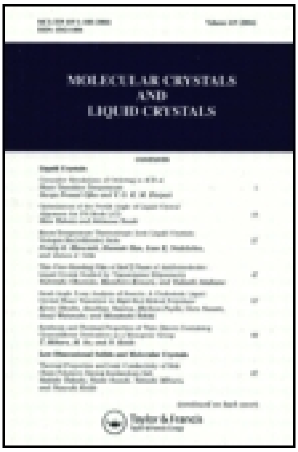

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Crystal Structure of the Organic Free Radical Perchlorotriphenylmethyl From Powder X-Ray Diffraction Data. Comparison with its Clathrate Structures

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CRYSTAL STRUCTURE OF THE ORGANIC FREE RADICAL PERCHLOROTRIPHENYLMETHYL FROM POWDER X-RAY DIFFRACTION DATA. COMPARISON WITH ITS CLATHRATE STRUCTURES.

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Abstract The perchlorotriphenylmethyl radical (PTM) is an exceptionally stable carbon free radical with considerable bulkiness showing a propeller-like conformation. Due to its inherent interest and since no large enough single-crystals were available, its crystal structure has been determined "ab initio" from powder X-ray diffraction data. To the authors' knowledge, this is the first molecular structure solved by powder methods. The crystal structure of pure PTM is also compared with the crystal structures of the clathrates that it forms with benzene and halogenobenzenes.

INTRODUCTION

The perchlorotriphenylmethyl radical (PTM) is prepared from tris-(pentachlorophenyl) methane in a "one pot" reaction by treatment with aqueous tetra-n-butylammonium hydroxide in tetrahydrofuran, followed by oxidation of the resulting carbanion with p-chloranil[1]. The PTM radical is obtained in the form of an amorphous powder that can be recrystallized from benzene and halogenobenzenes to form the corresponding clathrates. By heating at approx. 50°C, the clathrates decompose to give crystalline powder of PTM. Because of the impossibility of obtaining suitable crystals of pure PTM to perform a single-crystal X-ray diffraction experiment, the molecular structure of the PTM radical was first established in the benzene clathrate.

The present study has been undetaken in order to determine the crystal structure of pure PTM as well as to find the structural relationships existing between its crystal structure and those of the corresponding clathrates. This study also confirms the utility of the strategy described in [2] for the determination of crystal structures, with large known fragments, directly from measured X-ray powder diffraction intensities.

EXPERIMENTAL CONDITIONS

Microcrystalline powder of pure PTM was introduced in an upper-loaded sample holder. The powder diffraction pattern was scanned in steps of 0.02°(2θ) over the angular range 5-60°(2θ) and fixed-time counting (15 sec) was employed. Data were obtained by using a standard Siemens D500 powder diffraction system (40kV,20mA, copper target, graphite- monochromator, 293°K). The adjustment of the diffractometer was checked by using a Si standard.

The unit cells of the PTM clathrates with C_6H_5X (X= F, Cl and Br) were derived from single-crystal diffraction data measured on a four-circle CAD4 Enraf Nonius diffractometer.

DATA ANALYSIS

Indexing

It is a crucial stage in structural analysis, which needs high accuracy of the diffraction line positions. 28 lines of the powder diffraction pattern in the range $10 \leq 2\theta \leq 35°$ were introduced in the program TREOR[3]. The monoclinic test with $k_{max}=18$ yielded 16 possible solutions, of which only one showed no unindexed lines. This solution has refined cell parameters a=13.60(3), b=11.42(3), c=18.00(5)Å, β=108.2(3)°. The calculated density for Z=4 is 1.91 g cm^{-3} which is, as expected, higher than for the PTM.(C_6H_6) clathrate (1.80 g cm^{-3}). The unit cell found indexes all the observed lines of the diffraction pattern. From the list of unambiguous peaks, it could be seen that all lines can be indexed using the restriction h+k=2n which corresponds to a C-centered cell. According to the additional systematic absences for h0l with l=2n+1, the more probable space group C2/c was assumed (molecular formula: $C_{19}Cl_{15}$, Z=4).The final cell dimensions are: a= 13.612(2) b= 11.417(2), c=17.907(1)Å, β= 108.27(1)°, V= 2643$Å^3$.

Structure solution

To our knowledge, this is the first molecular crystal structure solved "*ab initio*" from powder diffraction data. Consequently, the determination procedure will be discussed in more detail. The main causes that make more difficult the resolution of molecular crystals by powder methods are two:

a) Unlike to most inorganic compounds,the diffraction interval is rather small (in general up to 2θ ≅ 60-70° for CuKα radiation). Due to the limited resolution, the application of conventional Direct Methods is problematic. Moreover, molecular crystals tend to have large cells. Hence the overlap problems at higher angles are severe.

b) The direct interpretation of the conventional Patterson map is normally impossible, due to the large number of equal-atoms in the asymmetric unit.

Recently,[2] have devised a new strategy that overcomes these difficulties provided that the geometry of a rather large fragment of the molecule is previously known. This strategy is based on the automated interpretation of the Patterson function in two stages. Firstly, the orientation of the molecule is found using the σ-function[4], and secondly, the oriented molecule is positioned in the unit cell with the τ-function[5]. The geometry of the known fragment of the PTM molecule i.e. the 15 Cl atoms, was obtained from the 1:1 benzene clathrate of PTM[1]. For practical efficiency and since the PTM fragment includes the twofold symmetry axis as pseudosymmetry, the Patterson search was done with all the 15 Cl atoms assuming the space group $C\bar{1}$. The program used was a slightly modified version of the ROTSEARCH program[6]. Table I summarizes the results of the Patterson search. It can be seen that the first and second rotation search solutions correspond to correct orientations of the molecule in the unit cell. The coarse rotation search was performed with 21 intramolecular Cl-Cl vectors in the range 2-5Å.

The positioning of the molecule, however, is not as clear as the rotation search. Fortunately, since the input fragment is large enough, the R-value is very reliable and the correct τ peak can easily be discriminated.

TABLE I Results of the automated full-symmetry Patterson search procedure applied to the PTM powder data (σ_w = height of the highest-ranked wrong σ peak).

σ / σ_w	solution with lowest R-value (%)	ranking n°. of the τ peak
1.82	14.4	46*
1.77	15.5	43*
1.00	16.5	7
0.95	22.6	32

* = correct solution

Structure refinement

In molecular crystals, the structure refinement from X-ray powder diffraction data is not trivial. On the one side, the number of positional parameters to refine is large and, on the other side, the 2θ interval of the diffraction pattern useful for the Rietveld refinement is rather small. Hence the refinement without constraints tends to produce wrong results as confirmed by several tests performed by the authors using the PTM data. To overcome this handicap, the Rietveld method[7] has been combined with the rigid- body strategy[8] in the RIBOLS[9] program. In this way, the number of free parameters is largely reduced, and the refinement from X-ray powder diffraction can furnish accurate information about the molecular shape and the crystal packing.

The refinement of pure PTM is a very good example of this drastic reduction. If no constraints are applied, the number of positional free parameters is 49. After introducing the rigid groups, it reduces to 8 only, i.e., three Euler angles φ, ψ, ϕ and three coordinates x, y, z defining, respectively, the orientation and the position of the phenyl ring not possessing crystallographic symmetry (ring A), and, for the phenyl ring on the crystallographic twofold axis (ring B), one Euler angle ψ with spin axis parallel to b and the y- coordinate of the center of mass.

Table II Details of the rigid-body Rietveld least-squares refinement (see text).

2θ range (°):	13-40
Step scan increment (°2θ):	0.02
N°. of structural parameters:	8

E.s.d.'s [σ] of the structural parameters:

ring	$\sigma(\varphi)$°	$\sigma(\psi)$	$\sigma(\phi)$	σ(x)Å	σ(y)	σ(z)
A	0.86	0.96	1.16	0.06	0.06	0.05
B	-	0.84	-	-	0.04	-

N°.of profile parameters:	3
Scale factor c:	$1.9(2) \times 10^{-4}$
FWHM (°):	0.106(8)
$B_{overall}$ ($Å^2$):	8.8(1.5)
Final R_{wp} (%):	21.3

$$\text{with} \quad R_{wp} = \left(\frac{\sum_i w_i [y_i(\text{obs}) - c\, y_i(\text{calc})]^2}{\sum_i w_i [y_i(\text{obs})]^2} \right)^{1/2}$$

and where y_i(obs) is the net intensity measured at the 2θ position of the i reflection.

Table II summarizes the most relevant refinement data. The profile function used to describe the peak shape was the Pseudo- Voigt one (0.8 Lorentzian + 0.2 Gaussian). Figure 1 shows the good agreement between observed and calculated powder diffraction patterns.

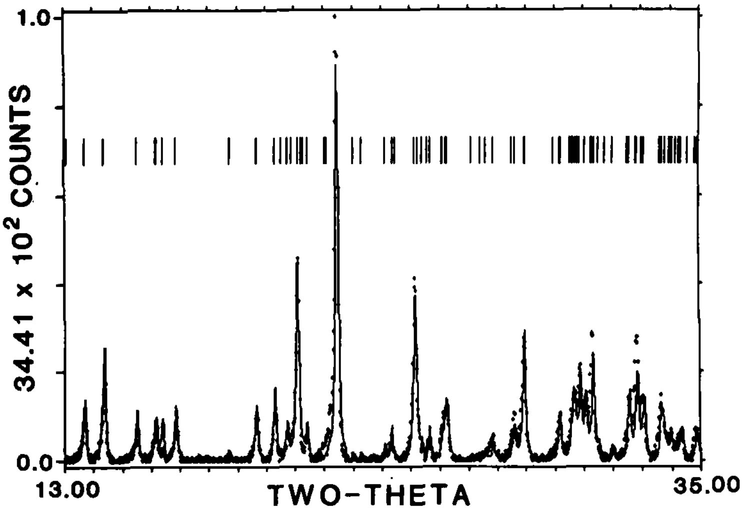

FIGURE 1 Plots of the observed and calculated powder diffraction patterns of PTM (dots = observed data; solid line = calculated data).

DISCUSSION OF THE STRUCTURE AND COMPARISON WITH ITS CLATHRATES.

The final atomic coordinates of the PTM molecule are given in Table III and Fig. 2 shows the corresponding atom numbering.

Since the molecule is placed on the twofold symmetry axis, the C1, C2, C8 and C2' atoms exactly lie on a plane (reference plane), confirming the expected sp^2 hybridation of C1. The conformation of the three pentachlorophenyl rings can be described by the dihedral angles between the reference plane and the mean planes of ring A and B i.e. 48.1° and 55.4° respectively. These values clearly indicate the non-symmetrical propeller conformation.

The PTM crystal structure is built by layers of molecules that are normal to the a^* direction and with a stacking distance of 6.48Å. The arrangement of the molecules in one such layer is shown in Figure 3 and can be described as formed by rows of molecules placed in a head-to-tail manner along the c- axis.

The PTM radical forms clathrates with small aromatic molecules with stochiometry 1:1. The most relevant crystal data of these

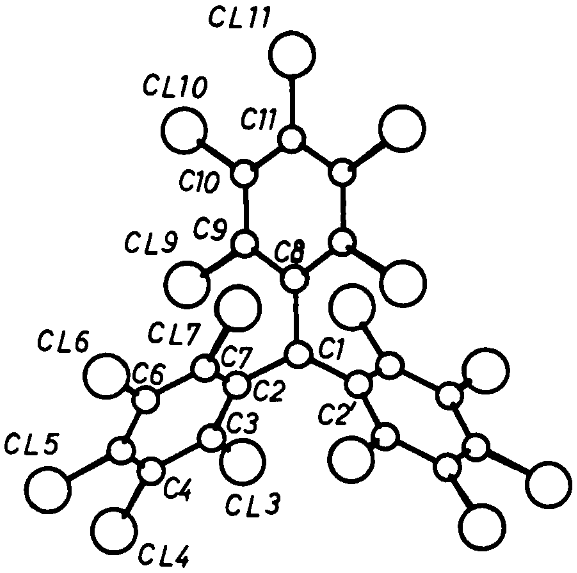

FIGURE 2 Atom numbering of the PTM radical molecule.

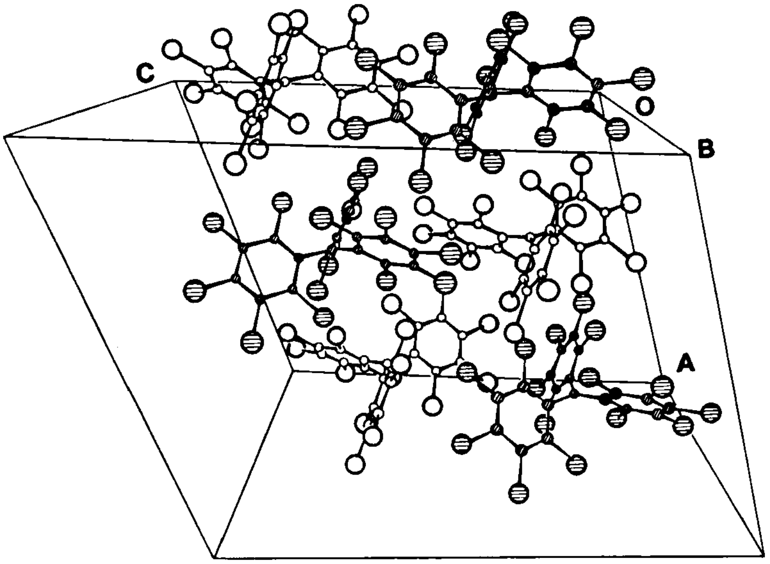

FIGURE 3 Perspective view of the unit cell of the PTM radical.

clathrates are given in Table IV.

Table III Fractional atomic coordinates ($x10^3$) for PTM with e.s.d.'s in parentheses.

atom	x/a	y/b	z/c
CL3	-0.161(5)	0.289(5)	0.209(4)
CL4	-0.199(5)	0.407(7)	0.049(3)
CL5	-0.072(4)	0.334(6)	-0.059(4)
CL6	0.089(5)	0.133(6)	-0.010(4)
CL7	0.134(6)	0.019(7)	0.152(3)
CL9	-0.194(2)	-0.024(4)	0.146(1)
CL10	-0.190(2)	-0.293(4)	0.145(1)
CL11	0	-0.421(5)	1/4
C1	0	0.099(5)	1/4
C2	-0.017(4)	0.153(6)	0.175(3)
C3	-0.087(4)	0.246(5)	0.151(3)
C4	-0.105(5)	0.301(6)	0.078(3)
C5	-0.050(4)	0.266(6)	0.030(3)
C6	0.021(4)	0.176(6)	0.051(3)
C7	0.038(5)	0.123(6)	0.124(3)
C8	0	-0.030(4)	1/4
C9	-0.084(1)	-0.095(3)	0.202(6)
C10	-0.084(1)	-0.215(3)	0.202(6)
C11	0	-0.275(4)	1/4

Table IV Cell parameters of some PTM clathrates with guests of the type C_6H_5X. All space groups are $P\bar{1}$ with Z=2.

X	a(Å)	b	c	α(°)	β	γ	V(Å^3)
H	8.771	13.416	13.537	96.91	90.14	101.85	1547
F	9.026	14.721	13.487	116.57	89.67	99.10	1578
Cl	8.882	13.456	13.557	97.65	91.25	98.90	1585
Br	8.933	13.484	13.575	97.97	91.55	98.31	1601

Inspection of Table IV indicates that the clathrates with X=H, Cl, Br correspond to the same structural type. Since the layered structure for X=H is already known[1], and to facilitate its comparison with that of pure PTM, the same portion of the layer of both structures are represented in figures 4 and 5. By heating at 50° the guest molecules included in the layers of the clathrate leave the crystal through the interlayer space, and, at the same time the PTM molecules rotate by ≅ ±25°.

Although the cell parameters of the clathrate with X=F are different from the rest, its structural type is essentially the same, as confirmed by x-ray analysis[10]. Here, the C_6H_5F molecules are partially placed in the interlayers. The measurement of the standard enthalpies associated with the process,

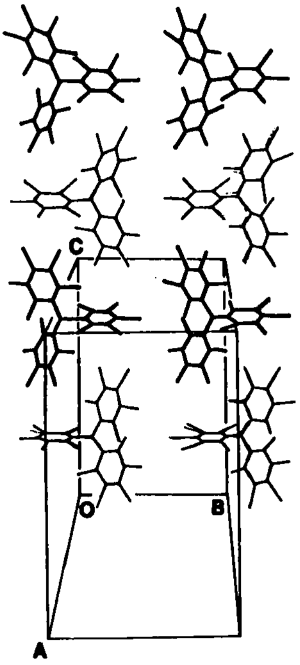

FIGURE 4 View of one layer of the PTM crystal structure.

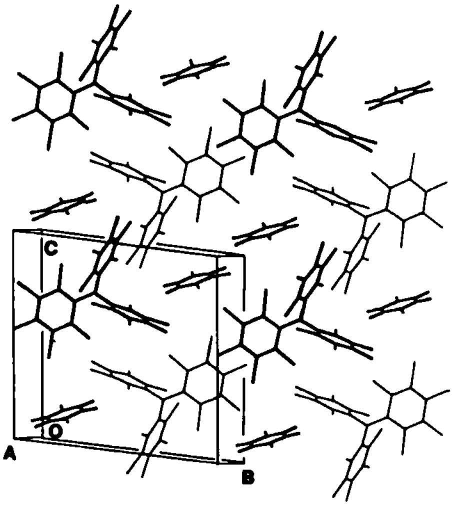

FIGURE 5 View of the same portion of one layer of PTM:C_6H_6. To visualize the correspondence between the molecules in both figures, they are drawn with different strengths.

$$\text{PTM:guest (s)} \xrightarrow{\Delta H_o} \text{PTM (s)} + \text{guest (g)} \quad (25^\circ C)$$

yields 17.4, 8.9, 47.5 and 52.6 KJ/mol for X=H,F,Cl and Br respectively, thus indicating that the fluorobenzene clathrate is also the less stable one.

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