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1,1′,3,3′,6,6′,8,8′-Octachloro-9,9′-bifluorenylidene and Perchloro-9,9′-bifluorenylidene, Two Exceedingly Twisted Ethylenes

Elies Molins,* Carlos Miravitlles, Enrique Espinosa, and Manuel Ballester*,†

Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari de Bellaterra, 08193 Cerdanyola, Spain

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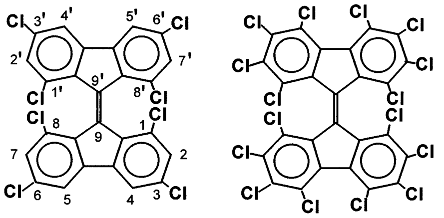
The syntheses of 1,1′,3,3′,6,6′,8,8′-octachloro-9,9′-bifluorenylidene (**1**), its precursors, and the byproduct 3,3′,5,5′-tetrachloro-4-(trichloromethyl)biphenyl (**5**) are described. Accurate structural X-ray data on **1** and on perchloro-9,9′-bifluorenylidene (**2**) are reported and discussed. Because of chlorine overcrowding, the dihedral angles between their two identical fluorenylidene moieties are abnormally large, the central-ethylene twist angles being 55 and 66°, respectively. Significant out-of-plane carbon−chlorine bond bending is likewise exhibited. Their ESR spectra and magnetic measurements prove that they are singlet species. The exceptionally large bathochromic displacements of their UV−vis absorption spectrum with respect to that of their parent hydrocarbon are mainly attributed to bond bending and molecular warping.

Introduction

How far an ethylene double bond could be twisted without becoming a single bond is a classical fundamental question including the conversion of a singlet ground state to a triplet (a diradical). It was argued that the synthesis and study of certain highly chlorinated ethylenes could afford some pertinent information on that subject. In fact, perchloro-organic chemistry is a domain that has often led to the discovery and allowed the study of some significant intra- and intermolecular structural, kinetic, spectral, electronic, and electrochemical phenomena due to the bulkiness of chlorine.[1,2]

Two extreme electronic conformations could be drawn for the perchlorinated “Chichibabin hydrocarbon” (perchlorotetraphenylbi-*p*-tolyl): the singlet, $(C_6Cl_5)_2C{=}C_6Cl_4{=}C_6Cl_4{=}C(C_6Cl_5)_2$, with a “flat” central ethylene bond, and the diradical $(C_6Cl_5)_2C{\bullet}{-}C_6Cl_4{-}C_6Cl_4{-}C{\bullet}(C_6Cl_5)_2$, with a central single bond. Magnetic susceptibility, ESR, and UV−vis data showed that this chlorocarbon is a diradical, because of the steric repulsions among its chlorine substituents.[2,3]

Unsubstituted 9,9′-bifluorenylidene, $C_{13}H_8{=}C_{13}H_8$, is a diamagnetic hydrocarbon with a highly twisted (~40°) central ethylene bond caused by steric repulsions between its two identical moieties.[4] Therefore, substitution of its 1,8,1′,8′ hydrogens by chlorines to give 1,1′,3,3′,6,6′,8,8′-octachloro-9,9′-bifluorenylidene (**1**) and perchloro-9,9′-bifluorenylidene (**2**) should greatly increase the twist. Therefore, it might be expected that, in the ground state, these compounds would be diradicals, as is the “perchloro-Chichibabin”.



1　　**2**

FIGURE 1. Flat structures of **1** and **2**.

Flat structures for bifluorenylidenes **1** and **2**, including atom and position numbers, are shown in Figure 1. They exhibit forbidding repulsions between 1/8′ and 1′/8 chlorine pairs.

Results and Discussion

The synthesis of bifluorenylidene **1** was carried out in two steps (Scheme 1): Friedel−Crafts condensation of

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* To whom correspondence should be addressed. E-mail: (E.M.) elies.molins@icmab.es.

† Alternative address: Turó de Monterols, 7.08006 Barcelona, Spain.

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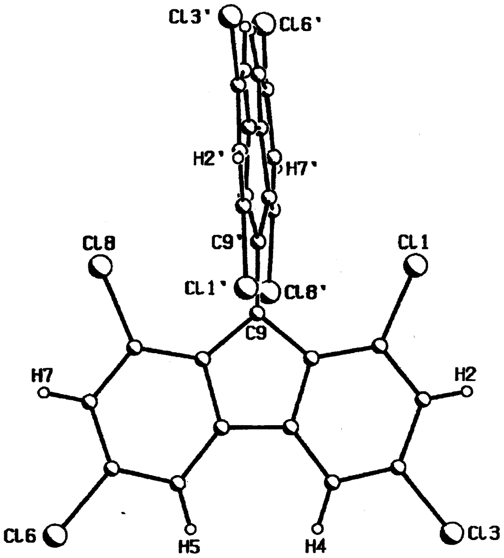


FIGURE 2. Perspective view of **1**.

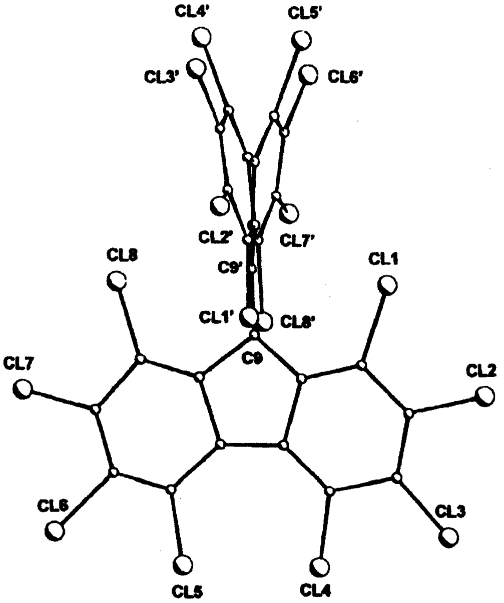
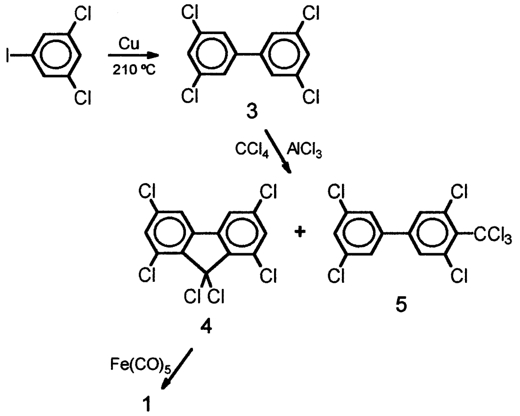


FIGURE 3. Perspective view of **2**.

3,3′,5,5′-tetrachlorobiphenyl (**3**) with carbon tetrachloride, to give 1,3,6,8,9,9′-hexachlorofluorene (**4**) (31% yield), and reductocondensation of the latter with copper dust in tetrachloroethylene (14% yield), $SnCl_2$, in dioxane (51%), or $Fe(CO)_5$, in benzene (75%). In the first case, 1,1′,3,3′,5,5′-tetrachloro-4-(trichloromethyl)biphenyl (**5**; 16%) is also formed. **2** was prepared as reported.[5]

X-ray Molecular Structures. Preliminary, unsatisfactory structural data on bifluorenylidene **2** has been reported.[6] Accurate data on both **1** and **2**, including atomic coordinates (with esd's), bond lengths, and bond angles are now available (Supporting Information). Perspective views for the molecules of **1** and **2** are displayed in Figures 2 and 3.

SCHEME 1. Synthesis of 1



The major structural feature of bifluorenylidenes **1** and **2** is the colossal torsion of their C9−C9′ ethylene bond, the twist angle being 55° and 66°, respectively. As far as the authors know, **2** *displays the highest ethylene bond twist ever reported due exclusively to intramolecular steric repulsions*. Also, this bond is unusually long (1.39 Å) for a double bond (cf. tetrachloroethylene, 1.29 Å.[7]). In hexachloroethane, the C−C single bond length is 1.578 Å.[8] In their parent hydrocarbon (9,9′-bifluorenylidene), it is (1.33 Å).[9]

That bond in **1** (1.392 Å) appears to be longer than in **2** (1.36 Å; see Supporting Information Tables S3 and S4). This paradox vanishes if it is taken into account that for large twist angles (week p-orbital overlap) substantial twist angle changes, such as going from **1** to **2**, would cause minor changes in the bond length.

Therefore, an underlying steric effect on the bond length may become dominant: the F-strain (front-strain, H. C. Brown). Consequently, because of chlorine buttressing, the "frontal" repulsion between the two bifluorenylidene moieties in **2** should be larger than in **1** and the C9−C9′ bond longer, as found. In fact, F-strain is a major factor in single bond dissociation leading to free radicals.[2]

The statistical error in the C9−C9′ bond length difference between **1** and **2** is 1 standard deviation. Therefore, although the above-given interpretation is reasonable and consistent with the data, nevertheless it is not firmly supported.

As anticipated, the additional ethylene bond torsion in **1** and **2** observed arises from the severe steric compression within chlorine pairs Cl1/Cl8′ and Cl1′/Cl8 (Figures 2 and 3), the contact distances being 3.66 and 3.79 Å, respectively. Torsion in **2** is greater than in **1** partly on account of the *buttressing* of chlorines 8 and 8′ with their vicinal chlorines (2,7 and 2′,7′), which enhance their effective size. It is pointed out that highly perchlorinated free radicals, such as perchlorotriphenylmethyl, owe their unique chemical inertness partly to buttressing by chlorine by enhancing the steric shielding of the sites where most of the *spin* density resides.[10]

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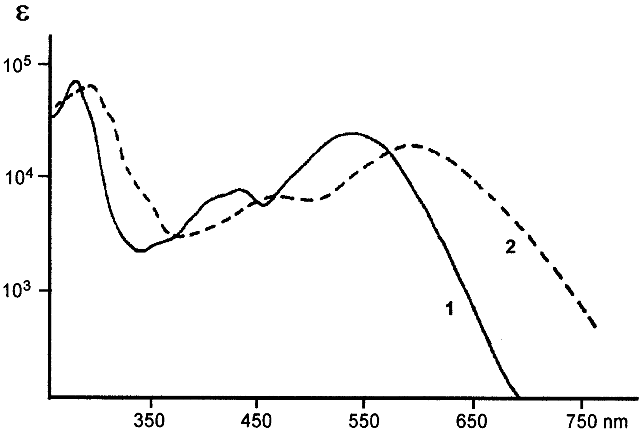

FIGURE 4. UV−vis spectra of **1** (—) and **2** (---) in cyclohexane.

Steric repulsions displace chlorines 1, 1′, 8, and 8′ out of the mean plane of the hexagonal (benzenoid) rings to which they are attached (0.10 and 0.31 Å and 0.16 and 0.27 Å for **1** and **2**, respectively).

In chlorocarbon **2**, a second major structural feature is the strong repulsions between chlorine pairs 4/5 and 4′/5′ (Figure 3), which force them out of the mean plane of each molecular moiety by 0.31 and 0.52 Å, causing warping of the latter by a 14° dihedral angle.

In bifluorenylidene **1**, unsubstituted in positions 4, 5, 4′, and 5′, the warping angle within each molecular moiety is about 3° instead; i.e., their two hexagonal rings are nearly coplanar.

The structures of some "overcrowded" perchlorocompounds, including bifluorenylidene **2**, had been reviewed and discussed by Herbstein.[11] As noted above, the reported X-ray data on **2** were not accurate.

Ultraviolet−Visible Spectra. Bifluorenylidenes **1** and **2** form violet and blue crystals, respectively. In cyclohexane, their absorption maxima are at 536 and 600 nm, respectively (Figure 4). Therefore, substitution of the eight hydrogens in **1** by chlorine to give **2** causes a 64 nm shift. This effect is due to (a) the usual substitution bathochromic effect of chlorine, (b) the out-of-plane bending of the C−Cl bonds by the added vicinal chlorines, and (c) the enhanced warping caused by chlorine buttressing. Factors b and c decrease the bonding character of the ground state so that they override the expected hypsochromic shift inherent in the central-ethylene bond twist (steric inhibition of resonance between the two fluorenylidene moieties).

Great bathochromic shifts are also encountered in other perchloroaromatic compounds.[2] As a dramatic example, while α,α,α,α′,α′,α′,2,5- and α,α,α′,α′,2,3,5,6-octachloro-*p*-xylenes are colorless, highly distorted perchloro-*p*-xylene, *p*-$Cl_3C-C_6Cl_4-CCl_3$, is yellow due to a huge (50 nm) bathochromic shift of its UV−vis ^1L_b benzenoid band.[2] This colossal effect is caused by *just two additional chlorines* (expected shift <10 nm).

Magnetism. **1**[5] and **2** are diamagnetic (**2**, $\chi \times 10^6$ (19 °C), −0.505). They display no ESR signal.

Experimental Section

3,3′,5,5′-Tetrachlorobiphenyl (3). Following the procedure reported by Van Roosmalen,[12] this compound was prepared by the self-condensation of 3,5-dichloroiodobenzene with copper: mp 166−8 °C (recrystallized from cyclohexane) (lit.[12] mp 162 °C); ^{1}H NMR, see ref 13; IR (KBr), 3085 (w), 1730 (w), 1587 (s), 1557 (s), 1433 (m), 1412 (m), 1370 (m), 1120 (s), 1098 (m), 842 (s), 797 (s), 663 (s) cm^{-1}.

Reaction of Biphenyl 3 with Carbon Tetrachloride. 1,3,6,8,9,9-Hexachlorofluorene (4). A mixture of biphenyl **3** (7.89 g), anhydrous $AlCl_3$ (10.0 g), and CCl_4 (250 mL) was refluxed (6 h), cooled, treated with water (50 mL), and extracted with $CHCl_3$. The resulting solution was washed with water, dried, evaporated, and chromatographed (silica gel, hexane). The solid residue was recrystallized from hexane, giving (a) **4** and (b) 3,3′,5,5′-Tetrachloro-4-(trichloromethyl)-biphenyl (**5**). Data for **4**: colorless needles (3.172 g, 31%); mp 228−30 °C; IR (KBr) 3090 (w), 1728 (w), 1602 (s), 1578 (s), 1570 (s), 1445 (m), 1370 (m), 1280 (m), 1205 (m), 1178 (s), 1128 (s), 1114 (s), 1080 (s), 918 (m), 890 (s), 858 (s), 800 (s), 680 (s), 550 (m) cm^{-1}; UV (C_6H_{12}) λ 240 (sh), 247, 255, 285, 312 (sh) nm (ϵ 29300, 47000, 53300, 6550, 1250); ^{1}H NMR (C_3D_6O), δ 7.440 (d, 2H, $J_H = 1.8$ Hz), 7.484 (d, 2H, $J_H = 1.8$ Hz). Anal. Calcd. for $C_{13}H_4Cl_6$: C, 41.8; H, 1.1; Cl, 57.1. Found: C, 42.1; H, 0.9; Cl, 57.0. Data for **5**: colorless crystals (1.814 g, 16%), mp 108−10 °C (from cyclohexane); IR (KBr), 3075 (w), 1745 (w), 1590 (s), 1570 (s), 1535 (s), 1363 (s), 1210 (s), 1180 (m), 1137 (m), 1093 (m), 1072 (m), 910 (m), 855 (s), 830 (s), 800 (s), 775 (s), 690 (s), 680 (s) cm^{-1}; UV (C_6H_{12}) λ 266 nm (ϵ 15120); ^{1}H NMR (C_3D_6O) δ 7.568 (t, 1 *p*-H, $J_H = 1.9$ Hz), 7.828 (d, 2 *o*-H, $J_H = 1.9$ Hz), 7.971 (s, 2 *o*-H). Anal. Calcd. for $C_{13}H_5C_{l7}$: C, 38.1; H, 1.2; Cl, 60.7. Found: C, 38.1; H, 1.2; Cl, 60.5.

A large amount of a resinous mixture was obtained, fluorene **4** being its major component (IR and UV spectra).

Reductocondensations of Fluorene 4. The synthesis of bifluorenylidene **1** has been effected in various ways, using preferentially $Fe(CO)_5$ as the reductocondensation agent (75% yield) (Scheme 1). It is a dark-violet, infusible (up to 350 °C) solid, being characterized by elemental analyses, IR, UV−vis, and MS.

(a) Synthesis of 1 with Copper Dust, in Tetrachloroethylene. A mixture of fluorene **4** (0.104 g), electrolytic copper dust (0.160 g), and anhydrous tetrachloroethylene (15 mL) was refluxed (24 h) with stirring under nitrogen. The resulting mixture was filtered and evaporated, giving, after chromatography (silica gel, CCl_4), bifluorenylidene **1** (0.012 g, 14%): infusible crystals (up to 350 °C); IR (KBr) 3185 (w), 1600 (s), 1585 (s), 1550 (s), 1437 (m), 1405 (s), 1368 (m), 1322 (m), 1280 (m), 1110 (s), 1088 (s), 860 (m), 850 (m), 827 (s) cm^{-1}; UV−vis λ 277, 408 (sh), 428, 536 nm (ϵ 61650, 5600, 5860, 22900); MS (all ^{35}Cl)[14] *m*/*e* (relative intensity), 600 (100, M$^+$), 530 (24, M$^+$ $^-$ 2Cl), 460 (23%, M$^+$ − 4Cl). Anal. Calcd for $C_{26}H_8Cl_8$: C, 51.7; H, 1.3; Cl, 47.0. Found: C, 51.5; H, 1.4; Cl, 47.0.

(b) Synthesis of 1 with Copper Dust, without Solvent. A mixture of fluorene **4** (0.100 g) and electrolytic Cu dust (0.065 g) was heated, first under vacuum at 120 °C and next under argon at 280 °C (10 min). The resulting mass was extracted with CCl_4. No identifiable substance was isolated.

(c) Synthesis of 1 with $Fe(CO)_5$, in Benzene. A solution of fluorene **4** (0.100 g) and $Fe(CO)_5$ (0.3 mL) in anhydrous benzene (15 mL) was refluxed (5 h) under nitrogen. The resulting solution was treated with I_2, to destroy the excess $Fe(CO)_5$, washed with aq $NaHSO_3$ and diluted HCl, dried, and evaporated. The residue was purified as before, yielding bifluorenylidene **1** (0.0629, 75%), identified by IR and UV−vis spectra.

(d) Synthesis of 1 with $SnCl_2$, in Dioxane. A mixture of fluorene **4** (0. 101 g) and $SnCl_2 \cdot 2H_2O$ (0.066 g) in anhydrous dioxane (10 mL) was refluxed with stirring (24 h), under

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[14] All peak clusters show isotopic distributions agreeing with the number of chlorines.

nitrogen. The resulting mass was diluted with aq HCl and extracted with CCl_4, and the solution was washed with water, dried, and evaporated to dryness. Only starting fluorene **4** (0.052 g, 51%) was isolated.

Perchloro-9,9′-bifluorenylidene (2). This chlorocarbon was prepared as described.[5]

X-ray Crystal Data.

Bifluorenylidene 1. $C_{26}H_8Cl_8$, $M_f = 603.7$, monoclinic, $P2_1/a$, $a = 11.390(2)$ Å, $b = 15.754(3)$ Å, $c = 13.788(4)$ Å, $\beta = 107.91(9)°$, $V = 2354.2(9)$ Å^3, $Z = 4$, $D_e = 1.704$ g cm^{-3}, radiation Mo Kα ($\lambda = 0.71073$ Å), $\mu = 9.8$ cm^{-1}, $F(000) = 1200$, $T = 21(1)$ °C, $R = 0.035$. Number of unique reflections 3280.

The resolution of its structure has been performed by a sequence of direct methods strategy[15] with partial refinement of chlorine positions and difference Fourier synthesis. The refinement of the structure was carried out by anisotropic full-matrix least-squares methods[15] up to $R = 0.035$. Atomic coordinates, bond lengths, and bond angles are available (Supporting Information).

Perchloro-9,9′-bifluorenylidene (2). $C_{26}Cl_{16}$, $M_f = 879.4$, monoclinic, $P2_1/c$, $a = 11.606(2)$ Å, $b = 21.144(5)$ Å, $c = 13.944(3)$ Å, $\beta = 104.92(3)°$, $V = 3306.5$ Å^3, $Z = 4$, $D_e = 1.770$ g cm^{-3}, radiation Mo Kα ($\lambda = 0.71073$ Å), $\mu = 13.6$ cm^{-1}, $F(000) = 1336$, $T = 21(1)$ °C, $R = 0.078$. Number of unique reflections 2820.

Resolution of the structure was not straightforward because of the somewhat defective quality of the crystals available. A sequence of direct methods strategy[15] with partial refinements of the chlorine positions and difference Fourier synthesis has afforded the complete model of the molecule. Refinement of the structure was performed by anisotropic full-matrix least-squares methods[15] up to a $R = 0.08$.[15] Difference Fourier synthesis shows peaks that might be attributed to a disordered tetrachloroethylene (solvent) molecule. Nevertheless, no disorder model could be established. Scattering factors have been taken from the *International Tables for X-ray Crystalography*.[16] Atomic coordinates, bond lengths, and bond angles are available (Supporting Information).

Conclusions

Because of their severe intramolecular steric interactions, bifluorenylidenes **1** and **2** display three remarkable features: (a) X-ray evidence of colossal torsions at their central ethylene bond, (b) ESR and magnetic susceptibility that show, despite their large torsion, that they are not diradicals as in related biphenyl structures, (c) UV−vis spectra of **2** that indicate that the overall bathochromic displacements due to the numerous molecular out-of-plane C−Cl bendings and aromatic-ring warpings override the underlying hypsochromic shift associated their huge central-ethylene bond twist (steric inhibition of resonance between their two molecular moieties).

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Supporting Information Available: Atomic coordinates, bond lengths, and bond angles for bifluorenes **1** and **2** (Tables S1, S3, S5 and S2, S4, S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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