

Table I. Comparison of Platyryn ¹H NMR Spectra (δ)

compound	[1,5,1,5]platyryn 2	[1,3,1,3]platyryn ref 5	OMP ^a
internal =CH—	-14.26	-8.97	
meso =CH—	11.75	11.64	10.98
CH ₃	4.51	4.22	3.76
	4.43	4.17	
>NH	-10.58	-5.6	-4.82

^a Octamethylporphyrin in trifluoroacetic acid.

1 H, CHO), 5.98 (s, 1 H, -CH-), 3.64 (d, 1 H, -CH-), 3.5-1.1 (br, -CH₂-), 2.24 (s, 6 H, CH₃), 2.05 (s, 3 H, CH₃), 1.98 (s, 3 H, CH₃); IR (HCCl₂) 1710 (C=O); mass spectrum, *m/z* (relative intensity) 376 (4, M⁺), 117 (100). Coupling of 5 with 6 to give a dihydro[1,5,1,5]platyryn, 7, was accomplished by simultaneous addition of separate methanol/dichloromethane solutions of 5 and 6 to a hot, oxygen-free solution of hydrobromic acid in methanol. Oxidation with oxygen, followed by rapid chromatographic workup gave a 2% yield of the dark purple platyryn 2 [mp > 350 °C; vis (CH₂Cl₂) λ_{max} (ε) 495 (123 000), 536 (144 000), 651 (15 700), 705 (12 300), 718 (13 500), 780 (9 400); 8 (diprotonated 2) ¹H NMR (Me₂SO-*d*₆/CF₃CO₂H): δ 11.75 (s, 2 H, meso-CH), 4.51 (s, 12 H, CH₃), 4.43 (s, 12 H, CH₃), 2.70-1.0 (m, 18 H, CH₂, -CH-), -10.58 (s, 4 H, NH), -14.26 (s, 4 H, =CH-); λ_{max} (ε) (bis-tetrafluoroborate salt 8): 495 (171 000), 536 (376 000), 651 (47 000), 703 (32 000), 719 (34 000), 780 (24 000), 830 (19 000)].

Both the platyryn 2 and its diprotonated form, 8, prove to be unstable (chemically reactive). Solutions of 2 and 8, as well as their solid forms, were observed to decompose in a few hours to a few days even at low temperatures. This high chemical reactivity suggests that there is little if any resonance stabilization⁵ in this 26 π-electron annulene.

A comparison (Table I) of the ¹H nuclear magnetic resonance spectrum of the diprotonated platyryn 8 with the acyclic salt 4 reveals that a very substantial diamagnetic ring current is present in 8. The internal vinyl protons of 8 are shifted some 21 ppm when compared to 4. The ring current effects in 8 are even greater than those corresponding effects exhibited by the diatropic⁴ [1,3,1,3]platyryn.²

Both of these properties, high chemical reactivity and a pronounced diamagnetic ring current, are consistent with the view that in the higher [4*n* + 2]annulenes, there will be little resonance stabilization (R.E. is inversely proportional to the number of π-electrons).⁶ In contrast, these same annulenes will exhibit increasingly higher diamagnetic ring currents (ring currents increase linearly with the number of π-electrons⁶).

Thus, in the series porphyrin, [1,3,1,3]platyryn, and [1,5,1,5]platyryn, a consistent picture of reactivity and ring currents is emerging.

Supplementary Material Available: Experimental details for compounds 2-8 (4 pages). Ordering information is given on any current masthead page.

(4) Sondheimer, F. *Acc. Chem. Res.* 1972, 5, 81.

(5) Figeys, H. P. *Tetrahedron* 1970, 26, 5225.

(6) Haddon, R. C. *J. Am. Chem. Soc.* 1979, 101, 1722.

E. LeGoff,* O. G. Weaver

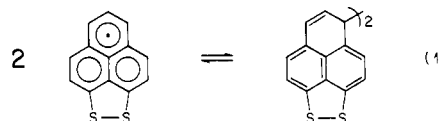
Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

*Received November 3, 1986

Perchloro-7H-cycloprop[a]acenaphthylene and the Perchlorophenalenyl System

Summary: Perchloro-7H-cycloprop[a]acenaphthylene (PCCPA) has been synthesized from the reaction of perchloroacenaphthylene with phenyl(bromodichloromethyl)mercury; PCCPA may be converted into perchlorophenalenyl (PCPLY) which has been detected by solution ESR spectroscopy.

Sir: Coplanar neutral radicals may exhibit interesting electronic properties in the solid state.¹ The primary obstacle to experimental test of this hypothesis is the propensity of such compounds to undergo σ-bond coupling to form a diamagnetic dimer in the condensed state.¹⁻⁸ Disulfide substitution in the phenalenyl (PLY) system has been shown to suppress the dimerization reaction (eq 1)



in the solution state^{1c} but probably not in the solid form of 1,9-dithiophenalenyl (DTPLY).

In the present paper we report the synthesis and characterization of perchloro-7H-cycloprop[a]acenaphthylene (PCCPA) and our initial entry into the perchlorophenalenyl (PCPLY) system. A number of novel aromatic chlorocarbons have been previously reported,⁹⁻¹² and perchlorination has been shown to be particularly effective in enhancing the stability of the triphenylmethyl-type radicals.^{12,13}

Perchloroacenaphthylene^{14,15} (PCAN) is expected to be a poor substrate for carbenoid addition as the peri double bond conjugates quite strongly with the naphthalene ring system and the presence of eight chlorine atoms directly attached to the π-system further deactivates the double bond toward electrophilic attack. Nevertheless, we found the Seyfreh reagent, phenyl(bromodichloromethyl)mercury (PhHgCCl₂Br),¹⁶ to be effective in transferring dichlorocarbene to perchloroacenaphthylene (although in low yield). Perchloroacenaphthylene was treated with 6 equiv

(1) (a) Haddon, R. C. *Nature (London)* 1975, 256, 394. (b) Haddon, R. C. *Aust. J. Chem.* 1975, 28, 2333, 2343. (c) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* 1978, 100, 7629.

(2) (a) Yamauchi, J. *J. Chem. Phys.* 1977, 67, 2850. (b) Azuma, N.; Tsutsui, K.; Miura, Y.; Higuchi, T. *Bull. Chem. Soc. Jpn.* 1981, 54, 3274.

(3) (a) Vegas, A.; Perez-Salazar, A.; Banister, A. J.; Hey, R. G. *J. Chem. Soc., Dalton Trans.* 1980, 1812. (b) Banister, A. J.; Smith, N. R. M.; Hey, R. G. *J. Chem. Soc., Perkin Trans. 1* 1983, 1181.

(4) Wolmershäuser, G.; Schnauber, M.; Wilhelm, T. *J. Chem. Soc., Chem. Commun.* 1984, 573.

(5) (a) Fairhurst, S. A.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Faraday Trans.* 1983, 79, 439, 925. (b) MacLean, G. K.; Passmore, J.; Schriver, M. J.; White, P. S.; Bethell, D.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* 1983, 807.

(6) Höfs, H.-U.; Bats, J. W.; Gleiter, R.; Hartmann, G.; Mews, R.; Eckert-Maksic, M.; Oberhammer, H.; Sheldrick, G. M. *Chem. Ber.* 1985, 118, 3781.

(7) Hayes, P. J.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* 1985, 107, 1346.

(8) Boudjouk, P., private communication.

(9) West, R. *Acc. Chem. Res.* 1972, 5, 65.

(10) Suschitzky, H., Ed. *Polychloroaromatic Compounds*; Plenum: London, 1974.

(11) Chivers, T. In *The Chemistry of the Carbon-Halogen Bond*; Patai, S., Ed.; Wiley: New York, 1973; Part 2, p 917.

(12) Ballester, M. *Acc. Chem. Res.* 1985, 18, 380.

(13) Ballester, M., ref 10, p 1.

(14) Mack, W. *Tetrahedron Lett.* 1966, 2875.

(15) Ballester, M.; Castaner, J.; Riera, J.; Pares, J. *An. Quim., Ser. C* 1980, 157.

(16) (a) Seyfreh, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y. P.; Simmon, H. D.; Treiber, A. J. H.; Dowd, S. R. *J. Am. Chem. Soc.* 1965, 87, 4259. (b) Seyfreh, D. *Acc. Chem. Res.* 1972, 5, 65.

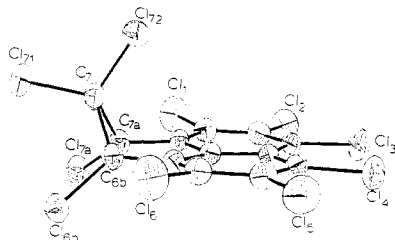
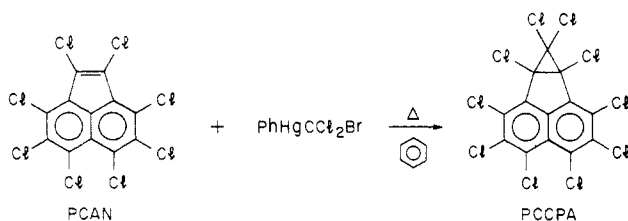


Figure 1. ORTEP drawing of the structure of perchloro-7H-cycloprop[*a*]acenaphthylene (PCCPA) found by X-ray crystallography.¹⁷

of phenyl(bromodichloromethyl)mercury in refluxing benzene. Phenyl mercuric bromide was removed by filtration, and the volatile components were removed by evaporation. The resulting orange solid was subjected to column chromatography on Florisil with hexane as eluant. The first compound to pass through the column was PCCPA, which could be recrystallized from heptane to give colorless, chunky needles, mp 195 °C, in 50% yield based on perchloroacenaphthylene (8% based on the mercurial).¹⁷ Further elution of the column allowed the recovery of most of the unreacted perchloroacenaphthylene.



The mass spectrum of PCCPA shows the characteristic chlorine isotope pattern, with a low intensity parent ion corresponding to $C_{13}Cl_{10}^+$ and a base peak at $C_{13}Cl_9^+$ (see below). An ORTEP view of the X-ray crystal structure¹⁷ of PCCPA is given in Figure 1. In contrast to perchloro-naphthalene the peri-chlorine atoms Cl_3 and Cl_4 in PCCPA remain essentially coplanar with the naphthalene ring system. In fact the largest deviations from planarity in this part of the molecule occur at Cl_1 and Cl_6 which lie about 0.2 Å above the mean plane formed by the acenaphthylene carbon atoms, presumably as a result of interactions with Cl_{6b} and Cl_{7a} . This degree of nonplanarity should exert a minimal perturbation on the naphthalene conjugation.¹⁹

The relatively stable PCCPA forms an interesting contrast with 7,7-dichloro-7H-cycloprop[*a*]acenaphthylene which has been suggested²⁰ as an intermediate in a dichlorocarbonoid addition to acenaphthylene to produce 2-chlorophenaleny (detected by ESR spectroscopy).²⁰

Addition of antimony pentachloride to a dichloromethane solution of PCCPA produces a red coloration which rapidly intensifies. A 2-h reflux of the solution leads to complete disappearance of the starting material.

By analogy with related chlorocarbon chemistry,^{9-13,20,21} it seems reasonable to assume that the perchlorophenaleny cation (PCPLY⁺) is formed in this reaction. Removal of the volatile components under high vacuum leaves a red

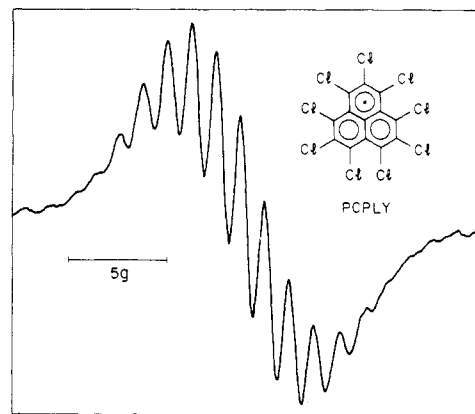
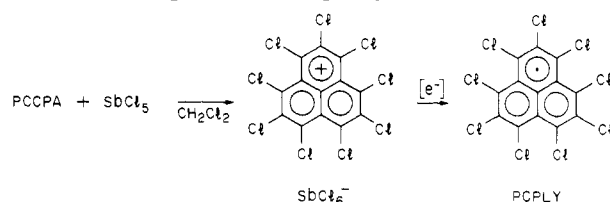


Figure 2. Electron spin resonance spectrum of a solution of perchlorophenaleny (PCPLY).

solid, which on stirring with mercury under dry, degassed benzene for 6 h gives rise to a pale yellow solution. If this



solution is examined in an ESR spectrometer a strong signal is observed (Figure 2). The same spectrum (and coloration) is produced by direct UV irradiation of a degassed benzene solution of PCCPA in a Pyrex ESR cell.

The ESR spectrum consists of at least 15 equally spaced lines, centered at $g = 2.0058$. The two chlorine isotopes (³⁵Cl, ³⁷Cl) each possess a nuclear spin $I = 3/2$, and it is clear from computer simulations that the principal features in the spectrum arise from the interaction of the unpaired electron with six equivalent chlorine atoms (hfs = 0.6 g).

In the parent phenaleny system,^{20,22} the six active positions (1, 3, 4, 6, 7, and 9) exhibit a hfs of 6.30 g, whereas the three inactive positions (2, 5, and 8) give rise to a splitting of 1.82 g. It is therefore apparent that the hfs in the ESR spectrum of PCPLY arises from the chlorine atoms at the 1, 3, 4, 6, 7, and 9 positions (theory: 19 lines). The splitting due to the remaining chlorine atoms (positions 2, 5, and 8) is apparently masked by the spectral line width (0.5 g). This analysis is supported by the hfs of 0.23 g found for the chlorine atom in 2-chlorophenaleny.²⁰

The chemical and physical properties of PCCPA and PCPLY are currently under investigation.^{17,23}

Acknowledgment. R.C.H. is grateful to Professor P. S. Skell for a valuable discussion.

(22) (a) Gerson, F. *Helv. Chim. Acta* 1966, 49, 146. (b) Gerson, F.; Heilbronner, E.; Reddock, H. A.; Paskovich, D. H.; Das, N. C. *Helv. Chim. Acta* 1967, 50, 813.

(23) We provide some details of our preliminary studies of the properties of PCPLY. If the benzene solution of PCPLY (text) is evaporated in a suitably constructed ESR cell, a yellow film may be sublimed up the walls of the tube at 130 °C (10^{-3} mm). This film gives rise to a broad ESR spectrum, and if the sublimate is redissolved in benzene, the solution ESR of PCPLY (Figure 2) is recovered. The same benzene solution of PCPLY (text) has also been successfully chromatographed over silica in the atmosphere. Quantitative data are not yet available, but these observations suggest that PCPLY possesses some stability toward oxygen, is thermally stable, and exhibits a degree of monomeric character in the solid state.

R. C. Haddon,* S. V. Chichester, S. M. Stein
J. H. Marshall, A. M. Mujsee
AT&T Bell Laboratories
Murray Hill, New Jersey 07974
Received November 24, 1986

(17) Full details will be published elsewhere.

(18) (a) Gafner, G.; Herbstein, F. H. *Acta Crystallogr.* 1962, 15, 1081. (b) Gafner, G.; Herbstein, F. H. *Nature (London)* 1963, 200, 130. (c) Avoyan, G. L.; Struchkov, Y. T. *J. Struct. Chem.* 1961, 2, 61.

(19) (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* 1986, 58, 137. (b) Haddon, R. C. *Chem. Phys. Lett.* 1986, 125, 231; *J. Am. Chem. Soc.* 1986, 108, 2837.

(20) (a) Biehl, R.; Hass, C.; Kurreck, H.; Lubitz, W.; Oestreich, S. *Tetrahedron* 1978, 34, 419. (b) Kirste, B.; Kurreck, H.; Fey, H. J.; Hass, C.; Schlömp, G. *J. Am. Chem. Soc.* 1979, 101, 7457. (c) Hass, C.; Kirste, B.; Kurreck, H.; Schlömp, G. *J. Am. Chem. Soc.* 1983, 105, 7375.

(21) Pettit, R. *J. Am. Chem. Soc.* 1960, 82, 1972.