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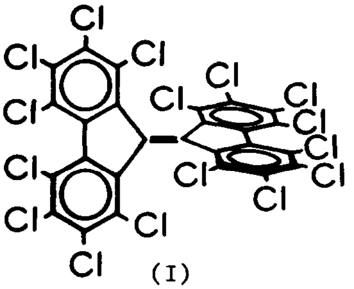
SYNTHESIS AND PROPERTIES OF PERCHLOROBI-9-FLUORENYLIDENE, AN EXCEPTIONALLY TWISTED ETHYLENE

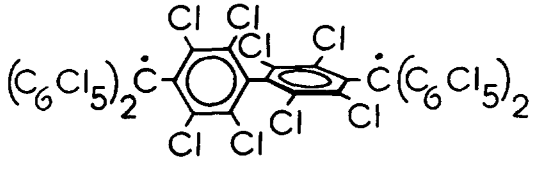
M. Ballester, J. Castañer, J. Riera and M. Camps
Instituto de Química Orgánica Aplicada (C.S.I.C.)
Jorge Girona Salgado, Barcelona, 34, Spain

Summary: The synthesis and properties of perchlorobi-9-fluorenylidene, a highly twisted ethylene, are reported. It is a diamagnetic chlorocarbon.

AS a continuation of the studies concerning steric distortion within the domain of perchloro-organic chemistry,[1] it was considered of significance to attempt the synthesis of a new chlorocarbon, the perchlorobi-9-fluorenylidene (I), and to study its properties and reactions. In fact its parent hydrocarbon, the bi-9-fluorenylidene, has given rise to numerous conflicting studies concerning its type of distortion.[2] However, it has been recently found that the latter hydrocarbon possesses a twisted (~42°) central (9,9') ethylene bond[3] on account of the repulsions between the 1 and 1', and the 8 and 8' substituents (hydrogens). In (I) -where these substituents are bulky chlorines- the angle of twisting should be much greater, as space-filling scale atomic models show. Therefore, the question of whether (I) would be a biradical was formulated.[+] It was previously found that the high twisting about the central bond in the "Chichibabin" chlorocarbon (II)[5] causes it to be a true, 100 per cent biradical, displaying two independent moieties in the electronic spectrum.



(I)



(II)

[+] Perchloro-9-phenylfluorenyl radical is a highly stable, completely disassociated carbon free radical.[4]

Perchlorobi-9-fluorenylidene (I), a dark-blue solid m.p. 358° (dec.) (DSC), is synthesized (84% yield) by dechlorination of perchlorofluorene (III)[5] with copper at 280°. UV-Vis. (C_6H_{12}): λ 209 (ε 35,700), 242 (46,000), 292 (57,500), 449 (6000), 591 (16,800) nm. MS: m/e 872 (M^+). Perchlorobenzo(e)indene(1,2,3--hi)acephenanthrylene (IV), an orange-yellow solid m.p. 420° (DSC) is a by-product (5%). UV-Vis. (CCl_4): 263 (54,600), 309 (38,000), 356 (17,400), 419 (22,900) nm. MS: m/e 802 (M^+). The latter is the major (88%) product at 330°. (I) is also converted into (IV) (94%) by mere heating at 350°.

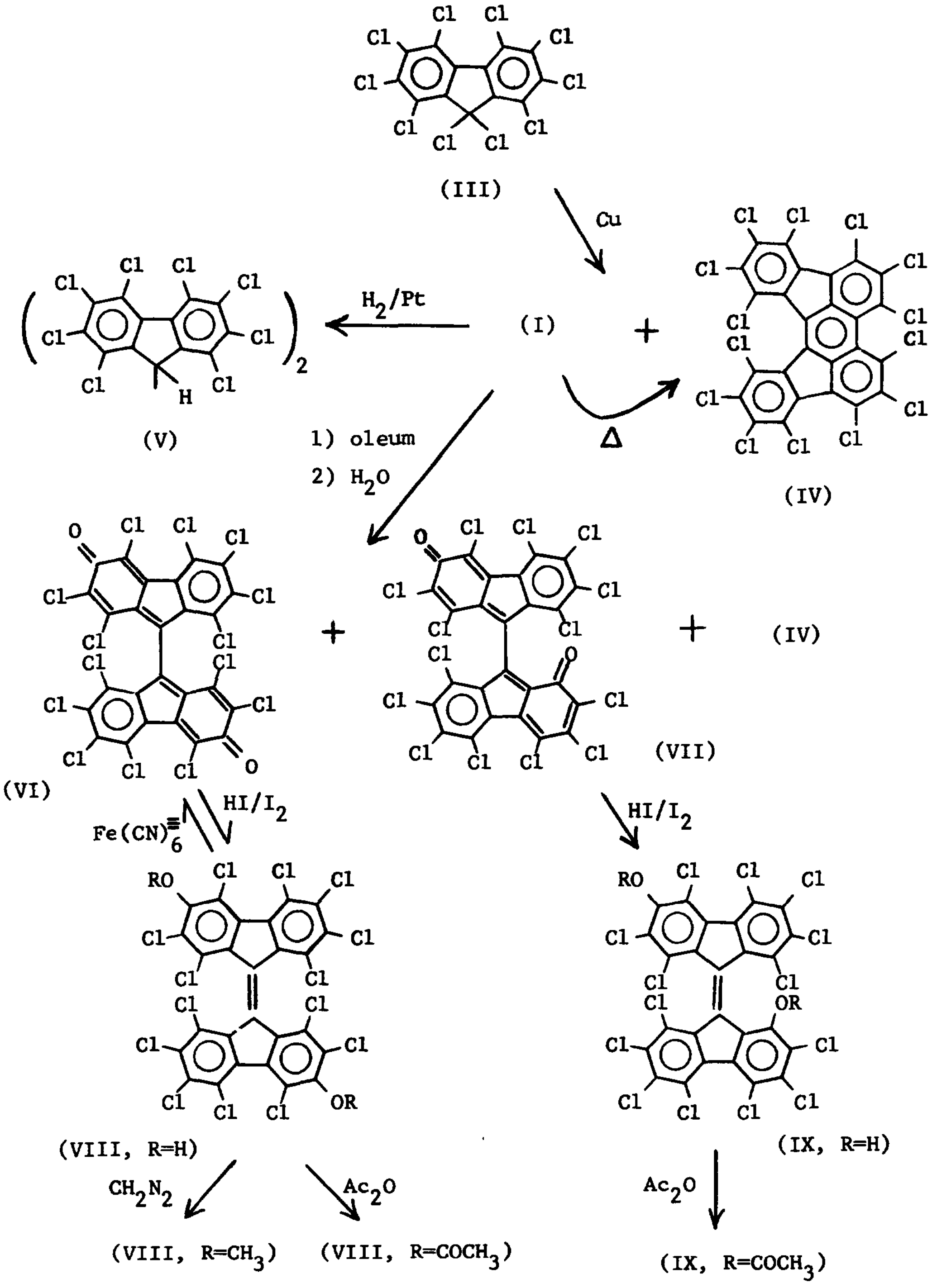
Ethylene (I) with H_2/Pt yields 9H,9'H-hexadecachlorobi-9-fluorenyl (V) (95%), a white solid m.p. 317-8°. UV-Vis. ($CHCl_3$): 309 (36,700) nm. MS: m/e 874 (M^+). X-ray analysis[6] shows that one moiety is on top of the other and rotated approximately 90° around the central C-C bond.

Treatment of (I) with 20% oleum at 100° gives a mixture of (IV) (12.6%), perchlorobi(3-oxofluoren-9-yl) (VI) (50.1%), dark-brown powder, dec. 330° (DSC), and perchloro-9-(3-oxofluoren-9-yl)-1-fluorenone (VII) (9.5%), red powder dec. 250° (DSC). Some (I) (16.5%) was recovered. Compound (VI) UV-Vis. (C_6H_{12}): 219 (52,400), 252 (30,000), 301 (56,200), 428 (17,300), 449 (17,600) nm. MS: m/e 834 (M^+). IR (KBr): 1655 cm^{-1}. Compound (VII) UV-Vis. (C_6H_{12}): 222 (51,100), 253 (37,200), 293 (44,600), 450 (13,800), 499 (11,600) nm. MS: m/e 834 (M^+). IR (KBr): 1655, 1642 cm^{-1}.

The reduction of ketone (VI) with HI/I_2 in benzene-water gives 3,3'-dihydroxytetradecachlorobi-9-fluorenylidene (VIII, R=H) (96%), a dark-blue powder m.p. 345-8°. UV-Vis. (C_6H_{12}): 240 (58,400), 290 (69,000), 450 (7110), 591 (21,000) nm. MS: m/e 836 (M^+).

Phenol (VIII, R=H) is methylated with CH_2N_2 in ether and acetylated with acetic anhydride to give 3,3'-dimethoxy- (VIII, $R=CH_3$) (98%) 3,3'-diacetoxytetradecachlorobi-9-fluorenylidene (VIII, $R=COCH_3$) (80%), both dark-blue powders dec. 340° and 290° (DSC), respectively. Compound (VIII, $R=CH_3$) UV-Vis. (C_6H_{12}): 241 (58,500), 292 (69,700), 460 (7150), 591 (21,200) nm. MS: m/e 864 (M^+). PMR ($CDCl_3$): τ 5,97 (s). Compound (VIII, $R=COCH_3$) UV-Vis. (C_6H_{12}): 239 (55,600), 286 (67,800), 455 (6700), 585 (19,100) nm. MS: m/e 920 (M^+). IR (KBr): 1785 cm^{-1}. PMR ($CDCl_3$): τ 7.55 (s). Phenol (VIII, R=H) reverts to (VI) (96%) by oxidation with potassium ferricyanide and Na_2CO_3 in benzene-water.

The reduction of (VII) under the same conditions as in (VI) gives 1,3'-dihydroxytetradecachlorobi-9-fluorenylidene (IX, R=H) which is not isolated but acetylated *in situ* as before, yielding (overall 49%) 1,3'-diacetoxytetradecachloro-


(III)
Cu
(I)
H_2/Pt
(V)
Δ
(IV)
1) oleum
2) H_2O
(VI)
(VII)
(IV)
$Fe(CN)_6^{\equiv}$
HI/I_2
HI/I_2
(VIII, R=H)
(IX, R=H)
CH_2N_2
Ac_2O
Ac_2O
(VIII, R=CH_3)
(VIII, R=$COCH_3$)
(IX, R=$COCH_3$)

bi-9-fluorenylidene (IX, R=$COCH_3$, dark blue powder m.p. 395-7°. UV-Vis. ($CHCl_3$): 239 (58,000), 305 (34,500), 448 (550), 592 (1300) nm. MS: m/e 920 (M^+). PMR ($CDCl_3$): τ 7.60 (*s*, 3H), 8.05 (*s*, 3H). IR (KBr): 1780, 1775 cm^{-1}.

All the new compounds give correct elemental analyses for C, H, and Cl. The structure of chlorocarbon (IV) has been assigned by comparison of its UV-Vis. spectrum with those of perchlorophenanthrene[7] and its parent hydrocarbon. The latter can be obtained analogously by pyrolysis of fluorene.[8] Assignments for ketones (VI) and (VII) are based on the data here reported.

Pure (I) does not show any EPR signal in solution, and magnetic susceptibility measurements indicate it is a diamagnetic compound.* Therefore, in spite of its being a highly twisted molecule, (I) is a singlet. This might be due to resonance in the biradical form being limited to two independent electrons, one in each molecular moiety, while resonance in the singlet form is extended to two paired electrons over the whole molecule. The microcrystalline character of chlorocarbon (I) does not permit X-ray measurements to be carried out on it.

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* Specific magnetic susceptibilities (x 10^6) at 292, 190 and 77°: -0,505, -0,511, and -0,492 e.m.u.

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