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THE CHEMISTRY OF PHENALENIUM SYSTEM—II*

7,8,2',3',4',5'-HEXACHLORO-11-METHOXY-6*H*-CYCLOPENTA[*a*]PYRENE -6-SPIRO-1'-CYCLOPENTA-2',4'-DIENE†

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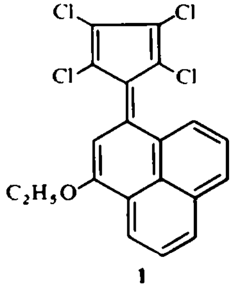
Abstract—7,8,2',3',4',5'-Hexachloro-11-methoxy-6*H*-cyclopenta[*a*]pyrene-6-spiro-1'-cyclopenta-2',4'-diene **5** has been obtained by the reaction of phenalenone and 1,2,3,4-tetrachlorocyclopentadiene. The gross structure of **5** has been determined by the X-ray analysis. The ground-state properties of **5** were discussed from the spectroscopic data, dipole moment and bond lengths.

WE HAVE previously described[1] a synthesis and some properties of 2-ethoxy-9,10,11,12-tetrachloropentaphenafulvalene (**1**) as a first example of the stable derivative of the pentaphenafulvalene which provided additional evidence for the ground-state properties of the cyclic cross-conjugated *pi*-electron system, mixed fulvalene.[2] Very recently Prinzbach and Woischnik[3] have reported a more simple derivative of this ring system, 7,8-dicyanopentaphenafulvalene (**2**) as a second instance.



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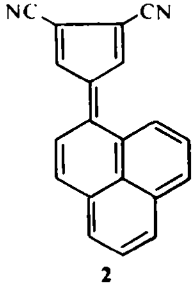

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As a part of our study of the phenalenium system, we wish to report the unusual product of the reaction between 1,2,3,4-tetrachlorocyclopentadiene (**3**) and phenalenone (**4**). One of the authors (I.M.) developed a method for the syntheses of sesquifulvalene and calicene derivatives by the reaction of **3** with 4,5-benzotropone and with the substituted cyclopropenones respectively.[4] Thus this synthetic means has been applied to phenalenone **4** which was assumed to be tricyclic 12 *pi*-electron vinylog of the tropone and the cyclopropenone.[5]

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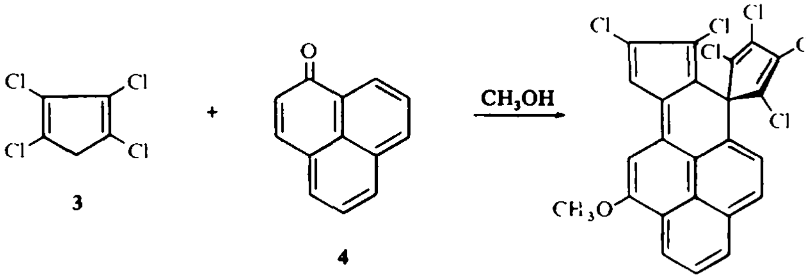
* Part I: see Ref. 1., Part III: see Ref. 18.

† We wish to thank Dr. K. Hirayama of Fuji Photofilm Co. for advice on the nomenclature of this compound.

A methanol solution of 3 and 4 was allowed to stand at 28–29° for 48 hr. During this period the solution changed from yellow to blue. From the above reaction mixture the violet crystals (5) were obtained in a poor yield [0·5%], accompanied with a large amount of resinous black powder. This violet substance 5 has a molecular formula of $C_{24}H_{10}OCl_6$ from the evidence of elemental analysis and molecular weight determination. It means that the two molecules of 3 were incorporated with phenalenone. The IR spectrum of 5 showed characteristic bands for phenafulvene moiety[6] at 1617, 1591 and 1566 cm^{-1}, and for aromatic ether linkage at 1248 and 1280 cm^{-1}. The electronic spectrum in *n*-hexane exhibited principal maxima at 286 nm (log ε 4·55), 295 (4·56), 388 (3·75), 406 (3·86), 517 (4·30), 548 (4·33), with the shoulders at 340 (3·86), 418 (3·78), 480 (4·10) and 592 (4·13). The longest wave length band at 548 nm shifted to 557 nm in methanol as expected for the solvent shift of the pentaphenafulvalene system.[3] The PMR spectrum [$CDCl_3$, internal TMS] at 100 MHz (Fig 1)



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4

5

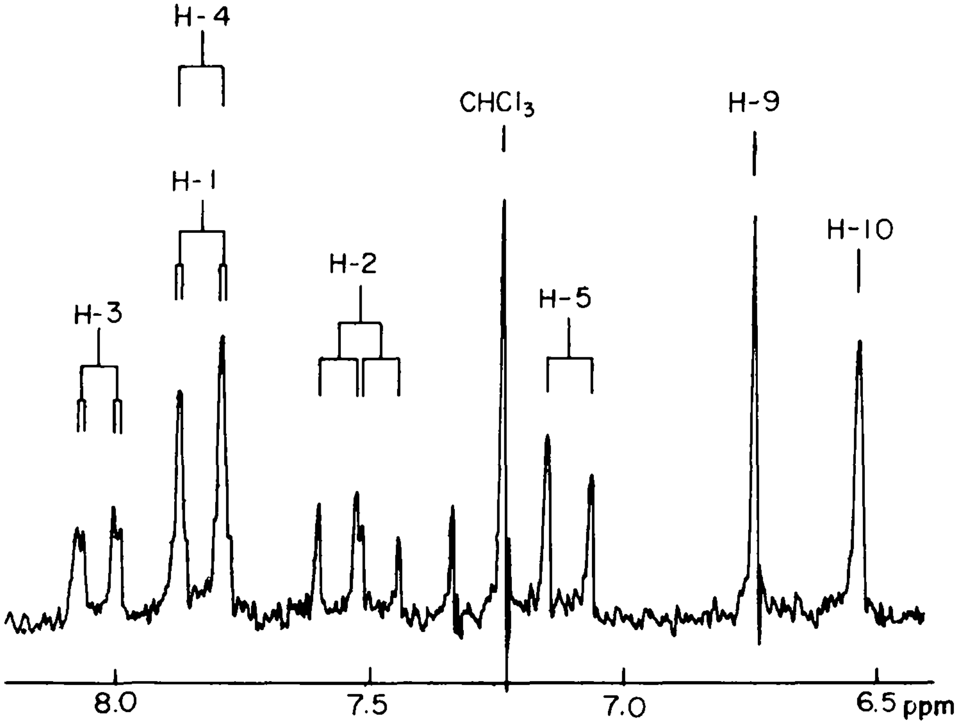

FIG 1. PMR spectrum of 5 in $CDCl_3$ at 100 MHz

showed a singlet for OMe hydrogens at δ 4·08 ppm (3H), a singlet for vinyl hydrogen H-10 at δ 6·54 ppm (1H),* a singlet for 5-membered ring hydrogen H-9 at 6·74 ppm, AB-quartet for aromatic ortho hydrogens H-4 and H-5 at δ 7·83 and δ 7·11 ppm with the coupling constant $J_{4,5}$ = 8·6 Hz, AMX-type signals for aromatic hydrogens H-1 at δ 7·83 ppm, H-2 at 7·52 ppm, H-3 at 8·03 ppm with the coupling constants $J_{1,2}$ = 7·4 Hz, $J_{2,3}$ = 8·3 Hz and $J_{1,3}$ = 1·6 Hz.

The dipole moment measurement in benzene solution at 25° gave a value of μ = 5·90 D which is of comparable magnitude to the reported value (6·33 D) of 2-ethoxy-9,10,11,12-tetrachloropentaphenafulvalene **1**.[1] This result indicates a definite degree of charge separation in the ground-state electronic structure of **5** and existence of the pentaphenafulvalene skeleton in its structure.

The definite conclusion of the gross structure of **5** was established from an X-ray crystallographic analysis.

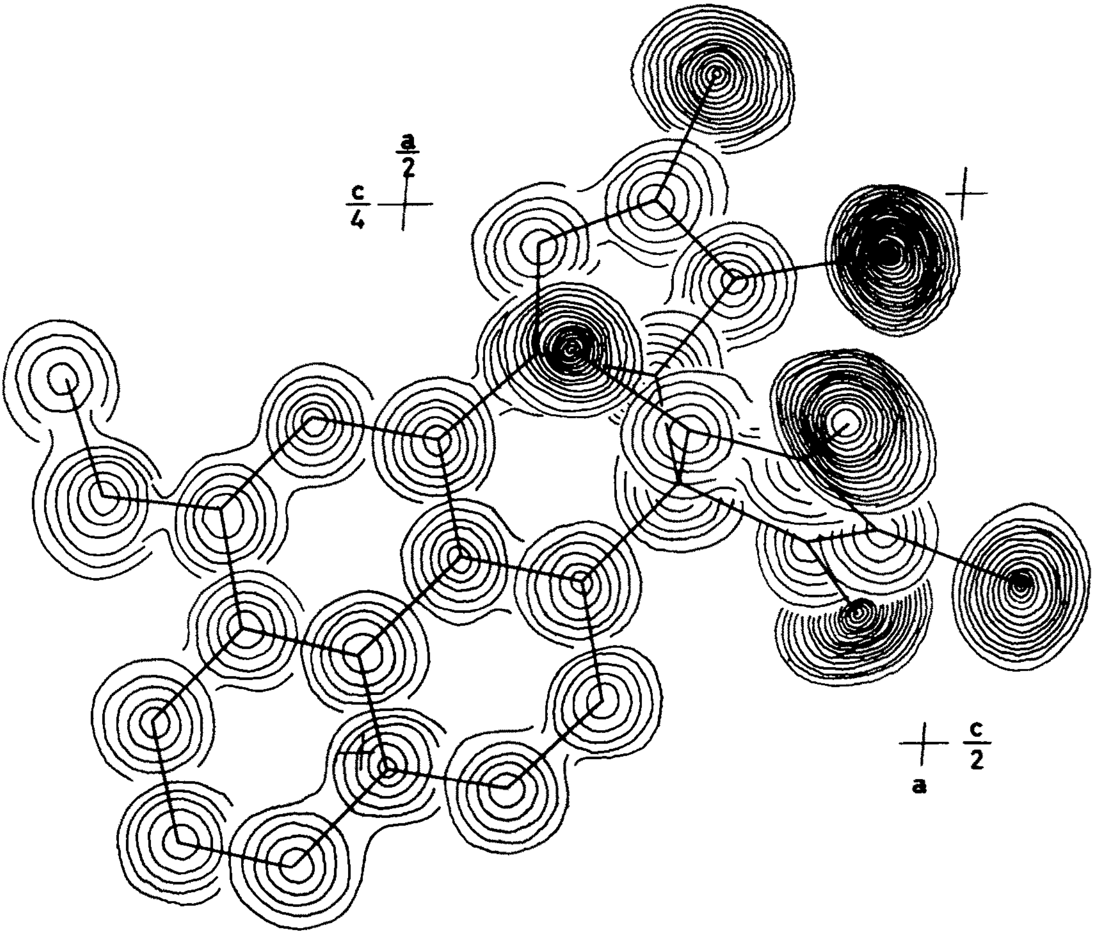

Fig 2. Composite electron density diagram of sections parallel to (010). The contours are drawn at equal intervals

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* This assignment is based on the observation that saturation of the OCH_3 resonance at δ 4·08 ppm causes a height increase of this signal.[17]

Crystals of **5** are monoclinic, with four molecules in a unit cell of dimensions, $a = 11{\cdot}866$, $b = 7{\cdot}983$, $c = 23{\cdot}122$ Å and $\beta = 95{\cdot}83°$, the space group is $P2_1/c$. Using the intensity data of independent 3948 reflections, the structure was solved by the symbolic addition method. The positional and thermal parameters of the non-H atoms were refined by the least-squares method. All the H atoms were located by the difference syntheses and were subjected to subsequent refinement. The final R factor for all the observed reflections was 0·071.

The 3-dimensional electron density distribution is shown in Fig 2. The structure of **5** should therefore be 7,8,2′,3′,4′,5′-hexachloro-11-methoxy-6*H*-cyclopenta[*a*]pyrene-6-spiro-1′-cyclopenta-2′,4′-diene (Fig 3).

The intramolecular bond lengths are listed in Table 1 with their estimated standard deviations.

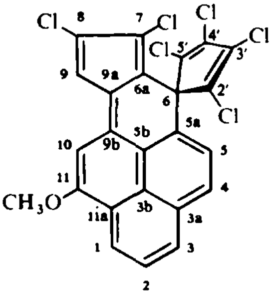


FIG 3. Numbering of **5**

TABLE 1. BOND LENGTHS WITH THEIR e.s.d.'s (Å)

Bond	Length	e.s.d.	Bond	Length	e.s.d.
C(1)–C(2)	1·397	0·008	C(11a)–C(3b)	1·424	0·007
C(2)–C(3)	1·359	0·008	C(11a)–C(1)	1·380	0·007
C(3)–C(3a)	1·415	0·007	C(3a)–C(3b)	1·407	0·007
C(3a)–C(4)	1·402	0·007	C(5b)–C(3b)	1·435	0·006
C(4)–C(5)	1·379	0·007	C(5a)–C(5b)	1·389	0·006
C(5)–C(5a)	1·402	0·007	C(6)–C(2′)	1·518	0·006
C(5a)–C(6)	1·528	0·006	C(2′)–C(3′)	1·318	0·007
C(6)–C(6a)	1·498	0·006	C(3′)–C(4′)	1·446	0·008
C(6a)–C(7)	1·356	0·007	C(4′)–C(5′)	1·329	0·008
C(7)–C(8)	1·439	0·007	C(5′)–C(6)	1·513	0·007
C(8)–C(9)	1·348	0·007	C(11)–O	1·342	0·007
C(9)–C(9a)	1·448	0·007	O–CH$_3$	1·434	0·009
C(9a)–C(6a)	1·440	0·006	C(7)–Cl	1·716	0·005
C(9a)–C(9b)	1·376	0·006	C(8)–Cl	1·725	0·005
C(9b)–C(10)	1·429	0·007	C(2′)–Cl	1·697	0·005
C(9b)–C(5b)	1·466	0·006	C(3′)–Cl	1·713	0·006
C(10)–C(11)	1·360	0·007	C(4′)–Cl	1·697	0·006
C(11)–C(11a)	1·451	0·007	C(5′)–Cl	1·689	0·005

We have already deduced the bond orders of the carbon skeleton of the pentaphenafulvalene from a VESCF molecular orbital treatment.[1] Theoretical bond lengths derived from the bond orders with the aid of the formula[7]

$$r_{ij}\,(\text{Å}) = 1{\cdot}520 - 0{\cdot}186\,p_{ij}$$

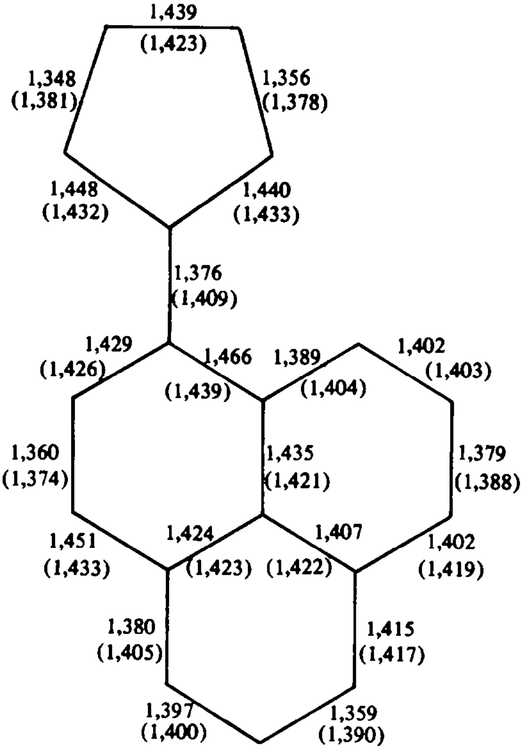
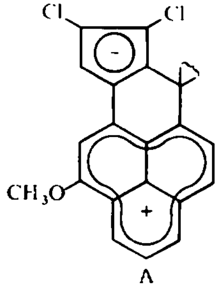
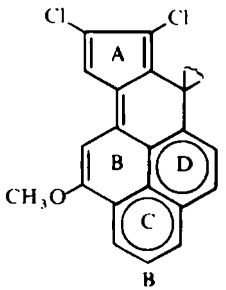


FIG 4. Comparison of theoretical and observed values of bond lengths (Å). Parenthesis indicates the theoretical values

are compared to the observed values in Fig 4. The agreement between them is fairly good. It should be noted that the intercyclic double bond C(9a)—C(9b), 1·376 Å, is significantly longer than that of ethylene, 1·337 Å[8] and is comparable to that of 1,2,3,4-tetrachloro-5,6-di-*n*-propylcalicene (1·370 Å).[9] Moreover, in the 5-membered ring of the pentaphenafulvalene moiety, the degree of bond fixation is smaller than that of the spiro 5-membered ring. It seems to suggest a considerable contribution of a dipolar phenalenium (12π)-cyclopentadienide (6π) form (A) to the ground-state structure of 5.[10] Although the bond lengths in C and D rings are almost equal to



A



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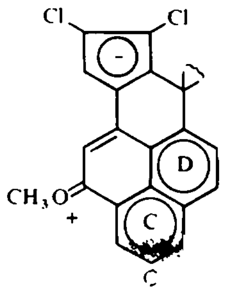
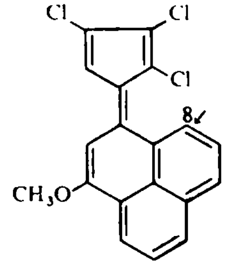


C

the normal benzenoid aromatic compounds, the apparent bond alternation is observed in the B-ring. The length of C (11) -O bond in 5 (1·342 Å) is shorter than that of normal C (sp^2) -O bond (1·38–1·39 Å).[11] It may be pointed out that the canonical forms such as (B) and (C) would participate to the resonance structure of this molecule.

This tendency is also revealed by the NMR spectroscopy. The observed ortho-coupling constants for C-, D-rings and the meta-coupling constant in C-ring are 8·3, 7·4, 8·6 and 1·6 Hz, respectively. These values are closely similar to those of naphthalene [$J_{1,2}$ = 8·1 Hz, $J_{2,3}$ = 6·4 Hz and $J_{1,3}$ = 1·4 Hz].[12] Moreover, the OMe hydrogen chemical shift of **5** [δ 4·08 ppm] is about 0·2 ppm lower field than the reported values for anisole [δ 3·78 ppm][13] and 1-methoxynaphthalene [δ 3·80 ppm].[14] We feel that the above mentioned NMR findings together with the bond lengths are due mainly to the appreciable contribution of the resonance forms B and C.

It is of interest to note that the present formation of **5** proceeded through the condensation of two molecules of 1,2,3,4-tetrachlorocyclopentadiene. Although detail routes remain unexplored, the present reaction would involve initial condensation of **3** and **4** to the 2-methoxy-9,10,11-trichloropentaphenafulvalene (**6**), followed by the attack of the second molecule of **3** at C-8 position and ring closure by dehydrochlorination would give the dihydro derivative (**7**), which might produce the final product **5** by dehydrogenation.* The intervention of an intermediate such as **6** is also seen in the reaction between **3** and the tropone in methanol to produce 1,2,3-trichloro-6-(*o*- and *p*-methoxyphenyl)-fulvenes.[15] Furthermore, the site of greatest reactivity towards nucleophilic attack for the pentaphenafulvalene is predicted to be the C-8 position by the VESCF-MO calculation for charge densities.[1]



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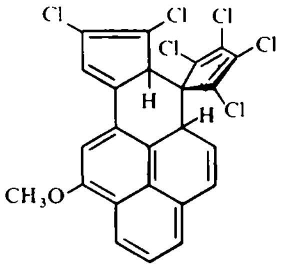

7

EXPERIMENTAL

PMR spectrum was recorded at 100 MHz on a Varian HA-100 spectrometer, with TMS (δ = 0·00 ppm) as field/frequency lock. IR spectrum was taken on a Hitachi Grating Infrared Spectrophotometer and UV and visible spectra was measured on a Hitachi 124 spectrophotometer.

Reaction of phenalenone with 1,2,3,4-*tetrachlorocyclopentadiene* A soln of 20 g of **3**, 15·1 g of **4** and 335 ml MeOH was warmed to 28–29° for 48 hr. The precipitated resinous black powder (6·1 g) was removed by suction filtration and thoroughly washed with 300 ml hot benzene. The MeOH filtrate was concentrated to about 50 ml under reduced pressure which was then diluted with water and extracted with benzene. The combined benzene extract was dried and the benzene was distilled. The residue was chromatographed on Al_2O_3. From the light petroleum eluted fraction, 6·9 g of **3** was recovered. Elution with benzene-light petroleum (1 : 10) yielded violet fractions, which on concentration gave crude **5** (0·382 g). Recrystallization of crude crystals from benzene afforded 0·203 g (0·5% based on phenalenone) of analytically pure **5**, violet needles, m.p. > 250°. (Found: C, 54·38, 54·53; H, 1·90, 1·84, Cl, 40·16, 40·16; mol. wt, 513 by vapour pressure osmometer; Calcd. for $C_{24}H_{10}OCl_6$: C, 54·69; H, 1·91; Cl, 40·36%; mol. wt., 527·07).

Dipole moment of **5**. The dipole moment of **5** was measured in benzene soln at 25° and calculated by Halverstadt–Kumler's method.[16]

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* This process would reasonably be interpreted by the hydride abstraction with the methoxyphenalenium cation which generated from **1** and methanol. The participation of methoxytropylium cation was also observed in the reaction of tropone with **3** in methanol.[15]

Mol. wt. = 527·07, MR$_D$ = 102·72

wt. fraction	ε		D	
0	2·2724		0·873285	
0·002671	2·2927	$\alpha_1 = 7{\cdot}60$	0·874632	$\beta_1 = 0{\cdot}504$
0·004570	2·3069	$\alpha_2 = 7{\cdot}55$	0·875328	$\beta_2 = 0{\cdot}447$
0·013252	2·3733	$\alpha_3 = 7{\cdot}61$	0·878654	$\beta_3 = 0{\cdot}405$

$\alpha = 7{\cdot}62$, $\beta = 0{\cdot}397$

$p_2 = 1{\cdot}621510$, P_{2}, $= 854{\cdot}6493$, $\mu = 5{\cdot}90$ D

X-Ray crystallographic analysis. The crystallographic and physical data obtained are: monoclinic, a = 11·866, b = 7·983, c = 23·122 Å and β = 95·83°. Space group, P2$_1$/c Four molecules per unit cell. Volume of the unit cell, 2179·0 A^3. Density (by flotation), 1·592 g.cm^{-3}. Density (calculated), 1·606 g.cm^{-3}. Linear absorption coefficient for MoKα radiation, μ = 7·95 cm^{-1}. Total number of electrons per unit cell, F(000) = 1056.

The intensities were collected on a Rigaku four circle automatic diffractometer using MoKα radiation, and all independent 3948 reflections with $\sin\theta/\lambda \leqslant 0{\cdot}60$ were measured. The moving-crystal moving counter technique was employed The dimensions of the crystal used was 0·04 × 0·03 × 0·03 cm.

The greater part of calculations was carried out on a HITAC 5020E computer in Computer Center of the University of Tokyo. Since the core storages available were short in number, initial calculations were based on the 3195 reflections with $\sin\theta/\lambda \leqslant 0{\cdot}56$.

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