first P–ONP linkage was monitored. In all cases, linear plots were obtained, to at least 80% reaction with typical correlation coefficients 0.997–0.999. Rate constants were reproducible to 3–6% of the average value.

phorochloridate, 6546-97-0; diphenyl phosphochloridate, 2524-64-3; 8-hydroxyquinoline sodium salt, 2872-54-0; 8-hydroxyquinoline, 148-24-3; *p*-nitrophenyl phosphorodichloridate, 34909-18-7.

Reductive Dimerizations of Perchlorofluorene. Synthesis of an Overcrowded, Twisted Ethylene

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Perchloro-9,9′-bifluorenylidene (2), a highly twisted ethylene, has been synthesized from perchlorofluorene (3) with Cu at 280 °C or from 9H-heptadecachloro-9,9′-bifluorenyl (1) by dehydrochlorination with NaOH. 1 has been obtained from 3 with SnCl₂. In spite of the high angle of twisting (67°), 2 is a diamagnetic chlorocarbon (magnetic susceptibility and ESR), i.e., a singlet. Hydrogenation of 2 gives 9H,9′H-hexadecachloro-9,9′-bifluorenyl (8). From 2 chlorocarbons perchlorobenzo[e]indeno[1,2,3-*hi*]acephenanthrylene (5), perchloro-14b,14c-dihydrobenzo[e]indeno[1,2,3-*hi*]acephenanthrylene (4), and perchloro-2,2′,3,3′-tetrahydro-1H,1′H-9,9′-bifluorenyl (10) have been obtained. The preceding compounds have given rise, either directly or indirectly, to perchlorofluorenone (12), perchloro-3,3′-dioxo-9,9′-bifluorenyl (13), perchloro-9-(3-oxo-9-fluorenyl)-1-fluorenone (14), tetradecachloro-3,3′-dihydroxy-9,9′-bifluorenylidene (15), tetradecachloro-1,3′-dihydroxy-9,9′-bifluorenylidene (16), 3,3′-diacetoxytetradecachloro-9,9′-bifluorenylidene (17), 1,3′-diacetoxytetradecachloro-9,9′-bifluorenylidene (18), and tetradecachloro-3,3′-dimethoxy-9,9′-bifluorenylidene (19). Chemical and ESR evidence for the formation of perchlorofluorenyl (PF) and 9H-octachlorofluorenyl (21) radicals is given, and the frontal strain of the relevant dimers is discussed. In the mechanistic interpretation of some reactions here reported, the role of steric distortion and shielding, due to chlorine overcrowding, is considered.

It has been reported that (trichloromethyl)benzenes such as *o*-H-heptachlorotoluene,[1] *p*-H-heptachlorotoluene,[2] and perchlorotoluene,[1,3,4] are reduced by iodide ion, by stannous chloride, or by ferrous chloride to give dimers and/or dimeric products therefrom. Those reactions take place through α,α-dichlorobenzyl radicals which yield α,α,α′,-α′-tetrachlorobibenzyls and/or α,α′-dichlorostilbenes. When the trichloromethyl group is flanked by *two ortho* chlorines, the isolated product is invariably a mixture of *cis*- and *trans*-α,α′-dichlorostilbenes, and this is due to frontal steric strain in the intermediate bibenzyl which favors vicinal chlorine elimination. If there is only *one ortho* chlorine, a mixture of the bibenzyl and the stilbenes is obtained.[1] In the case of perchlorotoluene (stannous chloride), the intermediate perchlorobenzyl has been detected by ESR spectrometry and found to be, at room temperature, in equilibrium with its dimer, the perchlorobibenzyl.[4]

Such a type of reduction takes place with the perchlorodiphenylmethane as well.[5,6] Nevertheless, the iso-lated product is neighter the perchlorotetraphenylethane nor the perchlorotetraphenylethylene, as it might be expected, but the perchlorodiphenylmethyl radical (PDM), a historical precursor of the "inert carbon free radicals".[5,6] This result is due to a prohibitive frontal strain in the hypothetical dimer of PDM. Similarly, the reduction of perchloro-9-phenylfluorene by ferrous chloride *does not* give dimeric products but inert perchloro-9-phenylfluorenyl radical (PPF),[7] and this is attributed to steric shielding of the 9-carbon by its four proximal chlorine atoms.

In spite of this hindrance to dimerization, and in connection with the problem of ethylene-bond twisting, it was regarded of significance to attempt the synthesis of related tetrasubstituted ethylenes provided with strong steric repulsions among their substituents.

It was reported long ago that steric interactions between the carbon pairs 1/1′ and 8/8′ in hydrocarbon 9,9′-bifluorenylidene are very significant,[8] the central ethylene (9,9′) bond being twisted about 42°.[9] Such a twisting confers a red color to that hydrocarbon, as well as thermochromy. Therefore, it was decided to attempt the

(1) Ballester, M.; Molinet, C.; Rosa, J. *Tetrahedron* **1959**, *6*, 109.
(2) Ballester, M.; Rosa, J. *An. R. Soc. Esp. Fis. Quim., Ser. B* **1960**, *56*, 203.
(3) Ballester, M. *Bull. Soc. Chim. Fr.* **1966**, 7.
(4) Olivella, S.; Ballester, M.; Castañer, J. *Tetrahedron Lett.* **1974**, 587.
(5) Ballester, M.; Riera, J. *J. Am. Chem. Soc.* **1964**, *86*, 4505.
(6) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215.

(7) Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J.; Armet, O. *J. Org. Chem.* **1984**, *49*, 770.
(8) Bergmann, E. D. *J. Chem. Soc.* **1935**, 987. Bergmann, E. D.; Berthier, G.; Pullman, A.; Pullman, M. B. *Bull. Soc. Chim. Fr.* **1950**, *17*, 1079. Rabinovitz, M.; Agranat, I.; Bergmann, E. D. *Tetrahedron Lett.* **1965**, 1265.
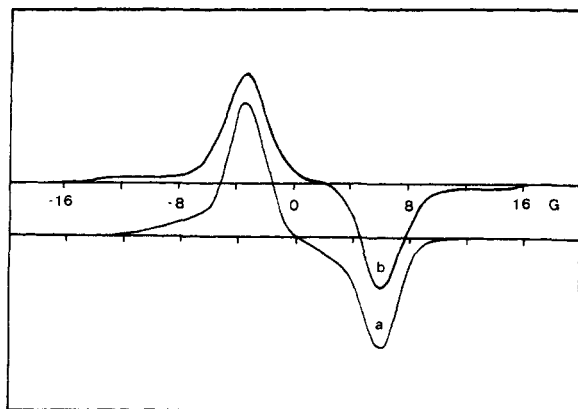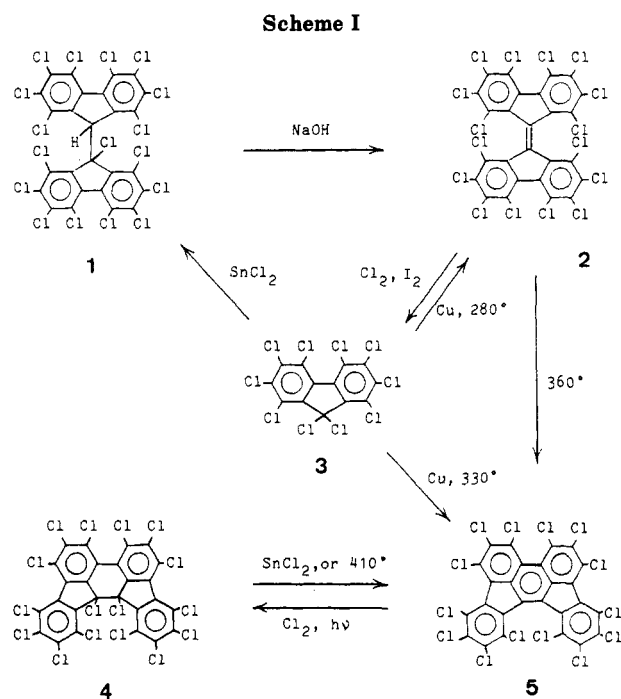(9) Bailey, N. A.; Hull, S. E. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3289.

Figure 1. (a) ESR spectrum of radical PF and (b) its computer simulation.

Scheme I

synthesis of perchloro-9,9′-bifluorenylidene (2), which would involve great repulsions between the chlorine pairs 1/1′ and 8/8′.[10]

Results and Discussion

Reductions of Perchlorofluorene[6] (3). (1) With SnCl₂ (Scheme I). Fluorene 3 reacts with SnCl₂ in dioxane, giving unexpectedly a very good yield of 9H-heptadecachloro-9,9′-bifluorenyl (1), the structure of which has been ascertained by analyses, spectra, and X-ray measurements.[12] Under the same conditions, related perchlorodiphenylmethane gives no dimer but perchlorodiphenylmethyl radical (PDM).[5] It is concluded therefore that perchloro-9-fluorenyl radical (PF) is formed. Also, as in the case of perchlorobenzyl radical,[4] it is assumed that radical PF is in equilibrium with a dimer. The transient formation of this radical has been confirmed by ESR. The hyperfine structure of the spectrum has been computer

Scheme II
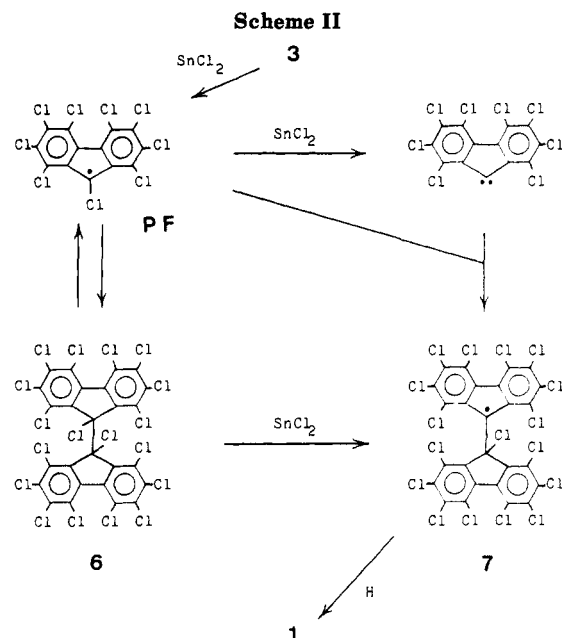
simulated, showing one main coupling (~2.3 G) with the 9-chlorine, and the usual line broadness (~3.0 G) of the fluorenyl radicals[7] due to the unresolved couplings with the aromatic chlorines (Figure 1).

The greater reactivity of radical PF, as compared to that of radical PDM, is attributed to a diminished steric shielding of the trivalent carbon atom, where presumably most of the spin density resides (three vicinal chlorines in PF vs. five in PDM). It is noteworthy that resonance stabilization in PF should be higher on account of its *quasi*-planar π-electron system.

With regard to the steps following the formation of radical PF, a conservative assumption (Scheme II) involves dechlorination of dimer perchloro-9,9′-bifluorenyl (6) with SnCl₂, giving dimeric fluorenyl radical 7 which picks up next a hydrogen atom from the medium to yield bifluorenyl 1. A remarkable feature of this mechanism is the failure of radical 7 to undergo further dechlorination to ethylene 2, as it occurs in the vicinal dechlorination of perchlorobibenzyl, which gives a mixture of cis- and *trans*-perchlorostilbene.[4] It is pointed out, however, that while such stilbenes are not strained, 2 is a highly twisted ethylene (see later) and consequently its formation from radical 7 should overcome a very high energy barrier. Nevertheless, it is surprising the high reactivity of radical 7 as a hydrogen acceptor. The trivalent 9-carbon of 7 is well shielded by one of its bulky perchloro-9-fluorenyl groups, much more so than radical PF. Consequently, radical 7 should be a poor hydrogen acceptor like perchloro-9-phenylfluorenyl radical (PPF), which, as mentioned before, is an inert free radical because of the shielding by its pentachlorophenyl group.[7] Radical 7 should therefore be more persistent than PF; yet, there is no ESR evidence for its formation during the dechlorination of chlorocarbon 3. The high chlorine coupling found (2.3 G) in the ESR spectrum of the reacting mixture (see before) corresponds certainly to a chlorine attached *directly* to the trivalent carbon. Therefore, such a spectrum is that of the radical PF (PDM(α-Cl) = 2.18 G[6]) and is inconsistent with that of radical 7. Alternative mechanistic possibilities, such as those involving a high-yield coupling of 9H-octachlorofluorenyl radical with radical PF (see Chart II), are also objectionable on other grounds.

(2) With Copper (Scheme I). In view of the preceding results, it was decided to perform the dechlorination of

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(10) A short notice on some aspects of this subject has been advanced.[11]

(11) Ballester, M.; Castañer, J.; Riera, J.; Camps, M. *Tetrahedron Lett.* **1980**, *21*, 193.

(12) Solans, X.; Miravitlles, C.; Declerq, J. P.; Germain, G. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2677.

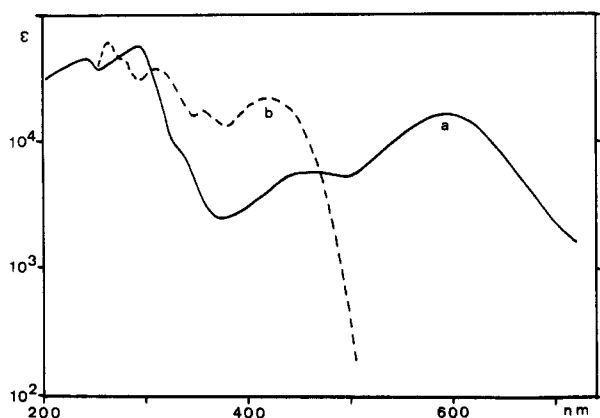(13) Perchloro-9-phenylfluorenyl radical (PPF)[7] *does not* extract hydrogen from ethers.

Figure 2. (a) UV–vis spectra of bifluorenylidene **2**, and (b) acephenanthrylene **5**.
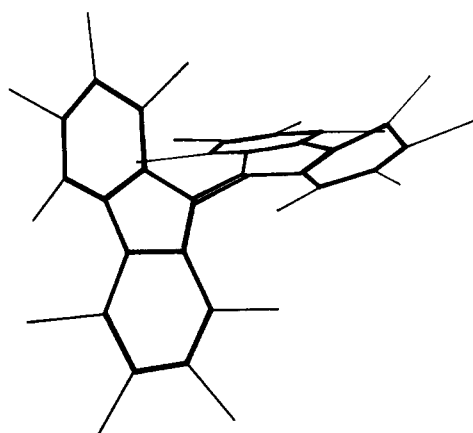

Figure 3. Molecular structure of bifluorenylidene **2** by X-ray measurements.

fluorene **3** under rather drastic conditions, i.e., by heating it with copper dust in a solvent (refluxing C_2Cl_4) or without (280–400 °C). As hoped for, in C_2Cl_4, an excellent yield of the perchloro-9,9′-bifluorenylidene (**2**) is obtained. Without solvent, at 280 °C, in addition to a very good yield of bifluorenylidene **2**, some perchlorobenzo[e]indeno-[1,2,3-*hi*]acephenanthrylene (**5**) is isolated. At higher temperatures (330 °C) the latter results in an excellent yield. Also, chlorine elimination from bifluorenylidene **2** by heating at 360 °C (without copper) affords an almost quantitative yield of the acephenanthrylene **5**. DSC and TG analyses show that bifluorenylidene **2** melts at 358 °C, giving acephenanthrylene **5**, this melting at 420 °C. It has also been found that bifluorenylidene **2** can also be obtained from bifluorenyl **1** by dehydrochlorination with base in an almost quantitative yield.

Bifluorenylidene **2** is a dark blue crystalline solid. Figure 2 shows its UV–vis spectrum, displaying a medium-intensity band about 590 nm. The molecular structure of bifluorenylidene **2** (X-ray analysis;[14] Figure 3) indicates that it is highly twisted (67°) about the central ethylene bond. Magnetic susceptibility measurements (from 77 K to room temperature) show that chlorocarbon **2** *is not* paramagnetic, i.e., neither a triplet nor a biradical, but a singlet. Furthermore, no significant ESR signal is observed at room temperature (in C_2Cl_4) and even at higher temperatures (up to 250 °C; C_6HCl_5).

In this connection, it should be pointed out that perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-diyl *is not* a singlet (quinonoid structure) but a double doublet (di-

Scheme III
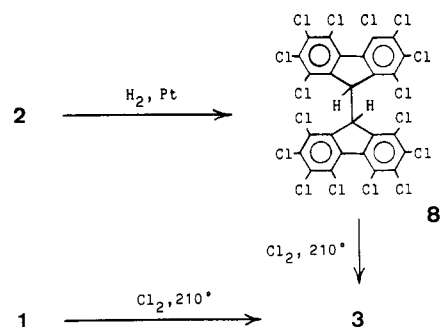
Scheme IV
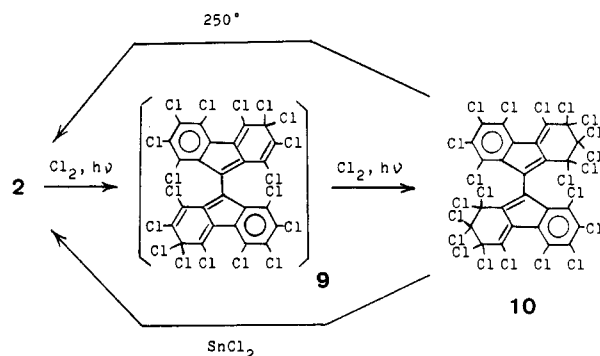
radical structure).[6] This is due to complete steric inhibition of resonance because of the perpendicularity of the two benzene rings in its biphenyl system.[6,15] The fact that bifluorenylidene **2** is a singlet indicates otherwise that, in spite of the twisting of its central ethylene bond, resonance is still significant, and consequently this singlet is stabilized over the double doublet and triplet structures.

Acephenanthrylene **5** is a new orange chlorocarbon, its UV–vis spectrum being shown in Figure 2. The formation of **5** is probably assisted by the twist strain of bifluorenylidene **2**, which is significantly released in the process. The structure of chlorocarbon **5** is derived from that of its precursor **2**, since it is reasonable to assume that the pair of chlorines of chlorocarbon **2** being eliminated in the cyclization process are those attached to carbons 1 and 1′. Also in such a cyclization, resonance is enhanced, and the steric strain is relieved (space-filling models). Similar thermal cyclizations take place in perchlorotriphenylmethyl (PTM) and perchloro-4-phenyltriphenylmethyl (PPTM) radicals[7] and perchlorofuchsone.[7]

Hydrogenation of Bifluorenylidene 2 (Scheme III). The hydrogenation of chlorocarbon **2** with H_2/Pt gives an almost quantitative yield of colorless 9H,9′H-hexadecachloro-9,9′-bifluorenyl (**8**). However, **2** does not react with $LiAlH_4$ in refluxing ether. X-ray analysis of **8** shows that one moiety of the molecule is on top of the other and rotated aproximately 90° around the central C–C bond.[12]

Chlorinations. (1) Both bifluorenyls 1 and 8 chlorinate with Cl_2 in refluxing commercial trichlorobenzene (~210 °C), in the dark, giving fluorene **3** in excellent yields (Scheme IV). The first step of these chlorinations is presumably homolysis to fluorenyl radicals (see Thermal Behavior of Bifluorenyls), which would then react with Cl_2, and so forth.

(2) Bifluorenylidene 2 reacts with Cl_2 in CCl_4 in the presence of I_2, at room temperature and in the dark, giving fluorene **3** in a very good yield (Scheme I). This reaction

(14) Molins, E.; Miravitlles, C. *Acta Crystallogr.*, in press.

(15) Ballester, M.; Castañer, J.; Riera, J.; Pascual, I. *J. Am. Chem. Soc.* **1984**, *106*, 3365.

Chart I

10   **11**

Scheme V

12
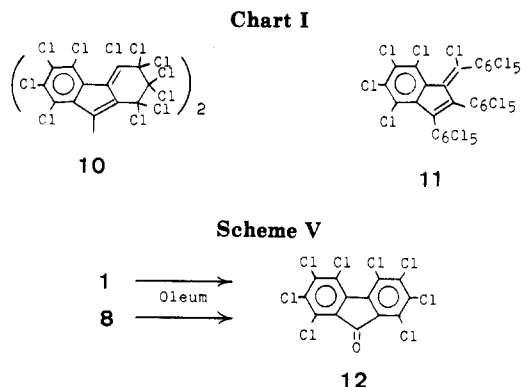
is accounted for by assuming an initial chlorine addition to the central ethylene bond of 2, which is assisted by its twist energy. The resulting perchloro-9,9'-bifluorenyl (6), in equilibrium with radical PF, would then chlorinate to fluorene 3. (The homolysis of 6 must be strongly assisted by its frontal strain; see Thermal Behavior of Bifluorenyls.)

(3) **Bifluorenylidene** 2 photochlorinates with Cl_2 and white incandescent light, in CCl_4 and at low temperature (5 °C), giving perchloro-2,2',3,3'-tetrahydro-1H,1'H-9,9'-bifluorenyl (10) (Scheme IV). The latter can be dechlorinated back to bifluorenylidene 2, in excellent yields, either with $SnCl_2$ or at 250 °C. At higher temperatures (refluxing CCl_4) that chlorination gives complex mixtures containing some fluorene 3.

The photochlorination is assumed to be initiated by photoexcitation of blue bifluorenylidene 2. Chlorine addition would take place preferentially at the least-shielded peripheral positions of the molecule, i.e., giving intermediate 9 (Scheme IV). Consequently, it is proposed that 10 is the structure of the product. Circumstantial evidence in favor of such a structural assignment derives from the fact that the UV–vis curve of chlorocarbon 10 and that of structurally related perchloro-2,3,8-triphenylbenzofulvene[16] (11) are similar (Chart I).[17]

(4) **Acephenanthrylene** 5 photochlorinates with Cl_2 and white incandescent light, in refluxing CCl_4, giving an orange-yellow chlorocarbon $C_{26}Cl_{16}$ in an excellent yield. Since it is well-known that additions to phenanthrenes occur at the 9,10-bond (as in the chlorination of perchlorophenanthrene[18]), it is assumed that chlorocarbon is perchloro-14b,14c-dihydrobenzo[e]indeno[1,2,3-hi]acephenanthrylene (4) (Scheme I). The latter can be dechlorinated back to acephenanthrylene 5 either with $SnCl_2$ or at 410 °C.

Reactions with Oleum. (1) Bifluorenyls 1 and 8 react with oleum at 100 °C, both giving an excellent yield of perchlorofluorenone[6] (12) (**Scheme V**).

The reason for these oxidations are explained as follows: Bifluorenyls 1 and 8 are provided with frontal strain at the 9,9'-bond. Moreover, the fragments resulting from rupture of that bond are resonance stabilized (see Thermal Behavior of Biphenyls). Consequently, it is reasonable that in a highly polar medium, such as oleum, protonation would initiate bond cleavage giving carbenium ion and 9H-fluorene, both being converted next to fluorenone 12.[6]

(2) **Bifluorenylidene** 2 reacts with oleum at 100 °C, giving dark brown perchloro-3,3'-dioxo-9,9'-bifluorenyl (13)

Scheme VI

2

13   **14**

15   **16**

17   **18**

19
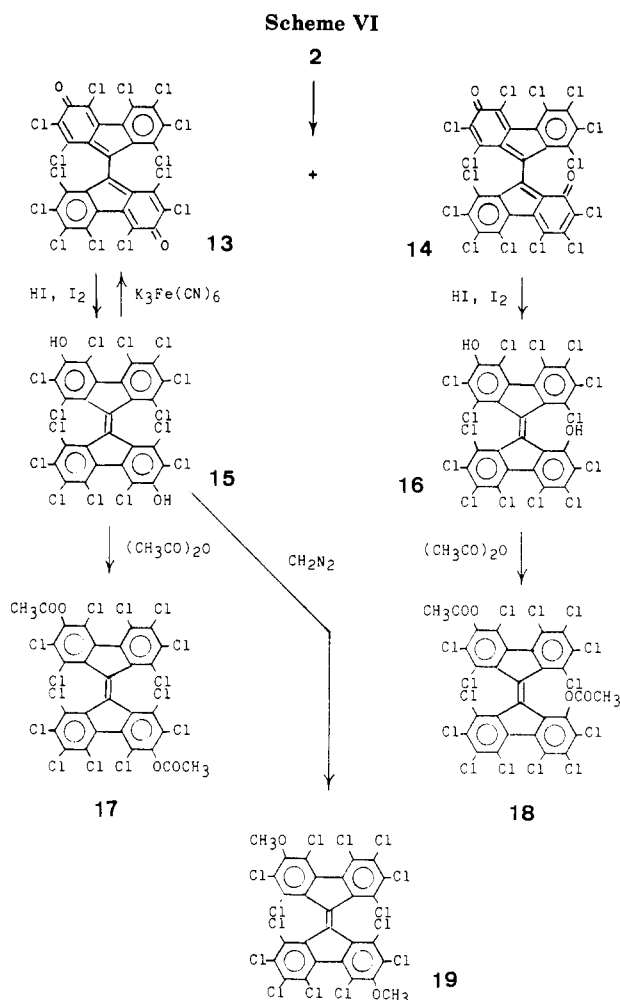
and some dark red perchloro-9-(3-oxo-9-fluorenyl)-1-fluorenone (14) (Scheme VI). The structure of these diketones has been assigned on the basis of spectral comparison with dark brown perchloro-9-phenyl-3-fluorenone[7] (20), the structure of which had been established by X-ray analysis.[19] According to the IR spectrum, the C=O and C=C stretching peaks of diketone 13 are coincident with those of ketone 20 (1654 and 1578 cm^{-1}), and therefore the carbonyl group is in position 3. Diketone 14 shows two C=O stretchings (1654 and 1595 cm^{-1}), one of them coincident with that of ketone 20, indicating that the other *is not* in position 3; i.e., it is in position 1. According to the UV–vis spectra, the locations of the maxima for diketone 13 and ketone 20 are almost coincident: 13, 301 nm (ϵ 56 000), 428 (17 300), 449 (17 600), and 480 (6100); 20, 305 nm (ϵ 26 300), 428 (6200), 452 (6700), 485 (2400). Also, the absorptivities of diketone 13 are about twice as high as those of ketone 20, since the two moieties of 13 can be assumed to be nearly electronically independent.

These diketones are reduced with HI/I_2,[20] giving tetradecachloro-3,3'-dihydroxy- (15) and tetradecachloro-1,3'-dihydroxy-9,9'-bifluorenylidene (16), respectively. Diphenol 15 gives back diketone 13 with $K_3Fe(CN)_6$. Those diphenols are acylated to 3,3'-diacetoxy- (17) and 1,3'-diacetoxytetradecachloro-9,9'-bifluorenylidene (18) (Scheme VI). Accordingly, the UV–vis spectra of these diacetates and diphenol 15 are almost coincident with that of bifluorenylidene 2. The ^{1}H NMR spectra of those di-

(16) Ballester, M.; Castañer, J.; Riera, J.; Armet, O. *Tetrahedron Lett.* **1980**, *21*, 2845.

(17) On account of their being almost perpendicular to the benzofulvene π-electron system, the three pentachlorophenyls of chlorocarbon 11 are supposed not to contribute significantly to the UV–vis spectrum.

(18) Ballester, M.; Castañer, J.; Riera, J.; Parés, J. *An. Quim., Ser. C* **1980**, *76*, 157.

(19) Solans, X.; Miravitlles, C.; Plana, F.; Declerq, J. P.; Germain, G. *Acta Crystallogr., Sect. B* **1981**, *B37*, 2079.

(20) Ballester, M.; Riera, J.; Castañer, J.; Rodríguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498.

Chart II

20   21   22
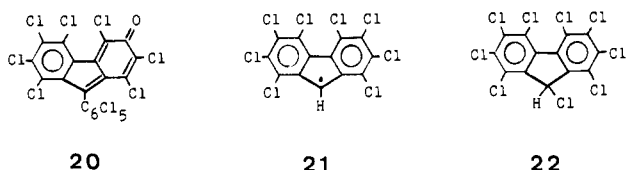
acetates confirm the structures of diketones 13 and 14, while 17 displays just one singlet at $\tau = 7.55$, indicating that the acetoxy groups are equivalent, and 18 shows two singlets at τ 7.60 and 8.05, indicating that in the latter only one acetoxy group is at an equivalent position to those in 17.

As far as the mechanism of those oxidations is concerned, it is suggested that they are initiated by protonation of the central (twisted) double bond of chlorocarbon 2, followed by solvolysis to two isomeric *o*- and *p*-quinomethanes which undergo oxidation to diketones 13 and 14.

Diphenol 15 is methylated with N_2CH_2 to give tetradecachloro-3,3'-dimethoxy-9,9'-bifluorenylidene (19) (Scheme VI).

Thermal Behavior of Bifluorenyls. Bifluorenyl 8 in C_6HCl_5, from 190 °C on, gives a transient ESR signal resulting from homolysis to 9H-octachlorofluorenyl radical (21) (Chart II). In fact, its hyperfine structure consists of two lines separated by 12.5 G due to coupling with the proton. Bifluorenyl 1 in that solvent, at 90 °C, gives an ESR signal that is coincident with that of radical PF, no indication of radical 21 being observed. This shows that bifluorenyl 1 dissociates, giving radicals PF and 21, and because of the lower temperature, the latter dimerizes to bifluorenyl 8. It is noted that the ease of homolysis in the bifluorenyls decreases in the order of decreasing frontal strain; i.e., $(PF)_2 > 1 > 8$.

Ultraviolet–Visible Spectra. The conjugation bands of bifluorenyls 1 and 8 show their maxima at 313 nm (ϵ 30 000) and 309 (36 700), respectively. In this connection it is mentioned that in 9H-nonachlorofluorene (22) (Chart II) it is found at 306 nm (ϵ 18 700).[21] It is remarked that the absorptivities of bifluorenyls 1 and 8 are about twice as high as that of 22, as expected. For the spectra of diketones 13 and 14, see before.

Experimental Section

General Methods. The IR, UV–vis, ^{1}H NMR, and mass spectra have been recorded with Perkin-Elmer 457, Beckman Acta M VI, Perkin-Elmer R 12B, and AEI MS-902S spectrometers, respectively. The magnetic susceptibilities have been measured in He with a Varian 4-in. magnet with constant force caps and a Cahn RG electrobalance.

The identification of the products of the reactions here described was effected at least by IR spectrum. Since the locations of the IR peaks of perchloro organic compounds differ markedly from those of their nonchlorinated counterparts, it is useful to include them in this section.

Reduction of Perchlorofluorene[6] **(3) with SnCl₂.** A mixture of 3 (0.258 g, 0.5 mmol), SnCl₂·2H₂O (0.126 g, 0.5 mmol), and purified dioxane (20 mL) was refluxed for 24 h under argon. The resulting mixture was treated with aqueous HCl (100 mL) and extracted with CHCl₃. This extract was washed with water, dried, and evaporated, giving a residue (0.220 g), which by crystallization from hexane–CHCl₃ afforded 9H-heptadecachloro-9,9'-bifluorenyl (1) (0.197 g, 88.5%): white crystals, mp 227–30 °C; UV (CHCl₃) 245 nm, 263 (sh), 313 (ϵ 62 100, 27 400, 30 000); IR (KBr) 1530 (w), 1390 (m), 1330 (s), 1322 (s), 1316 (s), 1250 (w), 1192 (s), 1178 (s), 1160 (m), 878 (m), 849 (m), 832 (m), 814 (s), 673 (s), 648 (s), 640 (s) cm⁻¹; mass spectrum, m/e (all ^{35}Cl) 872 (M⁺ − HCl). Anal.

(21) Ballester, M.; Castañer, J.; Riera, J.; Camps, M., unpublished results.

Calcd for $C_{26}HCl_{17}$: C, 34.1; H, 0.1; Cl, 65.8. Found: C, 34.1; H, 0.3; Cl, 65.6.

Reductions of Fluorene 3 with Copper. (1) Without Solvent. A mixture of 3 (2.10 g) and powdered electrolytic copper (1.03 g) was degassed under vacuum for 1 h at 120 °C and heated (45–120 min) at high temperature (280–300 °C) under argon. The resulting product was extracted with refluxing CCl₄. Evaporation of the solvent gave a residue, which by TLC over silica gel in hexane afforded the following. (a) Perchlorobenzo[e]indeno-[1,2,3-*hi*]acephenanthrylene (5): orange-yellow crystals, mp 420 °C (DSC); UV–vis (CCl₄) 263 nm, 280 (sh), 309, 356, 419 (ϵ 57 600, 45 100, 38 100, 17 400, 22 900); IR (KBr) 1378 (m), 1348 (s), 1325 (s), 1285 (s), 1234 (s), 1210 (m), 1176 (m), 915 (m), 858 (m), 842 (m), 790 (m), 637 (m), 484 (m) cm⁻¹; mass spectrum, m/e (all ^{35}Cl) 802 (M⁺). Anal. Calcd for $C_{26}Cl_{14}$: C, 38.5; Cl, 61.4. Found: C, 38.3; Cl, 61.2. (b) Perchloro-9,9'-bifluorenylidene (2): dark blue crystals, mp 358 °C dec (DSC); UV–vis (C_6H_{12}) 209 nm, 242, 292, 326 (sh), 449, 591 (ϵ 35 700, 46 000, 57 500, 10 100, 6020, 16 800); IR (KBr) 1362 (w), 1335 (s), 1315 (s), 1212 (s), 1120 (m), 840 (m), 800 (m), 642 (m) cm⁻¹; specific magnetic susceptibility, $\chi \times 10^6$, −0.505 (19 °C), −0.511 (−83 °C), −0.492 (−196 °C); mass spectrum, m/e (all ^{35}Cl) 872 (M⁺). Anal. Calcd for $C_{26}Cl_{16}$: C, 35.5; Cl, 64.5. Found: C, 35.3; Cl, 64.7. The main product was 2 and its yield decreased with temperature (from 84% to 69%) while that of 5 increased (from 5% to 25%). From 330 to 400 °C only 5 was obtained (88–78%).

(2) In Tetrachloroethylene. A mixture of 3 (0.300 g), powdered electrolytic copper (0.775 g), and tetrachloroethylene (10 mL) was refluxed for 18 h with stirring and under argon. The reaction mixture was filtered and evaporated to give a residue, which was passed through silica gel in CCl₄, yielding bifluorenylidene 2 (0.227 g, 88%).

Dehydrochlorination of Bifluorenyl 1. An aqueous saturated solution of NaOH (10 mL) was added to a solution of bifluorenyl 1 (0.040 g) in dioxane (40 mL), and the mixture was refluxed for 1 h with stirring. The blue reaction mixture was decanted, and the organic layer was diluted with CHCl₃, washed with water, dried, and evaporated. The resulting dark blue residue was identified as bifluorenylidene 2 (0.038 g, 99%).

Thermolysis of Bifluorenylidene 2. Bifluorenylidene 2 (0.100 g) was heated for 2 h at 360 °C under argon in a sealed glass tube. The resulting product was passed through silica gel in tetrachloroethylene, yielding acephenanthrylene 5 (0.086 g, 94%). The same thermolysis was repeated at 330 °C. Starting material was recovered (96%).

Reduction of Bifluorenylidene 2. Bifluorenylidene 2 (0.045 g) was hydrogenated for 70 h in a Parr apparatus in anhydrous tetrahydrofuran (40 mL) with Pt as catalyst. The resulting solution was filtered and evaporated to give a residue which by crystallization from hexane yielded 9H,9'H-hexadecachloro-9,9'-bifluorenyl (8) (0.043 g, 95%): white crystals, mp 317–318 °C; UV (CHCl₃) 273 (sh) nm, 309 (ϵ 24 700, 36 700); IR (KBr) 1520 (w), 1455 (w), 1390 (m), 1380 (w), 1340 (s), 1328 (s), 1242 (m), 1210 (m), 1192 (s), 1175 (s), 1168 (s), 870 (m), 844 (m), 820 (s), 812 (s), 760 (m), 641 (m) cm⁻¹; mass spectrum, m/e (all ^{35}Cl) 874 (M⁺). Anal. Calcd for $C_{26}H_2Cl_{16}$: C, 35.4; H, 0.2; Cl, 64.4. Found: C, 35.4; H, 0.2; Cl, 64.3.

Reaction of Bifluorenyl 8 with Cl₂. Dry Cl₂ was passed for 4 h through a refluxing solution of bifluorenyl 8 (0.040 g) in technical trichlorobenzene (4 mL) in the dark. Elimination of the solvent gave a residue which by TLC over silica gel in hexane afforded fluorene 3 (0.039 g, 84%).

Reaction of Bifluorenyl 1 with Cl₂. The preceding chlorination was repeated with bifluorenyl 1 (0.045 g) as starting material. Fluorene 3 (0.044 g, 85%) was also obtained.

Reactions of Bifluorenylidene 2 with Cl₂. (1) Dry Cl₂ was passed for 1 h through a solution of bifluorenylidene 2 (0.053 g) and I₂ (0.016 g) in CCl₄ (20 mL) in the dark, and the resulting solution was left undisturbed for 6 h. The resulting solution was washed with aqueous NaHSO₃ and water, dried, and evaporated. The residue, by several crystallizations from hexane, afforded starting bifluorenylidene 2 (0.014 g, 26% recovery) and fluorene 3 (0.028 g, 45%). This reaction was repeated with 94-h reaction time; fluorene 3 (81%) was isolated.

(2) Dry Cl₂ was passed for 30 h through a solution of bifluorenylidene 2 (0.490 g) in CCl₄ (150 mL) cooled at 5 °C, while

illuminating with a 600-W incandescent lamp at 20 cm. Evaporation of the solvent in vacuo gave a residue, which was crystallized from pentane, yielding perchloro-2,2',3,3'-tetrahydro-1H,1'H-9,9'-bifluorenyl (10) (0.420 g, 69%): orange-yellow solid, mp 280–282 °C dec; UV–vis (CHCl₃) 281 nm, 312 (sh), 356, 414 (sh) (ε 44 100, 22 100, 17 100, 3150); IR (KBr) 1580 (w), 1365 (s), 1315 (w), 1290 (s), 1275 (w), 1178 (m), 1114 (m), 1057 (m), 942 (m), 870 (m), 816 (m), 782 (m), 765 (m), 747 (s), 727 (m), 684 (m), 640 (m) cm⁻¹. Anal. Calcd for C₂₆Cl₂₂: C, 28.5; Cl, 71.5. Found: C, 28.6; Cl, 71.5.

Dechlorinations of Tetrahydrobifluorenyl 10. (1) With SnCl₂. A mixture of tetrahydrobifluorenyl 10 (1.102 g), SnCl₂·2H₂O (0.112 g), and ethyl ether (30 mL) was refluxed for 6 h under argon. The reaction mixture was treated with aqueous HCl, washed with water, dried, and evaporated. The residue was passed through silica gel in CCl₄, giving bifluorenylidene 2 (0.094 g, 99%).

(2) Thermal. Tetrahydrobifluorenyl 10 (0.042 g) was heated at 250 °C for 2 h under argon in a sealed glass tube. The resulting blue product was passed through silica gel in CCl₄ to give bifluorenylidene 2 (0.031 g, 92%).

Reaction of Acephenanthrylene 5 with Cl₂. Dry Cl₂ was passed for 24 h through a refluxing solution of acephenanthrylene 5 (0.110 g) in CCl₄, while illuminating with a 600-W incandescent lamp at 20 cm. The resulting solution was evaporated, and the residue was passed through silica gel in hexane and crystallized from hexane–CCl₄ to give perchloro-14b,14c-dihydrobenzo[e]-indeno[1,2,3-hi]acephenanthrylene (4) (0.109 g, 86%): orange-yellow solid, dec 367 °C (DSC); UV–vis (CCl₄) 260 nm, 300 (sh), 423, 485 (sh) (ε 50 000, 29 200, 3090, 11 900); IR (KBr) 1511 (w), 1402 (w), 1376 (w), 1320 (s), 1190 (m), 1160 (m), 915 (m), 860 (m), 844 (m), 785 (m), 630 (m), 500 (m), 480 (m) cm⁻¹; mass spectrum, m/e (all ³⁵Cl) 872 (M⁺). Anal. Calcd for C₂₆Cl₁₆: C, 35.5; Cl, 64.5. Found: C, 35.4; Cl, 64.5.

Dechlorinations of Dihydroacephenanthrylene 4. (1) With SnCl₂. This dechlorination was performed as in the case of tetrahydrobifluorenyl 10. Acephenanthrylene 5 (94%) was obtained.

(2) Thermal. This reaction was performed as in the case of tetrahydrobifluorenyl 10 but with a reaction temperature of 410 °C. Acephenanthrylene 5 (97%) was obtained.

Reaction of Bifluorenyl 8 with Oleum. A mixture of bifluorenyl 8 (0.040 g) and 20% oleum (15 mL) was heated at 100 °C for 24 h with stirring and in the dark. The resulting reaction mixture was poured onto cracked ice and extracted with CHCl₃. This organic extract was washed with water, dried, and evaporated to give a yellow solid, which was passed through silica gel in CHCl₃, yielding perchlorofluorenone⁶ (12) (0.038 g, 92%).

Reaction of Bifluorenyl 1 with Oleum. A mixture of bifluorenyl 1 (0.061 g) and 20% oleum (15 mL) was heated at 100 °C for 24 h with stirring and in the dark. The resulting reaction mixture was worked up as before to give fluorenone 12 (0.058 g, 92%).

Reaction of Bifluorenylidene 2 with Oleum. A mixture of bifluorenylidene 2 (0.120 g) and 20% oleum (60 mL) was heated at 100 °C for 24 h with stirring and in the dark. The resulting reaction mixture was worked up as before to give a brown residue (0.118 g), which was treated with refluxing CCl₄. The insoluble part was identified as acephenanthrylene 5 (0.014 g, 13%). The CCl₄ extract was submitted to column chromatography and TLC over silica gel in CCl₄–CHCl₃ mixtures to give the following. (a) Starting bifluorenylidene 2 (0.020 g, 16%). (b) Perchloro-9-(3-oxo-9-fluorenyl)-1-fluorenone (14) (0.012 g, 9.5%): dark red crystals, decomposing without melting around 250 °C (DSC); UV–vis (C₆H₁₂) 222 nm, 253, 278 (sh), 293, 353 (sh), 420 (sh), 450, 499 (ε 51 100, 37 200, 39 200, 44 600, 13 100, 11 700, 13 800, 11 600); IR (KBr) 1655 (s), 1571 (w), 1530 (m), 1500 (m), 1460 (s), 1320 (s), 1297 (s), 1245 (w), 1210 (s), 1183 (s), 1012 (s), 996 (m), 882 (m), 855 (m), 832 (m), 810 (m), 780 (m), 760 (m), 740 (m), 730 (m), 680 (m), 640 (m) cm⁻¹; mass spectrum, m/e (all ³⁵Cl) 834 (M⁺). Anal. Calcd for C₂₆Cl₁₄O₂: C, 37.1; Cl, 58.9. Found: C, 37.2; Cl, 58.9. (c) Perchloro-3,3'-dioxo-9,9'-bifluorenyl (13) (0.060 g, 50%): dark brown crystals, decomposing without melting around 330 °C (DSC); UV–vis (C₆H₁₂) 219 nm, 252, 276 (sh), 301, 343 (sh), 428, 449, 480 (sh) (ε 52 400, 30 000, 35 000, 56 000, 21 800, 17 300, 17 600, 6100); IR (KBr) 1655 (s), 1575 (w), 1534 (m), 1495 (w),

1375 (w), 1300 (m), 1180 (s), 1165 (m), 1120 (s), 1012 (s), 975 (m), 830 (m), 760 (m), 705 (m), 670 (m) cm⁻¹; mass spectrum, m/e (all ³⁵Cl) 834 (M⁺). Anal. Calcd for C₂₆Cl₁₄O₂: C, 37.1; Cl, 59.1. Found: C, 37.3; Cl, 59.2.

Reduction of Diketone 13 with HI. A mixture of diketone 13 (0.083 g), aqueous 57% HI (0.5 mL), I₂ (traces), and benzene (5 mL) was stirred for 24 h at room temperature. The resulting mixture was decanted, and the organic layer was washed with aqueous 50% H₃PO₂, with aqueous HCl, and with water, dried, and evaporated. The residue was crystallized from ether, giving trans(cis)-tetradecachloro-3,3'-dihydroxy-9,9'-bifluorenylidene (15) (0.080 g, 96%): dark blue crystals, mp 345–348 °C; UV–vis (C₆H₁₂) 240 nm, 290, 460, 591 (ε 58 400, 69 000, 7110, 21 000); IR (KBr) 3490 (w), 1530 (m), 1420 (m), 1345 (s), 1200 (s), 1170 (m), 960 (m), 890 (m), 835 (m), 664 (m) cm⁻¹; mass spectrum, m/e (all ³⁵Cl) 836 (M⁺). Anal. Calcd for C₂₆H₂Cl₁₄O₂: C, 37.1; H, 0.2; Cl, 59.1. Found: C, 36.9; H, 0.1; Cl, 59.0.

Oxidation of Diphenol 15 with K₃Fe(CN)₆. A mixture of diphenol 15 (0.048 g), K₃Fe(CN)₆ (0.300 g), Na₂CO₃ (0.300 g), benzene (10 mL), and water (10 mL) was stirred for 15 min. The organic layer was decanted, washed with water, dried, and evaporated. The residue was identified as diketone 13 (0.046 g, 96%).

Methylation of Diphenol 15. Diphenol 15 (0.095 g) was treated with an excess of an ethereal solution of CH₂N₂. Evaporation of the solvent gave a residue, which by crystallization from benzene gave trans(cis)-tetradecachloro-3,3'-dimethoxy-9,9'-bifluorenylidene (19) (0.096 g, 97%): dark blue crystals, decomposing without melting at 340 °C (DSC); UV–vis (C₆H₁₂) 225 nm (sh) 241, 270 (sh), 292, 460, 591 (ε 50 600, 58 500, 55 200, 69 700, 7150, 21 200; IR (KBr) 2930 (w), 2850 (w), 1545 (w), 1525 (w), 1450 (m), 1390 (m), 1343 (s), 1253 (w), 1227 (m), 1197 (m), 1143 (m), 1135 (m), 1040 (m), 1010 (m), 980 (m), 945 (m), 910 (m), 830 (m), 663 (m) cm⁻¹; ¹H NMR (CDCl₃) τ 5.97; mass spectrum, m/e (all ³⁵Cl) 864 (M⁺). Anal. Calcd for C₂₈H₆Cl₁₄O₂: C, 38.6; H, 0.7; Cl, 57.0. Found: C, 38.6; H, 0.7; Cl, 57.1.

Acetylation of Diphenol 15. A mixture of diphenol 15 (0.080 g) and acetic anhydride (50 mL) was refluxed for 4 h. Elimination of the solvent in vacuo gave a residue, which was dissolved in ether, washed with water, dried, and evaporated again. The resulting solid was purified by TLC over silica gel in CHCl₃, giving trans(cis)-3,3'-diacetoxytetradecachloro-9,9'-bifluorenylidene (17) (0.070 g, 70%): dark blue crystals, decomposing without melting at 290 °C; UV–vis (C₆H₁₂) 230 nm (sh), 239, 266 (sh), 286, 330 (sh), 455, 585 (ε 48 200, 55 600, 51 200, 67 800, 7440, 6670, 19 100); IR (KBr) 2915 (w), 2840 (w), 1785 (s), 1530 (w), 1478 (w), 1405 (w), 1340 (s), 1225 (m), 1198 (m), 1162 (s), 1140 (m), 1130 (m), 1008 (m), 905 (m), 850 (m), 843 (m), 832 (m), 700 (m), 675 (m) cm⁻¹; ¹H NMR (CDCl₃) τ 7.55; mass spectrum, m/e (all ³⁵Cl) 920 (M⁺). Anal. Calcd for C₃₀H₆Cl₁₄O₄: C, 38.8; H, 0.6; Cl, 53.6. Found: C, 38.8; H, 0.5; Cl, 53.8.

***trans*(*cis*)-1,3'-Diacetoxytetradecachloro-9,9'-bifluorenylidene (18).** The reduction of diketone 14 (0.091 g) was performed with HI as in the reduction of diketone 13. The crude diphenol 16 was acetylated with acetic anhydride as in the preceding paragraph, yielding diacetoxy compound 18 (0.049 g, 49%): dark blue crystals, mp 395–397 °C; UV–vis (CHCl₃) 305 nm, 448, 592 (ε 34 500, 550, 1305; IR (KBr) 2920 (w), 2850 (w), 1780 (s), 1411 (w), 1362 (s), 1346 (s), 1253 (m), 1182 (s), 1170 (s), 1118 (m), 1020 (m), 910 (m), 896 (m), 867 (m), 830 (m), 802 (m) cm⁻¹; ¹H NMR (CDCl₃) τ 7.60 (3 H), 8.05 (3 H); mass spectrum, m/e (all ³⁵Cl) 920 (M⁺). Anal. Calcd for C₃₀H₆Cl₁₄O₄: C, 38.8; H, 0.6; Cl, 53.6. Found: C, 38.9; H, 0.5; Cl, 53.7.