

Table 3. Important molecular parameters (\AA , $^\circ$) that define the molecular conformation (X-ray) compared with the values obtained by molecular-mechanics simulation (MM)

	(II)		(III)		(IV)		(V)	
	X-ray	MM	X-ray	MM	X-ray	MM	X-ray	MM
N—C(1)	1.357 (3)	1.353	1.356 (3)	1.351	1.373 (3)	1.356	1.363 (3)	1.353
N—C(4)	1.482 (3)	1.481	1.475 (3)	1.477	1.468 (3)	1.485	1.458 (3)	1.481
N—C(5)	1.404 (4)	1.407	1.423 (3)	1.403	1.415 (3)	1.409	1.418 (3)	1.407
O—C(1)	1.218 (3)	1.221	1.225 (3)	1.221	1.217 (3)	1.221	1.224 (3)	1.221
C(1)—N—C(5)—C(6)	34.9 (2)	27.0	63.3 (2)	53.7	155.2 (3)	153.3	-151.0 (2)	-153.6
C(1)—N—C(5)—C(10)	-147.4 (4)	-153.5	-119.6 (3)	-126.4	-26.6 (1)	-27.0	31.0 (1)	26.8

Table 4. Special bond-stretching [k (mdyne \AA^{-1}), r_o (\AA)] and angle-bending [k (mdyne $\text{\AA} \text{rad}^{-1}$), θ_o (rad)] force-field parameters

The parameters have been optimized, in combination with the standard parameters of Boyd (1968), to match the experimental structure of (II) and used to simulate the structures of (III), (IV) and (V), assuming a torsional attraction of $0.29 \text{ kJ mol}^{-1} \text{ deg}^{-1}$ towards the planar configuration of the phenyl rings. This corresponds to an estimated rotational barrier of 7 kJ mol^{-1} .

	k	r_o or θ_o
C(1)—C(2)	4.17	1.51
C(2)—C(3)	4.40	1.52
C(3)—C(4)	4.40	1.53
N—C(1)	8.33	1.34
N—C(4)	3.61	1.46
N—C(5)	7.50	1.39
N—C(1)—C(2)	0.41	2.094
N—C(1)—O	0.42	2.094
C(1)—N—C(5)	0.42	2.094
C(4)—N—C(5)	0.42	2.094
C(1)—N—C(4)	0.82	2.094
N—C—C	1.00	1.911

the torsional parameter of 7 kJ mol^{-1} at the central bond, favouring the planar configuration. Without this interaction the simulation converges to the fully staggered form. The comparison between some crucial bond parameters from crystallographic analyses and from the force-field simulation is shown in Table 3. The agreement is satisfactory.

Not surprisingly, efforts to observe the low barrier to rotation of the rings by NMR spectroscopy were

inconclusive. From the crystallographic results and the force-field simulation, however, the existence of the barrier is beyond dispute. Whether to interpret this result in terms of delocalization or nuclear screening (Boeyens, 1982) is not important. The distinguishing structural features would in either case be small, in view of the low barrier. The characteristic shortening of the N—C(1) bond, however, finds an easy explanation only in terms of nuclear screening by the N lone pair and C— $p\pi$ electron densities.

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Crystal and Molecular Structures of Overcrowded Halogenated Compounds. IX.* Stereochemistry of Molecules Containing the Perchlorofluorenyl and Perchlorofluorenylidene Moieties and of Their Hydrogen Analogues

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Abstract

The structures of the overcrowded perchlorofluorenyl moiety, on its own and in two poly-

chlorinated bifluorenyls, are compared among themselves and with those of the parent aromatic hydrocarbons; the comparison is extended to the perchlorofluorenylidene moiety in perchlorobifluorenylidene and the fluorenylidene moieties in

* Part VIII: Herbstein (1979).

various bifluorenylidenes. The perchlorinated molecules are distorted because of close intramolecular Cl...Cl nonbonded approaches across the bay regions of the molecules. The observed conformations can be explained by a simple hard-sphere rigid-moiety model; consideration of the variation of the intramolecular Cl...Cl nonbonded distances as one fragment is rotated with respect to another about the bond joining them provides explanations why only some of the formally possible diastereoisomers are actually found. The much smaller distortions found in the hydrocarbons are due to other interactions. Detailed analysis of the molecular and moiety geometries shows that there are appreciable intramolecular effects due to moiety interactions and also intermolecular influences due to neighbouring molecules ('packing effects'). This discussion shows that even routine crystal structure analyses, without pretensions to high precision, contain potentially useful stereochemical information which sometimes was not fully explored in the original reports.

1. Introduction

Highly overcrowded polyhalogenated aromatic hydrocarbons (Ballester, 1989) are distorted from planarity because the nonbonded distances between some halogen atoms in the hypothetical planar molecule are appreciably less than the van der Waals diameter of the halogen. Among the crystal and molecular structures reported are those of 1,4,5,8-tetrachloronaphthalene (Gafner & Herbstein, 1962), octachloronaphthalene (Gafner & Herbstein, 1963; Herbstein, 1979), decachloropyrene (Hazell, 1978), octabromonaphthalene (Brady, Redhouse & Wakefield, 1982), decachlorophenanthrene (Herbstein, Kapon & Merksamer, 1976), perchlorocoronene (Baird, Gall, MacNicol, Mallinson & Michie, 1988) and 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline (Herbstein, Kapon & Rabinovich, 1972).

Halogenated fluorenes are missing from the above list but information about their mode of distortion can be derived from two groups of compounds containing the perchlorofluorenyl moiety and one containing the perchlorofluorenylidene moiety. In this paper we compare in some detail the structures of the perchlorinated molecules with those of the parent hydrocarbons and among themselves, and attempt to account for the main structural features of the overcrowded molecules in terms of a simple hard-sphere model. This should be considered as a first step towards calculating the equilibrium structures of the isolated molecules by molecular mechanics. In addition, as structure analyses are available for a number of related molecules, intercomparisons of various kinds should provide some measure of the influence

of crystal packing on the details of molecular shape. The molecules discussed here can be described at a number of levels and we find it convenient to begin with the environments of individual atoms, then consider the shapes of the various rings, then the perchlorofluorenyl (perchlorofluorenylidene) moieties as units and finally compare the shapes of the whole molecules. In oversimplified terms the distortion in the perchlorofluorenyl (perchlorofluorenylidene) moiety can be described as a twist of the moiety about its long axis in order to increase the distance between the pair of chlorines in the 4,5-positions (the 'bay' region) to ~ 3.1 Å. Other pairs of adjacent chlorines are not overcrowded, as can be seen from the planarity of hexachlorobenzene (Brown & Strydom, 1974).

Our first group is based on fluorene which is planar or almost so in its crystals [Gerkin, Lundstedt & Reppart, 1984; crystal data for the molecules discussed are summarized in Table 1 (deposited*)]. Perchlorofluorene has been synthesized (Ballester, Riera, Castañer, Badía & Monsó, 1971; Ballester, Castañer & Riera, 1977) but its crystal structure does not appear to have been reported. Thus we use perchlorofluorene-9-spirocyclohexa-2',5'-diene as our perchlorinated reference compound; crystal structures have been reported for the neat compound and its isomorphous 2:1 inclusion complexes with benzene and cyclohexa-1,4-diene at 293 K and for the latter complex also at 168 K (Gall, MacNicol, Mallinson & Welsh, 1985).

The second group contains the compounds 9,9'-bi-9*H*-fluorenyl (Dougherty, Llort, Mislow & Blount, 1978), 9*H*,9*H*'-hexadecachloro-9,9'-bifluorenyl and 9*H*-heptadecachloro-9,9'-bifluorenyl (Solans, Miravittles, Declercq & Germain, 1980). The two overcrowded compounds are chemically related and were obtained in the same series of reactions, which were carried out under rather drastic conditions (Ballester, Castañer, Riera, de la Fuente & Camps, 1985). Thus both enantiomers of various intermediates would be expected to be present in the reaction mixtures and the fact that only one of the possible combinations of the enantiomeric intermediates was found has to be explained in thermodynamic rather than kinetic terms.

The third group contains the compounds 9,9'-bifluorenylidene [in two polymorphic forms and as 2:1 complexes with pyrene and perylene (Lee & Nyburg, 1985)], diisopropyl-9,9'-bifluorenylidene-1,1'-dicarboxylate (Bailey & Hull, 1978) and hexadecachloro-9,9'-bifluorenylidene [for synthesis see

* Tables 1, 2, 4, 5, 7 and 8, and Fig. 7 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53670 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ballester *et al.*, 1985)] as its 2:1 complex with tetrachloroethylene (Molins & Miravittles, 1990). These are all "strained ethylenes without push-pull effect" (Sandström, 1983, pp. 160–169; Shoham, Cohen, Suissa & Agranat, 1988) and contain fluorenylidene rather than fluorenyl moieties.

Comparisons throughout are made for molecules of the same sense of chirality, conversions of published data having been made where required. Our (arbitrary) choice of a standard conformation ["structures which differ... in their helical arrangements are of different conformation" (Prelog & Helmchen, 1982)] for the fluorenyl, perchlorofluorenyl, fluorenylidene and perchlorofluorenylidene moieties has $\tau[C(4)-C(5)-C(6)-C(7)]$ positive [our numbering of atoms, based on that Solans *et al.* (1980), is shown in Figs. 1 and 3 and is used throughout except in standard chemical formulae].

Geometrical and other calculations were made using the *GEOM* facility of the Cambridge Structural Database (Allen & Kennard, 1987), *MacMoMo* (Dobler, 1989) and *BMFIT* (Nyburg, 1974). Parameter e.s.d.'s were taken from the original sources if available, apart from some exceptions noted in the text. Lengths of C—Cl bonds of a variety of types are discussed in the *Appendix*.

2. Fluorene and perchlorofluorene-9-spirocyclohexa-2',5'-diene and its complexes

2.1. Fluorene

Fluorene has crystallographic symmetry C_{2v} with the mirror plane bisecting the molecule and containing the CH_2 group. Each half molecule is planar but the two halves are inclined at a dihedral angle of $1.28(4)^\circ$ and thus the overall shape is that of an almost flattened hinge. The distance between the two hydrogens in the bay region of fluorene and related

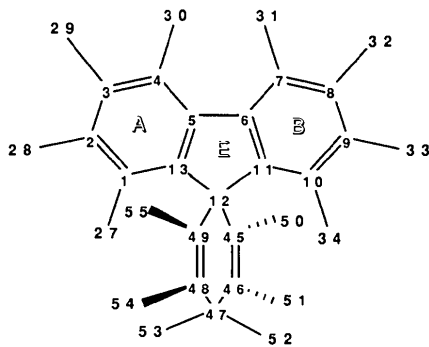


Fig. 1. Schematic diagram of perchlorofluorene-9-spirocyclohexa-2',5'-diene, showing nomenclature for the rings. The numbering of the atoms has been adapted to conform to that used by Solans *et al.* (1980); carbons are numbered 1–13, 45–49 and chlorines 27–34, 50–55.

moieties is $\sim 2.6 \text{ \AA}$, which is too large for repulsive interaction between these atoms. Thus we ascribe the small distortions of fluorene from strict planarity to intermolecular interactions.

2.2. Perchlorofluorene-9-spirocyclohexa-2',5'-diene and its complexes

The four structure analyses appear to be precise ($R = 0.030, 0.041, 0.035$ and 0.037 respectively). Gall *et al.* (1985) reported that the shapes of the host molecule in the three inclusion complexes were very similar and we therefore restrict ourselves to comparison of the extremes – the host molecule in its neat crystals at 293 K and in its 2:1 complex with cyclohexa-1,4-diene at 168 K.

We begin with the deviations of individual C atoms from the plane through the three atoms to which each is bonded [Table 2 (deposited)]. The largest deviation found is 0.055 \AA ; there do not seem to be any correspondences between values for chemically related atoms. The smallness of the distortions from planarity at individual carbons accords with remarks made by McIntosh, Robertson & Vand (1954) concerning analogous distortions in the overcrowded molecule 3:4:5:6-dibenzophenanthrene ([5]-helicene) – "the bending is distributed over the five fused rings in such a way as to cause no very severe buckling or angle distortions in any individual ring, and so the retention of aromatic properties can be understood."

The idealized molecule has a C_2 -2 axis running through carbons 47 and 12, with the plane of the cyclohexadiene moiety normal to the mean plane of the perchlorofluorenyl moiety; we test the extent to which this formal symmetry is achieved in practice, firstly with respect to deviations from planarity in the six-membered rings. In both molecules one ring (designated *A*) deviates less from planarity than the other (designated *B*) (Table 3). E.s.d.'s were not reported but we guess $\sigma(x)$ to be $\sim 0.004 \text{ \AA}$ for C atoms and $\sim 0.001 \text{ \AA}$ for Cl; thus both deviations from planarity and the differences between them are highly significant.

The overall deviations from idealized symmetry and non-planarity of the perchlorofluorenyl moieties in perchlorofluorene-9-spirocyclohexa-2',5'-diene ($C_{18}Cl_{14}$) and perchlorofluorene-9-spirocyclohexa-2',5'-diene-cyclohexa-1,4-diene (2/1) ($2C_{18}Cl_{14} \cdot C_6H_8$) (at 168 K) are considered next (Fig. 2). Both moieties deviate from C_2 -2 symmetry with deviations of up to 0.2 \AA from the hypothetical mean positions. In addition C(12) (values for the two molecules are $0.058; 0.068 \text{ \AA}$), C(47) ($0.288; 0.199 \text{ \AA}$), Cl(52) ($0.307; 0.045 \text{ \AA}$) and Cl(53) ($0.446; 0.446 \text{ \AA}$) deviate from the best plane through the carbons of the octachlorofluorenyl moiety to give a slight bow shape to the

Table 3. *R.m.s. deviations* (10^{-3} Å) of carbons and attached atoms (mainly chlorines) from the best planes of the various rings

Ring	$C_{18}Cl_{14}$		$2C_{18}Cl_{14}.C_6H_8$ (168 K)	
	Carbons	Attached atoms	Carbons	Attached atoms
A	38	199	31	181
B	51	246	50	259
E	42		52	

molecules along the C(12)···C(47) direction. The significantly different shapes of the moieties in the two crystals are conveniently demonstrated by the values of the C(4)—C(5)—C(6)—C(7) torsion angles [22.8 (4) and 27.5 (3)° respectively]; the analogous torsion angles in decachlorophenanthrene and 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline are 27.9 and 20.5° but larger values [mean 37.5 (7)°] are found in 1,2,5,6,7,8,11,12-octachloro-*N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (Sadrai, Bird, Potenza & Schugar, 1990). The 5-membered rings are fairly closely planar, as in fluorene, bifluorenyl, bifluorenylidene, diisopropyl 9,9'-bifluorenylidene-1,1'-dicarboxylate and hexadecachloro-9,9'-bifluorenylidene; however the 5-membered rings of the perchlorinated bifluorenyls considered in the next section have envelope conformations.

The nonbonded Cl···Cl distances in the two molecules lie in the range 3.06 to 3.12 Å, with the distances between the most overcrowded chlorines [Cl(30) and Cl(31)] at 3.07 and 3.10 Å in the two

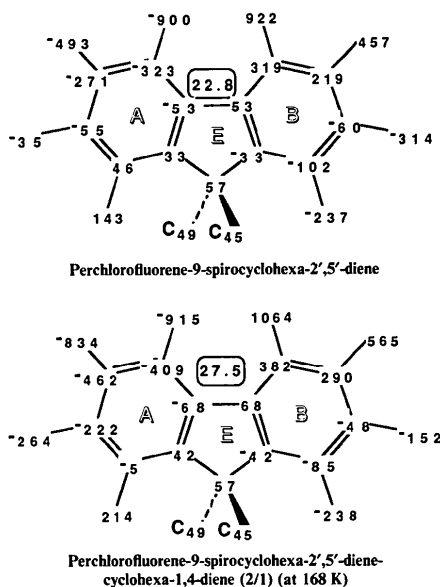


Fig. 2. Schematic diagram showing the deviations (10^{-3} Å) from the best plane through the four aromatic carbons of ring E of two perchlorofluorenyl moieties; negative signs are for deviations below the best plane. The torsion angles C(4)—C(5)—C(6)—C(7) (°) are boxed.

moieties [Table 4 (deposited)]. These values are similar to those found in decachlorophenanthrene, 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline and 1,2,5,6,7,8,11,12-octachloro-*N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide). The *peri* chlorines such as those in octachloronaphthalene [2.988 (2) and 3.019 (2) Å] and perchlorocoronene [3.021 (2) and 3.045 (2) Å] approach somewhat more closely.

The chirality of the molecules is due to the twist about C(5)—C(6) and the pairs of noncongruent molecules in the unit cells are conformational enantiomers; there will be a finite activation enthalpy of racemization in solution.

Analogous but smaller effects are found in 4,5-dimethylamine fluorenyl perchlorate (Staab, Saupe & Krieger, 1983; Staab & Saupe, 1988) which has twofold symmetry along the median molecular axis with the N atoms displaced above and below the mean molecular plane by 0.23 Å.

3. 9,9'-Bifluorenyl, 9*H*,9*H'*-hexadecachloro-9,9'-bifluorenyl and 9*H*-heptadecachloro-9,9'-bifluorenyl

A schematic diagram showing the numbering used for the molecules discussed in this section is given in Fig. 3.

3.1. 9,9'-Bifluorenyl

In crystalline 9,9'-bi-9*H*-fluorenyl the molecule is in the *gauche* conformation and has approximate (non-crystallographic) C_2 -2 symmetry, and this conformation, ascribed to steric rather than polar factors, also predominates in solution (Dougherty *et al.*,

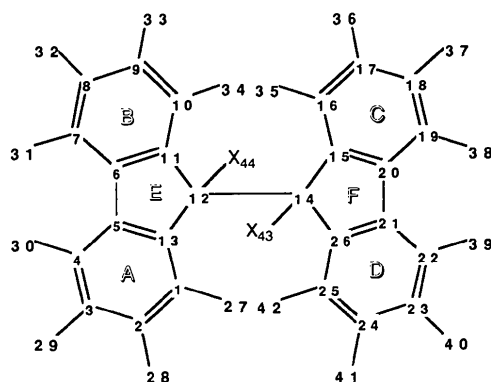


Fig. 3. Schematic diagram showing the numbering (Solans *et al.*, 1980; C 1–26, H 27–44) used for 9,9'-bifluorenyl, $C_{26}HCl_{17}$ (Cl 27–42, $X_{43} = Cl$, $X_{44} = H$) and $C_{26}H_2Cl_{16}$ (Cl 27–42, $X_{43} = X_{44} = H$). This diagram does *not* show the correct molecular shapes. Rings AEB are octachlorofluorenyl in $C_{26}H_2Cl_{16}$ and $C_{26}HCl_{17}$ while rings CFD are octachlorofluorenyl in $C_{26}H_2Cl_{16}$ but non-chlorofluorenyl in $C_{26}HCl_{17}$; we refer to these as polychlorofluorenyl moieties when differentiation between them is not necessary.

1978). The five-membered rings are planar to within 0.02 Å but the fluorenyl groups deviate from planarity. We show the projection of the molecule down the C(12)—C(14) bond in Fig. 4. It is convenient to describe the torsion about the ethane bond in terms of $\tau[C(11)—C(12)—C(14)—C(26)]$ (see Fig. 3) which would be 0° in the hypothetical eclipsed conformation. We choose as standard the bifluorenyl enantiomer with $\tau[C(11)—C(12)—C(14)—C(26)] = -62.1^\circ$ because this matches the molecular conformations obtained for the polychlorinated bifluorenyls described below when standard conformations are used for the polychlorofluorenyl moieties. However this choice gives the bifluorenyl enantiomer with *negative* values for its bay torsion angles. Both *AEB* and *DFC* moieties, which have the same relative conformation, are unsymmetrically distorted — the angles between the normals to the best planes through the rings *E*, *A* and *B* are 3.8 (*A/E*) and 1.8° (*E/B*) respectively; the analogous values for rings *F*, *D* and *C* are 4.4 (*D/F*) and 2.4° (*F/C*). Thus rings *A/E* and *D/F* have similar interplanar angles, as do *E/B* and *F/C*, in accord with the approximate twofold symmetry of the molecule. The larger bending found for *A/E* and *D/F* is presumably due to the intramolecular propinquity of *A* and *D* (Fig. 4).

We note that 10,10'-bianthronyl has a *gauche* conformation both in the solid [Ehrenberg, 1967; Ehrenberg uses the incorrect term "staggered configuration of the atoms in the neighbourhood of C(10)'" and in solution [from dipole moments (Huang, 1976)]. In the crystal there is an exact crystallographic twofold axis bisecting the C(10)—C(10') bond (chemical numbering) and directed analogously to the approximate twofold axis of bifluorenyl; thus Ehrenberg's Fig. 2 is similar in general appearance to our Fig. 4.

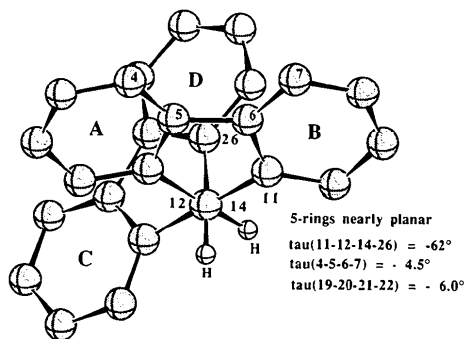


Fig. 4. Molecule of 9,9'-bifluorenyl viewed down the C(12)—C(14) bond [C(12) towards the observer]. The 'bay region' 4-5-6-7 is shown explicitly. The hydrogens of the aromatic rings have been omitted for clarity. Figs. 4 and 5 have been oriented on the page with C(5)—C(6) horizontal in order to facilitate comparison. The bay torsion angles are not significantly different.

3.2. 9*H*,9*H*'-Hexadecachloro-9,9'-bifluorenyl and 9*H*-heptadecachloro-9,9'-bifluorenyl

(i) *Introduction*. Room-temperature crystal structures have been reported for the similarly shaped molecules 9*H*,9*H*'-hexadecachloro-9,9'-bifluorenyl ($C_{26}H_2Cl_{16}$) and 9*H*-heptadecachloro-9,9'-bifluorenyl ($C_{26}HCl_{17}$) (Solans *et al.*, 1980). There are two crystallographically independent molecules (referred to as *A* and *B* respectively) in the crystals of $C_{26}H_2Cl_{16}$, and one in $C_{26}HCl_{17}$ so the structures of three independent molecules are available for study. Our calculations are based on coordinates corrected for three transcription errors (see CSD file for CLPFLC-10) and calculated tetrahedral positions for hydrogens [$d(C—H) = 1.0$ Å]. We estimate $\sigma(C—C)$ as ~ 0.02 Å and $\sigma(C—Cl)$ as ~ 0.015 Å instead of the values of 0.001–0.002 Å given originally (see *Appendix*). The projection of $C_{26}H_2Cl_{16}$ -*A* down the C(12)—C(14) bond is shown in Fig. 5 and a perspective view in Fig. 6.

(ii) *Description of the molecular shapes*. We begin with the deviations of individual C atoms from the planes through the three atoms to which each is bonded. The largest deviation for aromatic carbons is 0.08 Å, in general agreement with what has been noted above; the deviations for the two tetrahedral carbons are ~ 0.56 Å. The results are summarized in Table 5 (deposited).

The several six-membered rings and their attached atoms (mainly chlorines, with some carbons) are described in terms of deviations of these atoms from

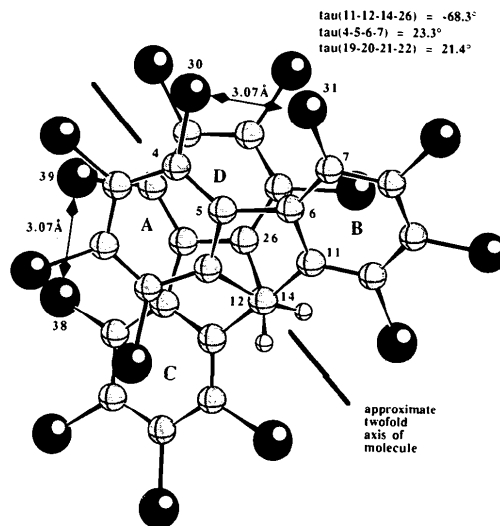


Fig. 5. Projection of $C_{26}H_2Cl_{16}$ -*A* down the C(12)—C(14) bond [C(12) towards the observer] showing the *gauche* conformation. The overcrowded pairs of chlorines [Cl(30), Cl(31) and Cl(38), Cl(39)] are shown explicitly. The bay torsion angles are significantly different at 29.6, 22.3° in $C_{26}HCl_{17}$ and 19.9, 23.3° in $C_{26}H_2Cl_{16}$ -*B*, but not in $C_{26}H_2Cl_{16}$ -*A*.

the best planes through the carbons of each ring. The rings can be divided into two groups on the basis of their deviations from planarity – rings *B* and *C* are less distorted than rings *A* and *D* in all three molecules. Furthermore ring *D* of $C_{26}HCl_{17}$, with Cl substituted at tetrahedral C(14), is less distorted than ring *A*, with H substituted at tetrahedral C(12) (Table 6).

We next consider the distortions of the polychlorofluorenyl moieties taken as units. Here we have calculated the best plane through the four aromatic carbons of the five-membered ring and the deviations of the other atoms from this plane and the results, which are similar to those shown in Fig. 2, are exemplified in Fig 7 (deposited). There are appreciable differences of detail among the six polychlorofluorenyl moieties [Table 7 (deposited)].

The overall type of distortion found for the polychlorofluorenyl moieties is the same as described above; in particular the values of $\tau[C(4)-C(5)-C(6)-C(7)]$ are in the range $19.9-29.6^\circ$. All the *AEB* and *DFC* moieties have the same relative conformation. The pattern of distortions given in Fig. 7 and Table 7 shows that the perchlorofluorenyl moieties are unsymmetrically distorted. The non-bonded Cl...Cl distances within polychlorofluorenyl moieties show the same features as described above; details have been deposited (Table 8). The distances of Cl(43) (bonded to sp^3 carbon) to its two nearest Cl neighbours in the nonachlorofluorenyl *CFD* moiety in $C_{26}HCl_{17}$ are 3.29 [Cl(43)...Cl(35)] and 3.19 Å [Cl(43)...Cl(42)].

(iii) *Comparison of the shapes of the polychlorofluorenyl moieties in the three molecules.* We have used the program *BMFIT* (Nyburg, 1974) to compare, pairwise, the shapes of the two polychlorofluorenyl moieties within each molecule. The fit has been made by matching the carbons of rings *AEB* to

Table 6. *R.m.s. deviations (10^{-3} Å) of carbons and attached atoms (mainly chlorines) from the best planes of the various rings*

Ring	$C_{26}HCl_{17}$		$C_{26}H_2Cl_{16}-A$		$C_{26}H_2Cl_{16}-B$	
	Carbons	Attached atoms	Carbons	Attached atoms	Carbons	Attached atoms
<i>A</i>	63	303	61	266	60	282
<i>B</i>	34	248	21	124	26	133
<i>C</i>	35	163	22	136	26	163
<i>D</i>	48	267	61	229	58	268

those of rings *DFC* (as units and in this order). This comparison has been extended to matching the *AEB* rings in one molecule to those in another. The shape differences between polychlorofluorenyl moieties are small and there is little difference between the intramolecular or intermolecular matches; the largest distances between carbons after matching are ~ 0.08 Å and those between chlorines ~ 0.30 Å. The results are summarized in Table 9.

(iv) *The overall shapes of the $C_{26}H_2Cl_{16}$ and $C_{26}HCl_{17}$ molecules.* The three molecules have been matched pairwise through their C atoms using *BMFIT* and the results are summarized in Table 10. The r.m.s. deviations are about twice as large for chlorines as for carbons. There are two aspects to the matching process – the relatively rigid polychlorofluorenyl moieties are not exactly congruent, as shown in Table 9, and the torsion angles about the ethane bond differ slightly. Thus the matching of whole molecules cannot be expected to be as close as that of individual polychlorofluorenyl moieties. The best match is obtained for $C_{26}HCl_{17}/C_{26}H_2Cl_{16}-B$ (the largest distance between carbons is 0.23 Å and between chlorines 0.37 Å) and then for $C_{26}H_2Cl_{16}-A/C_{26}H_2Cl_{16}-B$ ($0.33, 0.60$ Å); the greatest overall difference is between $C_{26}HCl_{17}$ and $C_{26}H_2Cl_{16}-A$ ($0.34, 0.50$ Å). This is in agreement with the relationships among the torsion angles. These comparisons are given in more detail in the histogram of Fig. 8, where the distributions of deviations are compared for the best and worst fits.

The values of $\tau[C(11)-C(12)-C(14)-C(26)]$ (which would be 0° in the hypothetical eclipsed conformation; see Fig. 3) are -72.1 for $C_{26}HCl_{17}$, -68.3 for $C_{26}H_2Cl_{16}-A$ and -74.4° for $C_{26}H_2Cl_{16}-B$, all for the enantiomers with polychlorofluorenyl moieties in their standard conformations. We now test the simple assumption that the 'ethane' torsion angles are determined by repulsive interactions between chlorines on the *AEB* and *DFC* polychlorofluorenyl moieties of the molecules. Using the 'rotation about a bond' facility of *MacMoMo* we calculate nonbonded Cl...Cl distances as this torsion angle is varied about its experimental value. In this simplified calculation of intramolecular strain we are assuming a hard sphere model for nonbonded atoms and rigidity of the *AEB, DFC* moieties. The results

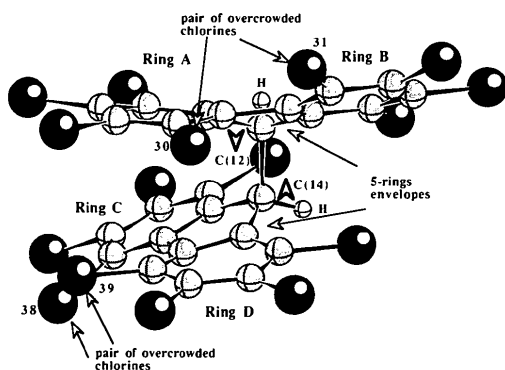


Fig. 6. Perspective diagram for $C_{26}H_2Cl_{16}-A$. The overcrowded pairs of chlorines are numbered. The directions of the deviations of the carbons of the ethane bond from the planes of the remaining four atoms of each of the five-membered rings are shown by the open arrow heads.

Table 9. *R.m.s. deviations* (Å, per atom) for polychlorofluorenyl groups matched pairwise through their carbons

The values for the carbons are given above the central diagonal (in bold) and for chlorines below. Intramolecular comparisons are plain and those between different molecules italicized.

	$C_{26}HCl_{17}$ <i>AEB</i>	$C_{26}HCl_{17}$ <i>DFC</i>	$C_{26}H_2Cl_{16-A}$ <i>AEB</i>	$C_{26}H_2Cl_{16-A}$ <i>DFC</i>	$C_{26}H_2Cl_{16-B}$ <i>AEB</i>	$C_{26}H_2Cl_{16-B}$ <i>DFC</i>
$C_{26}HCl_{17}$ <i>AEB</i>		C(intra) 0.063	C(inter) 0.046		C(inter) 0.051	
$C_{26}HCl_{17}$ <i>DFC</i>	Cl(intra) 0.179					
$C_{26}H_2Cl_{16-A}$ <i>AEB</i>	Cl(inter) 0.170			C(intra) 0.051	C(inter) 0.044	
$C_{26}H_2Cl_{16-A}$ <i>DFC</i>			Cl(intra) 0.135			
$C_{26}H_2Cl_{16-B}$ <i>AEB</i>	Cl(inter) 0.163		Cl(inter) 0.106			C(intra) 0.063
$C_{26}H_2Cl_{16-B}$ <i>DFC</i>					Cl(intra) 0.156	

for $C_{26}HCl_{17}$, given in Fig. 9, show that the lower limit to τ is determined by reduction of $d[Cl(27)\cdots Cl(35)]$ as τ is reduced. The upper limit is determined by the $Cl(28)\cdots Cl(39)$ and $Cl(30)\cdots Cl(41)$ approaches. The closer $Cl\cdots C$ distances when $\tau = -72^\circ$ are ~ 3.3 Å and lie within acceptable limits. Rather similar results are obtained for $C_{26}H_2Cl_{16-A}$ and $C_{26}H_2Cl_{16-B}$ except that the $Cl(34)\cdots Cl(42)$ interaction replaces the $Cl(28)\cdots Cl(39)$ interaction of $C_{26}HCl_{17}$, the other factors remaining the same. The small shape differences are large enough to play a role here. The closer $C\cdots Cl$ distances are ~ 3.4 Å for the observed torsion angles.

The stereoisomerism of bifluorenyl and of $C_{26}H_2Cl_{16}$ and $C_{26}HCl_{17}$ must be described separately. The relative conformation of the *AEB* fluorenyl moiety is *M* (minus) in terms of the twist about $C(5)-C(6)$ [nomenclature of Prelog & Helmchen (1982)] and the *DFC* moiety has the same relative conformation. Thus the bifluorenyl molecule has an $M_{AEB}-M_{DFC}$ relative conformation insofar as the two fluorenyl moieties are concerned. However one must

Table 10. *R.m.s. deviations* (Å, per atom) between the three molecules after pairwise matching through carbons

The deviations for the carbons are given, as before, above the principal diagonal in bold and those for the chlorines below this diagonal.

	$C_{26}HCl_{17}$	$C_{26}H_2Cl_{16-A}$	$C_{26}H_2Cl_{16-B}$
$C_{26}HCl_{17}$		0.178	0.126
$C_{26}H_2Cl_{16-A}$	0.353		0.148
$C_{26}H_2Cl_{16-B}$	0.221	0.301	

also take into account the sense of twist about the ethane bond, which has the relative conformation [$M_{C(12)-C(14)}$] (Figs. 3 and 4). Thus the overall relative conformation of the enantiomer taken here as standard is $M_{AEB}-[M_{C(12)-C(14)}]-M_{DFC}$; as noted before, in choosing the standard conformation of bifluorenyl we have given primacy to the sense of rotation about the ethane bond rather than to the signs of the torsion angles about $C(5)-C(6)$ [$C(20)-$

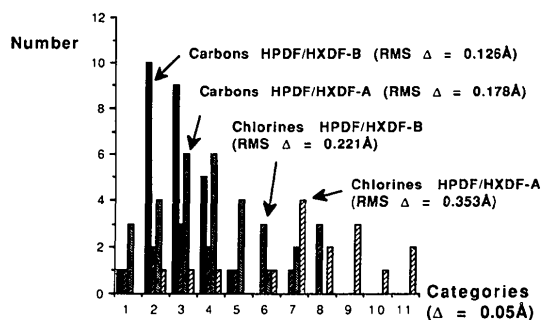


Fig. 8. The distribution of deviations (Å) for C and Cl atoms after matching (through carbons) the $C_{26}HCl_{17}$ molecule (designated as HPDF) with $C_{26}H_2Cl_{16-A}$ and $C_{26}H_2Cl_{16-B}$ (designated as HXDF-A,B) respectively. The categories are defined as follows in terms of range of deviations between matched atoms - 1: 0-0.05 Å; 2: 0.05-0.10 Å...11: 0.50-0.55 Å. The r.m.s. deviations for the various comparisons are summarized in Table 10.

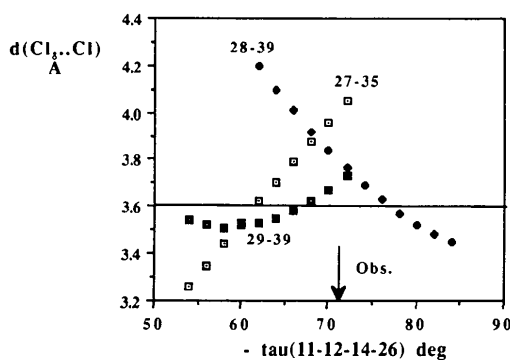


Fig. 9. The figure shows how the closer non-bonded distances between chlorines in different polychlorofluorenyl moieties in $C_{26}HCl_{17}$ would change if the torsion angle about the $C(12)-C(14)$ bond was altered from its observed value of -72° . The octa- and nonachlorofluorenyl moieties have been treated as rigid. The nominal van der Waals diameter of Cl (3.6 Å) is shown on the figure. $d[Cl(30)\cdots Cl(41)]$ has a very similar τ dependence to that shown for $d[Cl(28)\cdots Cl(39)]$. $d[Cl(34)\cdots Cl(43)]$ is essentially constant at 3.41 Å over the whole τ range shown.

C(21)]. The corresponding description for $C_{26}H_2Cl_{16}$ and $C_{26}HCl_{17}$ is $P_{AEB}[M_{C(12)-C(14)}]-P_{DFC}$. As a first approximation atoms C(12) and C(14) in bifluorenyl can be treated as prochiral and need not be included in the description. However this does not apply to $C_{26}H_2Cl_{16}$ and $C_{26}HCl_{17}$. In $C_{26}H_2Cl_{16}$ these two atoms are both *S*, the sequence rule having been applied as follows: with H at the rear of C(12) the groups C(14) with perchlorofluorenyl attached, C(13) and C(11) are in left-handed sequence (*S*) [C(13) has been given precedence over C(11) because the torsion angles C(12)—C(13)—C(5)—C(6) and C(12)—C(11)—C(6)—C(5) are -16.2 and 3.1° and *M* has precedence over *P*]. Thus the overall relative (standard) conformation of $C_{26}H_2Cl_{16}$ is $P_{AEB}-C(12)[S]-[M_{C(12)-C(14)}]-C(14)[S]-P_{DFC}$. For $C_{26}HCl_{17}$ the configuration at C(14) is *R* when the precedence of Cl(43) is taken into account and thus its overall relative (standard) conformation is $P_{AEB}-C(12)[S]-[M_{C(12)-C(14)}]-C(14)[R]-P_{DFC}$.

Using the same methods as before we have investigated the Cl...Cl and Cl...C distances in the hypothetical diastereomer $P_{AEB}[M_{C(12)-C(14)}]-M_{DFC}$ of $C_{26}H_2Cl_{16}$ as a function of $\tau[C(11)-C(12)-C(14)-C(26)]$. Satisfactory Cl...Cl distances are found in the regions of $\tau \approx -21$ and 180° . The first of these is ruled out by a C...Cl distance of 2.7 \AA , while the second is also somewhat unfavourable because of a number of C...Cl distances around 3.1 \AA . Thus steric considerations appear to eliminate the mixed diastereoisomer. Perchloro-9,9'-bifluorenyl ($C_{26}Cl_{18}$) has not been prepared although it has been postulated as an intermediate in some of the reaction schemes given by Ballester *et al.* (1985). We have replaced HC(12) of $C_{26}HCl_{17}$ by a Cl atom in the tetrahedral position with $d(C-Cl) = 1.80 \text{ \AA}$ and carried out a *MacMoMo* simulation test, by the methods described above, to check if an acceptable (in terms of Cl...Cl distances) conformation could be found for this molecule. One or other Cl...Cl distance was drastically too short ($< 2.5 \text{ \AA}$) for all values of $\tau[(C(11)-C(12)-C(14)-C(26))]$. Thus intramolecular Cl...Cl repulsions prevent the existence of perchloro-9,9'-bifluorenyl as a stable molecule, as indeed Ballester *et al.* surmised. Alternatively, appreciable changes in the shapes of the nonachlorofluorenyl moieties and of the molecule as a whole would be required, but we have not pursued this point.

4. 9,9'-Bifluorenylidene and hexadecachloro-9,9'-bifluorenylidene

4.1. 9,9'-Bifluorenylidene polymorphs, derivatives and complexes

Lee & Nyburg (1985) reported that bifluorenylidene is twisted by $\sim 39^\circ$ about its central double

bond and that the two fluorenylidene moieties (*i.e.* rings *AEB*, *DFC*) are not quite planar, as is shown by bay torsion angles of 7.5 (4) and 8.3 (4) $^\circ$ (Fig. 10); steric distortion of the fluorenylidene moieties was ascribed to interactions between hydrogens attached to C(1), C(16) and C(10), C(25). Similar geometrical results were reported for diisopropyl 9,9'-bifluorenylidene-1,1'-dicarboxylate (Bailey & Hull, 1978). Bi-4*H*-cyclopenta[*def*]phenanthren-4-ylidene has a shape similar to that of bifluorenylidene but with a twist angle (about the ethylenic bond) of 31° (Stezowski, Hildenbrand, Suissa & Agranat, 1989).

$\tau[C(4)-C(5)-C(6)-C(7)]$ was calculated by molecular mechanics as 4.7° for bifluorenylidene and 1,1'-dimethylbifluorenylidene (Favini, Simonetta, Sottocornola & Todeschini, 1982), but no comment was made apart from noting that the fluorenylidene fragments were approximately planar. (Parenthetically we remark that bifluorenylidene was incorrectly assigned C_i symmetry in their Table IV.)

4.2. Hexadecachloro-9,9'-bifluorenylidene

The crystal structure of the 2:1 complex of hexadecachloro-9,9'-bifluorenylidene (Ballester *et al.*, 1985) with tetrachloroethylene has been determined by Molins & Miravittles (1990) who have kindly provided me with atomic coordinates for the host molecule, and this is viewed in the direction of the double bond in Fig. 11. The results are not very precise, as can be gauged from the large e.s.d. (0.044 \AA) of the mean value of $d(C-Cl)$ (1.721 \AA). The torsion angles in the overcrowded regions are: $\tau[C(4)-C(5)-C(6)-C(7)] = 43.5$ and $\tau[C(19)-C(20)-C(21)-C(22)] = 52.2^\circ$ (numbering system adapted from that of Fig. 3); thus the *AEB* and *DFC* moieties again have the same conformation. The nonbonded Cl...Cl distances lie in the range 3.03 to 3.10 \AA and the perchlorofluorenylidene moieties are distorted from planarity as described above. The two five-membered rings have r.m.s. deviations (in Å) from planarity of 0.026 (*E*) and 0.029 (*F*), while for

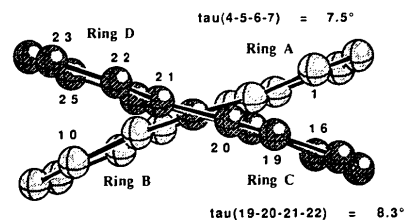


Fig. 10. The molecule of 9,9'-bifluorenylidene viewed down the double bond C(12)—C(14), with the rings *DFC* (emphasized) and C(14) towards the observer; thus the 'bay region' 19–20–21–22 is towards the observer. H atoms have been omitted for clarity. The torsion angles are given for the molecule in its 2:1 complex with perylene and have e.s.d.'s = $0.3-0.4^\circ$; the corresponding values in the β polymorph are 8.7 (6) and 11.2 (6) $^\circ$.

the carbons of the six-membered rings the values are 0.062 (*A*), 0.033 (*B*), 0.036 (*C*) and 0.046 (*D*), and for the attached atoms, in the same order, the values are 0.251, 0.256, 0.269 and 0.275; thus there are no clearcut distinctions among the degrees of distortion of the various rings.

In the molecule whose coordinates have been reported $\tau[\text{C}(11)\text{—C}(12)\text{—C}(14)\text{—C}(26)] = 116^\circ$ and the closest intramolecular approaches between non-bonded chlorines are for $\text{Cl}(34)\cdots\text{Cl}(35)$ (3.69 Å) and $\text{Cl}(27)\cdots\text{Cl}(42)$ (3.83 Å). We calculate these distances as a function of $\tau[\text{C}(11)\text{—C}(12)\text{—C}(14)\text{—C}(26)]$. The values of τ for which $d(\text{Cl}\cdots\text{Cl})$ falls below about 3.6 Å are ~ 83 and 116° (Fig. 12), the latter being close to the observed value. We conclude that only this range of τ values is permissible. At $\tau \approx 83^\circ$ the closest C \cdots Cl distances are about 3.1 Å, whereas these are about 3.4 Å for $\tau \approx 116^\circ$. Thus the $\tau \approx 116^\circ$ value is preferred both on account of a smaller twist energy about the double bond and lesser repulsion energy between closer nonbonded pairs of C and Cl atoms.

The stereoisomerism of bifluorenylidene and of hexadecachloro-9,9'-bifluorenylidene can be discussed together; we make the approximation that the *AEB* and *DFC* ring systems are congruent. The bifluorenylidene and hexadecachloro-9,9'-bifluorenylidene molecules have a $P_{AEB}\text{—}P_{DFC}$ relative conformation insofar as the two fluorenylidene (perchlorofluorenylidene) moieties are concerned. However one must also take into account the sense

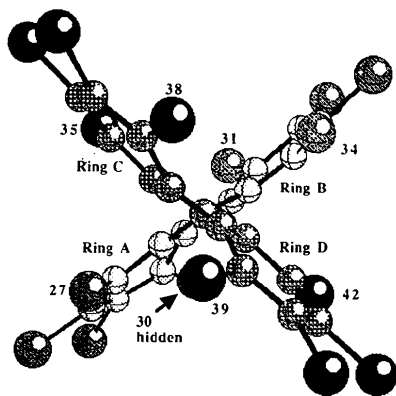


Fig. 11. The molecule of hexadecachloro-9,9'-bifluorenylidene (carbons stippled, chlorines dark, with front half of molecule emphasized) viewed down the double bond in perspective (view distance of $4 \times$ picture diagonal). C(14) is towards the observer. The interactions between the pairs of chlorines in the different perchlorofluorenyl moieties [$\text{Cl}(27)\cdots\text{Cl}(35)$; $\text{Cl}(27)\cdots\text{Cl}(42)$; $\text{Cl}(34)\cdots\text{Cl}(35)$; $\text{Cl}(34)\cdots\text{Cl}(42)$] determine (as shown in Fig. 12) the overall twisted shape of the molecule while the interactions between the overcrowded pairs of chlorines within each perchlorofluorenyl moiety [$\text{Cl}(30)\cdots\text{Cl}(31)$; $\text{Cl}(38)\cdots\text{Cl}(39)$] determine its shape. $\tau(\text{C}(4)\text{—C}(5)\text{—C}(6)\text{—C}(7)) = 43.5^\circ$ and $\tau(\text{C}(19)\text{—C}(20)\text{—C}(21)\text{—C}(22)) = 52.2^\circ$.

of twist about the double bond, which has the relative conformation [$M_{\text{C}(12)\text{—C}(14)}$] (Figs. 11 and 12). Thus the overall relative conformation of the enantiomer taken here as standard is $P_{AEB}\text{—}[M_{\text{C}(12)\text{—C}(14)}]\text{—}P_{DFC}$. We have already noted that a less stable diastereoisomer of hexadecachloro-9,9'-bifluorenylidene with $P_{AEB}\text{—}[P_{\text{C}(12)\text{—C}(14)}]\text{—}P_{DFC}$ relative configuration and $\tau[\text{C}(11)\text{—C}(12)\text{—C}(14)\text{—C}(26)] \approx 83^\circ$ is geometrically feasible.

We note that the mixed diastereoisomer $P_{AEB}\text{—}[\text{C}(12)\text{—C}(14)]\text{—}M_{DFC}$ has not been reported. We have investigated this point for hexadecachloro-9,9'-bifluorenylidene by using the 'change chirality' facility of *MacMoMo* to convert P_{DFC} to M_{DFC} and then fuse the two halves with the 'add molecule' facility to give $P_{AEB}\text{—}[\text{C}(12)\text{—C}(14)]\text{—}M_{DFC}$. Construction of a diagram analogous to Fig. 12 gives limiting $\tau[\text{C}(11)\text{—C}(12)\text{—C}(14)\text{—C}(26)]$ values of ~ 76 and 107° and in both instances the closer nonbonded C \cdots Cl distances are ~ 3.1 Å. Thus the most favourable structure in terms of strain energy is $P_{AEB}\text{—}[M_{\text{C}(12)\text{—C}(14)}]\text{—}P_{DFC}$, as found experimentally.

5. Concluding remarks

The fluorenyl moiety is found to be essentially planar in fluorene, where the small deviations from planarity are ascribed to crystal-packing effects, and slightly nonplanar in bifluorenyl because of mutual interactions between the two halves of the molecule, the hydrogens in the bay region being too far apart to contribute to steric effects. However the overcrowded chlorines in the bay region of the perchlorofluorenyl moieties of the perchlorinated analogues of the parent hydrocarbons cause twisting of the moiety about its long axis so that these two chlorines attain a separation of ~ 3.1 Å. Even in perchlorofluorene-9-spirocyclohexa-2',5'-

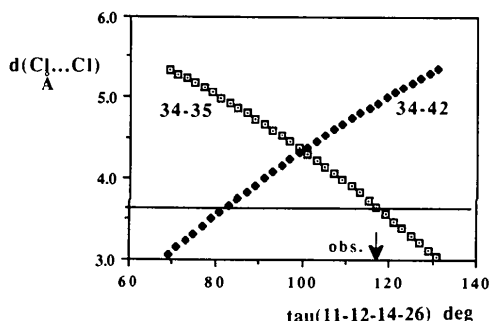


Fig. 12. Hexadecachloro-9,9'-bifluorenylidene — the variation of the nonbonded distances between the pairs of atoms Cl(34), Cl(35) and Cl(34), Cl(42) as the two moieties *AEB* and *DFC* are mutually rotated. The very similar values obtained for $d[\text{Cl}(27)\cdots\text{Cl}(35)]$ and $d[\text{Cl}(27)\cdots\text{Cl}(42)]$ are not included in the diagram for clarity. The 'limiting' nonbonded distance of 3.6 Å is shown as an horizontal line on the diagram.

diene (which serves here as surrogate for perchlorofluorene) the twisting is unsymmetrical along the molecule, suggesting that crystal packing exerts an appreciable influence on the details of the molecular shape. Thus some ambiguity seems unavoidable when comparing structures calculated by molecular mechanics with the results of crystal structure analyses. In the other perchlorinated molecules unsymmetrical distortions due to neighbouring molecules in the crystal are supplemented by intramolecular interactions between the two perchlorofluorenyl moieties. The *gauche* conformation assumed by bifluorenyl for steric reasons [following Dougherty *et al.* (1978)] is also taken up by its two polychlorinated analogues. Replacement of sp^3 carbons of fluorenyl and perchlorofluorenyl by sp^2 carbons in fluorenylidene and perchlorofluorenylidene does not lead to qualitative changes in the shapes of the respective moieties but their mutual disposition becomes quite different; the twisted configuration of bifluorenylidene about the central double bond is greatly accentuated in the hexadecachloro derivative.

The rich stereochemical information which can be extracted from the results of the crystal structure analyses represents in a sense answers to questions which still have to be posed.

I am grateful to Professor C. Miravittles and Dr E. Molins (Barcelona) for allowing me to use their (as yet) unpublished data for perchlorobifluorenylidene, to Professor M. Dobler (Zürich) for a copy of *Mac-MoMo*, to Professors X. Solans (Barcelona), A. Dreiding (Zürich) and M. B. Rubin (Haifa) for helpful discussions and to Dr M. Kapon (Haifa) for help with computing. This research has been supported by the P. & E. Nathan Research Fund and the Fund for the Promotion of Research at Technion.

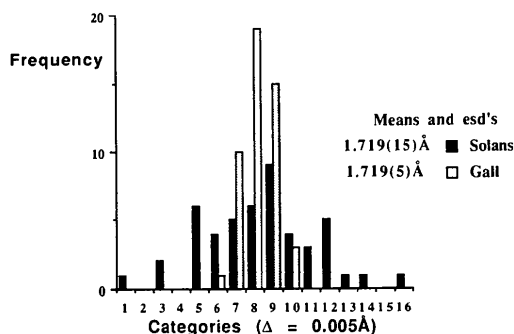


Fig. 13. The histogram of C—Cl distances obtained from the perchlorofluorene-9-spirocyclohexa-2',5'-diene molecule in its neat crystals and its complexes with benzene and cyclohexa-1,4-diene (at 298 and 168 K) is marked 'Gall' and that from the molecules $C_{26}HCl_{17}$, $C_{26}H_2Cl_{16}-A$ and $C_{26}H_2Cl_{16}-B$ is marked 'Solans'. Only chlorines bonded to sp^2 carbons are included. The categories are the following intervals of 0.005 Å — 1: 1.680 to 1.685, ... to 16: 1.750 to 1.755 Å.

APPENDIX

C—Cl distances

Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) give 1.720 (10) Å for the mean value of $C_{ar}-Cl$ ($o-Cl_2$) (364 entries); this should be compared with 1.719 (5) Å given by Gall *et al.* (1985) (32 entries) and an earlier value of 1.717 (8) Å (Herbstein, 1979). We obtain 1.718 (4) Å as the mean for the 16 C—Cl distances where chlorines are bonded to sp^2 carbons of the cyclohexadiene moieties; this does not differ significantly from the value of 1.711 (11) Å given by Allen, Kennard, Watson *et al.* (1987) for Cl—C=C—Cl fragments. Thus aromatic and ethylenic sp^2 carbons can be treated together. The histograms of C—Cl distances in the two groups of perchlorofluorenyl moieties discussed here are shown in Fig. 13, from which it is clear that there is good agreement between the means but that the Gall *et al.* (1985) values (e.s.d. 0.005 Å; 48 values) are more precise than those of Solans *et al.* (1980) (e.s.d. 0.015 Å; 48 values). The values for perchlorobifluorenylidene are not accurate enough to be included in this comparison.

The mean distance for $C(sp^3)-Cl$ in the hexachlorocyclohexa-1,4-diene moiety is 1.794 (4) Å (eight values) and the single $C(sp^3)-Cl$ distance in $C_{26}HCl_{17}$ [$C(14)-Cl(43)$] is 1.806 Å (e.s.d. uncertain). Kaftory (1983) found that the mean of 244 values for the $C(sp^3)-Cl$ distance (single chlorine substituted at carbon) was 1.788 (26) Å while Allen, Kennard, Watson *et al.* (1987) give 1.779 (15) Å for X_2-C-Cl_2 ($X = C, H, N, O$) fragments (18 values).

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Deformation-Density Studies of Thiathiophthenes. II. 2,4-Diphenyl-6a-thiathiophthene

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Abstract

A multipole model deformation-density study of 2,4-diphenylthiathiophthene is described. Like other thiathiophthene derivatives, the title compound contains two fused five-membered rings with a linear S—S—S part. However, it has two significantly different S—S distances [2.2125 (4) and 2.5087 (4) Å], in contrast to its 2,5-dimethyl derivative, which has been shown previously to have C_s molecular symmetry and hence two equal S—S distances [2.3510 (1) Å]. A comparison of the two derivatives is presented in terms of the multipole model deformation-density distribution. The net atomic charge of each atom obtained from the multipole refinements as well as from extended Hückel molecular orbital calculations is compared. The central S atom is more electron deficient than the other S atoms. Positive deformation densities are found along the C—C, C—H and C—S bonds. Small densities are found along the S—S bonds. In general, the multipole model density distributions give much clearer features than the experimental ones. Up to

hexadecapole terms are needed for S atoms in the multipole model refinements. The S atom further from the central S atom has a higher electron density than the nearer one. This is in agreement with the three-centre four-electron bond model.

Introduction

6a-Thiathiophthene derivatives have attracted considerable interest because of the unusual type of S—S bonding in these molecules (Hansen, Hordvik & Saethre, 1975; Gleiter & Cygax, 1976). The effect of alkyl substitution on the S—S bond length has been discussed at great length (Hordvik & Saethre, 1972; Wei, Paul, Beer & Naylor, 1975; Johnson, Llaguno & Paul, 1976; Wang, Chen & Wu, 1988; Wang, Wu & Cheng, 1990). Solid- and gas-state ESCA studies (Clark, Kilcast & Reid, 1971; Saethre, Svensson, Martensson, Gelius, Malmquist, Basilier & Siegbahn, 1977) were performed to try to solve the question of symmetry, *i.e.* whether the potential-energy curve for the S—S—S system has a single or double minimum. Several empirical and non-empirical calculations on the electronic structures of

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