

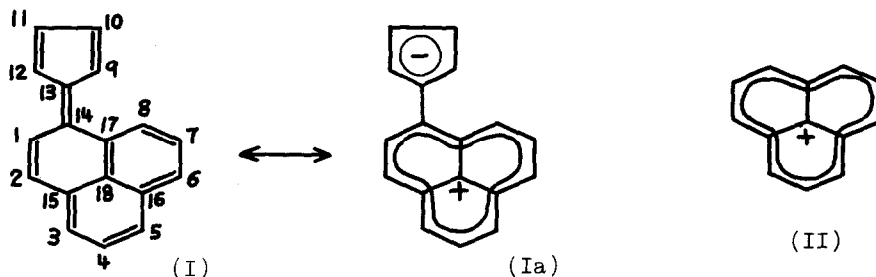
2-ETHOXY-9,10,11,12-TETRACHLOROPENTAPHENAFULVALENE

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CURRENT interest in the chemistry of nonbenzenoid aromatic hydrocarbons involving the contribution of a dipolar structure in its ground state (I) has led us to investigate the synthesis of a hitherto unknown ring system, pentaphenfulvalene (I) (2). HMO calculation predicts that the phenalenium cation (II) possesses twelve pi-electrons which exactly fill pairwise the six bonding MO's and has substantial pi-electron delocalization energy of  $5.83\beta$  (3). This means that the pentaphenfulvalene (I) would be especially notable because a significant contribution of the resonance form (Ia) would be expected as in the cases of calicene (4), sesquifulvalene (5) and pentahendecafulvalene (6).



Our VESCF-MO calculation (7) on (I) [charge densities and bond orders are shown in Fig. 1] indicate appreciable dipolar character to this hydrocarbon and predict a high dipole moment of 5.95 D directed from phenalenium to five-membered ring and a lowest singlet transition energy of 1.76 eV. The system (I) should therefore be a highly colored substance.

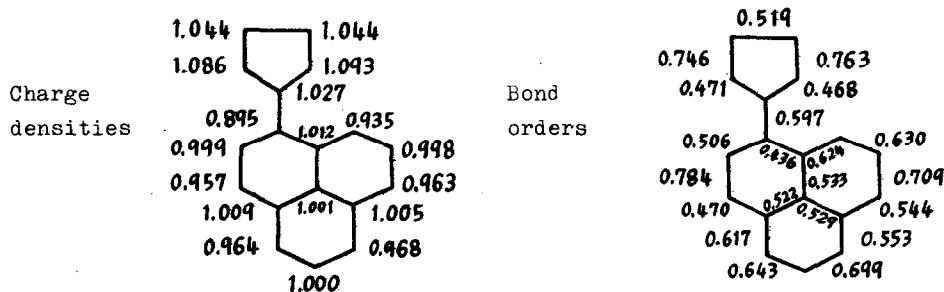
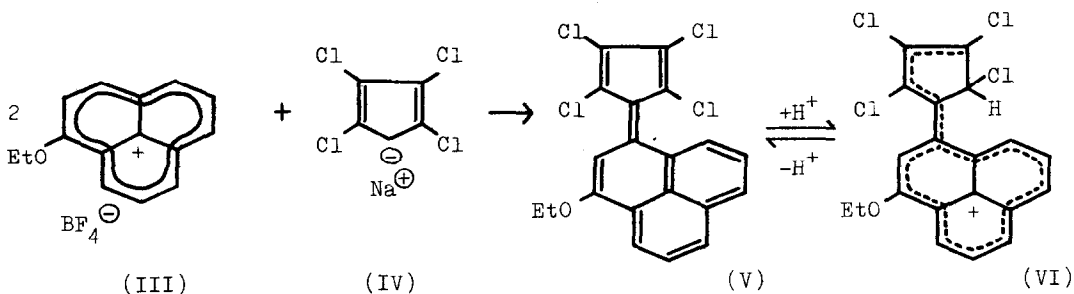


Fig. 1

We wish to report the first synthesis and some of the properties of a stable derivative of (I) with the substituents of four chlorines and a ethoxyl.

Compound (V) was obtained easily by the reaction of the ethoxyphenalenium fluoroborate (III) with sodium tetrachlorocyclopentadienide (IV). In a typical run, a solution of (III) [prepared by mixing a solution of 2.5 g (13 mmoles) of triethyloxonium fluoroborate and a solution of 1.98 g (11 mmoles) of phenalenone in 4 ml of methylenechloride. The resulting (III) was filtered in the nitrogen atmosphere and dissolved in 60 ml of dry acetonitrile] was cooled to 0°C and to it was added slowly a solution of sodium tetrachlorocyclopentadienide (IV) [to a solution of 1.02 g (5 mmoles) of tetrachlorocyclopentadiene in 10 ml of dimethoxyethane was added 0.227 g of a 52.9% suspension of sodium hydride in oil with 5 ml of dry benzene. This suspension was stirred at 0°C under nitrogen atmosphere, resulting in a deep violet suspension]. After a reaction time of 1 - 2 hr, the mixture was poured into water and the isolation with benzene and repeated chromatography on silica gel [pet. ether] afforded (V) in 0.189 g (9 %) yield as dark blue needles, m.p. above 250°C [recrystallized from benzene].



Anal. Calcd. for  $C_{20}H_{12}OCl_4$ : C, 58.57; H, 2.93; Cl, 34.60; mol. wt., 410. Found: C, 58.85; H, 3.02; Cl, 34.07%; mol. wt., 413 [by vapor pressure osmometer]; single spot on tlc. The ir spectrum [KBr] not only confirmed the presence of ethoxyl group (2980, 1263  $cm^{-1}$ ) but also showed strong evidence for the structure of the phenfulvene moiety (1620, 1581, 1555  $cm^{-1}$ ) (8). Difference in the polarity of the solvents used for taking the electronic spectrum of (V) influences mainly the longest wavelength band and the red shift of 19 nm is observed going from n-pentane to acetonitrile.  $\lambda^{n\text{-pentane}}$  nm (log  $\epsilon$ ): 244 (sh. 3.71), 305 (3.80), 387 (3.52), 408 (3.66), 587 (3.95);  $\lambda^{CH_3CN}$ : 245 (sh. 3.79), 313 (3.84), 370 (sh. 3.57), 409 (3.71), 606 (3.97). The pmr spectrum [ $CDCl_3$ , ppm down field from internal TMS] at 100 MHz showed a three-proton triplet at  $\delta$  1.58 ( $J = 7$  Hz) and a two-proton quartet at  $\delta$  4.36 ( $J = 7$  Hz) for ethoxyl group, a one-proton singlet at  $\delta$  7.32 (H-1) and two superimposed AMX-systems (H-3,4,5 and H-6,7,8) with identical chemical shifts and coupling constants at  $\delta$  7.66 (H-4, H-7; triplet,  $J_{3,4} = J_{4,5} = J_{6,7} = J_{7,8} = 8$  Hz),  $\delta$  8.07 (H-5, H-6; doublet of doublets,  $J_{4,5} = J_{6,7} = 8$  Hz,  $J_{3,5} = J_{6,8} = 3$  Hz),  $\delta$  8.30 (H-3, H-8; doublet of doublets,  $J = 8, 3$  Hz). Above mentioned spectral evidences clearly indicate the proposed structure (V).

Compound (V) is a weak base and dissolves reversibly in 80% sulfuric acid, with formation of a red cation. The electronic and the pmr spectra of (V) in conc. sulfuric acid present evidence supporting the formation of conjugate acid such as (VI), but the exact site of protonation is ambiguous.  $\lambda^{C \cdot H_2SO_4}$ : 368 (4.07), 417 (4.12), 460 (sh. 4.01);  $\delta^{C \cdot H_2SO_4}$  [ppm down field from external HMDS, 100 MHz]: 2.06, 5.20 ( $-OCH_2CH_3$ ), 7.89 (s, 0.9H, H-1), 8.55 (b.q., 2.OH, H-4 and H-7), 9.23 (b.q., 2.8H, H-3, H-5 and H-6), 9.74 (d. d., 1.OH, H-8) and 5.96 (s, 1.OH, proton on the five-membered ring). The high dipole moment of (V) [6.33 D measured in benzene at 25°C] together with the relatively low chemical shifts of H-3,4,5,6,7,8 and the identical vicinal coupling constants (9) in its pmr spectrum show a significant participation of a dipolar resonance structure such as (Ia) in the ground state of (V). Further studies of this system are currently in progress.

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