J. Am. Chem. Soc. **1994,** *116,* 9381-9382 9381

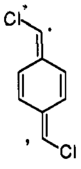
Substituent Switching of Biscarbene Electronic Configurations: *p*-Phenylenebis(fluoromethylene)

Peter S. Zuev and Robert S. Sheridan*

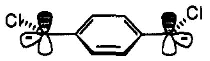
Department of Chemistry, University of Nevada
Reno, Nevada 89557

Received June 6, 1994

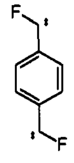
Motivated at least in part by the quest for organic magnetic materials, considerable effort has been focused on high-spin polycarbenes.[1] Systems comprised of triplet carbene subunits joined ferromagnetically across aromatic linkers have attracted the bulk of the attention. Yet, only a small fraction of the electronic states *potentially* arising from carbene–carbene interactions have high multiplicity.[2] Surprisingly, much less is known about lower-spin situations. In a general approach to this area, we have begun to explore aryl-coupled singlet carbene subunits.[3] Along these lines, we[4] and Tomioka and co-workers[5] recently described matrix isolation investigations of *p*-phenylenebis(chloromethylene) (**1**). Spectroscopic and reactivity evidence indicated that a diradical (**1a**, $\sigma^2\pi^2$) is favored over a biscarbene (**1b**, $\sigma^2\sigma^2$) electronic configuration. Hence, the gain in covalency appears to override the tendency of the "subunit" chlorocarbene centers to have closed-shell σ^2 configurations. We have reasoned that substituents that more strongly stabilize singlet carbenes might tip these systems toward biscarbene character. We now report investigations of *p*-phenylenebis(fluoromethylene) (**2**), where this appears to be the case.



1a



1b



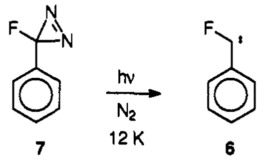
2

Bisdiazirine **3** was prepared from *p*-phenylenebis(bromodiazirine)[4] by reaction with *n*-Bu_4NF via procedures described for the synthesis of 3-fluoro-3-aryldiazirines (see supplementary material).[6] Irradiation (385 nm, 2.5 h) of a 12 K N_2 matrix containing **3** led to the disappearance of the starting material and gave primarily monocarbenemonodiazirine **4**, as judged by IR and UV/vis spectroscopy.[7] Intermediate **4** exhibited characteristic[8] diazirine absorptions in the IR (1563 cm^{-1}) and UV (376, 363, 356, and 338 nm), along with strong 300 nm and broad 450–750 nm (λ_{max} = 580 nm) electronic absorptions which are typical for arylhalocarbenes.[3,9] The matrix turned intense blue, reflecting the visible absorption of **4**.

Subsequent irradiation with 374 nm light slowly (ca. 13 h) transformed matrix-isolated **4** into a new species (Figure 1) which lacked the diazirine signatures in the IR and UV but still exhibited carbene UV (300 nm) and visible (480–800 nm, λ_{max} = 600 nm) absorptions. Trapping experiments verified that this species was biscarbene **2**. Warming an HCl-doped N_2 matrix (0.5% HCl) containing **2**, photochemically prepared as above, to 35–40 K resulted in the disappearance of the spectra of **2** and the growth of IR bands of α,α'-difluoro-α,α'-dichloro-*p*-xylene (**5**).[10] These results are summarized in Scheme 1.

The biscarbene **2** could also be generated and observed by IR and UV/vis in 3-methylpentane and CH_4 matrices, where it survived annealing to 60 and 46 K, respectively. Finally, **2** was stable in O_2 (2.5%) containing N_2 matrices up to 40 K, at which temperature the biscarbene slowly began to disappear to give uncharacterized products.

Although the matrix spectroscopy of phenylfluorocarbene (**6**) has been briefly described previously,[11] we repeated this work for purposes of comparison. Irradiation of 3-fluoro-3-phenyldiazirine (**7**) matrix isolated in N_2 at 13 K produced **6**, with IR spectra similar to those reported. A previously unreported deep blue color and attendant UV/vis absorptions at 300 nm and 450–740 nm (λ_{max} = 550 nm) were also observed, however.



7 **6**

It is instructive to compare the above results for **2** with those previously reported[4,5] for the chloro analog **1**. The conclusion that **1** is best described as a diradical (**1a**) rested on five pieces of evidence. (1) IR spectra indicated a quinonoid structure for **1**. (2) Compound **1** exhibited highly structured absorption in a region of the visible spectrum (400–500 nm) where phenylchlorocarbene does not absorb. (3) The diradical **1** was extremely reactive with hydrocarbons, abstracting H atoms from CH_4 at even 30 K. (4) In contrast to the usual CH insertion chemistry of singlet carbenes, **1** showed H-abstraction reactions. (5) Tomioka and co-workers have reported[5] that diradical **1** reacts readily with O_2 under matrix conditions, where phenychlorocarbene reacts only reluctantly.[12]

Analogous criteria indicate that **2** is a bis-closed-shell-carbene ($\sigma^2\sigma^2$) rather than a diradical. (1) The IR spectrum of **2** is characteristic for a *p*-disubstituted aromatic. In particular, strong ca. 1600 cm^{-1} bands corresponding to exocyclic C=C stretches (as seen in **1**) are not observed.[13] The major absorptions of **2** are

---

[1] For example, see the following along with references cited therein: (a) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179; (b) Iwamura, H. *Pure Appl. Chem.* **1993**, *65*, 57. (c) Furukawa, K.; Matsumura, T.; Teki, Y.; Kinoshita, T.; Takui, T.; Itoh, K. *Mol. Cryst. Liq. Cryst.* 1993, *232*, 251.

[2] Dougherty and co-workers have pointed out that a system comprising four electrons in four degenerate orbitals affords the possibility of 36 electronic states, including one quintet, 15 triplets, and 20 singlets. (a) McElwee-White, L.; Goddard, W. A., III; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3461. (b) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744.

[3] We have recently reported that *m*-phenylenebis(chloromethylene) is a closed-shell ground state singlet, in contrast to the multitude of previously studied *m*-arylbiscarbenes.[1] Zuev, P. S.; Sheridan, R. S. *J. Org. Chem.* **1994**, *59*, 2267.

[4] Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788.

[5] Tomioka, H.; Komatsu, K.; Nakayama, T.; Shimizu, M. *Chem. Lett.* **1993**, 1291.

[6] Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

[7] For matrix isolation and instrumentation details, see: (a) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. (b) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879. See supplementary material for a detailed description of the spectra of **4**.

[8] *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. I.

[9] (a) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576. (b) Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. *Tetrahedron Lett.* **1983**, *24*, 685. (c) Cox, D. P.; Gould, I. R; Hacker, N. P.; Moss, R. A.; Turro, N. J. *Tetrahedron Lett.* **1983**, *24*, 5313. (d) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday Jr., C.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

[10] Compound **5** was independently synthesized by solution irradiations of bisdiazirine **3** in the presence of HCl. See the supplementary material for details.

[11] McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456.

[12] (a) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517. (b) Sander, W. W. *Spectrochim. Acta* **1987**, *43A*, 637. (c) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

[13] If **2** exhibited quinonoidal character analogous to that of **1a**, F-substitution on the exocyclic double bonds would be expected to lead to 1600–1700 cm^{-1} bands, more intense than the corresponding strong 1580 cm^{-1} absorption observed in **1**.[14] Weak absorptions are observed in this region, which might arise from combination bands in **2**.

0002-7863/94/1516-9381$04.50/0

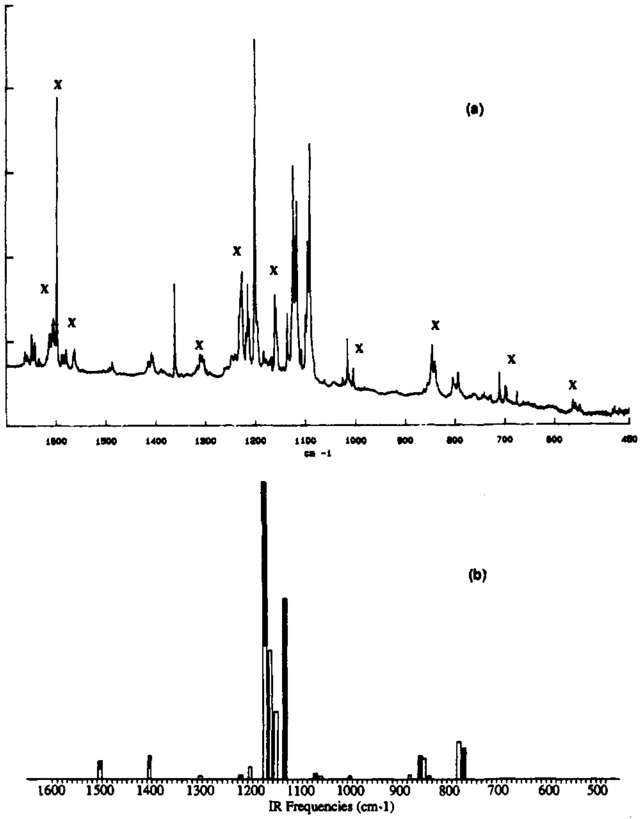
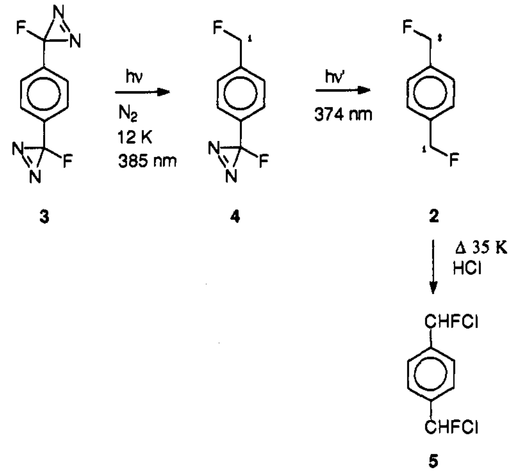


Figure 1. (a) IR absorbance spectrum of *p*-phenylenebis(fluoromethylene) (**2**) matrix isolated in N_2 at 12 K prepared as described in the text. Residual **3** and **4**, as well as H_2O at 1600 cm^{-1}, are indicated by **X**. (b) Ab initio (6-31G*) calculated IR spectra for *anti*-**2** (solid) and *syn*-**2** (open). Frequencies have been scaled by a factor of 0.9.

Scheme 1



found in the 1200–1100 cm^{-1} region, where electron withdrawing group disubstituted aromatics (and CF bonds) strongly absorb.[14] The IR of **2** closely resembles that of terephthaloyl fluoride (excluding C=O)[15] in the same fashion that **6**[11] and phenylchlorocarbene[3,12] have IR spectra similar to the corresponding benzoyl halides. (2) The UV/vis spectrum of **2** is nearly identical to those of monocarbenes **4** and **6**, exhibiting none of the radical-like structure seen in **1**.[4,5,16] (3) No H-abstraction from hydrocarbons by **2**, up to at least 60 K, is observed. (4) Biscarbene **2** does not react with O_2 under conditions where **1** reacts rapidly.[5,17] (5) The IR (Figure 1) and UV/vis spectra of **2** reasonably fit predictions of ab initio calculations. The geometry of biscarbene **2** was optimized in both the anti and syn conformations at the 6–31G* level, as was the geometry of monocarbene **6** for comparison.[18] The calculated geometries of the mono- and biscarbenes are very similar, with no indication of quinoidal distortions in **2**.[18] CIS/6-31G* calculations predict first excited singlet transitions at 438 nm for **6** and 470 nm for **2**.

In summary, *p*-phenylenebis(fluoromethylene) (**2**) and the bis(chloromethylene) **1** exhibit dramatically different spectroscopic and chemical properties. There exists a considerable amount of experimental[19] and calculational[20] data indicating that fluorine, due to stronger π-donor and σ-acceptor properties, is a more powerful stabilizer of singlet carbenes than is chlorine. Our results imply that the fine balance between electronic configurations in the *p*-linked systems can be selectively tipped toward either diradicals (**1a**) or biscarbenes (**2**) via these subtle substituent effects.[21-23]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-9215177) for generous support. We also thank the National Science Foundation for partial funding for the purchase of the Convex C210 computer used in this work.

Supplementary Material Available: Ab initio geometries for **2** (syn and anti) and **6**, synthetic procedures and spectral data for **3** and **5**, spectrocopic data for **4**, and IR spectrum of matrix-isolated terephthaloyl fluoride (4 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.

---

(14) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley and Sons: New York, 1980.

(15) Terephthaloyl fluoride was synthesized from reaction of terephthaloyl chloride with KF according to the procedure described in the following: Naumov, V. S.; Sokolov, A. B.; Ushakova, A. G. *J. Gen. Chem. USSR* **1968**, *38*, 2407. The matrix IR spectrum of the difluoride is displayed in the supplementary material.

(16) Singlet carbenes characteristically exhibit $\sigma \rightarrow \pi$ transitions in the visible.[3] See, for example: O'Gara, J. E.; Dailey, W. P. *J. Am. Chem. Soc.* **1992**, *114*, 3581.

(17) We have independently confirmed[5] that the bischloro diradical **1** reacts readily with 2.5% O_2-doped N_2 matrices at 30 K under conditions where **2** is stable.

(18) Ab initio calculations were carried out with Gaussian 90: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*, Revision J; Gaussian, Inc.: Pittsburgh, PA, 1990. The geometries of the syn and anti conformations of **2**, as well as that of **6**, were optimized at the RHF level of theory with the 6-31G* basis set under the constraint of C_{2v}, C_{2h}, and C_s symmetry, respectively. Vibrational frequency calculations gave zero imaginary frequencies for all three species. Geometric parameters are given in the supplementary material.

(19) (a) Moss, R. A.; Ho, G.-J.; Liu, W. *J. Am. Chem. Soc.* **1992**, *114*, 959 and references therein. (b) Gilles, M. K.; Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1992**, *96*, 1130.

(20) (a) Liebman, J. F.; Simons, J. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 1, p 51. (b) Shin, S. K.; Goddard, W. A., III; Beauchamp, J. L. *J. Chem. Phys.* **1990**, *93*, 4986 and references therein.

(21) We have further confirmed the assignment of monocarbene **4** by in situ trapping in an HCl-doped matrix. The experimental details will be given in a full paper.

(22) *p*-Phenylenebis(phenylmethylene) is reported to possess a singlet ground state with an excited triplet that can be thermally populated and observed by EPR.[23] Low temperature irradiations of the bisdiazirine precursor of **1** have as yet not yielded any triplet EPR spectra (Professor Paul Lahti, University of Massachusetts, Amherst, MA, personal communication). Based on the results described in the text, we believe that observation of a thermally accessible higher multiplicity state for **2** is even less likely.

(23) Sixl, H.; Mathes, R.; Schaupp, A.; Ulrich, K.; Huber, R. *Chem. Phys.* **1986**, *107*, 105.