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p-Phenylenebis(chloromethylene): Resonance Interaction of Two Singlet Carbenes

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Arylpolycarbenes and related species have been extensively explored as high-spin subunits with relevance to the search for organic magnetic materials.[1] The systems of greatest interest comprise triplet carbene centers coupled in ferromagnetic fashion, often with *m*-phenylene linkers, in attempts to maximize spin multiplicity. Direct resonance interaction of the carbenic centers, where covalent π-overlap would favor lower spin states, is purposely avoided. Hence, less is known about *p*-phenylenebiscarbenes.[2] A related but separate issue that appears not to have been previously addressed is the following: how would two inherently closed-shell ground-state singlet carbenes interact through a π-system? An appropriate subunit would be phenylchlorocarbene, which is known to have a σ^2 ground-state configuration stabilized by chlorine π-donation.[3] Herein we report the generation, characterization, and reactivity of a system comprising two chlorocarbenes linked para across a benzene ring (*p*-phenylenebis(chloromethylene), **1**).

Bisdiazirine **2** was prepared from terephthalamidine dihydrochloride[4] via the standard Graham procedure.[5] Irradiation[6] of **2** matrix-isolated in N_2 at 7 K (390 nm, 3 h) gave primarily a new species (**A**) in the IR and UV/vis spectra and a small amount of a second species (**B**). Subsequent irradiation of the matrix at 380 nm (2 h) converted **A** to **B** in the IR (Figure 1). At the same time, the matrix acquired a golden-yellow color, and weak but highly structured UV/vis absorbances grew in the region 410–460 nm (ϵ ca. 10 M^{-1} cm^{-1}, estimated by comparison with starting material UV). Extended broad-band irradiation (>220 nm) of the matrix containing **B** produced only minor changes in the spectra, with several bands splitting into two absorptions in the IR.

Trapping experiments aided identification of **A** and **B**. Irradiation (390 nm) of **2** in a N_2 matrix doped with 6% HCl gave the IR spectrum of **A**. Warming the matrix to 35 K caused disappearance of the bands of **A**, with concurrent increase of bands identified as those of monodiazirine **3** by comparison to authentic material. Thus, **A** can be assigned as monocarbene **4**. Subsequent irradiation (>220 nm) of **3** in the presence of HCl gave $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylene (**5**). In a separate experiment, **B** was generated in a 0.5% HCl-doped N_2 matrix by broad-band irradiation of bisdiazirine **2** (>220 nm). Warming the matrix to 35 K converted **B** to the bis-HCl adduct **5**, as observed by IR. We thus assign **B** the bis-denitrogenated structure **1** (Scheme I).[7]

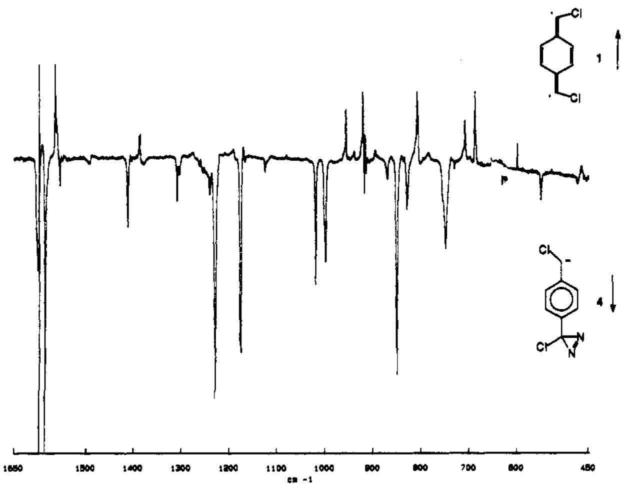
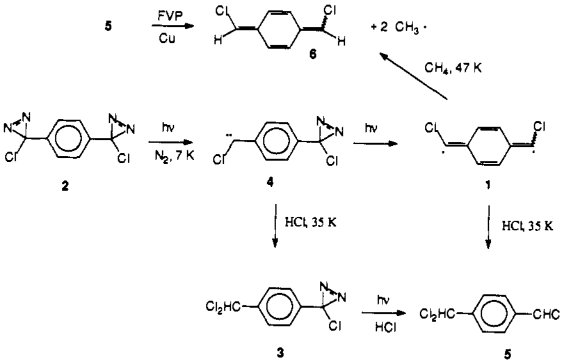


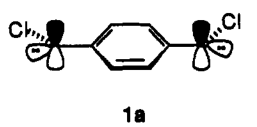
Figure 1. Difference spectrum showing IR of biradical **1** (positive peaks) and monocarbene **4** (negative peaks). The scale is in absorbance units. Spectrum generated by subtracting IR of N_2 matrix (7 K) after 3 h of irradiation of **2** at 390 nm from IR of same matrix after subsequent 2 h of irradiation at 380 nm. The sharp line at 1600 cm^{-1} is due to H_2O.

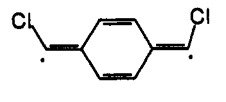
Scheme I



Compound **1** was found to be unusually reactive, even with hydrocarbons. Photolysis (390 nm) of a 3-methylpentane matrix (3-MP) of **2** at 7 K gave rise to the monocarbene **4**, observable by IR and UV. Subsequent irradiation at 380 nm, however, failed to produce any detectable amounts of **1** by IR or UV/vis; **4** was completely consumed, but no new products could be observed in the background absorptions of the matrix. Photolysis (>220 nm) of **2** in methane at 7 K, on the other hand, did give **1**. Among other products, we also observed methyl radical[8] and a new species (**C**) in the IR. On warming the matrix to 47 K, these IR bands increased simultaneously with decrease of those of **1**. We tentatively assign intermediate **C** the quinodimethane structure **6**, as shown in Scheme I. The same IR spectrum as **6** was produced by vacuum pyrolysis (750–950 °C) of **5** over a copper spiral, with trapping of the products directly in a N_2 matrix. Similar procedures have been utilized to generate related *p*-quinodimethanes.[9]

It is an interesting question whether **1** is electronically best described as the biscarbene structure **1a** or a diradical structure (**1b**). Although **1** reacts with HCl at low temperatures in a typical carbene fashion to give bis-adduct **5**, we believe that the other


1a


1b

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[7] A shift in the λ_{max} of the diazirine UV absorption on formation of **4** permits the selective formation of this species. Spectroscopic data on the starting material and on the various intermediates are contained in the supplementary material.

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properties of **1** are more consistent with diradical structure **1b**, based on several lines of reasoning. (1) The IR spectrum of phenylchlorocarbene resembles that of benzoyl chloride, with strong bands at ca. 1600 and 1200 cm^{-1} indicative of a strongly electron-withdrawing substituent on the benzene ring[3,10] (monocarbene **4** also exhibits such bands). The IR of **1** differs considerably from that of terephthaloyl chloride,[11] however, and has minimal absorption from 1300 to 1100 cm^{-1}. Moreover, although the ca. 1600-cm^{-1} ring-modes of benzenes with identical para substituents are IR forbidden[10] (e.g., terephthaloyl chloride has no absorption in this region), the strongest band of **1** is at 1582 cm^{-1}. *p*-Quinodimethanes[12] do show double-bond stretches at these frequencies (e.g., 1584 cm^{-1} in **6**). (2) The highly structured and long-wavelength electronic spectrum of **1** is absent in phenylchlorocarbenes, which generally have only broad absorbance at ca. 300 nm).[3,13,14] This weak band system is reminiscent of the visible spectrum of phenyl radical,[16] and we suggest that it similarly arises from a $\pi \rightarrow n$ transition in **1**. (3) Reacting with methane at 47 K, **1** is dramatically more reactive than phenylchlorocarbenes, which are stable at 77 K in organic matrices.[13] The failure to observe **1** in 3-MP at 7 K is likely also due to its reaction with the matrix, leading to product mixtures with IR absorbances obscured by the hydrocarbon background. (4) Compound **1** reacts with hydrocarbons via H-abstraction, whereas singlet carbenes such as phenylchlorocarbene show C–H insertion (at higher temperatures).[17]

We are continuing to investigate the properties of these highly reactive intermediates. The chemistry of a σ,σ-diradical such as **1b** is potentially related to that of didehydroaromatic species (where, in certain cases, alternate biscarbene structures can also be written).[18] The spin state of this species is also an open question.[19,20]

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Supplementary Material Available: Listings of spectral data for compounds **1–6** (1 page). Ordering information is given on any current masthead page.

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[14] A referee has suggested that (4-nitrophenyl)chlorocarbene might be a better model for biscarbene **1a**. The *p*-nitrocarbene, however, is reported to have a UV λ_{max} at 310 nm in solution, with no absorption in the visible.[15] Moreover, this carbene is not unusually reactive with hydrocarbons and has a lifetime of microseconds in organic solvents at room temperature.[15]

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[19] *p*-Phenylenebis(phenylmethylene) is reported, on the basis of EPR evidence, to have a singlet ground state with a low-lying excited triplet state.[2b]

[20] We have recently characterized *m*-phenylenebis(chloromethylene). This system shows no unusual electronic spectra and appears to behave as expected for a biscarbene (Zuev, P., unpublished results).