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Perchlorotriphenylene

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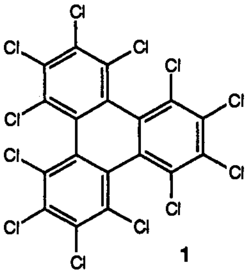
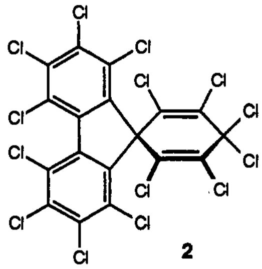
Perchlorotriphenylene (**1**) has proven to be unusually elusive. A recent review of its literature by Campbell et al.[1] indicates that the preparation of **1** has never been clearly described and that **1** has never been even minimally characterized. Attempts to prepare **1** by the exhaustive chlorination of triphenylene lead instead to the overchlorinated and rearranged compound **2**, first correctly described by the MacNicol group.[2] Campbell et al. explored several alternative syntheses 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 hydrocarbons[3] suggested that **1** should be at least marginally stable, though severely distorted from planarity. We now report the synthesis and crystallographic characterization of this extraordinary compound.

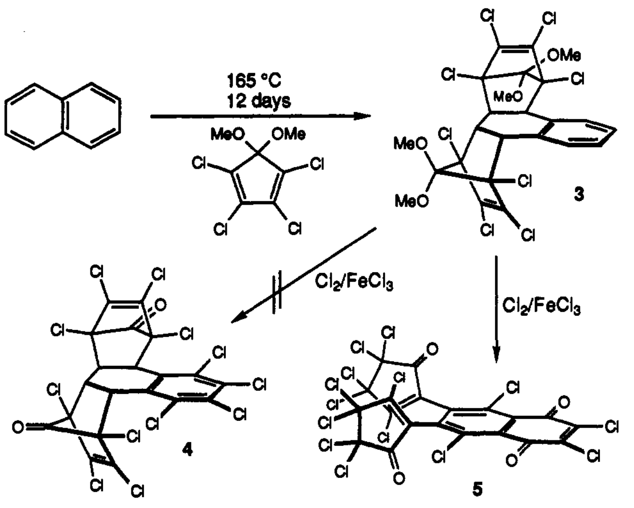


1

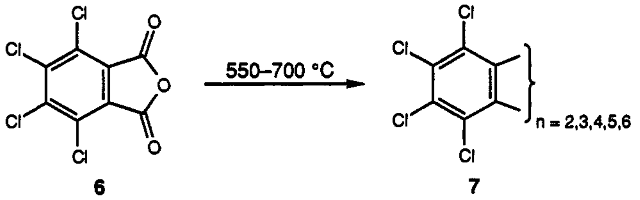


2

It is apparent from the earlier work that chlorination must be avoided in the final step of the synthesis of **1**. However, one might hope to chlorinate the Diels–Alder adduct **3** to give the relatively unstrained compound **4** by the same procedure used to prepare the commercially available 1,2,3,4-tetrachloronaphthalene–bis(hexachlorocyclopentadiene) adduct.[4] If this procedure were successful, then decarbonylation and dehydrogenation would give compound **1** under mild conditions. Compound **3**[5] was prepared easily by the prolonged heating of naphthalene with neat 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. Unfortunately, the chlorination of **3** invariably yielded complex mixtures, of which the most abundant component was the overchlorinated, oxidized, and rearranged product **5**.[6,7]



We then turned to the trimerization of tetrachlorobenzyne as a possible alternative synthesis. Initial experiments were conducted in solution, but neither the diazotization and decomposition of tetrachloroanthranilic acid[8] nor the treatment of hexachlorobenzene with butyllithium[9] led to the formation of any material with the necessary mass spectral characteristics. However, after solid tetrachlorophthalic anhydride (**6**) was roasted over a flame in an open Pyrex flask, mass spectral analysis of an organic extract of the product revealed several components with the general formula $(C_6Cl_4)_n$ (**7**).[10,11]



6 **7**

When the reaction was conducted under vacuum (~0.25 Torr) so that the material subliming upon decomposition of **6** would pass through a quartz tube at 700 °C, the product was somewhat enriched in the lower molecular weight components. After removal of unreacted **6** 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. From 1 g of **6** was obtained 8 mg of 80% pure compound **1** (the impurity was perchlorobiphenylene). Recrystallization of this material from dichloromethane–acetone gave crystals of pure **1**[12] suitable for X-ray analysis.[13]

The X-ray structure of perchlorotriphenylene is illustrated in Figure 1. The compound adopts a conformation with approximate C_2 symmetry, quite similar to that observed for perfluorotriphenylene,[14] but with much greater deviations from planarity. The rings C(1-2-3-4-14-13) and C(9-10-11-12-18-17) adopt boat conformations, with distortions similar in magnitude to those

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[1] Campbell, M. C.; Humphries, R. E.; Munn, N. M. *J. Org. Chem.* **1992**, *57*, 641–644.

[2] Gall, J. H.; MacNicol, D. D.; Mallinson, P. R.; Welsh, P. A. *Tetrahedron Lett.* **1985**, *26*, 4005–4008.

[3] (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.

[4] Danish, A. A.; Silverman, M.; Tajima, Y. A. *J. Am. Chem. Soc.* **1954**, *76*, 6144–6150.

[5] For **3**: mp 211–212 °C; ^{1}H NMR ($CDCl_3$) δ 3.14 (d, 2H, J = 9 Hz), 3.43 (s, 6H), 3.58 (s, 6H), 3.67 (d, 2H, J = 9 Hz), 7.07 and 7.53 (4H, AA′BB′ system); ^{13}C NMR ($CDCl_3$) 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 ($M - C_5Cl_4(OMe)_2 - Cl$, 39), 319 ($M - C_5Cl_4(OMe)_2 - Cl_2$, 41), 128 ($C_{10}H_8^+$, 100); exact mass 655.8816, calcd for $C_{24}H_{20}{}^{35}Cl_6{}^{37}Cl_2O_4$ 655.8811.

[6] For **5**: mp 302–304 °C dec; ^{13}C NMR ($CDCl_3$) 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 – Cl_2, 3), 273 (100).

[7] The structures of **3** and **5** were confirmed by X-ray crystallography; full details will be published elsewhere.

[8] Heaney, H.; Jablonski, J. M. *J. Chem. Soc. C* **1968**, 1895–1898.

[9] Hales, N. J.; Heaney, H.; Hollinshead, J. H.; Singh, P. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, pp 82–86.

[10] 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 ($C_{24}Cl_{16}$); the FAB mass spectrum of the same sample showed additional clusters at m/z 1070 ($C_{30}Cl_{20}$) and 1284 ($C_{36}Cl_{24}$).

[11] Perchlorobiphenylene, i.e. $(C_6Cl_4)_2$, has been prepared previously by flash vacuum pyrolysis of **6**, but no higher homologs were noted: (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.

[12] For **1**: mp 347–348 °C; MS, m/z 642 (M^+, 100), 605 (M – Cl, 25), 570 (M – Cl_2, 78), 500 (M – Cl_4, 70); exact mass 641.6180, calcd for $C_{18}{}^{35}Cl_9{}^{37}Cl_3$ 641.6174.

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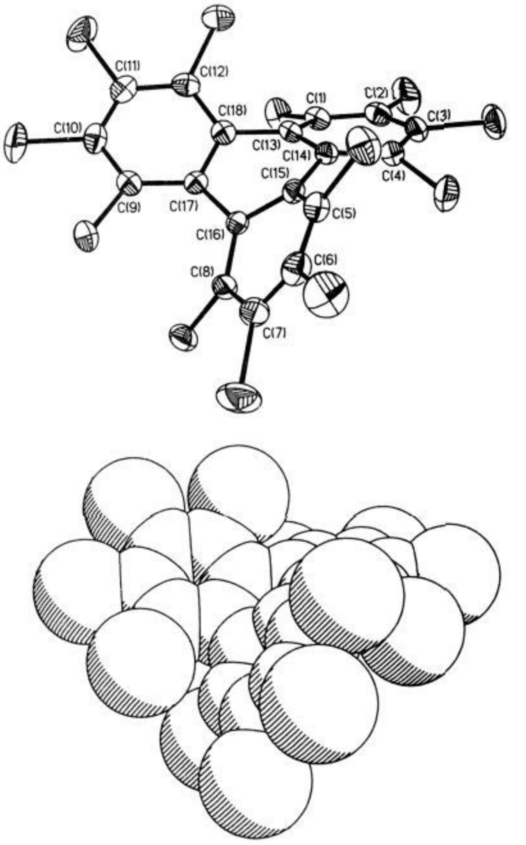

Figure 1. X-ray structure of perchlorotriphenylene (**1**). Both the thermal ellipsoid (above) and space-filling (below) drawings depict compound **1** in the same orientation. Thermal ellipsoids are drawn at the 50% probability level.

observed in an [8]paracyclophane.[15] The remaining naphthalene substructure [C(5–6–7–8–16–17–18–13–14–15)] exhibits a 56.6° end-to-end twist,[16] with the central ring and C(5–6–7–8–16–15) contributing 36.7° and 19.9°, respectively, to the overall twist. 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 highly twisted *anthracene* derivatives (60–69°).[3,17]

It is perhaps counterintuitive 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 calculations[18,19] 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 is favored by 1.6 kcal/mol. When the C_2 and D_3 conformations of **1** were examined by means of ab initio molecular orbital calculations at the STO-3G level,[20] the relative energy difference was found to be even more pronounced, with the C_2 conformer favored by 5.2 kcal/mol.[21]

In conclusion, perchlorotriphenylene, although difficult to synthesize and grossly distorted from planarity, is completely stable under ordinary conditions.

Acknowledgment. This work was supported by National Science Foundation Grants CHE-9106903 and CHE-9408295.

Supplementary Material Available: X-ray data for **1**, including a full description of data collection and crystal parameters, atomic coordinates, anisotropic displacement coefficients, bond lengths and bond angles, and least-squares planes (15 pages). This material is contained in many 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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(13) A crystal of **1** from CH_2Cl_2–acetone measuring 0.05 mm × 0.08 mm × 0.22 mm was used for X-ray measurements. Crystal data: $C_{18}Cl_{12}$; triclinic, space group $P\bar{1}$; $a = 8.811(1)$ Å, $b = 11.506(1)$ Å, $c = 11.537(1)$ Å, $\alpha = 74.146(8)°$, $\beta = 86.289(9)°$, $\gamma = 78.567(8)°$, $V = 1102.7(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.932$ g/cm^3. Intensity measurements were made with $4° \leq 2\theta \leq 50°$ by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at 296 K on a Siemens P4 diffractometer. A total of 3919 unique reflections were measured, of which 2642 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods using the SHELXTL PLUS software. Refinement of 271 parameters converged at $R = 0.036$, $R_w = 0.036$, with a goodness-of-fit of 0.86. Full details are provided in the supplementary material.

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

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

(16) See note 17 in ref 3a for the definition of "end-to-end twist".

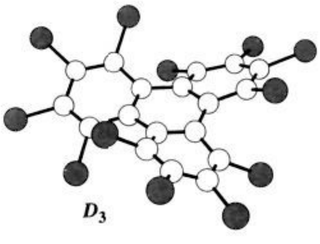
(17) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981–2983.

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

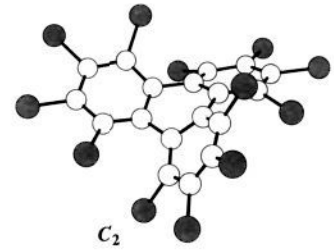
(19) All calculations were performed by using the SPARTAN 3.0 package of programs (Wavefunction, Inc.), and its built-in default thresholds for wave function and gradient convergence were employed. Frequency calculations were performed on all AM1-optimized geometries.

(20) 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.

(21) The fully optimized geometries from the ab initio calculations are illustrated below; the calculated C_2 conformation and the crystal structure (Figure 1) are extremely similar. Interestingly, the nonplanar distortions of the calculated D_3 conformation are relatively modest; for example, the end-to-end twists of the naphthalene subunits are less than 18°. However, 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.



D_3



C_2