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p-Phenylenebismethylene: Characterization, Calculation, and Conversion to a Conjugated Bis-Carbonyloxide

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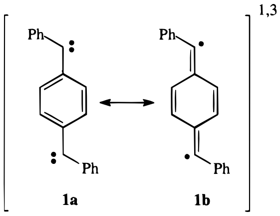
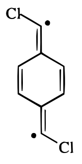
The search for new molecular magnetic materials has spawned numerous studies of high-spin systems built around triplet carbene subunits linked across *m*-phenylenes.[1] In these ferromagnetically coupled systems, covalent interaction between the triplet centers is topologically prohibited, but communication via shared π-space maximizes multiplicity. Considerably less is known about their conjugated cousins, *p*-phenylenebiscarbenes,[1a] where spin-pairing between the triplet carbene units leads to lower spin overall. For example, **1** has an EPR silent singlet ground state, but a thermally accessible triplet state ca. 1 kcal/mol higher in energy can be detected.[2−4] It has been suggested that this biscarbene system is represented more accurately as **1b**. Substituents can have a profound influence on the electronic configurations in these systems, however. For example, we have shown that the bischloro system **2** is best described as a quinonoidal biradical,[5] but bisfluoro-**3** is a closed shell bis-singlet carbene.[6,7] We now report the first spectroscopic characterization of the parent *para* system, *p*-phenylenebismethylene (**5**), a preliminary examination of its chemistry, and its conversion to a conjugated bis-carbonyl oxide.



1a **1b**



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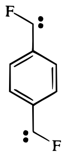

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Although bis-diazo compound **4** was first reported in 1964,[8] little of its chemistry has been described. However, we found that irradiation (334 nm) of **4** in a 10 K N_2 matrix produced a new species in the IR and UV/vis spectra that we attribute to biradical **5** (Figure 1).[9,10] Irrespective of irradiation conditions, all of the IR bands of **4** disappeared in concert, with simultaneous growth of those of **5**; no monodiazo compound could be observed. The matrix also developed a richly structured UV/vis spectrum, with strong bands at 365, 389, 418, and 460 nm, along with a long regularly structured tail extending to 700 nm.

In contrast to phenylcarbene itself, which is notoriously photolabile,[11] biscarbene **5** was surprisingly stable to photolysis. Broadband irradiation (>200 nm) for hours had negligible effect on the spectra of **5**. The biscarbene could be trapped in situ, however. Warming an HCl-containing nitrogen matrix (2% HCl in N_2) of **5** to 36 K caused the IR and UV/vis bands of **5** to disappear and those of **6** to appear concurrently. Again, no intermediates in this process were observed. Attempts to generate **5** in hydrocarbon matrices (CH_4 or 3-methylpentane) failed, giving only product tentatively identified by IR as *p*-quinodimethane.

Warming oxygen-doped nitrogen matrices (0.5% O_2 in N_2) of **5** to 30 K instantly converted the biscarbene to bis(carbonyl *O*-oxide) **7**, which exhibited multiple very strong bands in the 950−850 cm^{-1} region.[10] The matrix acquired a vivid orange hue, with the appearance of a broad absorption from 400 to 500 nm (λ_{max} 450 nm). Subsequent irradiation of the matrix with visible light (578 nm) rapidly destroyed the IR and visible spectra of **7**, producing weaker IR bands that we ascribe to bisdioxirane **8**.[10] Finally, broad-band irradiation (>400 nm) converted **8** mainly to terephthalic acid (**9**).[12] These results are summarized in Scheme 1.

Our spectral assignments were confirmed by DFT/ab initio calculations.[13] We have noted previously[5a] the electronic similarity between bis-carbenes such as **5** and singlet *p*-benzyne biradicals, where applicability of single determinantal density functional theory is currently under considerable discussion.[14] Bismethylene **5** likely also has a singlet-diradical ground state, as does **1**. We found, however, that UB3LYP/6-31G**[15] calculations on the corresponding *triplet* state of biradical **5** (syn and anti conformations, frequencies scaled by 0.96[16]) nicely fit the experimental IR spectra (Figure 1). Such an approach is not unreasonable given the expected small energy difference between the singlet and triplet biradical states (i.e. interaction between the

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[1] (a) Zuev, P. S.; Sheridan, R. S. *Tetrahedron* **1995**, *51*, 11337 and references therein. (b) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179 and references therein.

[2] (a) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526. (b) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251. (c) Sixl, H.; Mathes, R.; Schaupp, A.; Ulrich, K. *Chem. Phys.* **1986**, *107*, 105. (d) Teki, Y.; Sato, K.; Okamoto, M.; Yamashita, A.; Yamaguchi, Y.; Takkui, T.; Kinoshita, T.; Itoh, K. *Bull. Magn. Reson.* **1992**, *14*, 24. (e) Yamaguchi, Y.; Sato, K.; Teki, Y.; Kinoshita, T.; Takui, T.; Itoh, K. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1995**, *271*, 67.

[3] Nicolaides, Tomioka, and Murata have recently characterized *p*-phenylenebis(nitrene) by IR. Nicolaides, A.; Tomioka, H.; Murata, S. *J. Am. Chem. Soc.* **1998**, *120*, 11530.

[4] The mixed *p*-phenylenecarbenonitrene has also been observed, although experimental details were vague. Koseki, S.; Tomioka, H.; Toyota, A. *J. Phys. Chem.* **1994**, *98*, 13203.

[5] (a) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788. (b) Tomioka, H.; Komatsu, K.; Nakayama, T.; Shimizu, M. *Chem. Lett.* **1993**, 1291. These workers also reported the reaction of **2** with O_2, although intermediates were not characterized.

[6] Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 9381.

[7] Trindle and co-workers have recently described calculations on **2** and **5**. Trindle, C.; Datta, S. N.; Mallik, B. *J. Am. Chem. Soc.* **1997**, *119*, 12947.

[8] Murray, R. W.; Trozzolo, A. M. *J. Org. Chem.* **1964**, *29*, 1268.

[9] For a description of the matrix isolation instrumentation and experimental techniques, 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. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

[10] For tabulations of experimental and calculated IR spectra of species reported in this work, see the Supporting Information.

[11] (a) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779. (b) 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 minor amount of an additional carbonyl-containing product was also observed, whose identity is still under investigation.

[13] Gaussian 94, Revision D.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc.: Pittsburgh, PA, 1995. Geometric parameters are given in the Supporting Information.

[14] (a) Cramer, C.; Nash, J. J.; Squires, R. R. *Chem. Phys. Lett.* **1997**, *277*, 311. (b) Schreiner, P. R. *J. Am. Chem. Soc.* **1998**, *120*, 4184. (c) For an in-depth discussion of similarly successful use of broken-spin symmetry unrestricted DFT methods with singlet diradicals see: Cramer, C. *J. Am. Chem. Soc.* **1998**, *120*, 6261.

[15] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988,** *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

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

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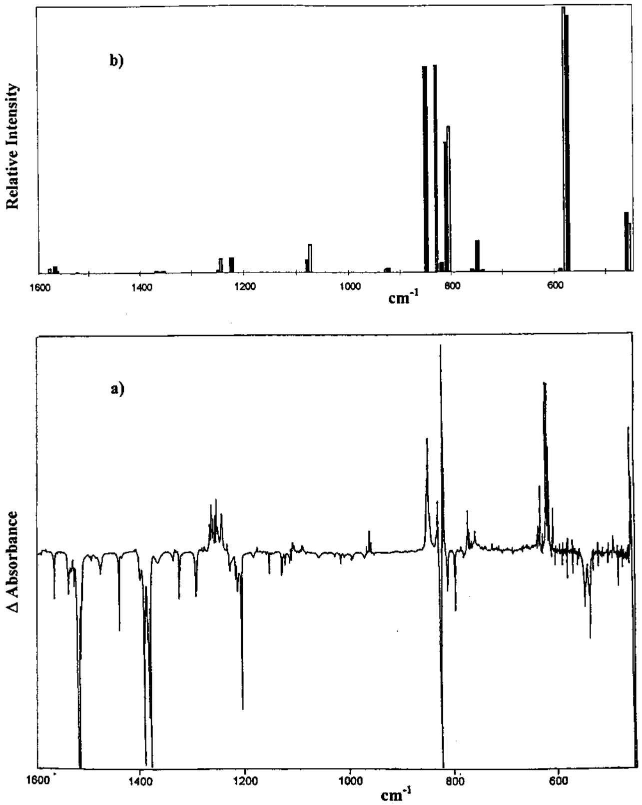
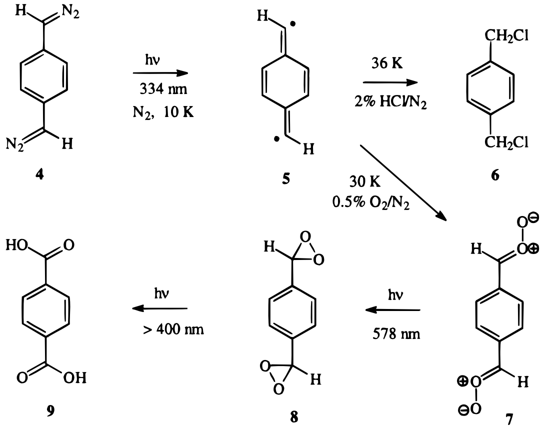


Figure 1. (a) Difference of IR spectra of bis-diazo compound **4** matrix isolated in N_2 at 10 K, before and after irradiation at 313 nm for 12 h. Positive peaks correspond to biradical **5** and negative peaks to **4**. (b) UB3LYP/6-31G** calculated IR spectra for triplet *anti*-**5** (solid) and *syn*-**5** (open). Freqencies have been scaled by a factor of 0.96.[16]

Scheme 1



“σ-radical” centers in **5** is small).[17] Indeed, CAS[10,10]/6-31G** calculations on singlet **5** predicted a quinonoidal geometry very similar to that from the triplet DFT calculations (see Supporting Information).[18] Moreover, broken spin-symmetry UB3LYP calculations[14c] on the *singlet* biradical state of **5** (with an $\langle S^2\rangle$ value of 1.17 indicating an approximate 50:50 singlet/triplet mixed state) gave nearly the same geometry and IR predictions as for the triplet, but 1.2 kcal/mol lower in energy.[13] Davidson has suggested recently that CAS calculations predict the ground state of **5** to be a quintet bis-carbene.[19] Our UB3LYP calculations,[20,21] however, place the quintet 24 kcal/mol higher in energy than triplet **5**. The predicted IR spectrum of quintet biscarbene also bears little resemblance to experiment.[10]

B3LYP/6-31G** calculations on bis-carbonyloxide **7** gave a less satisfactory fit to the experimental spectra. Following the lead of Warner,[22] however, we found that addition of diffuse functions (B3LYP/6-31+G**) significantly improved the agreement between experiment and theory.[10] The simpler 6-31G** basis set sufficed to confirm the assignment of bis-dioxirane **8** based on IR spectra.[10]

The lack of photochemical reactivity of **5** is striking. Phenylcarbene readily ring expands on irradiation under similar conditions.[11] Nicolaides, Tomioka, and Murata also have found recently that the corresponding *p*-bisnitrene undergoes photochemical rearrangement.[3] The UV/vis spectra of **5** and phenylcarbene[11] are superficially similar, but that of **5** is substantially broader and more intense. The very different electronic nature of the excited states of the mono- and bis-carbenes may account for the photolability contrast. The difference between the biscarbene and bisnitrene[3] is even less clear. Although it has been suggested that carbonyl *O*-oxides possess considerable biradical character,[23] the bis-O_2 adduct **7** shows little indication in its spectra for interaction between the methylene centers. The IR spectra for **7** show numerous, strong O−O stretching bands, identified by ^{18}O labeling and DFT calculations, in the region 950−850 cm^{-1},[10] analogous to those reported for benzaldehyde *O*-oxide (915 and 890 cm^{-1}).[24] The complexity of the IR in this band group likely reflects the multiple conformational isomers of **7**, supporting its assignment. The visible spectrum observed for **7** is unremarkable, and is in a wavelength region similar to that described for the parent mono-carbonyl oxide.[24] Finally, photochemical rearrangement of **7** to bisdioxirane **8**, and thence to **9**, is in line with the behavior of other carbonyl oxides.[23]

In summary, our results confirm that *p*-phenylenebismethylene (**5**) is a quinoidal biradical. Although photochemically stable, the bis-methylene shows carbene-like reactivity with HCl and O_2, giving in the latter case a novel bis-carbonyl *O*-oxide.[25]

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Supporting Information Available: Tabulated experimental/calculated IR spectra and geometric parameters for **5**, **7**, and **8**, and UV/vis spectrum and calculated energies for **5** (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[17] D. A. Hrovat and W. T. Borden (personal communication) have found that CASPT2 calculations place the triplet states 2.0 kcal/mol above the singlets of syn and anti **5**. They also see evidence for dynamic spin polarization in the π system incited by the σ nonbonding orbitals, accounting for the singlet stabilization.

[18] The IR spectrum predicted for **5** by CAS[10,10]/6-31G** calculations fits the experiment less well than did DFT (on C_{2h} isomer, see Supporting Information). This discrepancy may be due to lack of σ-electron correlation in the CAS calculations or subtle complications with numeric frequency calculations.

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

[20] The calculational results reported by Trindle and co-workers in ref 7 also do not support a quintet ground state for **5**.

[21] For successful applications of DFT to aryl carbene energetics, see: (a) Cramer, C. J.; Dulles., F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787. (b) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (c) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v.-R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030. (d) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022.

[22] Warner, P. M. *J. Org. Chem.* **1996**, *61*, 7192.

[23] Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

[24] Sander, W. *J. Org. Chem.* **1989**, *54*, 333.

[25] Attempts to observe a low-temperature EPR spectrum of the excited triplet state of **5** have thus far been unsuccessful (Paul Lahti, personal communication). The extreme reactivity of the diradical may explain why its EPR has not been reported previously.