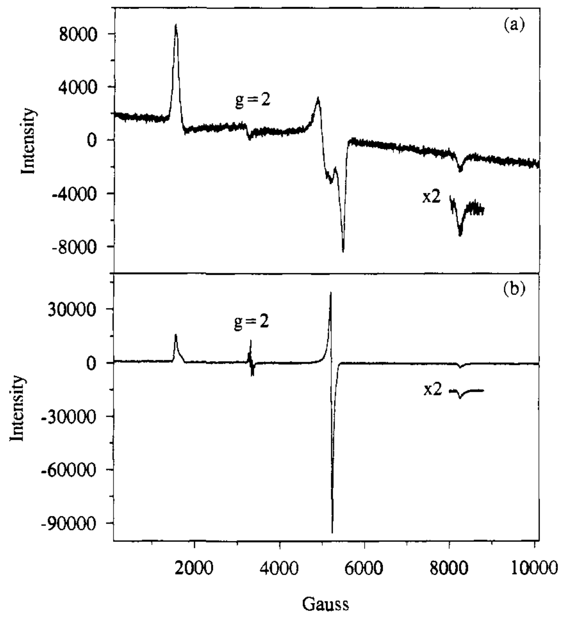
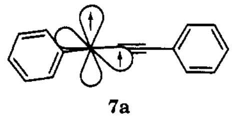


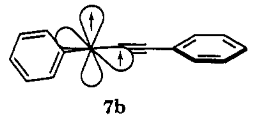
Figure 1. (a) ESR spectrum of 1,3-diphenylpropynylidene (**7a**) obtained upon photolysis (λ > 571 nm) of 1,3-diphenyldiazopropyne (**6**) matrix-isolated in MTHF at 4 K. (b) ESR spectrum obtained after warming the matrix in spectrum a to 90 K for 15 min and cooling back to 4 K. Spectrum shows disappearance of **7a** and appearance of **7b**.

as the cause of the two observed ESR signals. Long-wavelength irradiation (λ > 534 nm, 1 h) of 1,3-diphenyldiazopropyne (**6**) matrix-isolated in a 2-methyltetrahydrofuran glass (MTHF, 5.3 mM) at 4 K in the cavity of an ESR spectrometer produces the triplet ESR signal of **7a** (Figure 1a).[15,16] Warming the matrix to 90 K causes the original triplet signal to disappear almost completely, with concomitant growth of a new triplet ESR signal of **7b** (Figure 1b). Similar behavior is observed upon irradiation of diazo compound **6** in a methylcyclohexane (MCH) glass.[15,16] In MCH, photolysis produces **7a** and a small amount of **7b**. Warming the matrix to 65 K results in a large decrease of the ESR signals of **7a** and concomitant growth of the ESR signals of **7b**. Subsequent warming to 80 K followed by recooling to 4 K results in essentially complete conversion of **7a** to **7b**. These results suggest that the barrier to rearrangement of **7a** to **7b** is matrix-dependent.[20]

The chemical reactivity of **7a** and **7b** is consistent with the proposed structure. Photolysis (λ > 261 nm) of 1,3-diphenylpropynylidene (**7a** and **7b**) in argon at 10 K results in the disappearance of the IR, UV/vis, and ESR signals of **7a** and **7b**, and in the appearance of diphenylcyclopropenylidene (**8**) (Scheme I).[21] The structural assignment of **8** is based on the observation of the strong symmetric C–C stretch of the cyclopropenylidene moiety at 1332 cm^{-1}.[5,8,22] As in the parent system,[5,8] this process is photochemically reversible. Photolysis (λ = 232 ± 7 nm) of cyclopropenylidene **8** results in the disappearance of its IR and UV/vis signals with the concomitant appearance of the IR, UV/vis, and ESR signals of both **7a** and **7b**.[23] Interestingly, 1,3-migration of a phenyl group to form diphenylvinylidenecarbene (**9**) does not occur under any photolysis conditions, as demonstrated by the absence of a strong infrared absorption in the vicinity of 1950 cm^{-1}. Photolysis (λ > 571 nm, 15 h) of 1,3-diphenyldiazopropyne (**6**) in an argon matrix doped with 5.0% O_2 results in chemical trapping of **7a** and **7b** to yield 1,3-diphenylpropynone as the major product, a reaction characteristic of triplet carbenes (Scheme I).[24]

Isomerism in triplet 1,3-diphenylpropynylidenes could, in principle, arise due to the existence of two conformations that differ in the relative orientations of the two phenyl substituents.[25,26] In **7a**, the aryl rings are coplanar, which permits delocalization of one unpaired electron at the carbene center. In **7b**, the aryl rings are perpendicular, which permits delocalization of both unpaired electrons at the carbene center. As long as the bond angle at the carbene carbon in **7a** is comparable to or smaller than the angle in **7b**,[27] the structure of **7a** deviates more strongly from axial symmetry than the structure of **7b**. Assuming the point dipole approximation,[26] this results in a larger value of $|E/hc|$ for **7a**. The perpendicular arrangement of the phenyl rings in **7b** is also consistent with the observation that **7b** exhibits shorter-wavelength electronic absorptions than **7a**. Our explanation of isomerism in terms of the relative orientation of the two phenyl substituents is independent of the precise geometry of the propynylidene moiety;[27,28] further experimental and computational studies will be required to fully elucidate the detailed structure of triplet 1,3-diphenylpropynylidene.


7a


7b

Our results concerning 1,3-diphenylpropynylidene bring into question recent conclusions drawn by Iwamura and co-workers in their study of phenylpropynylidenes **2** and **3**[9] and diphenylpentadiynylidenes **4** and **5**.[11] We find that conformational isomerism, in a system that cannot exhibit bond-shift isomerism, produces ESR spectra that are virtually identical to spectra reported by Iwamura and interpreted in terms of bond-shift isomerism.[9,11] In light of these results, we believe that additional experimental evidence is required to substantiate the existence of bond-shift isomerism in acetylenic carbenes.

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Supplementary Material Available: IR, UV, and ESR spectra for 1,3-diphenylpropynylidene (**7a,b**) and diphenylcyclopropenylidene (**8**) matrix-isolated in argon and experimental and spectroscopic data for 1,3-diphenyldiazopropyne (**6**) (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) The observation of the triplet ESR signal at 10 K implies that the triplet state either is the ground state or lies within several calories/mole of the ground state: Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 208.

(19) The absence of the corresponding absorptions for **7b** could signal a significant structural difference between **7a** and **7b**, or it could simply reflect our inability to generate a sufficiently high concentration of **7b**.

(20) Dougherty has investigated matrix site effects and the matrix dependence of unimolecular rearrangements: Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240–2252.

(21) Diphenylcyclopropenylidene (**8**): IR (Ar, 10 K) 1332 s, 1051 m, 762 s, 690 s, 583 m, 518 m cm^{-1}; UV/vis (Ar, 10 K) λ_{max} 220.0, 225.2, 244.8, 255.2, 266.8, 272.8, 280.0, 286.4, 295.6 nm. Carbene **8** possesses a singlet electronic ground state.[5]

(22) Lee, T. J.; Bunge, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, *107*, 137–142.

(23) The reversible formation of *both* carbenes (**7a** and **7b**) upon photolysis of **8** establishes that **7a** and **7b** do not differ simply in the orientation of the carbene and N_2 in the matrix site.

(24) (a) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344–354. (b) Sander, W. *J. Org. Chem.* **1988**, *53*, 121–126. (c) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 988.

(25) 1,3-Diphenylpropynylidene cannot exhibit the type of conformational isomerism displayed by carbenes that bear substituents lacking C_2 symmetry (e.g., 1-naphthylcarbene).[26]

(26) Roth, H. D.; Hutton, R. S. *Tetrahedron* **1985**, *41*, 1567–1578.

(27) Calculations predict a 140–150° bond angle at the carbene carbon in triplet propynylidene (**1**),[4,5] and ^{13}C hyperfine coupling constants establish a 160° bond angle in triplet 1-phenylpropynylidene (**2**) and 3-phenylpropynylidene (**3**).[8]

(28) Recent QCISD 6-31G* calculations predict an allenic 1,3-diradical structure (C_2) for triplet propynylidene: R. Herges (Erlangen), personal communication.