Tetrahedron Vol. 49, No. 30, pp. 6561-6568, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

SYNTHESIS AND CHEMISTRY OF A FACIALLY DISSYMMETRIC CAGE-CONDENSED *p*-BENZOQUINONE; A SYNTHETIC ENTRY INTO NOVEL DOUBLY-CAGED SYSTEMS

Alan P. Marchand*, Simon G. Bott*, and Vijay R. Gadgil
Department of Chemistry, University of North Texas, Denton, TX 76203-0068

William H. Watson*, Mariusz Krawiec, and Ram P. Kashyap
Department of Chemistry, Texas Christian University, P. O. Box 32908, Fort Worth, TX 76129

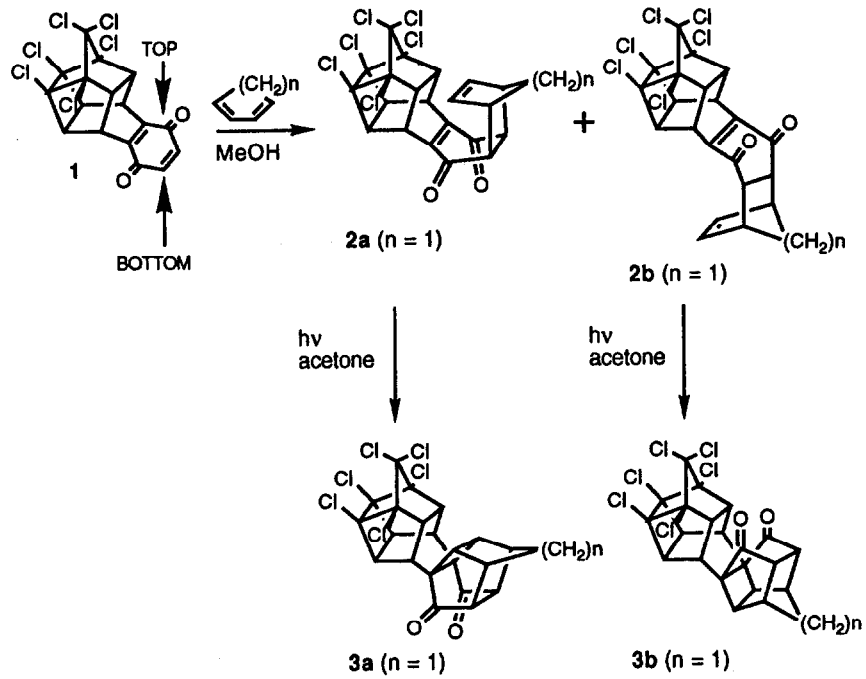
(*Received in USA* 3 *March* 1993)

Absract. The synthesis of a novel caged quinone, **1**, is reported. Diels-Alder cycloaddition of cyclopentadiene to **1** results in the formation of two *endo* adducts, **2a** and **2b**, each of which can be photocyclized to the corresponding "doubly-caged" diketone (**3a** and **3b**, respectively).

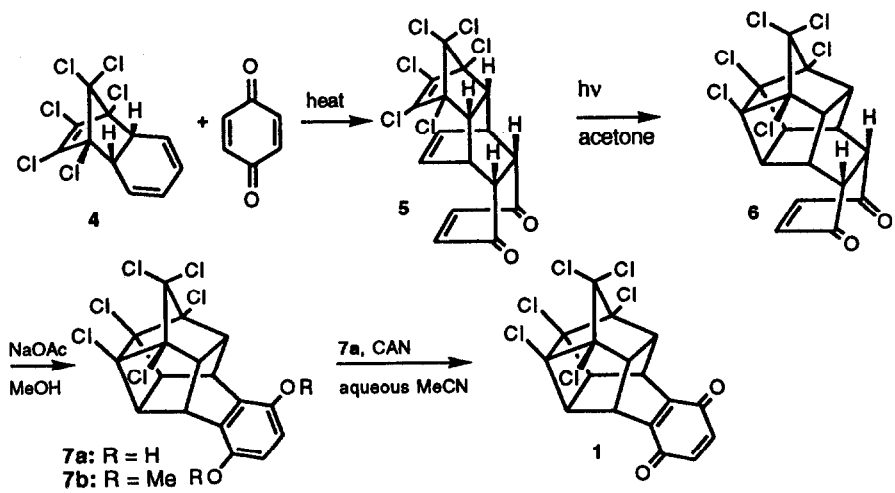
Introduction. As part of a continuing program which is concerned with the synthesis and chemistry of novel polycyclic "cage" compounds,[1] we have undertaken the synthesis of an unusual, facially dissymmetric cage-condensed *p*-benzoquinone, **1** (Scheme 1). This compound is of interest as a dienophile for use in Diels-Alder cycloadditions with cyclic dienes (*e.g.*, cyclopentadiene, n = 1). We anticipated that the *endo* [4 + 2] cycloadducts which result via topside and/or bottomside attack of the diene upon **1** subsequently might be induced to undergo intramolecular [2 + 2] photocylization, thereby affording a new class of "doubly-caged" systems, e.g., **3a** and **3b**. The parent hydrocarbons derived via reductive dechlorination-deoxygenation of **3a** and **3b** are expected to be relatively nonvolatile solids which posseses unusually high crystal densities. In addition, each of these hydrocarbons contains strain energy associated with the cage moieties which is expected to re-sult in a relatively large, negative heat of combustion. Thus, hydrocarbons of this type are of considerable interest as a potential new class of energetic materials (e.g., as fuels for volume-limited applications).[2]

Results and Discussion. Our synthesis of caged *p*-benzoquinone **1** is shown in Scheme 2. We find that Diels-Alder cycloaddition of *p*-benzoquinone to tricyclic diene **4**[3] occurs in accordance with the Alder-Stein "principle of maximum accumulation of unsaturation"[4] and proceeds exclusively via attack upon the "top" (exo) face of the diene to afford **5** as the sole [4 + 2] cycloadduct. Subsequent intramolecular [2 + 2] photocyclization of **5** might proceed via either of two pathways, i.e., cyclobutane formation via [2 + 2] cycloaddition (i) of the dichlorinated C=C double bond to the central C=C double bond or (ii) of the enedione C=C double bond to the central C=C double bond in **5**. In fact, we find that only the first of these two pathways is followed; the corresponding caged enedione system, **6**, is formed exclusively.

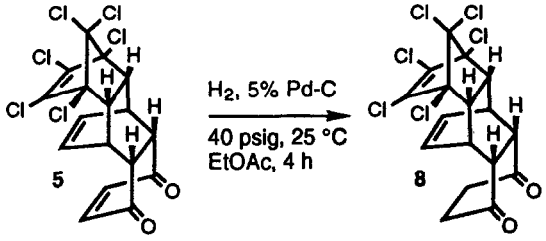
Scheme 1



Scheme 2

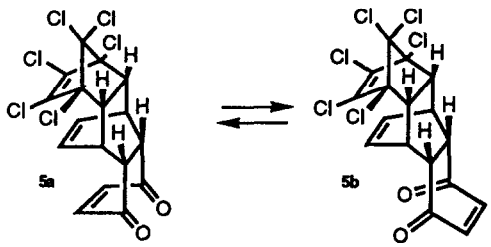


Since the photocyclization was performed by irradiating **5** with an ordinary tungsten filament lamp, it seems reasonable to expect that the enedione system is the active chromophore. This expectation was verified by the results of a simple control experiment. The enedione C=C double bond in **5** was selectively hydrogenated, and the resulting "dienedione" (**8**, see below) was irradiated by using a tungsten filament lamp. It was observed that the dienedione failed to photocyclize when subjected to the same photochemical conditions which resulted in photocyclization of **5** to **6**.



5 **8**

Thus, it is apparent that the enedione system is the active chromophore in **5** under the photochemical conditions employed. Yet, the resulting photocyclization of **5** to **6** does not directly involve cycloaddition across this chromophore. There are two factors which might be invoked to account for this result: (i) It seems likely that the 1,4-cyclohexendione moiety will exhibit a strong conformational preference which favors the (less hindered) "transoid" configuration, with the consequence that the enedione C=C does not lie in close proximity to the H-C=C-H moiety (see the equilibrium between **5a** and **5b**, below). (ii) Intramolecular transfer of the absorbed photochemical energy occurs, probably to the distant C=C double bond which is substituted by two heavy atoms (i.e., Cl).[5]



5a **5b**

(cisoid) *(transoid)*

Diels-Alder [4 + 2] cycloaddition of cyclopentadiene to **1** afforded a mixture of *endo* cycloadducts **2a** and **2b** (product ratio **2a** : **2b** = 1 : 1.5, as determined by integration of the ^{1}H NMR spectrum of the product mixture). Subsequent intramolecular photocyclizations of **2a** and of **2b** were performed by using a 250 W tungsten lamp. In each case, this procedure afforded the corresponding intramolecular [2 + 2] cycloadduct (i.e., **3a** and **3b**, respectively, see Scheme 2).

Summary and Conclusions. An unusual, facially dissymmetric cage-condensed *p*-benzoquinone, **1**, has been synthesized. The first step in this synthesis, which involves Diels-Alder cycloaddition of facially dissymmetric diene **4** to *p*-benzoquinone, with (i) regiospecific addition to the "bottom" face of the diene and (ii) stereospecific endo addition. In the course of pursuing this synthesis, it was observed that a precursor trienedione, **5**, undergoes intramolecular [2 + 2] photocyclization in such a way that the enedione chromophore

in **5** does not directly participate in the ring closure reaction. This unusual photochemical reaction is currently undergoing intensive scrutiny in our laboratory. In addition, Diels-Alder cycloaddition of cyclopentadiene to quinone **1** was studied. Two products, **2a** and **2b**, were obtained (product ratio **2a:2b** = 1:1.5). Subsequent intramolecular cyclization of **2a** and of **2b** resulted in the formation of the corresponding "doubly-caged" diketone sytstems (**3a** and **3b**, respectively).[6]

Experimental Section

Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were obtained by using a Nicolet 20SXB FT IR spectrometer. ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Varian Gemini-200 NMR spectrometer. Chemical shifts are reported in parts per million (δ) downfield from $SiMe_4$. Elemental microanalyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, NY and by M-H-W Laboratories, Phoenix, AZ.

Trienedione 5. To a solution of 1,2,3,4,9,9-hexachloro-1α,4α,4aα,8aα-tetrahydro-1,4-methanonaphthalene[2] (**4**, 8.0 gm, 20 mmol) in toluene (30 mL) was added freshly sublimed *p*-benzoquinone (2.2 g, 20 mmol), and the resulting mixture was heated under argon at 95 °C for 12 h. The reaction mixture then was concentrated *in vacuo*, and EtOAc (25 mL) and hexane (15-20 mL) were added to the residue. Crude **5** (3.5 g, 38%) gradually preciptated when this mixture was allowed to stand at room temperature for several hours. Recrystallization of the material thereby obtained from EtOAc afforded pure **5** (3.0 g, 33%) as a yellow microcrystalline solid: mp 198 °C; IR (KBr) 3030 (w), 2980 (w), 2855 (w), 1670 (s), 1600 (s), 1390 (m), 1280 (s), 1110 (m), 1070 (s), 1060 (m), 880 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 3.00 (s, 4 H), 3.58 (br s, 2 H), 6.04 (dt, J_1 = 8.0 Hz, J_2 = 4.6 Hz, 2 H), 6.70 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.4 (d), 49.5 (d), 49.6 (d), 80.7 (s), 103.9 (s), 128.8 (d), 129.7 (s), 142.0 (d), 196.2 (s). Anal. Calcd for $C_{17}H_{10}Cl_6O_2$: C, 44.49; H, 2.20. Found: C, 44.56; H, 2.17.

Intramolecular [2 + 2] Photocyclization of 5. A solution of **5** (2.0 g, 4.4 mmol) in anhydrous acetone (800 mL) was irradiated under argon for 4 h with a 250 W tungsten lamp. The heat out-put of the lamp was sufficient to cause the reaction mixture to reflux vigorously. The reaction mixture was concentrated *in vacuo*, and the residue, a viscous, pale yellow oil, was taken up in acetone (50 mL). Hexane (100 mL) was added, and the resulting mixture was allowed to stand overnight, whereupon a colorless semi-solid precipitated (900 mg). The results of NMR analysis of this material suggest that it consists of a mixture of **6** and **7a**, the latter compound being the major component of the mixture.

Repeated attempts to purify this material by recrystallization invariably led to mixtures of **6** and **7a**. Accordingly, an attempt was made to convert **6** into **7a** via base promoted isomerization, Thus, to a solution of **6** and **7a** (3.3 g, 7.2 mmol) in MeOH (120 mL) at room temperature was added NaOAc (5.0 g, 60 mmol), and the resulting mixture was stirred overnight. The reaction mixture was concentrated *in vacuo*, and saturated aqueous NH_4Cl solution (100 mL) was added to the residue. The resulting mixture was extracted with EtOAc (3 x 30 mL), and the combined organic extracts were washed sequentially with water (25 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. Crude **7a** (3.0 g, 91%) was thereby obtained as a dark oil which gradually solidified upon standing at room temperature for several hours.

Characterization of **7a** was completed by converting it to the corresponding di-O-methyl ether, **7b**. Thus, to a mixture of crude **7a** (500 mg, 1.08 mmol) and anhydrous K_2CO_3 (1.0 g, 7.0 mmol) in acetone (25 mL) was added $(MeO)_2SO_2$ (500 mg, 4.0 mmol, excess), and the resulting mixture was refluxed for 6 h. The reaction mixture was concentrated *in vacuo*, and water (50 mL) was added to the residue. The resulting mixture was stirred at room temperature overnight and then was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed sequentially with water (25 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. Crude **7b** (500 mg, 94%) was thereby obtained as a yellow microcrystalline solid. The crude product was purified via column chromatography on silica gel by using 15% EtOAc-hexane as eluent. Pure **7b** (300 mg, 60%) was thereby obtained as a pale yellow microcrystalline solid: mp 241-242 °C; IR (KBr) 2941 (w), 2923 (w), 1498 (s), 1450 (m), 1288 (m),

1253 (s), 1107 (s), 1091 (s), 1006 (m), 858 (m), 802 (m), 760 (w), 710 cm-1 (w); ^{1}H NMR ($CDCl_3$) δ 2.80 (t, J = 2.2 Hz, 4 H), 3.78 (s, 6 H), 4.38 (m, 2 H), 6.72 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.5 (q), 50.3 (d), 53.9 (d), 53.9 (d), 77.1 (s), 82.3 (s), 95.4 (s), 109.3 (d), 124. (s), 149.7 (s). Anal. Calcd for $C_{19}H_{16}Cl_6O_2$: C, 46.85; H, 2.89. Found: C, 47.07; H, 2.92.

Dienedione 8. To a solution of **5** (50 mg, 0.11 mmol) in EtOAc (25 mL) was added 5% palladized charcoal catalyst (20 mg). The resulting mixture was hydrogenated by using H_2 (40 psig) in a Parr Shaker apparatus at 25 °C for 4 h. Methylene chloride (25 mL) was added, and the resulting mixture was filtered. The filtrate was concentrated *in vacuo*, and the residue was recrystallized from MeOH. Pure **6** (40 mg, 80%) was thereby obtained as a colorless microcrystalline solid: mp 208-209 °C; IR (KBr) 2951 (w), 2880 (w), 1697 (vs) 1591 (m), 1429 (w), 1401 (w), 1269 (m), 1175 (m), 1070 (m), 1042 (m), 879 (m), 754 (m), 694 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 2.55 (centrosymmetric A_2B_2 pattern, 4 H), 2.91 (s, 2 H), 3.02 (s, 2 H), 3.54 (br t, J = 3.5 Hz, 2 H), 6.06 (ddd, J = 7.7, 4.4, 3.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.7 (t), 37.1 (d), 49.4 (d), 53.2 (d), 80.7 (s), 103.9 (s), 129.4 (d), 129.7 (s), 206.2 (s). Anal. Calcd for $C_{17}H_{12}Cl_6O_2$: C, 44.29; H, 2.62. Found: C, 44.04; H, 2.60.

Oxidation of Hydroquinone 7a to Quinone 1. To a solution of **7a** (300 mg, 0.70 mmol) in CH_3CN (20 mL) and water (4 mL) was added Ceric ammonium nitrate (847 mg, 1.55 mmol). The reaction mixture was stirred at room temperature for 10 minutes and then was poured into water (100 mL). The resulting suspension was extracted with Et_2O (4 x 25 mL). The combined ethereal extracts were washed sequentially with water (25 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by using 10% EtOAc-hexane as eluent. Pure **1** (100 mg, 33%) was thereby obtained as a bright orange microcrystalline solid: mp 251-252 °C; IR (KBr) 1657 (s), 1591 (m), 1344 (w), 1323 (w), 1287 (m), 1126 (m), 1020 (m), 870 (m), 845 (m), 752 cm-1 (m); ^{1}H NMR ($CDCl_3$) δ 2.84 (m, 4 H), 4.24 (m, 2 H), 6.79 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.0 (d), 50.7 (d), 54.3 (d), 76.8 (s), 81.9 (s), 95.2 (s), 136.4 (d), 142.8 (s), 182.6 (s). Anal. Calcd for $C_{17}H_8Cl_6O_2$: C, 44.68; H, 1.76. Found: C, 44.75; H, 1.78.

Diels-Alder Cycloaddition of Cyclopentadiene to Quinone 1. To a solution of quinone **1** (200 mg, 0.434 mmol) in MeOH (20 mL) at room temperature was added with stirring cyclopentadiene (200 mg, excess), and the resulting mixture was stirred at room temperature. After 2-3 h, a mixture of [4 + 2] cycloadducts, **2a** and **2b** (ratio 1:1.5, by integration of the ^{1}H NMR spectrum), gradually precipitated. The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5 mL). Hexane (5 mL) was added, and the resulting mixture was allowed to evaporate slowly at room temperature. After having stood for 12 h, roughly half of the solvent had evaporated, and a yellow microcrystalline solid had precipitated. The solvent was decanted, and the residue was washed with hexane. Further concentration of the mother liquor by evaporation resulted in the formation of reddish-yellow crystals mixed with yellow crystals. The solvent was decanted, the residue was washed with hexane, and the differently colored crystals we separated mechanically. Recrystallization of the yellow crystals from CH_2Cl_2-hexane furnished pure **2a** (50 mg, 22%): mp 230-231 °C; IR (KBr) 1654 (s), 1619 (m), 1269 (m), 1354 (m), 1008 (w), 858 (w), 717 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.45 (*AB*, J_{AB} = 8.9 Hz, 1 H), 1.56 [t(*AB*), J_{AB} = 8.9 Hz, J_1 = 1.6 Hz, 1 H], 2.64 (m, 2 H), 2.75 (m, 2 H), 3.27 (m, 2 H), 3.55 (br s, 2 H), 4.18 (dt, J_1 = 5.3 Hz, J_2 = 2.0 Hz, 2 H), 5.98 (t, J = 1.74 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.1 (d), 49.1 (d), 49.2 (t), 49.3 (d), 50.5 (d), 54.2 (d), 76.9 (s), 81.9 (s), 95.2 (s), 135.1 (d), 140.3 (s), 194.6 (s). Anal. Calcd for $C_{22}H_{14}Cl_6O_2$: C, 50.52; H, 2.69. Found: C, 50.49; H, 2.56.

Recrystallization of the reddish-yellow crystals from CH_2Cl_2-hexane afforded pure **2b** (60 mg, 26%): mp 212-213 °C; IR (KBr) 2908 (w), 2859 (w), 1666 (s), 1612 (w), 1253 (m), 1182 (w), 1006 (m), 858 (w), 740 cm-1 (w); ^{1}H NMR ($CDCl_3$) δ 1.44 (*AB*, J = 8.8 Hz, 1 H), 1.55 [t(*AB*), J = 8.8, 1.6 Hz, 1 H), 2.69 (m, 2 H), 2.76 (m, 2 H), 3.27 (dd, J = 2.5, 1.4 Hz, 2 H), 3.54 (m, 2 H), 4.18 (dt, J = 5.0, 2.0 Hz, 2 H), 5.89 (t, J = 1.9 Hz, 2 H). Anal. Calcd for $C_{22}H_{14}Cl_6O_2$: C, 50.52; H, 2.69. Found: C, 50.32; H, 2.59.

Intramolecular [2 + 2] Photocyclization of 2a. A solution of **2a** (25 mg, 0.05 mmol) in acetone (25 mL) was irradiated under argon with a 250 W tungsten lamp for 3 h. The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in hot CH_2Cl_2 (5 mL). Hexane (10 mL) was added,

and the resulting solution was allowed to stand overnight at room temperature, whereupon **3a** precipitated as a colorless solid. Recrystallization of this material from EtOAc-hexane afforded pure **3a** (20 mg, 80%) as a colorless microcrystalline solid: mp 351-352 °C (dec.); IR (KBr) 2965 (w), 1750 (sh, s), 1733 (vs), 1274 (w), 1218 (w), 1182 (w), 1105 (m), 1084 (m), 1070 (m), 985 (m), 861 (m), 738 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.91 (*AB*, J_{AB} = 11.5 Hz, 1 H), 2.08 (*AB*, J_{AB} = 11.5 Hz, 1 H), 2.63 (dt, J_1 = 1.5 Hz, J_2 = 3.5 Hz, 2 H), 2.75 (d, J = 1.3 Hz, 2 H), 2.98 (m, 2 H), 3.15 (m, 4 H), 3.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.2 (d), 40.9 (t), 42.0 (d), 44.0 (d), 44.9 (d), 47.4 (s), 50.3 (d), 54.9 (d), 78.4 (s), 82.3 (s), 94.0 (s), 210.2 (s). Anal. Calcd for $C_{22}H_{14}Cl_6O_2$: C, 50.52; H, 2.69. Found: C, 50.42; H, 2.56.

Intramolecular [2 + 2] Photocyclization of 2b. A solution of **2b** (30 mg, 0.057 mmol) in acetone (25 mL) was irradiated under argon with a 250 W tungsten lamp for 3 h. The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in hot acetone (5 mL). Hexane (10 mL) was added, and the resulting solution was allowed to stand overnight at room temperature, whereupon **3b** precipitated as a colorless solid. Recrystallization of this material from EtOAc-hexane afforded pure **3b** (25 mg, 83%) as a colorless microcrystalline solid: mp 365-366 °C (dec.); IR (KBr) 2965 (w), 1750 (sh, s), 1733 (vs), 1274 (w), 1218 (w), 1182 (w), 1105 (m), 1084 (m), 1070 (m), 985 (m), 861 (m), 738 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.89 (*AB*, J = 11.3 Hz, 1 H), 2.07 (*AB*, J = 11.3 Hz, 1 H), 2.66 (dt, J = 7.5, 1.8 Hz, 2 H), 2.77 (br s, 2 H), 2.94 (br s, 4 H), 3.15 (m, 2 H), 3.20 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.3 (d), 40.8 (t), 41.6 (d), 43.9 (d), 47.1 (d), 47.2 (d), 47.9 (d), 55.0 (s), 77.2 (s), 83.0 (s), 93.6 (s), 210.4 (s). Anal. Calcd for $C_{22}H_{14}Cl_6O_2$: C, 50.52; H, 2.69. Found: C, 50.33; H, 2.58.

X-ray Structure Determinations: Compounds 1, 7b, and 8. Suitable crystals were affixed to glass fibers and mounted on the goniometer of an Enraf-Nonius CAD-4 diffractometer. Data were collected by using the ω–2θ technique, Mo Kα radiation (λ = 0.71073 Å). and a graphite monochromator. The structures were solved by direct methods, and the model was refined by using full-matrix least-squares techniques. The data were corrected for absorption by using DIFABS. Hydrogen atoms were located on difference Fourier maps and then included in the model in idealized positions [$U(H) = 1.3\ B_{eq}(C)$]. Crystal and refinement data are given in Table 1.[6]

X-ray Structure Determinations: Compounds 2a, 2b, 3a, 3b, and 5. All data were colleced on a Rigaku AFC6S diffractometer. Data were collected by using the ω–2θ scan technique with monochromated CuKα radiation (λ = 1.54178 Å). Lorentz-polarization and an empirical Ψ-scan absorption correction were applied. Cell parameters were obtained by a least-squares refinement of 25 high angle reflections. Crystal and refinement data are given in Table 1.[6]

Acknowledgment. We thank the Robert A. Welch Foundation [Grants B-963 (A. P. M.), B-1202 (S. G. B.) and P-074 (W. H. W.)] and the United States Air Force (Contract F29601-92-K-0018, to A. P. M.) for financial support of this study. Helpful discussions with Professor Richard A. Caldwell (University of Texas at Dallas) are gratefully acknowledged.

Table 1. X-ray structure data

Compound	1	2a	2b	3a	3b	5	7b	8
Formula	$C_{17}H_8O_2Cl_6$	$C_{22}H_{14}O_2Cl_6$	$C_{22}H_{14}O_2Cl_6$	$C_{22}H_{14}O_2Cl_6$	$C_{22}H_{14}O_2Cl_6$	$C_{17}H_{10}O_2Cl_6$	$C_{19}H_{14}O_2Cl_6$	$C_{17}H_{12}O_2Cl_6$
Size (mm)	.08x.10x.12	.15x.15x.15	.40x.30x.50	.15x.15x.60	.30x.25x.10	.37x.27 x.45	0.2x0.3x0.08	.25x.32x.35
Space Group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
# refl. for cell	25	22	24	16	23	16	25	25
2θ range (°)	40-44	18.8-49.1	78.1-79.2	39.4-44.3	34.5-43.3	47.3-54.0	36-44	30-37
a (Å)	7.724 (1)	12.301 (3)	11.583 (2)	7.397 (4)	7.634 (4)	12.008 (2)	11.1413 (8)	14.418 (1)
b (Å)	18.113 (4)	12.236 (3)	11.784 (1)	13.721 (3)	11.050 (5)	10.713 (2)	11.9473 (8)	9.0359 (6)
c (Å)	12.251 (1)	7.820 (1)	7.6270 (9)	19.829 (5)	23.932 (4)	13.918 (2)	16.595 (1)	15.436 (1)
α (°)	90.00	99.20 (2)	90.876 (9)	90.00	90.00	90.00	106.463 (6)	90.00
β (°)	90.00	91.99 (2)	97.50 (1)	98.52 (4)	91.25 (3)	91.08 (1)	98.485 (6)	116.020 (6)
γ (°)	90.00	113.28 (2)	97.472 (9)	90.00	90.00	90.00	103.221 (6)	90.00
V (Å^3)	1713.9 (5)	1061 (1)	1022.8 (4)	1990 (1)	2018 (2)	1790.2 (7)	2008.1 (3)	1807.1 (2)
Z	4	2	2	4	4	4	4	4
D_c (g-cm^{-3})	1.771	1.637	1.698	1.745	1.721	1.703	1.611	1.694
μ (cm^{-1})	10.17	77.32	80.20	82.43	81.29	90.70	8.73	9.65
Corr. Fac.	0.90-1.12	0.81-1.00	0.55-1.00	0.21-1.00	0.30-1.00	0.43-1.00	0.73-1.24	0.86-1.14
ω–2θ (2θ_{max})	44	163.1	257.1	157.3	157.6	131.7	44	44
Total refl.	1249	4581	6054	4805	6019	3489	4906	2475
Unique refl.	1249	4374	4219	4384	4216	3168	4906	2378
R_{int}	- -	0.083	0.071	0.106	0.099	0.119	- -	0.0118
$I \geq 3\sigma(I)$	1065	1485	3612	3525	2595	2152	4149	1881
Parameters	141	272	328	328	322	266	487	226
R, wR	.0294, .0308	.13, .10	.070, .078	.062, .067	.085, .079	.073, .072	.0409, .0448	.0416, .0586
$(\Delta/\sigma)_{max}$	<0.01	7.2	9.2	0.03	0.94	0.07	<0.01	<0.01
ρ_{min}; ρ_{max}	-0.33; 0.27	-0.57; 0.65	-0.60; 0.91	-0.65; 0.49	-0.59; 0.61	-0.62; 0.80	-0.44; 0.34	-0.25; 0.33

REFERENCES & FOOTNOTES

1. Marchand, A. P. In *Advances in Theoretically Interesting Molecules;* Thummel, R. P., Ed.; JAI: Greenwich, CT; 1989, Vol. 1, pp 357-399.

2. Burdette, G. W.; Lander, H. R.; McCoy, J. R. *J. Energy* **1978**, *2*, 289.

3. Chow, T. J.; Chao, Y. S. *Synth. Commun.* **1988**, *18*, 1875.

4. (a) Alder, K.; Stein, G. *Angew. Chem.* **1937**, *50*, 510. (b) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16; (c) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537.

5. (a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969. (b) Caldwell, R. A.; Jacobs, L. D.; Furlani, T. R.; Nalley, E. A.; Laboy, J. *J. Am. Chem. Soc.* **1992**, *114*, 1623.

6. Tables of positional parameters and their estimated standard deviations, general displacement parameter expressions, bond distances, bond angles, and torsion angles (135 + iv pages) for **1**, **2a**, **2b**, **3a**, **3b**, **5**, **7b**, and **8** are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CV2 1EW, U. K. Requests should be accompanied by the full literature citation for this article.