CRYSTAL STRUCTURE OF HEXADECACHLORO-9,9'-BIFLUORENYLIDENE: THE TWISTEST CARBON DOUBLE BOND

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INTRODUCTION

For several years we have been undertaken the systematic structural study of overcrowded chlorinated aromatic compounds (Miravitlles, Solans, Germain, Declercq, 1979; Galí, Miravitlles, Solans, Font-Altaba, 1979; Solans, Galí, Miravitlles, Font-Altaba, 1978; Galí, Solans, Miravitlles, Plana, 1978; Galí et al., 1978; Galí et al., 1978; Miravitlles et al., 1985; Molins, Rius, Miravitlles, 1984). Due to its own bulkiness, chlorine atoms often produce strong steric hindrance in organic molecules. These hindrances can only be relaxed assuming extreme molecular conformations, sometimes at the border of molecular stability. This is an important source of information about the elasticity and interatomic potentials in stable configurations far from the usual ones. Otherwise, hydrogen substitution by halogen atoms is a natural way to enhance steric restraints: chlorine atom has three times the volume of an hydrogen atom and about the same of methyl groups.

EXPERIMENTAL

Some prismatic dark blue crystals of hexadecachloro-9,9'-bifluorenylidene were used for several X-ray data collections on an Enraf-Nonius CAD4 diffractometer. Unit cell were determined by centering 25 high angle reflections

and refining the orientation matrix and unit cell parameters by least-squares. A summary of crystal data measurements are shown in Table 1 for the best crystal. The intensities were corrected for Lorentz and polarization effects. Resolution of the structure was difficult because of not too good quality of crystals. A sequence of direct methods strategy (MULTAN 11/82: Main et al., 1982) with partial refinement chlorine positions and difference Fourier synthesis finally gives the complete model of the molecule.

Table 1. Crystal and data measurement parameters.

SUMMARY OF X-RAY ANALYSIS

A/ Crystal Parameters at 21 °C

$C_{26}Cl_{16}$	Mol wt = 980
a = 11.606 (2)	Space group: $P2_1/c$
b = 21.144 (5)	Z = 4
c = 13.944 (3) Å	d (calcd) = 1.77 g/cm^3
	μ (calcd) = 13.6 cm^{-1}
β = 104.92 (3) °	size = 0.15 x 0.23 x 0.37 mm.
V = 3306.5 Å^3	

B/ Data Measurement Parameters

Radiation	Mo Kα (λ = 0.71069 Å)
N. of collected reflections	2820
N. of observed reflections	1336 (I > 2.5 σ (I))
Data collection range (2θ)	2-47 °
Scan method	ω-2θ
Range of hkl	-13-13; 0-23; 0-15
Standard reflection decay	1.8 %

C/ Data Refinement Parameters

N. of refined parameters	379
R factor	0.080
R_w	0.078
w = $1/(\sigma^2(F) + 0.000228\ F^2)$	

Refinement of the structure was performed by anisotropic full-matrix least-squares methods (SHELX-76: Sheldrick, 1976) up to a final R of 0.08. Difference Fourier synthesis showed peaks which might be attributed to a disordered tetrachloroethylene solvent molecule, but no disorder model could be established. Scattering factors were taken from International Tables for X-ray Crystallography. Atomic fractional coordinates and equivalent temperature

factors are listed in Table 2. Bond lenghts and bond angles are given in Tables 3 and 4.

Table 2. Fractional atomic coordinates (x104) with their e.s.d.'s and equivalent temperature factors.

	X/A		Y/B		Z/C	
CL3	8180	(8)	3433	(4)	1900	(9)
CL4	5803	(9)	3201	(5)	2375	(10)
CL5	4594	(8)	1888	(5)	2029	(9)
CL6	5801	(7)	800	(4)	1219	(8)
CL9	6323	(7)	511	(4)	−792	(8)
CL10	8291	(8)	−99	(4)	−1542	(9)
CL11	10764	(8)	538	(4)	−1196	(9)
CL12	11320	(7)	1752	(4)	40	(9)
CL3'	10868	(7)	1536	(4)	2512	(8)
CL4'	13101	(8)	1876	(5)	4168	(9)
CL5'	14189	(8)	3206	(5)	4268	(8)
CL6'	13110	(7)	4209	(4)	2755	(9)
CL9'	12705	(8)	4397	(4)	491	(9)
CL10	10786	(9)	4936	(5)	−1215	(9)
CL11	8322	(9)	4310	(5)	−1880	(9)
CL12	7758	(7)	3120	(5)	−839	(8)
C1	9074	(22)	2240	(13)	790	(26)
C2	7894	(23)	2281	(13)	1067	(29)
C3	7456	(25)	2746	(15)	1540	(26)
C4	6381	(25)	2621	(15)	1808	(25)
C5	5840	(27)	2042	(17)	1583	(30)
C7	7289	(25)	1681	(14)	757	(27)
C6	6337	(25)	1556	(18)	1194	(31)
C8	8008	(25)	1297	(14)	308	(26)
C9	7746	(23)	810	(12)	−337	(24)
C10	8612	(31)	541	(15)	−856	(30)
C11	9725	(25)	841	(15)	−631	(24)
C12	9980	(27)	1360	(16)	11	(30)
C13	9155	(25)	1607	(13)	437	(24)
C1'	9951	(23)	2685	(14)	1044	(25)
C2'	11121	(21)	2665	(13)	1705	(21)
C3'	11546	(25)	2236	(13)	2426	(27)
C4'	12535	(26)	2409	(18)	3269	(28)
C5'	13009	(26)	2999	(16)	3260	(26)
C6'	12617	(25)	3456	(15)	2511	(27)
C7'	11710	(25)	3299	(13)	1721	(26)
C8'	10983	(26)	3620	(14)	908	(27)
C9'	11267	(25)	4102	(14)	349	(32)
C10'	10413	(30)	4332	(16)	−539	(29)
C11'	9318	(27)	4039	(16)	−828	(25)
C12'	9069	(27)	3543	(15)	−269	(29)
C13'	9898	(24)	3310	(14)	519	(26)

Table 3. Bond lenghts in Å with e.s.d.'s.

C3 —CL3	1.69	(3)	C13 -C1 -C2	106	(3)
C4 —CL4	1.69	(3)	C1' -C1 -C2	124	(3)
C5 —CL5	1.74	(4)	C1' -C1 -C13	128	(3)
C6 —CL6	1.72	(3)	C3 -C2 -C1	130	(3)
C9 —CL9	1.73	(3)	C7 -C2 -C1	106	(3)
C10 —CL10	1.64	(3)	C7 -C2 -C3	124	(3)
C11 —CL11	1.72	(3)	C2 -C3 -CL3	123	(2)
C12 —CL12	1.75	(3)	C4 -C3 -CL3	119	(3)
C3' —CL3'	1.70	(3)	C4 -C3 -C2	117	(3)
C4' —CL4'	1.69	(3)	C3 -C4 -CL4	118	(3)
C5' —CL5'	1.75	(3)	C5 -C4 -CL4	123	(3)
C6' —CL6'	1.70	(3)	C5 -C4 -C3	119	(3)
C9' —CL9'	1.74	(3)	C4 -C5 -CL5	117	(3)
C10'—CL10	1.71	(4)	C6 -C5 -CL5	118	(3)
C11'—CL11	1.72	(3)	C6 -C5 -C4	123	(3)
C12'—CL12	1.77	(3)	C6 -C7 -C2	114	(3)
C2 —C1	1.52	(4)	C8 -C7 -C2	110	(3)
C13 —C1	1.44	(4)	C8 -C7 -C6	134	(3)
C1' —C1	1.36	(3)	C5 -C6 -CL6	120	(3)
C3 —C2	1.35	(4)	C7 -C6 -CL6	120	(3)
C7 —C2	1.46	(4)	C7 -C6 -C5	119	(3)
C4 —C3	1.42	(4)	C9 -C8 -C7	132	(3)
C5 —C4	1.37	(4)	C13 -C8 -C7	108	(3)
C6 —C5	1.36	(4)	C13 -C8 -C9	118	(3)
C6 —C7	1.42	(4)	C8 -C9 -CL9	124	(2)
C8 —C7	1.42	(4)	C10 -C9 -CL9	112	(2)
C9 —C8	1.35	(4)	C10 -C9 -C8	123	(3)
C13 —C8	1.45	(4)	C9 -C10 -CL10	121	(3)
C10 —C9	1.49	(4)	C11 -C10 -CL10	124	(3)
C11 —C10	1.40	(4)	C11 -C10 -C9	115	(3)
C12 —C11	1.40	(4)	C10 -C11 -CL11	115	(3)
C13 —C12	1.35	(4)	C12 -C11 -CL11	122	(3)
C2' —C1'	1.43	(3)	C12 -C11 -C10	122	(3)
C13'—C1'	1.50	(4)	C11 -C12 -CL12	115	(3)
C3' —C2'	1.35	(3)	C13 -C12 -CL12	122	(3)
C7' —C2'	1.50	(3)	C13 -C12 -C11·	122	(3)
C4' —C3'	1.46	(4)	C8 -C13 -C1	110	(3)
C5' —C4'	1.36	(4)	C12 -C13 -C1	129	(3)
C6' —C5'	1.41	(4)	C12 -C13 -C8	120	(3)
C7' —C6'	1.35	(4)	C2' -C1' -C1	132	(3)
C8' —C7'	1.40	(4)	C13'-C1' -C1	123	(3)
C9' —C8'	1.37	(4)	C13'-C1' -C2'	105	(2)
C13'—C8'	1.40	(3)	C3' -C2' -C1'	127	(3)
C10'—C9'	1.46	(4)	C7' -C2' -C1'	110	(2)
C11'—C10'	1.38	(4)	C7' -C2' -C3'	121	(2)
C12'—C11'	1.38	(4)	C2' -C3' -CL3'	123	(2)
C13'—C12'	1.35	(4)	C4' -C3' -CL3'	116	(3)

Table 4. Bond angles in ° with e.s.d.'s.

C4'-C3'-C2'	119	(3)
C3'-C4'-CL4'	120	(3)
C5'-C4'-CL4'	122	(3)
C5'-C4'-C3'	117	(3)
C4'-C5'-CL5'	117	(3)
C6'-C5'-CL5'	117	(2)
C6'-C5'-C4'	125	(3)
C5'-C6'-CL6'	118	(2)
C7'-C6'-CL6'	123	(3)
C7'-C6'-C5'	118	(3)
C6'-C7'-C2'	119	(3)
C8'-C7'-C2'	104	(2)
C8'-C7'-C6'	136	(3)
C9'-C8'-C7'	129	(3)
C13'-C8'-C7'	112	(3)
C13'-C8'-C9'	117	(3)
C8'-C9'-CL9'	124	(2)
C10'-C9'-CL9'	114	(3)
C10'-C9'-C8'	121	(3)
C9'-C10'-CL10	120	(3)
C11'-C10'-CL10	121	(3)
C11'-C10'-C9'	118	(3)
C10'-C11'-CL11	118	(3)
C12'-C11'-CL11	123	(3)
C12'-C11'-C10'	119	(3)
C11'-C12'-CL12	114	(3)
C13'-C12'-CL12	122	(3)
C13'-C12'-C11'	122	(3)
C8'-C13'-C1'	108	(2)
C12'-C13'-C1'	130	(3)
C12'-C13'-C8'	122	(3)

RESULTS AND DISCUSSION

Perspective views of the molecule are shown in Figure 1. The C1-C1' central bond distance is 1.36 (1) Å corresponding to a double bond. In α- and β-modifications of 9,9'-bifluorenylidene (BFL) and in their complexes with perylene and perylidene (Jung-Si Lee and S.C. Nyburg, 1985) this double bond distance has the same value. Similar compounds but not completely perchlorinated, 9H-Heptadecachloro-9,9'-bifluorenyl and 9H, 9'H hexadecachloro-9,9'-bifluorenyl, show a sp_3 hybridation at C1 and C1' (Solans, Miravitlles, Declercq and Germain, 1980) allowing perchlorofluorenyl groups to adopt a relative orientation with a low degree of steric hindrance. In the title molecule the relative disposition of the perchlorofluorenyl groups is given by the dihedral angle between planes C2-C1-C3 and C2'-C1'-C13 (66(1)º).
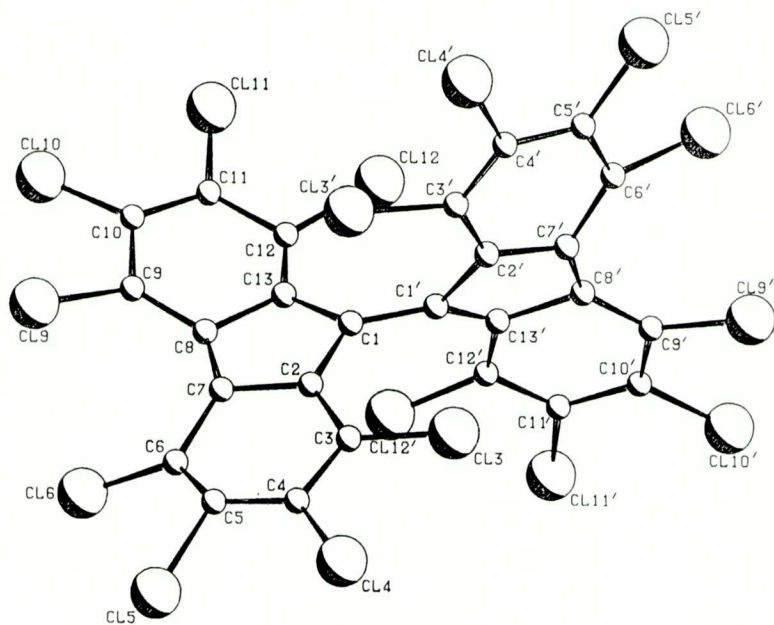
Fig. 1. Perspective view of the molecule with atom numbering.

This value can be attributed to the twisting of the double bond and that is the twistest double bond from the references we got. This magnitude for the non-chlorinated molecule (BFL) is 39.3 (1)°. Similar values were obtained in perchlorofuchsone ((33°): (Molins, Rius and Miravitlles, 1984) and per-chloro (diphenylmethylene)-cyclohexa-1, 4-diene (27°) (Ballester et al., 1989).

Five membered rings are nearly planar (r.m.s.d. of 0.027 and 0.029 Å), and similarly the six-membered rings (range r.m.s.d. 0.032-0.062 Å). In each perchlorofluorenyl moiety the dihedral angle between five-membered ring and six-membered rings is about 14°, these later are oriented up and downwards from the five-membered ring mean plane. Otherwise, the 3, 6, 9 and 12 chlorine atoms are removed out of plane from his own phenyl ring (in the same sense in each ring: like a boat conformation): 3 and 12 between 0.16 and 0.27 Å; 6 and 9 between 0.31 and 0.52 Å.

The strong strength in the molecule is related with the steric impediment at 3, 6, 9 and 12 chlorine atoms (Cl6 ... Cl9: 3.07, Cl6' ... Cl9': 3.10, Cl3 ... Cl3': 3.79, Cl12 ... Cl12': 3.65 Å). The Cl6 ... Cl9 and Cl9' are the shortest Cl ... Cl non-bonded referenced distances and are within the same order of those in perchlorophenyl groups. The twist conformation is adopted for this overcrowded symmetric ethylene R2=C=C=R2, and the internal angles are [R-

C-R = 105.1, 1.6.4 °] instead of double bent conformation as has been stated by Lee & Nyburg (1985).

In conclusion, there are four sites with strong steric hindrance in the molecule:

– The most importants (Cl6 ... Cl9 and Cl6' ... Cl9') produce the double bending of prechlorofluorenyl groups and the out-of-plane displacement of these Cl-atoms.

– The remaining ones (Cl3 ... Cl3' and Cl12 ... Cl12') lead to the twisting of double bond.

A full revision of the structures of overcrowded perchloro compounds is developed by Herbstein (1991); in this paper, the present compounds is compared with the others.

Abstract

The X-Ray crystal structure of the hexadecachloro-9,9'-bifluorenylidene has been determined. Crystals were monoclinic $P2_1/c$, a=11.606(2), b=21.144(5), c=13.944(3) Å, β=104.92(3)°, Z=4 D_x=1.77 g cm^{-3}, λ(MoKα)=0.71069 Å. The structure was solved by direct methods and refined with 1336 reflections to a final R value of 0.078. The twisting of the C1-C1' double bond (1.36(1)Å) is 66(1)°.

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B) PROPIETATS FÍSIQUES DE CRISTALLS I SUPERCONDUCTORS.

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V.I. Simonov. Crystal structure of high-temperature superconductors

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