

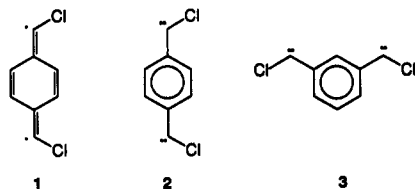
Substituent Control of Biscarbene Electronic Configurations: *m*-Phenylenebis(chloromethylene)

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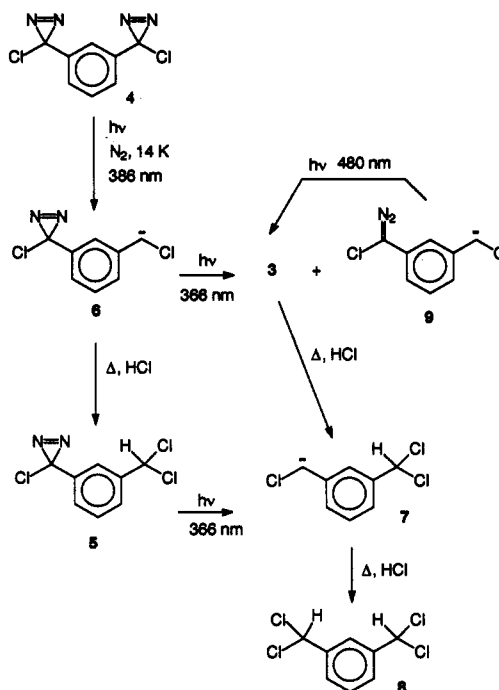
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In the search for organic magnetic materials, there has been considerable interest in molecules comprising high-spin subunits joined through ferromagnetic coupling units.^{1,2} The *m*-phenylene linker, where covalent interactions between appended groups are inhibited, has proven especially effective in this regard.^{1–3} Hence, *m*-phenylene biradicals,⁴ tetraradicals,³ biscarbenes^{1,4,5} and bisnitrenes^{5b} all exhibit high-multiplicity ground states. High-spin systems, however, represent only a small fraction of the potential electronic states arising from the interaction of two biradicaloid moieties.^{6,7} As part of a program aimed at a broader understanding of the factors that influence the electronic configurations in coupled reactive intermediates, we⁸ (and Tomioka and co-workers⁹) recently reported the first investigations of a system incorporating two singlet carbene subunits. It was found that *p*-phenylenebis(chloromethylene) exhibited spectroscopic and reactivity properties consistent with a biradical (1) rather than a bis-closed shell singlet carbene structure (2). We now wish to report the characterization of a system comprised of two *inherently singlet* carbenes linked *meta* across an aromatic ring, *m*-phenylenebis(chloromethylene) (3).



The *m*-bisdiazirine 4 was straightforwardly synthesized from isophthalamidine dihydrochloride¹⁰ via Graham¹¹ methods. Irradiation of N₂ matrix isolated 4 at 386 nm (3 h, 10 K) converted the bisdiazirine mainly to a new compound (A), as judged by IR and UV/vis (Scheme 1). Subsequent irradiation at 366 nm (3 h) destroyed A and increased the IR absorptions of another product, B. Long-

Scheme 1



term irradiation of the matrix with broad-band light (>220 nm) slowly destroyed B and produced new species with absorptions in the IR in the 1815–1770 cm⁻¹ region.

Trapping experiments were carried out to identify A and B. Compound A was photochemically generated as above (386 nm) in a N₂ matrix containing 1% HCl. Annealing the matrix at 30–38 K transformed A into 5, identified by comparison with the matrix IR of an authentic sample. Hence, A corresponds to monocarbene-diazirine 6. Irradiation of a N₂ matrix of diazirine 5 (independently synthesized) at 366 nm gave a new product in the IR spectrum, presumed to be carbene 7. In a separate experiment, B was generated directly in a 1% HCl-containing N₂ matrix by 366-nm irradiation of bisdiazirine 4. Warming the matrix to 32 K caused the slow disappearance of the IR bands of B with concurrent growth of 7. When the temperature was raised to 37 K, both sets of IR bands rapidly disappeared and those of doubly-trapped product $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*m*-xylene (8) appeared. Compound B is thus biscarbene 3. Small amounts of a diazo compound believed to be 9, signified by a small band at 2052 cm⁻¹, were also observed in the photolyses of 6.¹² The diazo absorption could be selectively destroyed, with a corresponding increase in 3, by irradiation of the matrices at 480 nm. These transformations are summarized in Scheme 1.

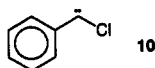
Both mono- (6) and biscarbene (3) exhibited strong UV/vis absorptions at ca. 300 nm, and weak, very broad bands in the region 600–850 nm (λ_{\max} 740 nm). The diazo compound 9 showed a visible absorption at 480 nm, which appeared and disappeared in concert with the 2052-cm⁻¹ IR band.¹²

Our results appear to indicate that 3 is a closed-shell ground-state singlet. Our reasoning is based on several factors. (1) The IR spectrum of 3 is very similar to that

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 (6) As described by Dougherty, and co-workers,^{2,7} a tetraradical with four electrons in four degenerate orbitals affords the possibility of 36 electronic states, including 1 quintet, 15 triplets, and 20 singlets.
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- (12) Similar electronic and vibrational transitions are observed in other aryl diazomethanes. See, for example: Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* 1993, 115, 855.

of isophthaloyl chloride¹³ (excluding carbonyl bands), in the same fashion that phenylchlorocarbene (10) resembles benzoyl chloride.^{8,9,14} In particular, the observed strong absorptions at ca. 1600 and 1150 cm⁻¹ are consistent with strongly electron-withdrawing aromatic substitution.¹⁵ The vibrational spectrum of **3** predicted by ab initio calculations at the 6-31G* level for the singlet biscarbene electronic configuration also fits the observed spectrum well (see Experimental Section and supplementary material).¹⁶ (2) The UV/vis spectrum of **3** is nearly identical to that of phenylchlorocarbene.¹⁴ The long-wavelength $\sigma \rightarrow \pi$ transition for phenylchlorocarbene (10) has not been reported previously, but we have observed a broad, weak absorption for this carbene, in nitrogen matrices, at 600–850 nm (λ_{\max} 750 nm). CIS/6-31G* calculations¹⁶ predict similar transitions for **3** and **10** at ca. 560 nm. Quintet *m*-biscarbenes that have been spectroscopically observed show π -radical-like structured absorption in the 400–500-nm region in the visible.¹⁷ Similarly, biradical **1** exhibits highly structured absorption in the neighborhood of 400–500 nm.^{8,9} (3) The biscarbene **3** is stable on annealing in an O₂-containing nitrogen matrix, under conditions where triplet carbenes rapidly react.^{14,18,19} Snyder and McMasters (personal communication)²⁰ have also found that extended irradiation of the bis-bromo analog of **4** gives no EPR spectrum at low temperatures. (4) In contrast to **1**, *meta* system **3** appears to undergo photochemical ring expansion analogous to **10**^{14b,c} (signaled by the appearance of the 1815 cm⁻¹ absorption).



Previously studied *m*-phenylenebiscarbenes,^{1,4} incorporating triplet carbene subunits, have possessed quintet ground states. Polycarbenes based on this structural motif have exhibited even higher spin multiplicities.¹ It is perhaps not surprising, however, that robustly-singlet closed-shell carbene subunits, as in **3**, maintain their identity when *meta*-coupled. It is not clear that the stabilization to be gained by exchange interaction in the π -system of a higher-multiplicity electronic state could

overcome the energy increase necessary for promotion of both carbene centers from closed- to open-shell. We are continuing to investigate the influence of substituents on these interesting systems.

Experimental Section

General. Unless otherwise noted, solvents and reagents were used as obtained. NMR spectra were obtained on a General Electric QE-300 instrument and were referenced to residual protio solvent. General descriptions of the low temperature apparatus and matrix isolation techniques have been previously published.²¹

***m*-Phenylenebis(amidine hydrochloride).**¹⁰ Dry HCl was passed into a cooled suspension of 1,3-dicyanobenzene (Aldrich, 32 g, 0.25 mol) in anhydrous ethanol (50 mL) until 37 g (1 mol) of the gas was absorbed. The reaction mixture was allowed to stand at room temperature for 48 h. The solvent was then removed in vacuo to give crude bis-imido ether dihydrochloride as a white solid. The solid was crushed in a mortar and transferred to a 1-L flask, and a solution (300 mL) of dry NH₃ (30 g) in anhydrous ethanol was added slowly in small portions. The mixture was stirred for 24 h and then allowed to stand for 48 additional hours at room temperature. The solution was filtered to remove the precipitated NH₄Cl, and the solvent was removed in vacuo to give *m*-phenylenebis(amidine hydrochloride) as a white solid (33 g, 56%), which was used without further purification: ¹H NMR (DMSO-*d*₆) 9.55 (s, 8 H), 8.54 (s, 1 H), 8.19 (d, 7.2 Hz, 2H), 7.84 (t, 7.2 Hz, 1H).

***m*-Phenylenebis(chlorodiazirine) (4).** The general method of Graham¹¹ was used to prepare this compound. A 1-L flask equipped with magnetic stirrer, a dropping funnel, and a thermometer was charged with *m*-phenylenebis(amidine hydrochloride) (5 g, 20 mmol), Me₂SO (200 mL), and NaCl (19 g). After the salts dissolved, 50 mL of *n*-pentane was added, and the reaction mixture was cooled to 5 °C using an ice-water bath. An aqueous 12% solution of NaOCl (commercial Purechlor Sanitizer, 300 mL), saturated with NaCl, was added dropwise to the stirred reaction mixture over the period of 30 min. The reaction temperature was maintained below 30 °C by a cooling bath. After the addition was completed, the reaction mixture was stirred for an additional hour and diluted with 200 mL of water. The pentane layer was separated, and the aqueous layer was extracted with 3 × 100 mL of pentane. The combined pentane portions were washed with 2 × 100 mL of water, dried (MgSO₄), filtered, and concentrated under reduced pressure at 25 °C. The oily residue was dissolved in a minimum amount of methylene chloride and purified by flash chromatography²² (silica gel, 200–425 mesh, CH₂Cl₂), where **4** eluted in the first fractions. The solvent was stripped under reduced pressure, leaving neat **4** as light yellow oil solidifying at about 0 °C (0.34 g, 7.5%): IR (N₂ matrix, 10 K, deposited from room temperature) 1577 (vs), 1493 (m), 1486 (m), 1435 (m), 1430 (w), 1336 (w), 1300 (w), 1281 (m), 1213 (m), 1120 (w), 1059 (m), 1022 (m), 1009 (m), 975 (s), 902 (m), 895 (m), 798–795 (m), 720 (w), 702 (m), 692 (s), 650 (m), 558 (w), 493 (w) cm⁻¹; UV/vis (N₂ matrix, 10 K) λ_{\max} 385, 378, 373, 365, 355, 347, 331 nm; ¹H NMR (CDCl₃) 7.46 (t, 7.8 Hz, 1H), 7.13 (d, 7.8 Hz, 2H), 6.9 (s, 1H) ppm; ¹³C NMR (CDCl₃) 136.1, 128.5, 126.3, 123.4, 46.0 ppm. *Caution: diazirines such as 4 and 5 are potentially shock sensitive.*¹¹

(3-(Dichloromethyl)phenyl)chlorodiazirine (5). Bisdiazirine **4** (300 mg, 1.3 mmol) dissolved in *n*-pentane (50 mL) was irradiated at 350 nm (Rayonet) at –30 °C with continuous HCl purge for 10 min. After removal of the solvent in vacuo, the residue was purified by flash chromatography²² (silica gel, 200–425 mesh, CH₂Cl₂), giving **5** as an oil (10 mg, 0.3%): IR (N₂ matrix, 10 K, deposited from 44 °C) 1577 (s), 1492 (m), 1439 (m), 1176 (w), 1106 (w), 1043 (m), 994–989 (m), 852–849 (m), 693 (w), 669 (m) cm⁻¹; UV/vis (N₂ matrix, 10 K) λ_{\max} 386, 365 nm. Major product **8** was isolated as a white solid from later fractions (235

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(19) Tomioka and co-workers⁹ reported that the *p*-biscarbene **1** reacts with O₂ at low temperatures. PM3-ROHF CI calculations were also purported to confirm the σ, σ -biradical structure. We believe, however, that such semiempirical calculations should be applied with caution on these compounds. Analogous calculations carried out in our laboratory predict a quintet ground state for **3**.

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mg, 75%);²³ IR (N₂ matrix, 12 K, deposited from 50 °C) 1464 (m), 1452 (w), 1396 (m), 1385 (w), 1348 (w), 1339 (w), 1262 (w), 1249 (w), 1219 (m), 1176 (m), 1159 (m), 1098 (w), 953 (w), 844 (m), 829 (w), 811 (m), 798 (w), 729 (s), 719–714 (sh), 591 (w), 576 (w), 557 (m), 541 (w) cm⁻¹; ¹H NMR (CDCl₃) 7.78 (s, 1H), 7.63 (d, 7.5 Hz, 2H), 7.50 (t, 7.8 Hz, 1H), 6.73 (s, 2H) ppm.

m-Phenylenebis(chloromethylene) (3): IR (N₂ matrix, 12 K) 1573 (s), 1282 (m), 1247 (m), 1230 (w), 1166 (w), 1147 (s), 1141 (s), 963 (m), 829 (m), 820 (w), 777 (m), 756 (m), 729 (w), 708 (w), 565 (w), and 553 (w) cm⁻¹. Calculated vibrational spectrum (6-31G*, frequencies × 0.9, 1600–400 cm⁻¹, relative intensity ≥ 1 in parentheses) 1587 (65), 1572 (8), 1474 (2), 1384 (9), 1227 (22), 1218 (19), 1148 (100), 1096 (1), 998 (1), 950 (38), 823 (5), 716 (71), 653 (7), and 552(22) cm⁻¹.

(3-(Chloromethylene)phenyl)chlorodiazirine (6): IR (N₂ matrix, 12 K) 1589 (m), 1474 (w), 1418 (w), 1410 (w), 1326 (m), 1289 (w), 1272 (m), 1185 (m), 1170 (s), 1043 (w), 999 (m), 990 (m), 959 (m), 857 (w), 851 (w), 807 (w), 748 (s), and 676 (m) cm⁻¹.

(3-(Dichloromethyl)phenyl)chloromethylene (7): IR (N₂ matrix, 13 K) 1270 (w), 1261 (m), 1235 (m), 1213 (w), 1158 (m),

953 (m), and 816 (w) cm⁻¹; UV/vis (N₂ matrix, 13 K) 300–360 nm (λ_{max} 325 nm).

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Supplementary Material Available: Experimental and calculated IR spectra of 3 and ¹³C and ¹H NMR spectra of 4 (3 pages). This material is contained in 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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