toluene solutions of $[IrA(CO)(Ph_3P)_2]$ (A = Cl, Br, I) under hydrogen (p_{H_2}, 650 mm) show no evidence for reduction to metallic Ir at 60° for several days. It should also be noted that the sequence of catalytic activity of these three complexes for the H_2–O_2 combination, Cl > Br > I, is the same as found for the homogeneous catalysis of H_2–D_2 equilibration and para hydrogen conversion in toluene solution under mild conditions.[8]

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. HE-09678), the Environmental Protection Agency (Grant No. AP-00574), and Matthey Bishop, Inc.

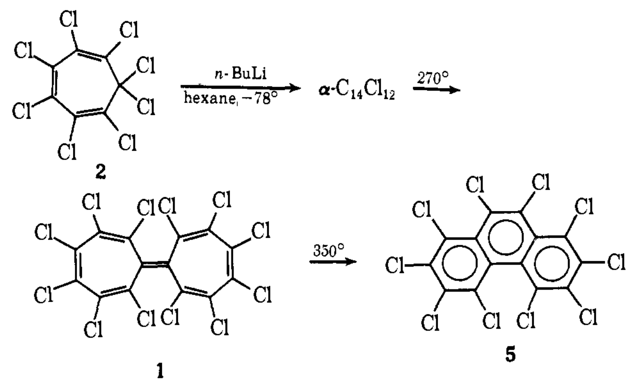
(8) L. Vaska and M. E. Tadros, unpublished results.

L. Vaska,* Maher E. Tadros
Department of Chemistry, Clarkson College of Technology
Potsdam, New York 13676
Received August 21, 1971

Perchloroheptafulvalene. Its Synthesis, Structure, and Bonding[1]

Sir:

The preparation of octachlorocycloheptatriene (**2**) and its derivatives was described recently.[2,3] In continuing our studies of **2**, we now report the synthesis of dodecachloroheptafulvalene (**1**). Unlike other known heptafulvalenes,[4] **1** does not oxidize in air and is highly stable. Although heptafulvalene is a 14 π-electron system and so has sometimes been classed as aromatic, recent theoretical studies[7–9] suggest that it should contain localized single and double bonds. Thus, the preparation and structural characterization of **1** are of some theoretical as well as experimental interest.

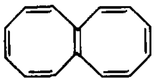


Treatment of **2** with 1 equiv of *n*-butyllithium at −78° led to the formation of α-$C_{14}Cl_{12}$[10] in 90% yield. The latter is transformed quantitatively into **1** upon heating to 270°. The product was recrystallized from carbon tetrachloride to give pure **1** as lemon-yellow crystals, mp 290°.

Anal. Calcd for $C_{14}Cl_{12}$: C, 28.32; Cl, 71.68; mol wt ($^{12}C_{14}{}^{35}Cl_{12}$), 587.626. Found: C, 28.26; Cl, 71.67; mol wt (high-resolution mass spectroscopy), 587.619.

Crystalline **1** shows a six-line ^{35}Cl nqr spectrum (77°K) with resonances in the vinyl Cl region[11] at 37.12, 37.31, 37.92, 37.94, 38.01, and 38.20 MHz, all equally intense. This spectrum is consistent with the presence of three different kinds of vinylic chlorines with each of the three nqr lines split to a doublet by crystal effects. The infrared solid-state spectrum (KBr disk) of **1** is very simple with bands at 1566 (m), 1250 (m), 1155 (s), 1060 (m), 935 (m), 798 (w), 719 (s), 578 (m), 557 (m), and 523 (w) cm^{-1}; the ir spectrum in solution is very similar.

The observed dipole moment value of 0 ± 0.5 D[12] indicates a centrosymmetric geometry for **1** in solution. These data are not only consistent with the heptafulvalene structure but also with the alternate structure **3** and perhaps **4**.


3


4

A single-crystal X-ray diffraction investigation[13] shows **1** to have the heptafulvalene structure. The molecule has idealized C_{2h}-$2/m$ geometry and is decidedly nonplanar with *strongly alternating bond lengths* (Figure 1). The X-ray crystal structure of heptafulvalene itself has recently been published by Coppens.[14] The parent hydrocarbon also shows bond alternation which is however less marked than in **1**. The C–C bond lengths for **1** correspond well with those expected for localized double bonds and sp^2–sp^2 single bonds, so the electronic structure of **1** appears to be highly localized.

The ultraviolet spectrum of **1** in cyclohexane shows λ_{max} values at 218 ($\log \epsilon = 4.41$), 239 (4.43), 275 (4.33), and 350 (3.68) nm. This spectrum is very similar to that[3] of **2** except for the additional band at 350 nm. However, the lemon-yellow color of **1** is strikingly different from that reported for heptafulvalene itself and its simple derivatives, which are described as reddish black crystals.[5,6]

Upon heating to 340°, **1** loses chlorine and converts in high yield to the known decachlorophenanthrene

---

(1) M. I. and R. W. acknowledge partial support of this work by a U. S. Public Health Service–National Institutes of Health grant, while B. K. T. and L. F. D. acknowledge support of the crystallographic study by the National Science Foundation (GP-19175X). The use of the UNIVAC 1108 computer at the University of Wisconsin Computing Center was made possible from support of the National Science Foundation and the Wisconsin Alumni Research Foundation through the University Research Committee.

(2) R. West and K. Kusuda, *J. Amer. Chem. Soc.*, **90**, 7354 (1968).

(3) K. Kusuda, R. West, and V. N. M. Rao, *ibid.*, **93**, 3627 (1971).

(4) Heptafulvalene itself has been reported by Doering,[5] and the dimethyl and diphenyl derivatives have been described by Jones and his coworkers.[6] The parent compound and the dimethyl derivative were so oxygen sensitive at room temperature that analyses could not be obtained.

(5) W. von E. Doering, *Theor. Org. Chem., Pap. Kekule Symp.*, 44 (1959).

(6) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970); W. M. Jones and C. L. Ennis, *ibid.*, **91**, 6391 (1969).

(7) M. J. S. Dewar and G. J. Gliecher, *ibid.*, **87**, 685 (1965).

(8) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963).

(9) A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962).

(10) Colorless crystals, mp (apparent) 262–263°. This compound will be discussed in a subsequent paper.

(11) R. M. Smith and R. West, *J. Org. Chem.*, **35**, 2681 (1970).

(12) We are grateful to Professor W. E. Vaughan and Dr. E. M. Turner of the University of Wisconsin for the dipole moment measurement.

(13) Triclinic; $P\bar{1}$; $a = 8.5682$ (5), $b = 8.6905$ (5), $c = 7.6811$ (5) (Å), $\alpha = 85.073$ (2), $\beta = 81.055$ (2), $\gamma = 62.927$ (2); $\rho_{obsd} = 1.95$ g cm^{-3} *vs.* $\rho_{calcd} = 1.96$ g cm^{-3} for $Z = 1$. The crystal structure was solved by an application of the Karle–Hauptman symbolic addition procedure and was refined by anisotropic least squares to $R_1 = 2.9\%$ and $R_2 = 4.2\%$ for 1185 independent diffraction maxima collected with an automated diffractometer.

(14) P. Coppens, *Mol. Cryst. Liq. Cryst.*, **9**, 25 (1969).

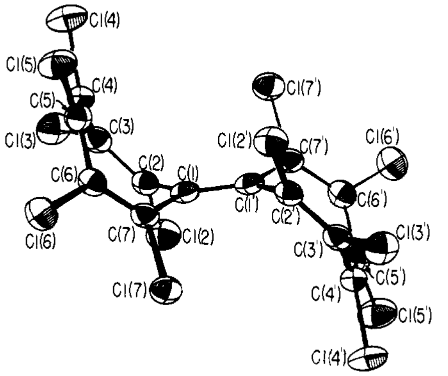


Figure 1. Configuration of the perchloroheptafulvalene molecule, $C_{14}Cl_{12}$, which possesses crystallographic site symmetry C_i-1; its geometry closely conforms to C_{2h}-$2/m$ symmetry. Intra-ring bond lengths are C(1)–C(1′), 1.332 (5) Å; C(1)–C(2), 1.484 (4) Å; C(2)–C(3), 1.331 (4) Å; C(3)–C(4), 1.459 (4) Å; C(4)–C(5), 1.342 (4) Å; C(5)–C(6), 1.465 (4) Å; C(6)–C(7), 1.333 (4) Å; C(7)–C(1), 1.487 (4) Å. The six independent C–Cl bond lengths range from 1.724 (3) to 1.728 (3) Å. The nonbonding intra-ring Cl· · ·Cl contacts range from 3.098 (1) to 3.170 (1) Å. Intra-ring angles subtended at C(*n*) are C(1), 112.3 (2)°; C(2), 121.7 (2)°; C(3), 122.3 (2)°; C(4), 124.1 (2)°; C(5), 125.2 (2)°; C(6), 122.3 (2)°; C(7), 121.2 (2)°. The anisotropically refined carbon and chlorine atoms are shown as 50% probability ellipsoids.

(5), mp 255° (lit.[15] 255°), with an infrared spectrum identical with that of an authentic sample. In view of the lability of the analogous hydrocarbon the remarkable thermal stability and resistance to oxidation of **1** provide another dramatic example of the great change in properties often conferred on a hydrocarbon by complete chlorine substitution.

---

[15] J. D. Brooks, P. J. Collins, and H. S. Silberman, *Aust. J. Chem.*, **19**, 2401 (1966); M. Ballester, *Bull. Soc. Chim. Fr.*, 7 (1966). We are grateful to Dr. Brooks of CSIRO, Australia, and Professor Ballester of Instituto de Quimica "Alonso Barba," Spain, for authentic decachlorophenanthrene samples.

Michihiro Ishimori, Robert West*
Boon Keng Teo, Lawrence F. Dahl
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received July 31, 1971

Electron Paramagnetic Resonance Spectra of Semiquinone Intermediates Observed during the Photooxidation of Phenol in Water

Sir:

We wish to report the observation of electron paramagnetic resonance (epr) signals of semiquinone intermediates during the photooxidation of phenol in water containing NaOH. These spectra were obtained at room temperature using a Varian E-12 spectrometer[1] to which we have added a flow system driven by a peristaltic pump. With this system, flow rates could be varied between 0.1 and 36 ml/min. Oxygen was excluded by purging the solution with argon which was bubbled through a series of chromous ion scrubbers.[2]

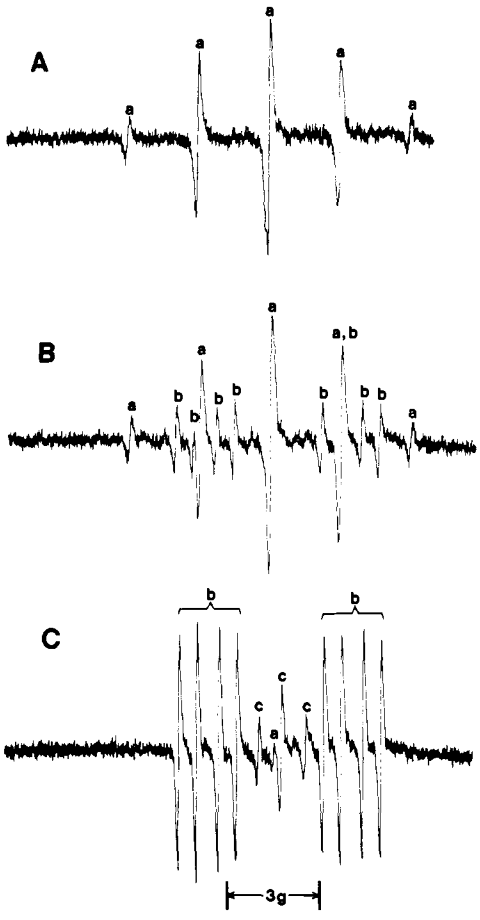


Figure 1. Epr spectra during irradiation of a solution of 0.02 *M* phenol in water at pH 12. Flow rate: (A) 1.5 ml/min, (B) 0.3 ml/min, and (C) 0.1 ml/min.

The epr spectrum obtained during irradiation with the full spectrum of a Hanovia mercury–xenon arc lamp is dependent upon the flow rate as can be seen in Figure 1. Figure 1A which is the spectrum of *p*-benzosemiquinone (proton–electron hyperfine, 2.37 G)[3] is obtained at flow rates greater than 1.5 ml/min. The spectrum in Figure 1B is obtained at flow rates between 0.3 and 1.5 ml/min and is a superposition of spectra due to *p*-benzosemiquinone and oxybenzosemiquinone (three inequivalent protons with hyperfine 4.82, 1.32, and 0.60 G).[4] At flow rates below 0.3 ml/min, the spectrum given in Figure 1C is obtained. This is a superposition of spectra due to oxybenzosemiquinone and dioxybenzosemiquinone (two equivalent protons with hyperfine 0.79 G).[5] A weak line due to *p*-benzosemiquinone can be detected, also.

The appearance of these spectra depends upon the pH of the media. Between pH 11 and 12, only *p*-benzosemiquinone is observed, even at very low flow rates. Above pH 12, all of the intermediates are observed depending upon the flow rate employed as illustrated above. In addition we have observed a dependence upon the phenoxide ion concentration. This dependence does not appear to be the result of only the change in the absorbance of the solution. For example, changing the phenoxide concentration from 5 × 10^{-2} to 1 × 10^{-3} *M* decreases the amount of light absorbed by a

---

[1] The authors are indebted to Dr. M. Fujimoto for allowing the use of his spectrometer.

[2] N. Bunce, personal communication.

[3] Reported value, 2.37 G: M. Adams, M. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

[4] Reported values, 4.8, 1.3, and 0.60 G: J. Stone and W. Waters, *J. Chem. Soc.*, 1488 (1965).

[5] Reported value, 0.79 G: M. Das and G. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).