The authors thank the Centro de Proceso de Datos de la Junta de Energía Nuclear (Madrid), for providing facilities for the use of the 1108 Univac computer.

References

BROWN, W. A. C., EGLINTON, C., MARTIN, J., PARKER, W. & SIM, G. A. (1964). *Proc. Chem. Soc. London*, pp. 57–58.

FLORENCIO, F., SMITH-VERDIER, P. & GARCÍA-BLANCO, S. (1978). *Acta Cryst.* B**34**, 2220–2223.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS. A Computer Program for the Automatic Treatment of Weighting Schemes.* Instituto 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TAMURA, C. & SIM, G. A. (1968). *J. Chem. Soc. B*, pp. 1241–1248.

WEBB, N. C. & BECKER, M. R. (1967). *J. Chem. Soc. B*, pp. 1317–1321.

Acta Cryst. (1981). B**37**, 2079–2082

Perchloro(9-phenyl-3-fluorenone). A Disordered Structure

BY X. SOLANS, C. MIRAVITLLES AND F. PLANA

UEI de Difracción de Rayos-X y Estructuras Cristalinas, Instituto 'Jaime Almera' del CSIC, Egipciacas 15, *Barcelona*-1, *Spain*

AND J. P. DECLERCQ* AND G. GERMAIN

Laboratoire de Chimie-Physique et de Cristallographie, Université de Louvain, 1 *place Louis Pasteur, B*-1348 *Louvain-la-Neuve, Belgium*

(*Received* 24 *July* 1979; *accepted* 27 *April* 1981)

Abstract. $C_{19}Cl_{12}O$, M_r = 669·64, $F(000)$ = 1304, monoclinic, $C2/c$, a = 16·420 (4), b = 15·005 (3), c = 10·478 (3) Å, β = 119·36 (2)°, V = 2250·0 (9) Å^3, Z = 4, D_c = 1·97 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·48 mm^{-1}. Direct methods were used to determine the structure from X-ray data. Block-diagonal least-squares refinement based on 1419 reflections converged with R at 0·045 and with occupation factors for the Cl(14) and O(14) atoms equal to 0·5. The molecule is located at a special position (twofold axis) and is slightly distorted as a consequence of steric interactions between Cl atoms.

Introduction. The success achieved in the synthesis of functionalized radicals of the perchloro(triphenylmethyl) free-radical series (Ballester, Riera, Castañer, Badía & Monsó, 1971) and their bonding to molecules of biological interest (Ballester, Riera, Rodriguez & Rovira, 1977; Ballester, Castañer, Riera & Veciana, 1978) prompted Ballester and co-workers to try the same functionalization in fluorene radicals; for this reason, the title compound was synthesized as the first step towards obtaining these radicals.

Perchloro(9-phenyl-3-fluorenone) (PPF) is obtained together with its isomer perchloro[4-(9-fluorenylidene)-2,5-cyclohexadien-1-one] and with the free radical 9-phenyl-9-fluorenyl which is one of the original products in the synthesizing process (Armet, 1978). In order to make a decisive confirmation of the structural hypotheses established by means of spectral and chemical techniques by the aforementioned authors, the structure of PPF was determined by X-ray diffraction methods.

Irregular black crystals were obtained by evaporation in chloroform. Initially a crystal 0·2 × 0·2 × 0·2 mm was selected and an attempt to determine its structure was made without success. A second crystallization (also by evaporation in chloroform), but slower and more controlled, produced new black crystals with a more defined habit and of generally better quality, and so a second crystal was chosen (0·2 × 0·2 × 0·3

---

[*] Charge de Recherches of the Fonds National de la Recherche Scientifique.

0567-7408/81/112079-04$01.00

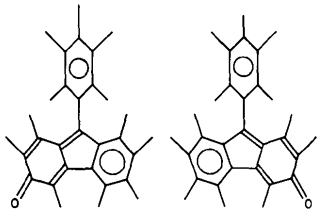
mm). Although no great differences were observed between the two crystals as regards intensities measured and Wilson statistics, the distribution of the values of $|E_{hkl}|^2$ in terms of the parity groups was significantly better in the second crystal. This would explain the failure of the first attempt at a structural resolution.

The crystal data and the intensity measurements were made on a Syntex $P2_1$ diffractometer. The unit cell was determined automatically by centering 15 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. The intensities were collected by the ω-scan technique. 1671 independent reflections were measured within the range $2 \leq \theta \leq 23{\cdot}5°$, 1419 of which were considered as observed according to the condition $I \geq 2{\cdot}5\sigma(I)$. Lorentz–polarization corrections were made. The systematic absences observed indicated two possible space groups, Cc and $C2/c$. The statistical results of $\langle||E|^2 - 1|\rangle$, $\langle|E|\rangle$ and the $N(z)$ distribution (Howells, Phillips & Rogers, 1950) indicated the space group was $C2/c$. However, this conclusion does not concur with the results obtained by spectroscopic and chemical techniques. According to these, the ketonic function must be linked to the atoms C(3) or C(3′), because $Z = 4$ and in group $C2/c$ the molecule must be situated in a special position. However, this is not possible due to the lack of symmetry of the PPF molecule. In view of this fact, the structure was considered as noncentrosymmetric during the resolution process.

The phase problem was solved by direct methods (Main, Woolfson, Lessinger, Germain & Declercq, 1977) using 300 reflections with $|E| \geq 1{\cdot}31$ and 2000 $\sum_2$ relationships. An E map computed with the phase from the set with the highest combined figure of merit revealed peaks for all the atoms, but it was not possible to differentiate the position of the ketonic group according to the height and the distances of peaks linked to the C(3) and C(3′) atoms.

In considering that these two atoms could be Cl, we decided to perform a block-diagonal least-squares refinement (a modified version of *SFLS*, Ahmed, Hall, Pippy & Huber, 1966) and this gave a value of $R = 0{\cdot}12$. A difference synthesis at this point revealed negative maxima for these two Cl atoms and another electron density synthesis indicated that the integration of these two maxima corresponds to a total number of electrons equal to 13. Moreover, the bond distances between C(3), C(3′) and these two maxima have an average value equal to that of the C—Cl and C=O distances.

Refinements considering a Cl atom bonded to C(3) and an O atom to C(3′), and inversely, did not solve the problem of the location of the ketonic group. In the same way, in none of these models did the distances and angles clearly indicate which of the groups showed a benzenic or quinoid structure. All this led us to think that the Cl and O atoms are fractionally in statistical disorder. New refinements with, in the first place, an occupation factor of 0·5 for Cl and O atoms bonded to C(3) and C(3′), and secondly, anisotropic cycles with a free occupation factor gave a final R value of 0·045 for 1419 reflections, and the occupation factors for Cl(14), O(14), Cl(14′) and O(14′) are very close to 0·5.



(I) (II)

Fig. 1. Two possible stereochemical configurations for the PPF molecule.

A subsequent refinement with space group $C2/c$, and an occupation factor of 0·5 for Cl and O atoms 14 and 14′, gave the same final R value.* Thus, we must consider that (a) the molecule is located at a special position (twofold axis) and (b) there is disorder not only for the Cl and O atoms but also for the rings to which these atoms are linked, since the presence of the C=O bond conditions the existence of a quinoid ring. Fig. 1 shows a diagram of the two conformations.

Table 1. *Final atomic parameters* ($\times 10^5$) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^2$) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = 1/6\pi^2 \textstyle\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	87727 (36)	67373 (37)	82706 (60)	8 (1)
C(2)	83145 (36)	60921 (38)	86199 (61)	8 (1)
C(3)	85016 (37)	51895 (38)	85408 (62)	7 (1)
C(4)	91775 (36)	49330 (34)	80929 (56)	6 (1)
C(5)	96377 (33)	55686 (32)	77530 (53)	6 (1)
C(6)	94370 (35)	64874 (31)	78479 (56)	7 (1)
C(7)	100000	70384 (44)	75000	6 (1)
C(8)	100000	80242 (43)	75000	7 (1)
C(9)	94065 (34)	85069 (32)	62345 (54)	7 (1)
C(10)	94234 (34)	94268 (31)	62328 (59)	9 (1)
C(11)	100000	98931 (43)	75000	8 (1)
Cl(12)	85433 (12)	78312 (10)	84278 (24)	16 (1)
Cl(13)	75200 (11)	63773 (13)	91556 (21)	14 (1)
O(14)	80586 (56)	45749 (65)	88847 (97)	15 (2)
Cl(14)	79424 (22)	44275 (19)	90245 (37)	10 (1)
Cl(15)	93608 (15)	38080 (10)	81523 (26)	17 (1)
Cl(16)	86598 (10)	79142 (9)	46961 (15)	7 (1)
Cl(17)	87259 (9)	99859 (9)	46124 (15)	11 (1)
Cl(18)	100000	110359 (11)	75000	10 (1)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36141 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

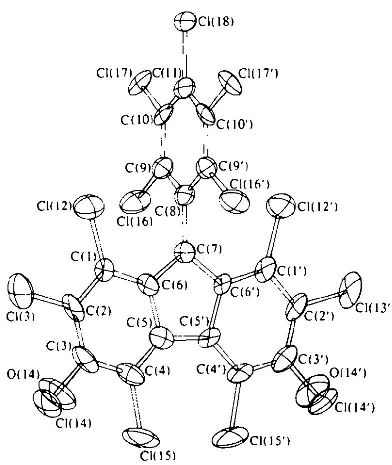


Fig. 2. View of the molecule drawn by *ORTEP* showing thermal ellipsoids and the numbering of the atoms.

The function minimized in the refinement process was $w||F_o| - |F_c||^2$ with $w = 1/(a + |F_o| + c|F_o|^2)$; $a = 2F_{\min}$, $c = 2/F_{\max}$ and $R = \sum||F_o| - |F_c||/\sum |F_o|$.

A difference map showed no significant features. The final atomic parameters are given in Table 1. Fig. 2 shows a view of the molecule and the numbering of the atoms drawn by the program *ORTEP* (Johnson, 1965).

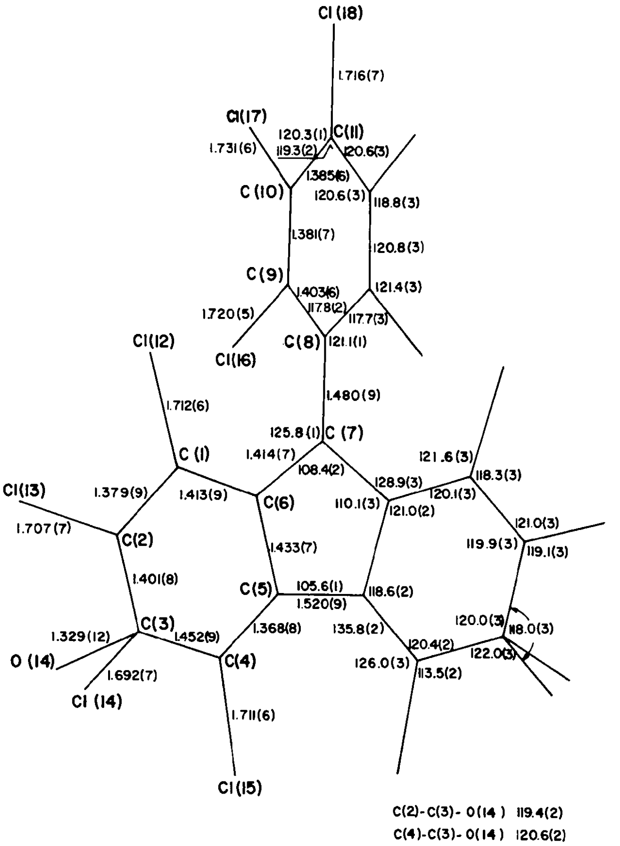


Fig. 3. Bond lengths (Å) and angles (°); standard deviations are in parentheses.

Table 2. *Selected intramolecular distances* (Å)

Cl(12)–Cl(13)	3·069 (3)	Cl(16)–Cl(17)	3·114 (2)
Cl(13)–Cl(14)	3·026 (4)	Cl(17)–Cl(18)	3·134 (2)
Cl(14)–Cl(15)	3·033 (5)	O(14)–Cl(13)	2·903 (10)
Cl(15)–Cl(15')	3·011 (4)	O(14)–Cl(15)	2·843 (11)

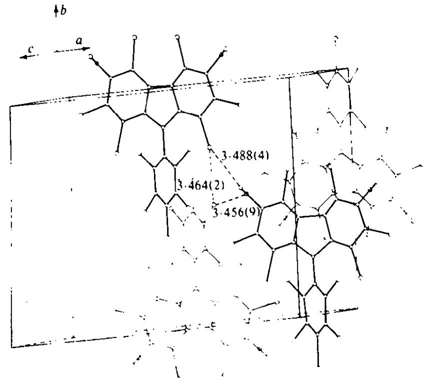
Discussion. Fig. 3 shows the bond distances and angles of the PPF molecule. The bond lengths and bond angles in the pentachlorophenyl group do not differ from those values obtained in other structures containing this group {mean values of C–C = 1·39 (2), C–Cl = 1·72 (2) Å and C–C–C = 120 (1)° as in perchloro(5,10-diphenyldibenzo[*a,e*]pentalene) (Miravitlles, Solans, Germain & Declercq, 1979), decachlorobiphenyl (Pedersen, 1975; Galí, 1975), perchloro(diphenylnitroxide) (Solans, Galí, Miravitlles & Font-Altaba, 1978), perchloro(1-benzylidene-2,5-cyclohexadiene) (Galí, Solans, Miravitlles & Plana, 1978) or in perchloro(1,2,3-triphenylnaphthalene) (Galí, Solans, Miravitlles, Font-Altaba & Armet, 1978)}. The C–Cl distances coincide with values given by Herbstein (1982).

The average C–C distance in the six-membered rings of the fluorenone group is 1·41 (5) Å. This is longer than the accepted value of 1·394 Å (Sutton, 1958) for a benzo ring, and shorter than the average value of 1·450 Å for a quinoid ring substituted by Cl atoms as, for example, in perchloro(1-benzylidene-2,5-cyclohexadiene) (Galí, Solans, Miravitlles & Plana, 1978) and in perchloro-*p*-xylylene (Galí, Miravitlles & Font-Altaba, 1976).

The distance C(3)–O(14) is appreciably longer than it should be, especially bearing in mind the electronegativity of the Cl atoms (Yates, Ardao & Fieser, 1956). Nevertheless, this difference could be attributed to partial errors due to the difficulty of refining a disordered structure, as in the case of the distance C(3)–Cl(14) which is significantly shorter than the average accepted value.

On the other hand, the average value of the remaining C–Cl bond distances of the fluorenone group is 1·71 (2) Å which concurs with the above-mentioned accepted value (Herbstein, 1982).

The PPF molecule is slightly distorted as in the majority of perchlorinated compounds in which there is severe internal overcrowding as a consequence of steric interactions between Cl atoms (Table 2). Accordingly, the C(5)–C(5') bond distance is longer (1·520 Å) than in the above-mentioned structures, the C(6)–C(5)–C(4) angles are appreciably less than 120° and the torsion angle C(4)–C(5)–C(5')–C(4') is 4·04°. The dihedral angle between the perchlorophenyl and fluorenone groups is 89·5°.



Fg. 4. Perspective view of the unit-cell contents, showing shortest intermolecular distances (Å).

The PPF molecules are stacked in layers parallel to the (103) planes in the crystal (Fig. 4).

We thank the Chlorocarbon Group of the Insituto de Química Aplicada de Catalunya (CSIC) for valuable discussions and for providing the samples; one of us (CM) is grateful for the financial assistance provided by the University of Louvain and the CSIC (Consejo Superior de Investigaciones Científicas).

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. National Research Council, Ottawa, Canada.

Armet, O. (1978). Thesis, Univ. of Barcelona, Spain.

Ballester, M., Castañer, J., Riera, J. & Veciana, J. (1978). *Tetrahedron Lett.* p. 479.

Ballester, M., Riera, J., Castañer, J., Badía, C. & Monsó, J. M. (1971). *J. Am. Chem. Soc.* **93**, 2215–2225.

Ballester, M., Riera, J., Rodriguez, A. & Rovira, C. (1977). *Tetrahedron Lett.* p. 2355.

Galí, S. (1975). Thesis, Univ. of Barcelona, Spain.

Galí, S., Miravitlles, C. & Font-Altaba, M. (1976). *Acta Cryst.* B**32**, 3112–3114.

Galí, S., Solans, X., Miravitlles, C., Font-Altaba, M. & Armet, O. (1978). *Acta Cryst.* B**34**, 1011–1014.

Galí, S., Solans, X., Miravitlles, C. & Plana, F. (1978). *Acta Cryst.* B**34**, 1739–1741.

Herbstein, F. H. (1982). *Acta Cryst.* To be published.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210–214.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

Miravitlles, C., Solans, X., Germain, G. & Declercq, J. P. (1979). *Acta Cryst.* B**35**, 2809–2812.

Pedersen, B. F. (1975). *Acta Cryst.* B**31**, 2931–2933.

Solans, X., Galí, S., Miravitlles, C. & Font-Altaba, M. (1978). *Acta Cryst.* B**34**, 2331–2333.

Sutton, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* London: The Chemical Society.

Yates, P., Ardao, M. I. & Fieser, L. F. (1956). *J. Am. Chem. Soc.* **78**, 650–652.

Acta Cryst. (1981). B**37**, 2082–2085

Crystallographic Studies of High-Density Organic Crystals, 3,5-Diamino-2,4,6-trinitrophenol

By S. K. Bhattacharjee and H. L. Ammon

Department of Chemistry, University of Maryland, College Park, Maryland 20742, *USA*

(*Received* 22 *January* 1981; *accepted* 29 *April* 1981)

Abstract. $C_6H_5N_5O_7$, $M_r = 259\cdot1$, orthorhombic, $P2_12_12_1$, $a = 4\cdot9653\,(5)$, $b = 8\cdot8984\,(5)$, $c = 20\cdot607\,(3)$ Å, $D_{\rm calc} = 1\cdot89$ Mg m^{-3} for $Z = 4$; Cu $K\alpha$ ($\lambda = 1\cdot5418$ Å) diffractometer data; 909 intensities; 860 I's $> 3\sigma$ above background; final $R = 0\cdot044$. The effects of both nitro and amino substitution are exhibited by the aromatic ring. All H atoms are involved in strong intramolecular and weaker intermolecular H···O contacts. The C—N and N—O distances, O—N—O angles and C—N torsion angles of the nitro groups show trends which could be related to different degrees of negative-charge delocalization by the groups.

Introduction. The densities of organic crystals containing atoms no heavier than O are typically 1·1–1·3 Mg m^{-3}. Nitro-group substitution can produce a dramatic increase in crystal density, with some polynitro compounds approaching 2·0 Mg m^{-3}. We are in the process of investigating the crystal structures of

0567-7408/81/112082-04$01.00