

The Pursuit of Perchlorotriphenylene

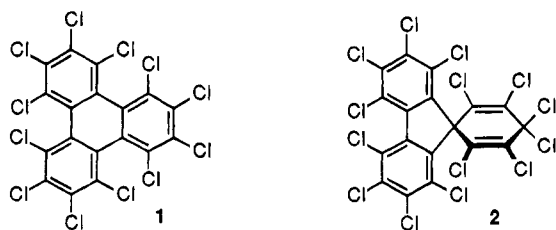
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The synthesis of the polycyclic aromatic chlorocarbon perchlorotriphenylene (**1**, dodecachlorotriphenylene) from tetrachlorophthalic anhydride is described, and several approaches to the synthesis of **1** via Diels–Alder additions of 2,3,4,5-tetrachlorothiophene 1,1-dioxide and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene to naphthalene are also reported. The X-ray structure of compound **1** shows it to adopt a C_2 conformation which is highly distorted from planarity, but the compound is stable under ordinary conditions. Semiempirical and ab initio molecular orbital calculations indicate that the C_2 conformation is preferred to a D_3 conformation in the gas phase as well, and these calculations also indicate that compound **1** is highly flexible and can undergo rapid enantiomerization.

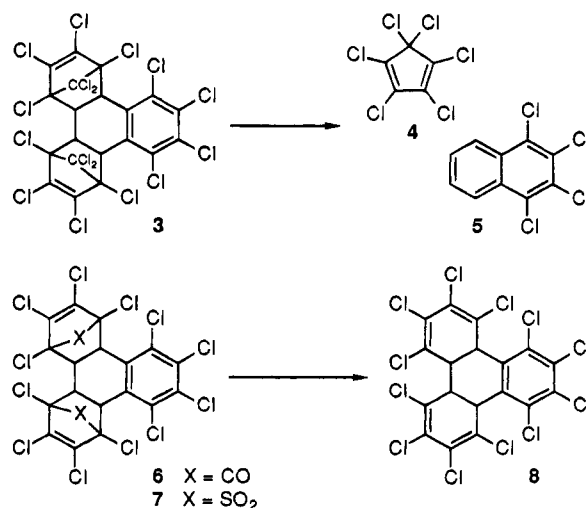
Perchlorotriphenylene (**1**, dodecachlorotriphenylene) has been elusive. A recent review of its literature by Campbell et al.¹ indicates that the synthesis of **1** has never been clearly described and that **1**, if ever prepared, has not been even minimally characterized. Attempts to prepare **1** by the exhaustive chlorination of triphenylene lead instead to overchlorination and rearrangement; for example, BMC chlorination^{2,3} of triphenylene gives primarily the rearranged compound **2** as well as tetradecachloro-*o*-terphenyl (both compounds were unambiguously characterized by X-ray crystallography).⁴ Campbell et al. explored several alternative syntheses of **1** without success, leading them to speculate that “severe molecular twisting to relieve steric interactions of “ortho” chlorines may preclude any stable existence [for **1**]”.¹ Our own experience with highly twisted polycyclic aromatic hydrocarbons⁵ suggested that **1** should be at least marginally stable, although severely distorted from planarity. We now describe the synthesis, isolation, and characterization of **1**, as well as a few unsuccessful but instructive approaches to it, and computational studies of this highly strained molecule.⁶



Results and Discussion

Diels–Alder Syntheses of Highly Chlorinated Derivatives of Triphenylene. It is clear from the

results of earlier studies^{1,2,4} that vigorous chlorination reactions must be avoided in the final step of any synthesis of **1**. Instead, all of the chlorine atoms should be in place in a less highly strained precursor which could then be converted to **1** by a series of steps not involving strong electrophiles. Campbell et al.¹ attempted to prepare **1** by the thermal decomposition of commercially available compound **3**, which has the full chlorocarbon skeleton of **1** in place, but pyrolysis of **3** gave only retro-Diels–Alder reaction products. That attempt required that dichlorocarbene be expelled to form **1**, a relatively difficult proposition. However, if either compound **6** or **7** could be prepared and pyrolyzed instead, the expulsion of CO or SO₂ might be preferred to the retro-Diels–Alder process, yielding a tetrahydro-**1** (**8**) which should in turn be convertible to **1** by dehydrogenation. Interestingly, compound **3** is prepared by the chlorination of the naphthalene bis(hexachlorocyclopentadiene) adduct without unwanted rearrangements,⁷ so the chlorination of similar naphthalene adducts might also be possible.



[®] Abstract published in *Advance ACS Abstracts*, January 1, 1995.
(1) Campbell, M. C.; Humphries, R. E.; Munn, N. M. *J. Org. Chem.* **1992**, *57*, 641–644.

(2) Ballester, M. *Adv. Phys. Org. Chem.* **1989**, *25*, 267–445.

(3) Ballester, M.; Molinet, C.; Castaner, J. *J. Am. Chem. Soc.* **1960**, *82*, 4254–4258.

(4) Gall, J. H.; MacNicol, D. D.; Mallinson, P. R.; Welsh, P. A. *Tetrahedron Lett.* **1985**, *26*, 4005–4008.

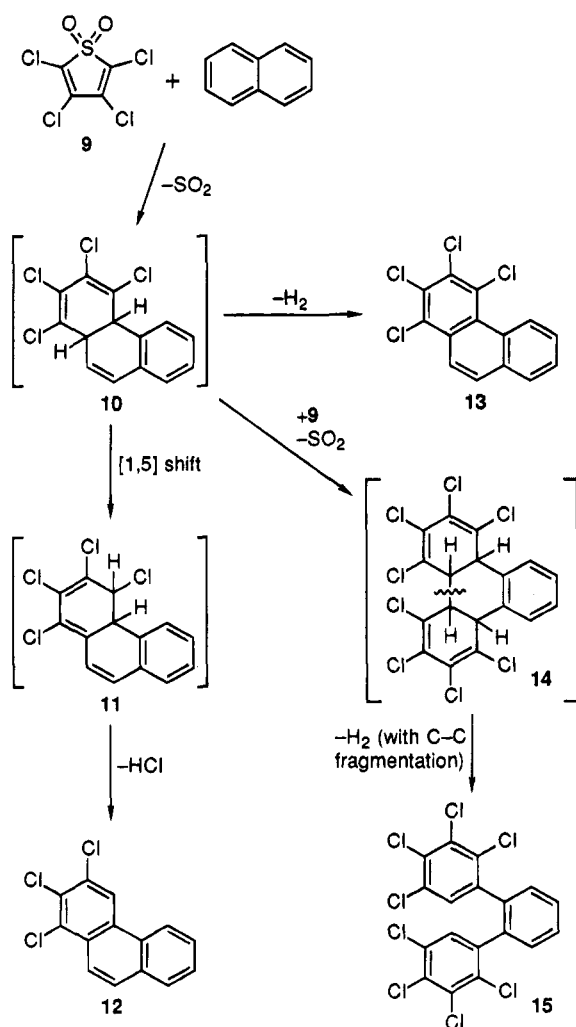
(5) (a) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660–4665. (b) Smyth, N.; Van Engen, D.; Pascal, R. A., Jr. *J. Org. Chem.* **1990**, *55*, 1937–1940. (c) Pascal, R. A., Jr. *Pure Appl. Chem.* **1993**, *65*, 105–110.

(6) A preliminary communication describing the synthesis of **1** has been published: Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5983–5984.

In a first test of the feasibility of such syntheses, we investigated the reactions of tetrachlorothiophene derivatives with naphthalene. Tetrachlorothiophene itself failed to condense with naphthalene even after prolonged heating, but tetrachlorothiophene dioxide⁸ (**9**) gave a

(7) Danish, A. A.; Silverman, M.; Tajima, Y. A. *J. Am. Chem. Soc.* **1954**, *76*, 6144–6150.

Scheme 1



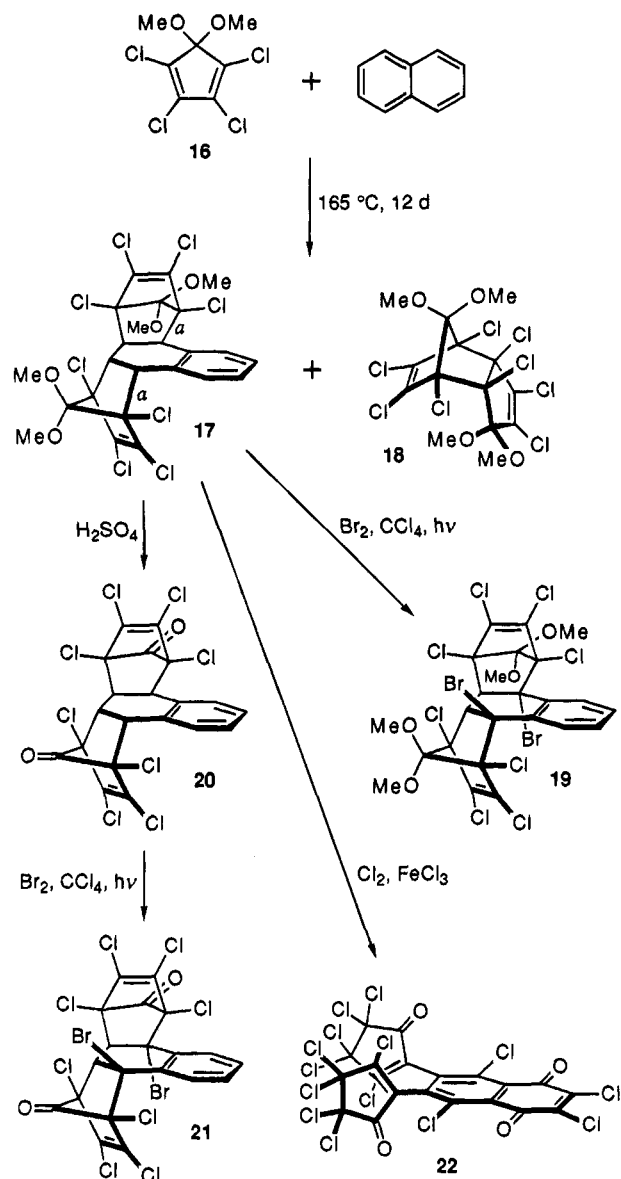
mixture of adducts when heated with naphthalene at 165–170 °C (see Scheme 1). The bulk of this material (~75%) was 1,2,3-trichlorophenanthrene (**12**). This monoadduct must be formed by Diels–Alder reaction of the starting materials followed by expulsion of SO₂ to give **10**, double bond isomerization to **11**, and dehydrochlorination to yield **12**. Only the 1,2,3-isomer is observed; the loss of the C-4 chlorine may relieve an intramolecular steric conflict in the precursors.⁹ Interestingly, a small amount (2%) of 1,2,3,4-tetrachlorophenanthrene¹⁰ (**13**) is also found in the reaction mixture, presumably formed by the dehydrogenation of **10** or **11**. The ¹H NMR spectrum of **13** shows a very low field doublet (δ 9.69) which is the C-5 proton forced to be in very close contact with the C-4 chlorine. The chief product resulting from the addition of two molecules of **9** to naphthalene was 2,3,4,5,2'',3'',4'',5''-octachloro-*o*-terphenyl (**15**). The mechanism of formation of **15** is uncertain, but it probably arises by fragmentation and dehydrogenation of the "normal" diadduct **14**, a process driven by the relief of strain and the formation of two new aromatic rings.

(8) (a) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 856–867. (b) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 867–870.

(9) The proposed intermediate **11** is formed via a [1,5] sigmatropic shift of the C(10a)-hydrogen in **10**. AM1 calculations indicate that **11** is 3.5 kcal/mol lower in energy than the isomer which would be formed by an alternative [1,5] shift of the C(4a)-hydrogen of **10**. We thank a referee for pointing out this possibility.

(10) Harrison, R.; Heaney, H.; Jablonski, J. M.; Mason, K. G.; Sketchley, J. M. *J. Chem. Soc. (C)* **1969**, 1684–1689.

Scheme 2



Similar fragmentations to give a tetrachlorophenyl group have been reported in the reactions of **9** with furans.^{8b} The ¹H NMR spectrum of **15** clearly shows it to be a mixture of *cis* and *trans* rotational isomers on the NMR time scale, but only a single component was observed in gas chromatographic analyses.

In contrast to the above reaction, the addition of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (**16**) to naphthalene gave primarily the desired diadduct **17** along with some of the dimer **18** (see Scheme 2). The X-ray structure of **17** is shown in Figure 1. This is the first X-ray structure of a naphthalene bis(cyclopentadiene) adduct, and this determination unambiguously establishes the stereochemistry of addition of the cyclopentadienes to be *endo*, as well as *trans* to one another.¹¹ Most significantly, there is ample space for the introduction of four chlorine atoms on the benzene ring, which would be required for the synthesis of **1**, and such a chlorination

(11) The stereochemistry of the diadduct **3** is also believed to be *trans* on the basis of zero field NMR and multiple-quantum NMR analyses: (a) Zax, D. B.; Bielecki, A.; Zilm, K. W.; Pines, A.; Weitkamp, D. P. *J. Chem. Phys.* **1985**, *83*, 4877–4905. (b) Baum, J.; Pines, A. *J. Am. Chem. Soc.* **1986**, *83*, 7447–7454. (c) Bielecki, A.; Zax, D. B.; Thayer, A. M.; Miller, J. M.; Pines, A. *Z. Naturforsch.* **1986**, *41a*, 440–444.

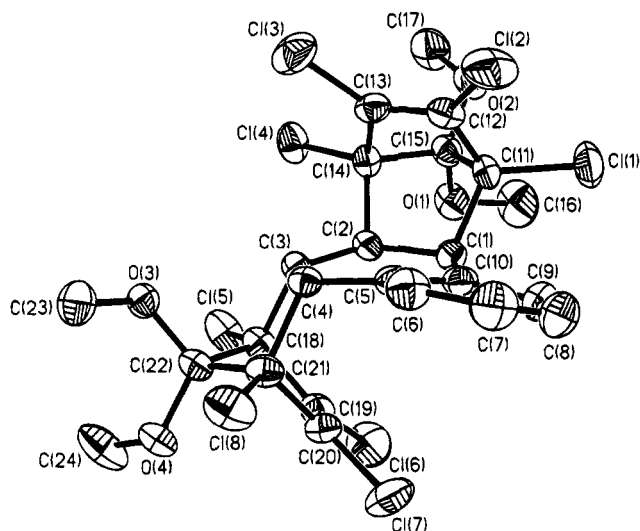


Figure 1. X-ray structure of compound **17**. Thermal ellipsoids are drawn at the 50% probability level.

has been previously demonstrated in the synthesis of compound **3**.⁷ Thus, from the readily available **17**, it seemed to be only a short step to both octachloro- and dodecachlorotriphenylene, but this proved not to be the case.

Photobromination of **17** with a large excess of bromine gave the benzylic dibromide **19** in quantitative yield,¹² but attempts to dehydrobrominate **19** with triethylamine or KOH were without success. In order to reduce the steric encumbrance of the central ring hydrogens, the ketals of **17** were cleaved with concentrated sulfuric acid to give diketone **20** in 95% yield, and photobromination as before gave the benzylic dibromide **21** in 94% yield. Dehydrobromination of **21**, if successful, would yield a double norbornadienone, which should immediately lose two molecules of CO to give the fully aromatic octachlorotriphenylene **23**.

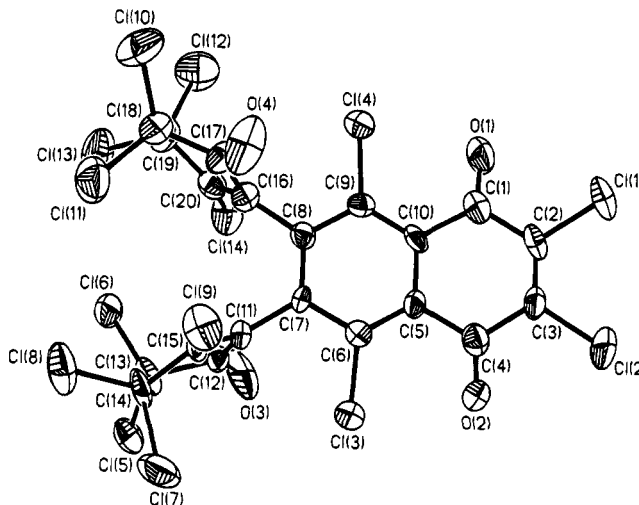
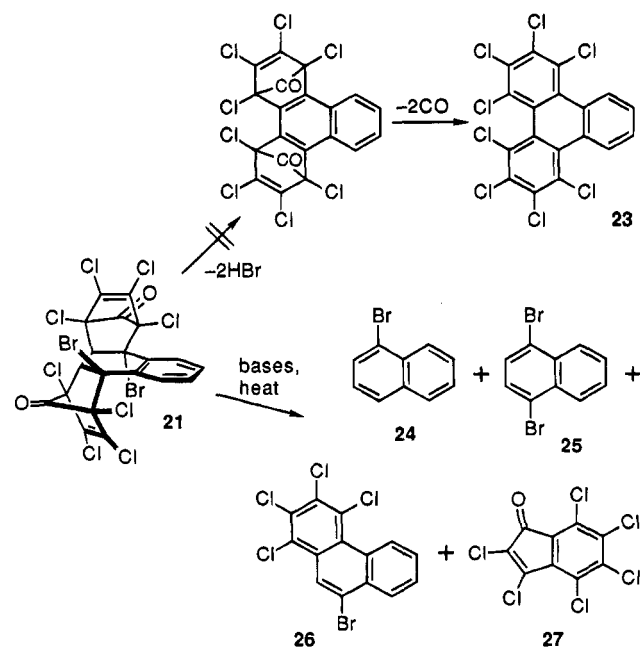


Figure 2. X-ray structure of compound **22**. Thermal ellipsoids are drawn at the 50% probability level.

tions, KOH in triglyme,¹³ or KF on alumina¹⁴ gave unidentifiable decomposition products, and treatment with triethylamine¹⁵ or sodium acetate¹⁶ returned starting material. Treatment of **21** with DBU in refluxing dichlorobenzene,¹⁷ or with refluxing 2,6-lutidine, or simply heating in nitrobenzene or DMF¹⁸ gave mixtures which included the bromonaphthalenes **24** and **25**, as well as compounds tentatively identified as **26** and **27** on the basis of GC-MS analysis, without any detectable formation of **23**. These results strongly suggested that retro-Diels–Alder reactions would preclude formation of the desired triphenylenes even when expulsion of CO was a possibility. That the extrusion of CO is difficult in these molecules was further emphasized by the reactivity of compound **20**: thermolysis of **20** in refluxing nitrobenzene or *o*-dichlorobenzene gave no reaction, nor did photolysis in hot CCl₄, and attempts to dehydrogenate **20** with DDQ or *o*-chloranil were also unsuccessful.

The final attempts to prepare **1** via the diadduct **17** were direct, though perhaps ill-advised, chlorinations of **17**. Unfortunately, these reactions invariably yielded complex mixtures of products, few of which were conclusively identified because of their lack of ¹H NMR resonances and relative insolubility. One very interesting product was obtained by vigorous chlorination of **17** with iron and chlorine, conditions similar to those employed for the literature synthesis⁷ of compound **3**. The ¹³C NMR spectrum of this material (**22**) showed only 10 resonances (including two carbonyl resonances), which in conjunction with the mass spectrum indicated a highly chlorinated compound with two-fold symmetry. X-ray analysis was required to determine the structure of this material, which is illustrated in Figure 2. Compound **22** arises by chlorinolysis of the bonds marked *a* in compound **17**, which probably proceeds by electrophilic attack

A variety of established procedures for dehydrohalogenation were recruited for this task. Unfortunately, treatment of **21** with NaOH under phase transfer condi-

(12) Interestingly, attempted photobromination and photochlorination of compound **3** returned only starting material.

(13) Mizuno, K.; Kimura, Y.; Otsuji, Y. *Synthesis* **1979**, 688.

(14) Yamawaki, J.; Kawate, T.; Ando, T.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1885–1886.

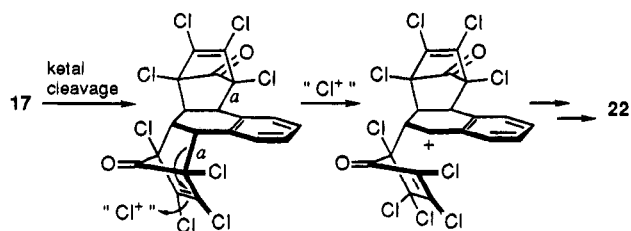
(15) Price, C. C.; Judge, J. M. *Org. Synth.* **1965**, *45*, 22–24.

(16) Cromwell, N. H.; Cram, D. J.; Harris, C. E. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, pp 125–127.

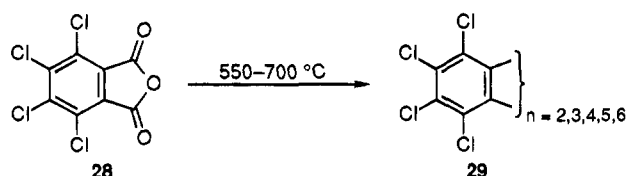
(17) Oediger, H.; Moller, F. *Angew. Chem., Int. Ed. Engl.* **1967**, *79*, 76.

(18) Heller, M.; Lenhard, R. H.; Bernstein, S. *J. Am. Chem. Soc.* **1964**, *86*, 2309–2310.

on the olefins and fragmentation of the resulting cation. This, along with ketal cleavage, extensive chlorination, and oxidation of the naphthalene to the quinone, eventually leads to compound **22**. There is little space to add any additional chlorines to this highly crowded molecule.



Perchlorotriphenylene from Tetrachlorobenzene. With the failure of the Diels–Alder approach to **1**, we turned to the trimerization of tetrachlorobenzene as a possible alternative synthesis. Initial experiments were conducted in solution, but neither the diazotization and decomposition of tetrachloroanthranilic acid¹⁹ nor the treatment of hexachlorobenzene with butyllithium²⁰ led to the formation of any material with the necessary mass spectral characteristics. However, perchlorobiphenylene has been prepared previously by flash vacuum pyrolysis of tetrachlorophthalic anhydride, presumably via tetrachlorobenzene, but no higher molecular weight products were noted in these experiments.²¹ If the local concentration of tetrachlorobenzene could be increased, perhaps the trimer **1** would be formed to some extent. We therefore heated solid tetrachlorophthalic anhydride (**28**) over a flame in an open Pyrex flask for several minutes, and mass spectral analysis of an organic extract of the green-black residue revealed several components of the general formula $(C_6Cl_4)_n$ (**29**). Indeed, progressive heating of the sample in an electron impact mass spectrometer showed components with apparent molecular ion clusters at m/z 428 ($C_{12}Cl_8$), 642 ($C_{18}Cl_{12}$), and 856 ($C_{24}Cl_{16}$), and the FAB mass spectrum of the same sample showed additional clusters at m/z 1070 ($C_{30}Cl_{20}$) and 1284 ($C_{36}Cl_{24}$).



When the reaction was conducted under vacuum (~ 0.25 Torr) so that the material subliming upon decomposition of **28** would pass through a quartz tube at 700 °C, the product was somewhat enriched in the lower molecular weight components. After removal of unreacted **28** by hydrolysis and extraction with ethanolic KOH, the remaining material was subjected to two cycles of preparative TLC (hexanes), each time isolating the band with $R_f = 0.84$. Finally, recrystallization of this material from dichloromethane and acetone gave crystals of pure **1** suitable for X-ray analysis.

(19) Heaney, H.; Jablonski, J. M. *J. Chem. Soc. (C)* **1968**, 1895–1898.

(20) Hales, N. J.; Heaney, H.; Hollinshead, J. H.; Singh, P. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. 6, pp 82–86.

(21) (a) Cava, M. P.; Mitchell, M. J.; DeJongh, D. C.; Van Fossen, R. Y. *Tetrahedron Lett.* **1966**, 2947–2951. (b) Brown, R. F. C.; Gardner, D. V.; McOmie, J. F. W.; Solly, R. K. *J. Chem. Soc., Chem. Commun.* **1966**, 407–408.

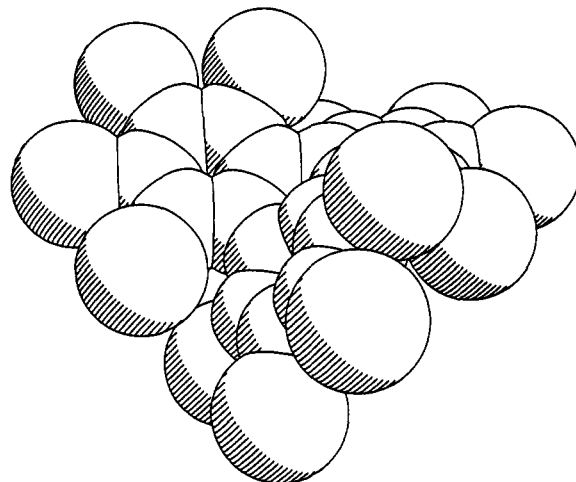
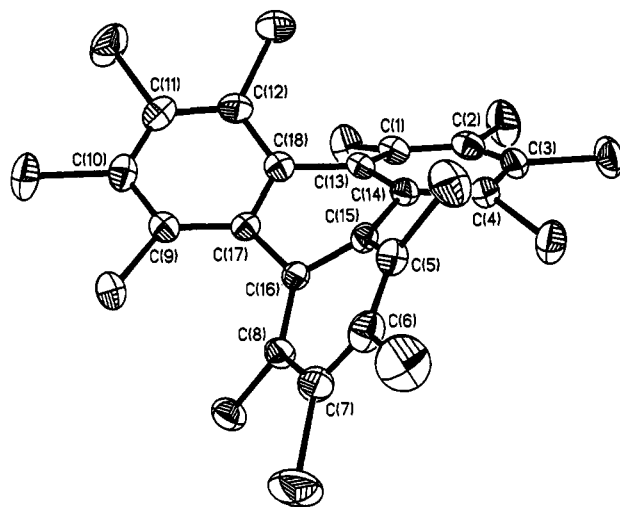


Figure 3. X-ray structure of perchlorotriphenylene (**1**). Both the thermal ellipsoid (above) and space filling (below) drawings depict compound **1** in the same orientation. Thermal ellipsoids are drawn at the 50% probability level.

The X-ray structure of perchlorotriphenylene is illustrated in Figure 3. Compound **1** adopts a conformation with approximate C_2 symmetry, quite similar to that observed for perfluorotriphenylene,²² but with much greater deviations from planarity. The molecule distorts to relieve the intramolecular Cl–Cl nonbonded contacts, which remain very close: for example, Cl(4)–Cl(5), 3.059 Å; Cl(8)–Cl(9), 3.035 Å; and Cl(1)–Cl(12), 3.141 Å. The result of these distortions is that the rings C(1–2–3–4–14–13) and C(9–10–11–12–18–17) adopt boat conformations, with geometries similar to those found in [8]paracyclophane,²³ and the remaining naphthalene substructure [C(5–6–7–8–16–17–18–13–14–15)] displays a 56.6° end-to-end twist,²⁴ with the central ring and C(5–6–7–8–16–15) contributing 36.7° and 19.9°, respectively, to the overall twist.²⁵ Indeed, the distortions of the central ring are greater than those in any other substituted triphenylene, and the 57° twist of the naphthalene subunit approaches the overall twists of the most

(22) Hursthouse, M. B.; Smith, V. B.; Massey, A. G. *J. Fluorine Chem.* **1977**, *10*, 145–155.

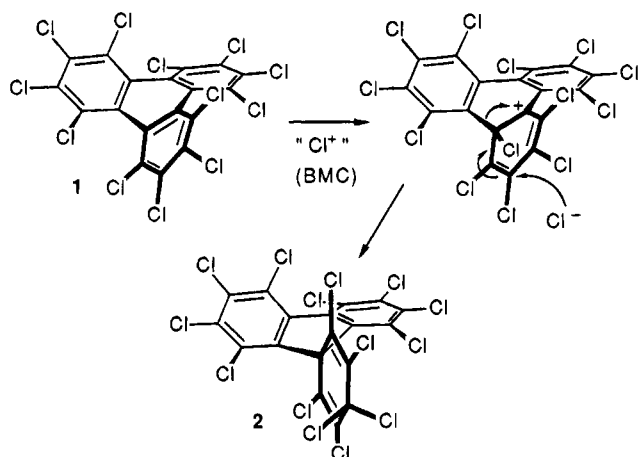
(23) Newton, M. G.; Walter, T. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1973**, *95*, 5652–5658.

(24) See note 17 in ref 5a for the definition of “end-to-end twist”.

(25) The corresponding twists in perfluorotriphenylene²² are 40.5°, 28.0°, and 12.4°, respectively.

highly twisted *anthracene* derivatives (60–69°).^{3,26} One other point should be noted: the central ring of compound **1** shows strong bond alternation. Triphenylene itself is known from both experimental²⁷ and computational²⁸ studies to exhibit a great deal of bond alternation in the central ring, and it is perhaps best regarded as three fully delocalized benzene rings linked by bonds of low order.^{28a} In compound **1** the bond alternation of the center ring is at least as pronounced, with the short bonds averaging 1.414 Å (1.411 Å for triphenylene²⁷) and the long bonds 1.478 Å (1.470 Å).

Perchlorotriphenylene is a high-melting solid (347–348 °C) which is perfectly stable under ordinary conditions. However, such a strained aromatic system cannot be expected to survive the attack of strong electrophiles, and, indeed, the easy formation of the spiro compound **2** by the chlorination of triphenylene⁴ is readily understood from the structure of **1**. Compound **1** is probably formed under the BMC chlorination conditions,³ but the 57° twist of the naphthalene moiety in **1** brings the molecule more than halfway to the relatively strain-free spiro geometry observed in **2**. The addition of one more equivalent of chlorine to **1**, as illustrated below, yields a carbonium ion distorted in such a way as to favor further rearrangement to compound **2**.



Computational Studies of the Conformations of Perchlorotriphenylene. It is perhaps unexpected that perfluoro- and perchlorotriphenylene should adopt conformations of C_2 rather than D_3 symmetry, but the experimental solid state structures are consistent with the results of gas-phase computational studies of these molecules. AM1 calculations²⁹ indicate that both the C_2 and D_3 conformations of **1** reflect true potential energy minima, but the C_2 form is calculated to be 1.0 kcal/mol lower in energy than the D_3 conformer. Similarly, C_2 perfluorotriphenylene and C_2 perbromotriphenylene (which is unknown) are favored by 1.6 kcal/mol and 0.3 kcal/mol, respectively, over their D_3 conformers. When the C_2 and D_3 conformations of **1** were examined by means of ab initio molecular orbital calculations at the HF/STO-3G level,³⁰ the relative energy difference was found to be even greater, with the C_2 conformer favored by 5.2 kcal/mol.

(26) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981–2983.

(27) Filippini, G. *J. Mol. Struct.* **1985**, *130*, 117–124.

(28) (a) Glidewell, C.; Lloyd, D. *Tetrahedron* **1984**, *40*, 4455–4472.

(b) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583–9587.

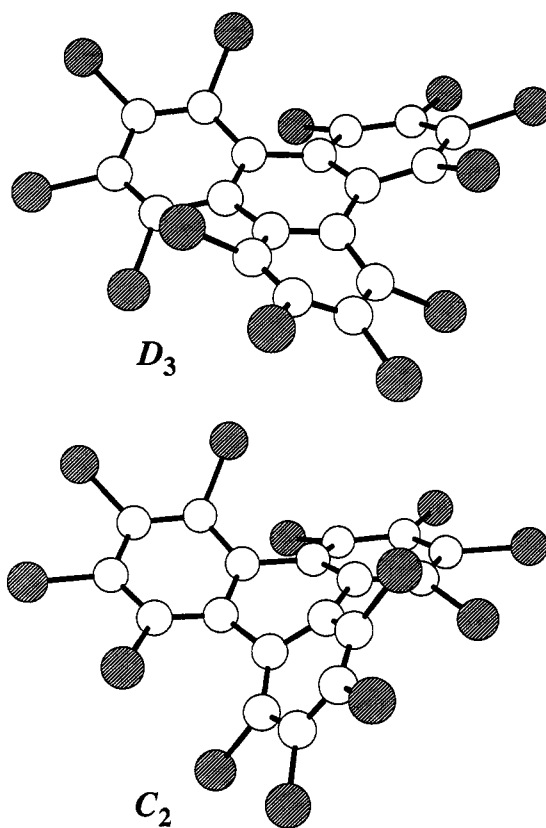
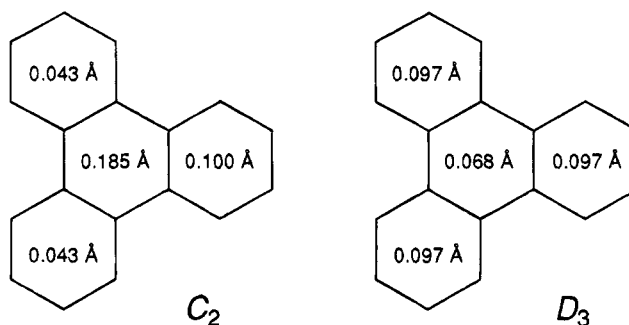


Figure 4. C_2 and D_3 conformations of perchlorotriphenylene from ab initio calculations at the HF/STO-3G level of theory.

The fully optimized geometries from the ab initio calculations are illustrated in Figure 4; the calculated C_2 conformation and the crystal structure (Figure 3) are extremely similar. But why is the C_2 structure favored over D_3 ? Given below are the RMS deviations from planarity of the atoms in each ring of the calculated C_2 and D_3 conformations. In the D_3 conformation the greatest distortions are found in the three outer rings, but in the C_2 conformation the greatest distortion is



observed in the central ring. Two of the outer rings of the C_2 conformation show less than half of the RMS deviation from planarity (0.043 Å) than that calculated for the three outer rings of the D_3 conformation (0.097 Å), and the distortion of the remaining C_2 outer ring is about the same (0.100 Å) as that for the D_3 conformation. Thus the C_2 conformation minimizes the distortion of the more highly delocalized, aromatic, outer rings of the

(29) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(30) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; pp 63–100.

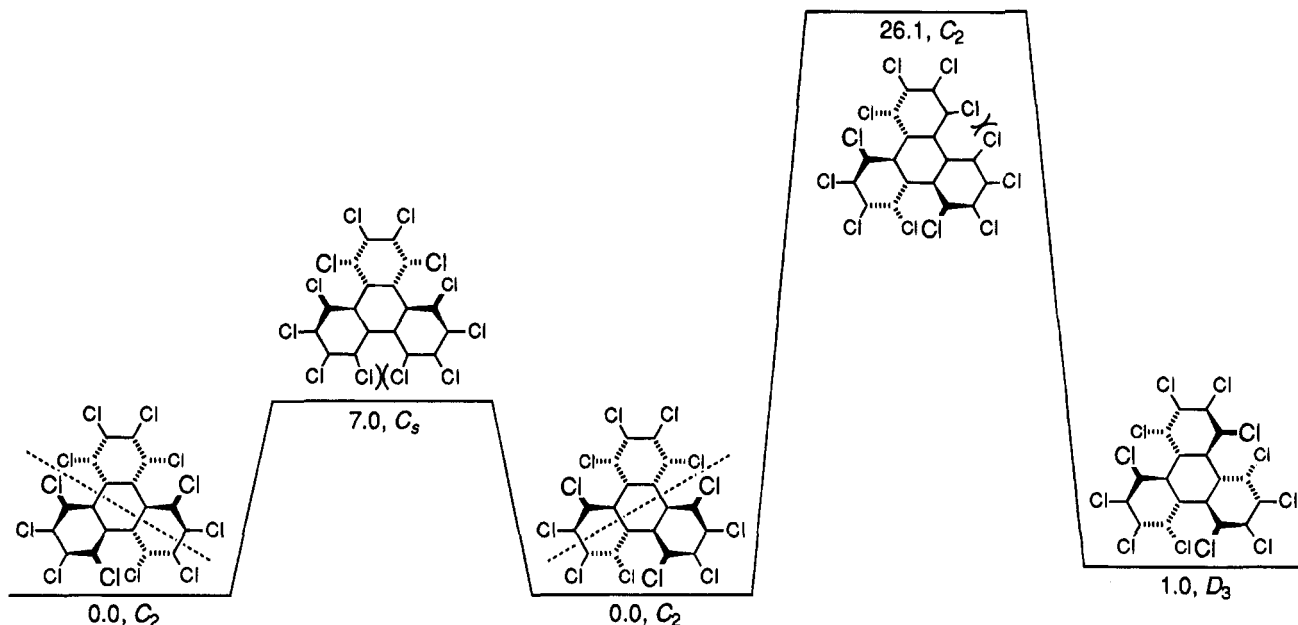


Figure 5. Potential energy diagram illustrating the calculated (AM1) relative energies of ground state, intermediate, and transition state conformations of perchlorotriphenylene. The information just below each plateau indicates the energy (in kcal/mol relative to the C_2 ground state) and symmetry of the illustrated conformation.

triphenylene at the expense of the bond-alternate central ring, while the opposite trend is observed in the D_3 conformation. The preservation of planarity in the delocalized outer rings of the C_2 conformation probably accounts for its slightly greater stability.³¹

Finally, the observed conformation of **1** is chiral, and if resolved, the separate enantiomers might exhibit very high optical activity. However, an initial attempt to resolve **1** on a chiral chromatography column³² was unsuccessful, and subsequent AM1 calculations suggested that further attempts would be futile. Figure 5 shows the potential energy minima and transition states for the interconversion of the conformers of compound **1**. Interconversion of the C_2 and D_3 conformations is difficult, with a calculated barrier of 26 kcal/mol. If the enantiomerization of **1** required the compound to pass through this transition state, then resolution might be relatively simple. However, the direct interconversion of the C_2 enantiomers can occur through a lower energy pathway. This transition state possesses C_s symmetry and lies only 7 kcal/mol above the equilibrium geometry of **1**. Under such circumstances, the resolution of **1** can only be successful at liquid nitrogen temperatures or below.

Conclusion

Perchlorotriphenylene is a difficult molecule to prepare, and even the one-step synthesis reported herein is not amenable to the preparation of large quantities. In addition, the molecule is highly distorted from planarity, with a greater degree of distortion than has been observed for any other triphenylene. However, despite the synthetic challenge and the high degree of strain

present in the molecule, perchlorotriphenylene is completely stable under ordinary conditions, and computational studies indicate that it possesses a high degree of conformational flexibility.

Experimental Section

Reaction of Naphthalene and Tetrachlorothiophene Dioxide. A mixture of 2,3,4,5-tetrachlorothiophene 1,1-dioxide⁸ (**9**, 714 mg, 2.81 mmol) and naphthalene (10.20 g, 79.6 mmol) was heated at 167 °C for 41 h. After removal of the naphthalene under vacuum a dark brown solid remained (909 mg). A portion of this material (815 mg) was fractionated by silica gel column chromatography (hexanes) to yield five fractions, designated α (3.8 mg), β (9.4 mg), γ (655.2 mg), δ (7.8 mg), and ϵ (17.0 mg).

Fraction α proved to be pure **1,2,3,4-tetrachlorophenanthrene (13)**: ¹H NMR (500 MHz, CDCl₃) δ 7.67 (m, 2H), 7.87 (d, 1H, $J = 9$ Hz), 7.91 (m, 1H), 8.22 (d, 1H, $J = 9$ Hz), 9.69 (d, 1H, $J = 9$ Hz) [lit.⁹ ¹H NMR (60 MHz, CDCl₃) δ 7.55–7.85 (m), 8.10–8.25 (m), 9.60–9.75 (m)]; MS, m/z 316 (M^+ , 100), 280 ($M - HCl$, 4), 244 ($M - Cl_2$, 25). Fractions β , γ , and δ were mixtures of three components, the least abundant of which ($\sim 2\%$) was compound **13**. A portion of fraction γ was recrystallized from benzene to give **1,2,3-trichlorophenanthrene (12)**, which was the major component ($\sim 75\%$) of fractions β , γ , and δ : ¹H NMR (CDCl₃) δ 7.67 (m, 2H), 7.85 (d, 1H, $J = 9$ Hz), 7.90 (d, 1H, $J = 8$ Hz), 8.14 (d, 1H, $J = 9$ Hz), 8.53 (d, 1H, $J = 8$ Hz), 8.69 (s, 1H); MS, m/z 280 (M^+ , 100), 244 ($M - HCl$, 4), 210 ($M - Cl_2$, 34). The third component was purified by sublimation of a portion of fraction γ , which removed compounds **12** and **13**, and left **2,3,4,5,2'',3'',4'',5''-octachloro-o-terphenyl (15)**: ¹H NMR (benzene-*d*₆, mixture of two conformers in an approximately 3:2 ratio) δ 6.75 (s, 0.8H), 7.01 (m, 1.2H), 7.11 (m, 0.8H), 7.25 (m, 2H), 7.29 (s, 1.2H); ¹H NMR (acetone-*d*₆, mixture of two conformers in an approximately 1:1 ratio) δ 7.46 (m, 1H), 7.50 (s, 1H), 7.54 (m, 1H), 7.63 (m, 1H), 7.64 (s, 1H), 7.65 (m, 1H); MS, m/z 506 (M^+ , 35), 469 ($M - Cl$, 6), 434 ($M - Cl_2$, 100), 399 ($M - Cl_3$, 8), 364 ($M - Cl_4$, 36); exact mass 505.7926, calcd for C₁₈H₈³⁵Cl₈³⁷-Cl₂ 505.7919.

1,2,3,4,5,6,7,8-Octachloro-13,13,14,14-tetramethoxy-1,4,4a,4b,5,8a,12b-octahydro-1,4:5,8-dimethanotriphenylene (17). A mixture of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (**16**, 19.7 g, 74.6 mmol) and naphthalene (10.2

(31) It is also notable that the central ring in the D_3 conformer must adopt a chair conformation, and in our experience it is rare to observe chairlike distortions in structures of polycyclic aromatic compounds. Boat and twist conformations, such as those in the C_2 conformer, are much more commonly observed and may provide better orbital overlap for the π -systems in these molecules.

(32) West, A. P., Jr.; Smyth, N.; Kraml, C. M.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1993**, *58*, 3502–3506.

g, 79.6 mmol) was stirred for 12 d at 165 °C. After cooling, CH₂Cl₂ (500 mL) was added, and the mixture was filtered through a pad of silica gel, which was rinsed with another 500 mL of CH₂Cl₂. The filtrate was concentrated to yield an orange oil (29.1 g). Hexanes (350 mL) were added, and the mixture was filtered through a second pad of silica gel, which was rinsed with another 500 mL of hexanes. The hexane filtrate was put aside, the pad was rinsed with 1.2 L of CH₂Cl₂, and this filtrate was concentrated to give a brown oil. Crystallization from ethanol yielded compound **17** (11.2 g, 17.1 mmol, 46%): mp 211–212 °C; ¹H NMR (CDCl₃) δ 3.24 (d, 2H, *J* = 9 Hz), 3.53 (s, 6H), 3.68 (s, 6H), 3.77 (d, 2H, *J* = 9 Hz), 7.77 and 7.63 (AA'BB' system, 4H); ¹³C NMR (CDCl₃) δ 40.8, 47.6, 51.9, 52.6, 78.8, 81.1, 110.6, 126.6, 127.1, 128.9, 129.5, 130.9; MS, *m/z* 656 (M⁺, 0.7), 621 (M - Cl, 64), 355 (M - C₅Cl₄(OMe)₂ - Cl, 39), 319 (M - C₅Cl₄(OMe)₂ - Cl₂, 41), 128 (C₁₀H₈⁺, 100); exact mass 655.8816, calcd for C₂₄H₂₀³⁵Cl₈³⁷Cl₂O₄ 655.8811. Anal. Found for C₂₄H₂₀Cl₈O₄: C, 43.87; H, 3.50. Calcd: C, 43.94; H, 3.07. The stereochemistry of **17** was established by X-ray analysis (see Figure 1).

Concentration of the mother liquor from the crystallization of **17** and recrystallization of the residue from methanol gave the dimer **18** (6.97 g, 13.2 mmol, 35%): mp 258–259 °C dec; ¹H NMR (CDCl₃) δ 3.36 (s, 3H), 3.53 (s, 3H), 3.56 (s, 3H), 3.61 (s, 3H); ¹³C NMR (CDCl₃) δ 52.3, 52.67, 52.74, 53.1, 80.0, 81.5, 83.5, 85.8, 106.4, 115.0, 129.2, 133.9, 134.5, 135.2. Anal. Found for C₁₄H₁₂Cl₈O₄: C, 31.80; H, 2.30. Calcd: C, 31.86; H, 2.29.

8a,12b-Dibromo-1,2,3,4,5,6,7,8-octachloro-13,13,14,14-tetramethoxy-1,4,4a,4b,5,8,8a,12b-octahydro-1,4:5,8-dimethanotriphenylene (19). A solution of compound **17** (147.6 mg, 0.225 mmol) and bromine (0.20 mL, 3.9 mmol) in CCl₄ (13 mL) was irradiated with a tungsten lamp for 3 h at room temperature. Chloroform (100 mL) was added and the solution was washed with 1 N aqueous Na₂SO₃ (100 mL) and water (100 mL). After drying over MgSO₄, the organic layer was concentrated to yield white solid **19** (182.4 mg, 0.225 mmol, 100%): mp 267–268 °C dec; ¹H NMR (CDCl₃) δ 3.57 (s, 6H), 3.76 (s, 6H), 3.90 (s, 2H), 7.22 and 8.05 (AA'BB' system, 4H); ¹³C NMR (CDCl₃) δ 52.1, 52.7, 54.1, 61.0, 84.7, 112.1, 128.3, 130.5, 131.2, 133.4 (10 of 12 possible resonances reliably observed); MS, *m/z* 812 (M⁺, 8), 777 (M - Cl, 15), 733 (M - Br, 73), 697 (M - Br - HCl, 11), 545 (37), 434 (58), 287 (97), 156 (100); exact mass 811.7022, calcd for C₂₄H₁₈⁷⁹Br₂³⁵Cl₈³⁷-Cl₂O₄ 811.7022.

1,2,3,4,5,6,7,8-Octachloro-13,14-dioxo-1,4,4a,4b,5,8,8a,12b-octahydro-1,4:5,8-dimethanotriphenylene (20). A mixture of compound **17** (6.89 g, 10.5 mmol) and concentrated H₂SO₄ (100 mL) was stirred for 21 h at room temperature and then poured into ice-water (900 mL). The mixture was extracted with chloroform (6 × 200 mL), and the combined organic layers were washed with water (400 mL) and saturated NaHCO₃ (2 × 400 mL). After drying over MgSO₄, the organic layer was concentrated to yield white solid **20** (5.65 g, 10.0 mmol, 95%): mp 279–280 °C dec; ¹H NMR (CDCl₃) δ 3.39 (d, 2H, *J* = 8 Hz), 3.99 (d, 2H, *J* = 8 Hz), 7.22 and 7.42 (AA'BB' system, 4H); IR (KBr) ν_{max} (cm⁻¹) 1751, 1588, 1224, 713.

8a,12b-Dibromo-1,2,3,4,5,6,7,8-Octachloro-13,14-dioxo-1,4,4a,4b,5,8,8a,12b-octahydro-1,4:5,8-dimethanotriphenylene (21). A solution of compound **20** (5.65 g, 10.0 mmol) and bromine (13.0 mL, 252 mmol) in CCl₄ (300 mL) was irradiated with a tungsten lamp for 16 h at room temperature. Concentration of the mixture yielded a light yellow solid. This material was taken up in chloroform (900 mL), and the resulting suspension was washed with saturated

NaHCO₃ (400 mL). After drying over MgSO₄, the organic layer was concentrated to yield white solid **21** (6.78 g, 9.39 mmol, 94%): mp 261–262 °C dec; ¹H NMR (CDCl₃) δ 3.86 (s, 2H), 7.47 and 7.67 (AA'BB' system, 4H). Anal. Found for C₂₀H₆Br₂Cl₈O₂: C, 33.08; H, 0.74. Calcd: C, 33.29; H, 0.84.

2,3,5,8-Tetrachloro-6,7-bis(2,3,3,4,4-pentachloro-5-oxocyclopentenyl)-1,4-naphthoquinone (22). A mixture of **17** (1.03 g, 1.57 mmol), iron powder (370 mg, 6.63 mmol), and FeCl₃ (375 mg, 2.31 mmol) in 1,1,2,2-tetrachloroethane (110 mL) was heated at 120 °C for 5 h while a stream of chlorine was passed through the mixture. After cooling, the mixture was filtered through a pad of Celite, and the pad was rinsed with chloroform (600 mL). The filtrate was concentrated to give a brown oil (2.72 g). Chloroform (500 mL) was added, and the organic solution was washed with 1.2 N aqueous Na₂SO₃, dried over MgSO₄, and concentrated to give a mixture of a yellow solid and a brown oil. Recrystallization of the solid from chloroform-ethanol yielded bright yellow **22** (106.1 mg, 0.133 mmol, 8%): mp 302–304 °C dec; ¹³C NMR (CDCl₃) δ 87.6, 90.3, 131.0, 131.6, 135.0, 135.3, 143.0, 163.6, 173.3, 180.7; FAB MS, *m/z* 802 (M⁺, 2), 732 (M - Cl₂, 3), 273 (100). The structure of **22** was established by X-ray analysis (see Figure 2).³³

Perchlorotriphenylene (1). In the best of several runs, tetrachlorophthalic anhydride (0.4 g, 1.4 mmol) was placed in the sealed end of a 1 cm × 60 cm quartz tube, and the tube was attached to a vacuum pump and evacuated (~0.25 Torr). The center section of the tube (~20 cm) was placed in a tube furnace, and the furnace was heated to 700 °C. At this point, a Bunsen burner was used to heat and sublime the anhydride (with considerable decomposition) into the center section of the tube. When this process was complete, a large amount of material had emerged from the other side of the furnace and condensed in the unheated part of the tube. This material was stirred with a solution of 75 mL of ethanol, 25 mL of water, and 5 g of NaOH overnight. The resulting mixture was filtered, the collected solid was mixed in warm chloroform, and the mixture was filtered again. The latter filtrate was concentrated and fractionated by preparative silica gel TLC (solvent, hexanes). Three major nonpolar bands were observed with *R*_f's of 0.93, 0.90, and 0.84. The material with *R*_f 0.84 was collected and rechromatographed under the same conditions to yield 8 mg of ~80% pure compound **1**. Recrystallization of this material from CH₂Cl₂-acetone gave golden yellow crystals of **1**: mp 347–348 °C; MS, *m/z* 642 (M⁺, 100), 605 (M - Cl, 25), 570 (M - Cl₂, 78), 500 (M - Cl₄, 70); exact mass 641.6180, calcd for C₁₈³⁵Cl₉³⁷Cl₃ 641.6174. The structure of **1** was established by X-ray analysis of these crystals (see Figure 3).³³

Computational Studies. All semiempirical (AM1) and ab initio (HF/STO-3G) molecular orbital calculations were performed by using the SPARTAN 3.0 package of programs (Wavefunction, Inc.), and its built-in default thresholds for wave function and gradient convergence were employed. Frequency calculations were performed on all AM1-optimized equilibrium and transition state geometries.

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Supplementary Material Available: Copies of ¹H NMR spectra of **12**, **13**, **15**, **17–21** (8 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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(33) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.