

servations reported here indicate that individual rotational states within a given vibronic level may show irregular variations of lifetime, the variation being linked to "accidental" singlet-triplet degeneracies. In order to observe these variations, the half-width of the excitation source should be  $< 0.1 \text{ cm}^{-1}$ , a range that may soon be realized for tunable lasers.

The measurements described below are not time resolved; instead, they represent an analysis of mild perturbations observed in the 3260-Å ( $2\nu_2 + \nu_4$ ) vibronic band of the  ${}^1A_2 \leftarrow {}^1A_1[1(n\pi^*)]$  band system of  $\text{CH}_2\text{O}$  vapor,<sup>6,7</sup> a band also known to give rise to a magnetic rotation spectrum.<sup>8</sup> This band was therefore recorded in an external magnetic field (13 kg) and a Zeeman effect observed for about 25 out of a total 800 lines present in the band. Every Zeeman-sensitive line corresponds to a transition found to be perturbed in the field-free absorption spectrum. Thus the perturbation is not induced by the Zeeman field; rather, the perturbation present at zero external field develops a magnetic moment which is observed through a shift or broadening of the line when the Zeeman field is switched on.

The rotational perturbations in the 3260-Å band occur in each subband for  $K' = 0-7$ , the point of resonance shifting progressively from  $J' = 12$  at  $K' = 0$  to  $J' = 17$  at  $K' = 7$ . A number of otherwise unassigned extra lines associated with the perturbation are observed, and the available information is sufficient to obtain approximate values of the constants of the *perturbing* state from the analysis of the perturbation. The constants obtained in this way,  $A = 8.58$ ,  $B = 1.166$ , and  $C = 1.042 \text{ cm}^{-1}$ , resemble closely those of the zero-point  $0^+$  level of the triplet state ( $A = 8.67$ ,  $B = 1.156$ ,  $C = 1.042 \text{ cm}^{-1}$ )<sup>9</sup> and so establish that the perturbing state must be a vibronic level of  ${}^3A_2$ , a fact which provides a natural explanation for the appearance of magnetically sensitive lines. It also emerges that the perturbation is not satisfactorily explained unless (a) the perturbing triplet state has the same vibronic symmetry,  ${}^{e\nu}B_2$ , as the ( $2\nu_2 + \nu_4$ ) vibronic state of  ${}^1A_2$ ,<sup>10</sup> (b) the interaction matrix elements have appreciable  $N, K$  dependence, and (c) the perturbing triplet state lies 5455.6  $\text{cm}^{-1}$  higher in energy than the vibrationless  ${}^3A_2$  state so that the perturbation is probably  $2\nu_2 + \nu_4({}^1A_2) \leftrightarrow \nu_1 + 2\nu_2 + \nu_4({}^3A_2)$ . Since the coupled states have the same vibronic symmetry, the interaction must be rotational in character.

Vibronic  $B_2$  states of the electronic  ${}^1A_2$  and  ${}^3A_2$  states of  $\text{CH}_2\text{O}$  cannot interact by spin-orbit coupling (the spatial part of  $\text{H}_{\text{SO}}$  has no totally symmetric component) or by vibronic spin-orbit coupling, so that a third mechanism of interaction must be considered. An indirect second-order mechanism involving electronic orbital-rotation and spin-orbit coupling, analogous to the interactions that account for spin-rotation coupling in multiplet states,<sup>11</sup> does have the requisite prop-

(5) E. S. Yeung and C. B. Moore, *J. Amer. Chem. Soc.*, **93**, 2059 (1971).

(6) J. E. Parkin, H. G. Poole, and W. R. Raynes, *Proc. Chem. Soc., London*, 248 (1962).

(7) V. Sethuraman, V. A. Job, and K. K. Innes, *J. Mol. Spectrosc.*, **33**, 189 (1970).

(8) P. Kusch and F. W. Loomis, *Phys. Rev.*, **53**, 850 (1939).

(9) W. T. Raynes, *J. Chem. Phys.*, **44**, 2755 (1966).

(10) Selection rules for the perturbation are then  $\Delta N = \Delta K = 0$  and  $\Delta J = \Delta M = 0$ .

(11) J. H. Van Vleck, *Rev. Mod. Phys.*, **23**, 213 (1951); R. S. Hender-son, *Phys. Rev.*, **100**, 723 (1955).

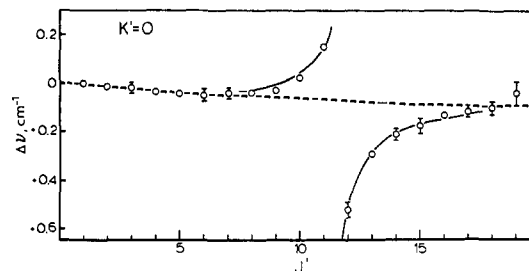


Figure 1. Calculated and observed perturbations in the  $K' = 0$  submanifold (3260-Å band of  $\text{CH}_2\text{O}$ ). The solid line shows the course of the perturbation calculated from the constants of the  ${}^1A_2$  and  ${}^3A_2$  states<sup>7,9</sup> with the coefficient  $a_{xx} + a_{yy} = 0.043 \text{ cm}^{-1}$  (see eq 1). The points represent "observed" values, obtained by subtracting the calculated *unperturbed* energy from the rotational term value. Owing to small errors in the rotational constants, the unperturbed term values (broken line) do not coincide exactly with  $\Delta\nu = 0$ .

erties and leads to the interaction matrix element

$$W({}^1A_2; {}^3A_2) = (a_{xx} + a_{yy})[N(N + 1)]^{1/2} + (a_{zz} - a_{xx} - a_{yy})K/[N(N + 1)]^{1/2} \quad (1)$$

in which the coefficients  $a_{qq}$ ,  $q = x, y, z$ , are integrals over the electronic, vibrational, and spin coordinates. Figure 1 illustrates the analysis of the  $K' = 0$  perturbation on the basis of eq 1. The interaction is weak, but leads to observable singlet-triplet mixing between nearly degenerate levels. This mechanism has recently been discussed theoretically<sup>12</sup> but has not previously been identified for polyatomic molecules.

(12) M. A. Ratner and B. R. Sundheim, *Chem. Phys. Lett.*, **10**, 56 (1971).

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Contribution No. 25

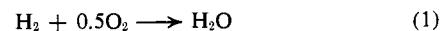
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## Catalytic Hydrogenolysis of Molecular Oxygen by Transition Metal Complexes in Nonaqueous Solution

Sir:

We wish to report some observations on what appears to be a homogeneous catalytic combination of molecular hydrogen and oxygen to form water (eq 1) in the



presence of some triphenylphosphine complexes of platinum, iridium, rhodium, and ruthenium in toluene solutions under ambient conditions (Table I). Although the heterogeneous catalysis of this reaction (eq 1) by metal surfaces is among the first recognized catalytic reactions at large, for the corresponding homogeneous catalysis we find references only to systems involving copper ion in aqueous solution at elevated temperatures and under high pressures of the gases (eq 1).<sup>1</sup>

Our discovery originates from the observation that a volumetric uptake of a mixture of  $\text{H}_2$  and  $\text{O}_2$  by a

(1) (a) H. F. McDuffie, E. L. Compere, H. H. Stone, L. F. Woo, and C. H. Secoy, *J. Phys. Chem.*, **62**, 1030 (1958); (b) T. V. Berlina and V. A. Tulupov, *Katal. Reakts. Zhidk. Faze, Tr. Vses. Konf.*, 1962, 330 (1963).

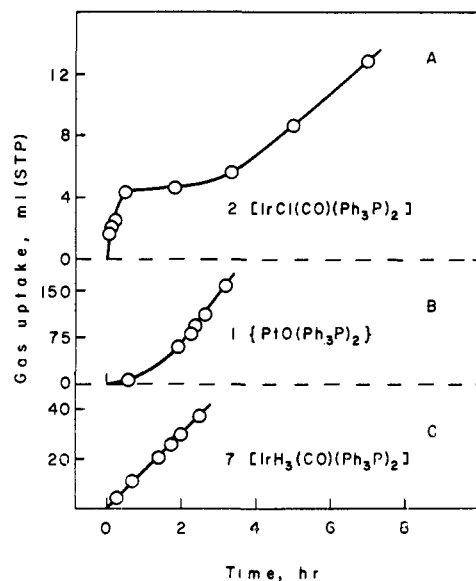


Figure 1. Rate curves for hydrogen and oxygen absorption by toluene solutions of three complexes at 25°C: 2,  $2.8 \times 10^{-3} M$  in 50 ml; 1,  $2.0 \times 10^{-3} M$  in 50 ml; and 7,  $2.8 \times 10^{-3} M$  in 300 ml of solution; see Table I and text. Note that the gas uptake scale is different for each complex.

solution of  $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$  proceeded beyond the stoichiometric amount required to produce the 1:1 hydrogen and oxygen adducts,  $[(\text{XY})\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$  ( $\text{XY} = \text{H}_2, \text{O}_2$ );<sup>2</sup> cf. curve A of Figure 1.<sup>3</sup> A subse-

Table I. Rate and Activation Parameters for the Combination of Molecular Oxygen and Hydrogen Catalyzed by Some Metal Complexes in Toluene Solution at 25°C<sup>a</sup>

| No. | Complex   | $10^6 k_0$ ,<br>$M \text{ sec}^{-1}$ | $\Delta H^*$ ,<br>kcal/mol <sup>b</sup> |
|-----|---|--------------------------------------|---|
| 1   | $\{\text{PtO}(\text{Ph}_3\text{P})_n\}^c$                       | 13.2                                 | 2.8                                     |
| 2   | $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$               | 9.6                                  | 8.8                                     |
| 3   | $[\text{Rh}(\text{OClO}_3)(\text{CO})(\text{Ph}_3\text{P})_2]$  | 6.9                                  | 6.1                                     |
| 4   | $[\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2]$               | 5.9                                  |   |
| 5   | $[\text{RuCl}_3(\text{Ph}_3\text{P})_3]$                        | 1.1                                  |   |
| 6   | $[\text{IrBr}(\text{CO})(\text{Ph}_3\text{P})_2]^d$             | 0.76                                 |   |
| 7   | <i>fac</i> - $[\text{IrH}_3(\text{CO})(\text{Ph}_3\text{P})_2]$ | 0.43                                 |   |
| 8   | $[\text{IrH}(\text{CO})(\text{Ph}_3\text{P})_3]$                | 0.26                                 |   |
| 9   | $[\text{RhCl}(\text{Ph}_3\text{P})_3]^e$                        | 0.20                                 |   |
| 10  | $[\text{IrH}_3(\text{Ph}_3\text{P})_3]^e$                       | 0.07                                 | 10.0                                    |

<sup>a</sup> Uptake was measured volumetrically;  $p_{\text{H}_2}$ , 460 mm;  $p_{\text{O}_2}$ , 230 mm. Solutions of 7, 8, 2, and 10 were  $2.8 \times 10^{-3} M$ , others  $2.0 \times 10^{-3} M$  in the complex as formulated. The pseudo-zero-order rate constants,  $k_0$  (eq 2), were calculated by  $k_0 = \text{slope}$  (moles of gas uptake per second)<sup>2/3</sup>/(liters of solution). <sup>b</sup> 25–65°. <sup>c</sup> See ref 4. <sup>d</sup> 65°. <sup>e</sup> 45°.

quent study with this and other group VIII metal complexes has shown the following. (a) The stoichiometry of the catalytic  $\text{H}_2\text{-O}_2$  combination was found to be as expressed in eq 1, *i.e.*, the gas uptake at constant pressure,  $p_{\text{H}_2}:p_{\text{O}_2} = 2$ , was linear with time (Figure 1),<sup>3</sup> eq 2. The pseudo-zero-order rate constants,  $d[\text{H}_2\text{O}]/dt = -d[\text{H}_2]/dt =$

$$(-2/3)d[\text{H}_2 + \text{O}_2]/dt = k_0 \quad (2)$$

(2) L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968), and references therein.

(3) The first plateau of curve A in Figure 1 corresponds to about 1 mol of gas ( $\text{H}_2, \text{O}_2$ ) per mole of Ir. This is followed by a gradual increase in uptake rate (autocatalysis) which later becomes constant; the last portion of the curve, not shown, is similar to B and C.

$k_0$  (eq 2),  $M \text{ sec}^{-1}$ , are given in Table I. (b) Water has been identified as the only product of the reaction, by gas chromatography and quantitatively through absorption by  $\text{CuSO}_4$ . Formation of over 200 mol of  $\text{H}_2\text{O}$  per mole of the metal complex has been followed in some experiments (with 1 and 2). Tests for the presence of hydrogen peroxide (KI,  $\text{CrO}_3$ ) were negative. (c) The catalytic activity and initial behavior in solution vary greatly among the several complexes which we have examined. (i) Most of the complexes showed autocatalysis (Figure 1A,B), which demonstrates that in these cases the active species are different from the starting materials. Once active, however, catalysts 1<sup>4</sup> and 2<sup>5</sup> exhibited an undiminished activity for several days; when reused after recovery,<sup>4,5</sup> they catalyzed the reaction immediately upon contact with the reagents in solution. (ii) The hydrido complexes 7 and 10, on the other hand, did not initially require clearly discernible induction periods (see curve C of Figure 1). (iii) Some complexes (5, 7, 8, and 9) showed declining catalytic rates with time. Notably, 8 became inactive rather abruptly after *ca.* 50 hr of continuous catalysis. Recovery of crystalline materials from the solutions of catalysis by 7 and 8 showed that both had been converted to their respective isomers: 7 to *mer*- $[\text{IrH}_3(\text{CO})(\text{Ph}_3\text{P})_2]$ , and 8 to another form of  $[\text{IrH}(\text{CO})(\text{Ph}_3\text{P})_3]$  whose structure is unknown. Freshly prepared solutions of these recovered isomers did not catalyze the  $\text{H}_2\text{-O}_2$  combination. (iv) The following complexes exhibited no catalytic activity under the conditions cited (See Table I):  $[\text{Ir}(\text{CO})(\text{Ph}_3\text{P})_2]$  (55–65°, 120 hr),  $[\text{Ir}(\text{OClO}_3)(\text{CO})(\text{Ph}_3\text{P})_2]$  (25–65°, 60 hr),  $[\text{Ir}(\text{CO})(\text{Ph}_3\text{P})_3]\text{ClO}_4$  (25–65°, 25 hr),  $[\text{OsBr}_2(\text{Ph}_3\text{P})_3]$  (25–45°, 50 hr),  $[\text{CoCl}_2(\text{Ph}_3\text{P})_2]$  (25–65°, 65 hr),  $[\text{CoCl}(\text{Ph}_3\text{P})_3]$  (25–65°, 70 hr). (d) Mechanistic studies of the catalyses by 1 and 2, to be detailed elsewhere, show that these reactions are first order in both  $\text{H}_2$  and  $\text{O}_2$ , and about half order in the complex.<sup>6</sup> It should be noted that no satisfactory mechanism seems to have been advanced for the metal surface-catalyzed reaction.<sup>7</sup>

The question of whether or not the catalyses reported here are caused by traces of (colloidal) metal formed by reduction of the complexes is a critical one whenever the reaction is known to be catalyzed also by the metallic form of the central atom in the complex. Although we can offer no "absolute proof" for the homogeneity of these catalyses, the observations (c) cited above, *especially ii and iii*, together with the rate (Table I, Figure 1) and mechanistic (d)<sup>6</sup> data, strongly support the premise that the reactions are not surface catalyzed. Furthermore, separate experiments with

(4) The precise composition and nature of this material have not yet been established. It is a Pt, O, and  $\text{Ph}_3\text{P}$  containing brown species ( $\text{Ph}_3\text{P}:\text{Pt} \approx 1.5$ ) which is formed from  $[\text{O}_2\text{Pt}(\text{Ph}_3\text{P})_2]$  and  $\text{H}_2$  (or  $[\text{Pt}(\text{Ph}_3\text{P})_4]$ ,  $\text{O}_2$ , and  $\text{H}_2$ ), and is different from previously reported Pt– $\text{Ph}_3\text{P}$  compounds. The ir of 1 shows bands attributable to  $\text{Ph}_3\text{P}$  and  $\text{Ph}_3\text{PO}$  only. The species remains perceptibly unchanged after catalysis.

(5) The ir of the recovered species derived from 2 exhibits vibrations characteristic of the  $\text{H}_2$  and  $\text{O}_2$  adducts of 2,<sup>2</sup> and some other bands in the 1900–2200- $\text{cm}^{-1}$  region.

(6) Rate =  $k_2 \cdot n[\text{H}_2][\text{O}_2][\text{C}]^n$ ; C = 1,  $n = 0.65$ ; C = 2,  $n = 0.50$ ; at 45° in toluene,  $k_2 \cdot 55(1) = 260 M^{-1.65} \text{ sec}^{-1}$ ,  $\Delta S^* = -39 \text{ eu}$ ; at 65° in chlorobenzene,  $k_2 \cdot 5(2) = 62 M^{-1.5} \text{ sec}^{-1}$ ,  $\Delta S^* = -25 \text{ eu}$ .

(7) (a) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, pp 447–451; (b) E. N. Khárkovskaya, G. K. Borezkov, and M. G. Slin'ko, *Dokl. Akad. Nauk SSSR*, 127, 145 (1959); *Chem. Abstr.*, 55, 21755e (1961); (c) M. Ladacki, T. J. Houser, and R. W. Roberts, *J. Catal.*, 4, 239 (1965); (d) G. J. K. Acres, *Platinum Metals Rev.*, 10, 60 (1966), and references therein.

toluene solutions of  $[\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2]$  ( $\text{A} = \text{Cl}, \text{Br}, \text{I}$ ) under hydrogen ( $p_{\text{H}_2}$ , 650 mm) show no evidence for reduction to metallic Ir at  $60^\circ$  for several days. It should also be noted that the sequence of catalytic activity of these three complexes for the  $\text{H}_2\text{-O}_2$  combination,  $\text{Cl} > \text{Br} > \text{I}$ , is the same as found for the homogeneous catalysis of  $\text{H}_2\text{-D}_2$  equilibration and para hydrogen conversion in toluene solution under mild conditions.<sup>8</sup>

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

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### Perchloroheptafulvalene. Its Synthesis, Structure, and Bonding<sup>1</sup>

Sir:

The preparation of octachlorocycloheptatriene (**2**) and its derivatives was described recently.<sup>2,3</sup> In continuing our studies of **2**, we now report the synthesis of dodecachloroheptafulvalene (**1**). Unlike other known heptafulvalenes,<sup>4</sup> **1** does not oxidize in air and is highly stable. Although heptafulvalene is a 14  $\pi$ -electron system and so has sometimes been classed as aromatic, recent theoretical studies<sup>7-9</sup> 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  $-78^\circ$  led to the formation of  $\alpha\text{-C}_{14}\text{Cl}_{12}$  in 90% yield. The latter is transformed quantitatively into **1** upon heating to  $270^\circ$ . The product was recrystallized from carbon tetrachloride to give pure **1** as lemon-yellow crystals, mp  $290^\circ$ .

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

(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,<sup>5</sup> and the dimethyl and diphenyl derivatives have been described by Jones and his coworkers.<sup>6</sup> 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).

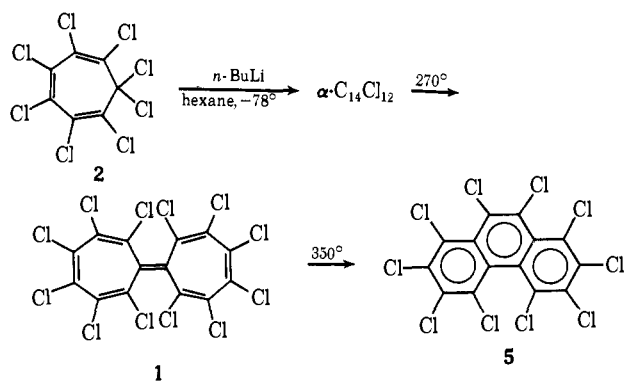
(6) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970); W. M. Jones and C. L. Ennis, *ibid.*, **91**, 6391 (1969).

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

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

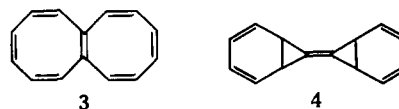
(9) A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962).

(10) Colorless crystals, mp (apparent)  $262\text{-}263^\circ$ . This compound will be discussed in a subsequent paper.



Crystalline **1** shows a six-line  $^{35}\text{Cl}$  nqr spectrum ( $77^\circ\text{K}$ ) with resonances in the vinyl Cl region<sup>11</sup> 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)  $\text{cm}^{-1}$ ; the ir spectrum in solution is very similar.

The observed dipole moment value of  $0 \pm 0.5 \text{ D}^{12}$  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**.



A single-crystal X-ray diffraction investigation<sup>13</sup> shows **1** to have the heptafulvalene structure. The molecule has idealized  $C_{2h}\text{-}2/m$  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.<sup>14</sup> 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  $\text{sp}^2\text{-sp}^2$  single bonds, so the electronic structure of **1** appears to be highly localized.

The ultraviolet spectrum of **1** in cyclohexane shows  $\lambda_{\text{max}}$  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<sup>8</sup> 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.<sup>5,6</sup>

Upon heating to  $340^\circ$ , **1** loses chlorine and converts in high yield to the known decachlorophenanthrene

(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);  $\rho_{\text{obs}} = 1.95 \text{ g cm}^{-3}$  vs.  $\rho_{\text{calcd}} = 1.96 \text{ g cm}^{-3}$  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).