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The Crystal and Molecular Structures of Overcrowded Halogenated Compounds. I. Introductory Survey

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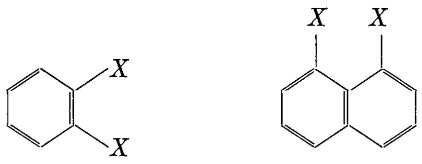
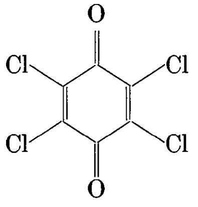
Crystallographic data are reported for the α (stable below −85 °C.) and β phases of 1:2-4:5-tetrachlorobenzene, and for the β and γ (stable above 46 °C.) phases of 1:2-4:5-tetrabromobenzene; the relationship between X-ray diffraction and nuclear-quadrupole resonance measurements for these compounds is discussed. Crystallographic data are also given for chloranil, hexabromobenzene, 1:4-5:8-tetrachloronaphthalene and octachloronaphthalene.

1. Introduction

Although overcrowded aromatic hydrocarbons show large deviations from regular forms (Harnik, Herbstein, Schmidt & Hirshfeld, 1954), the details of the distortion in the overcrowded region are difficult to study because the positions of hydrogen atoms must be determined. When the overcrowded atoms are halogens this difficulty does not arise; in addition some molecules become overcrowded only when bulky halogens are substituted for hydrogen atoms. We have therefore begun a systematic study of molecules in which the overcrowded atoms are halogens in order to obtain information about the molecular shapes and the interactions among the various halogen atoms. In the present paper crystallographic data are given for various compounds of interest. Determinations of the crystal structures of some of these compounds will be reported in later papers of this series. The compounds investigated fall into two categories of the classification introduced by Harnik *et al.* (1954) viz. Group I, where the overcrowding is due to bulky substituents ortho to one another in a benzene ring; and Group IV, where the overcrowding is due to bulky substituents in the 1:8 positions of a naphthalene ring (see Fig. 1).



Compounds of Group I. Compounds of Group IV.



Chloranil.

Fig. 1. Classification of compounds.

Crystallographic data for the various compounds were derived from equi-inclination photographs on a Weissenberg camera adapted for use at high and low temperatures in a manner similar to that described by Kreuger (1955).

2. Compounds in Group I

The ortho-dihalogenated benzenes are liquid at room temperature and it is therefore more convenient to work with the sym-tetrasubstituted (1:2-4:5) derivatives. The sym-tetrachloro and tetrabromobenzenes were investigated at −130 °C. and over the temperature range 20 to 120 °C.* In addition crystallographic data are reported for chloranil and hexabromobenzene at room temperature.

(*a*) 1:2-4:5-*tetrachlorobenzene*

This compound was obtained from British Drug Houses (Laboratory Chemicals Group), Poole, England; crystals were grown by slow cooling of ethanol–benzene solutions. Many of these crystals were found to be twinned; similar twinning is found in β-1:2-4:5-tetrabromobenzene and is discussed in more detail in Part II (Gafner & Herbstein, 1960).

Lattice parameters determined at room temperature by front and back-reflexion Weissenberg methods (Herbstein, 1957) are given in Table 1. Reasonably good agreement with the results of Dean, Pollak, Craven & Jeffrey (1958) was found and the axial ratios calculated from the present results ($a:b:c = 0{\cdot}9153:1:0{\cdot}3626$) also agree well with those given by Groth (1919) (0·9041:1:0·3650). There is, however, a difference of 4° 6′ in the values of β (103° 28′ and 99° 22½′ respectively). Photographs taken at temperatures up to 100 °C. (this limit was set by sublimation of the crystals) showed no evidence of a phase change. Photographs at −130 °C. showed that a phase change had taken place between this temperature and room temperature. Monfils (1955) has reported a phase change at −85 °C. (188 ± 2 °K.) from nuclear quadrupole resonance (NQR) measurements. Our photographs show that the new (α) phase differs from the β phase primarily in an increase of the length of the a axis by a factor of about six. Both $hk0$ and $hk1$ Weissenberg photographs show many absences and these made an accurate determination of the length of the new a axis difficult. The α and β phases have the same orientation and the appearance of comparable photographs suggests that there must be a close resemblance between the crystal structures. However, we have not been able to determine accurate cell dimensions or a space group for the α-phase because of the difficulties mentioned above.

The NQR spectrum of the β-phase is a doublet; this is in agreement with the X-ray results which show that there are two independent chlorine atoms in the unit cell. Below 188 °K. the spectrum consists of four lines. More information about the unit cell of the α-phase is needed before it can be decided whether these four lines have a multiple structure.

(*b*) 1:2-4:5-*tetrabromobenzene*

This compound was also obtained from B.D.H.; crystals were grown by slow cooling of ethanol–xylene solutions. Lattice parameters measured at room temperature are given in Table 1. The agreement of the present axial ratios ($a:b:c = 0{\cdot}9643:1:0{\cdot}3753$) with those given by Groth (0·949:1:0·347) is good. There is a large difference of 7° 58′ in the values of β (102° 22′ and 94° 24′ respectively). Crystals were photographed at −130 °C. but no phase change was found. Weissenberg photographs were also taken at temperatures of up to 120 °C. and a phase change was found in the region 40–50 °C. The phase stable at room temperature has been termed the β-phase, and that stable at higher temperatures the γ-phase. Lattice parameters of the latter are also given in Table 1.

The $\beta \rightleftharpoons \gamma$ transition in 1:2-4:5-tetrabromobenzene seems to have been observed first by Schaum, Schaeling & Klausing (1916) with the polarizing microscope, but no details were given.

There is a close relationship between the crystal structures of the β and γ-phases; in particular the molecules in both phases are at centres of symmetry and thus there are two independent bromine atoms in the asymmetric unit in each polymorph. A three-dimensional analysis of the crystal structure of the β-phase has been reported briefly (Gafner & Herbstein, 1958) and is described in detail in Part II; the crystal structure of the γ-phase will be reported later.

These X-ray results can be compared with those obtained from nuclear quadrupole resonance measurements. Bray & Barnes (1954) have reported a doublet

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* We are grateful to Mr C. A. R. Philpotts and Mr J. Shochot for their help in this part of the work.

Table 1. *Crystallographic data*

Compound	Phase	a (Å)	b (Å)	c (Å)	β	Space group	Density		Z	Morphology	Stability range
							Meas. (g.cm.$^{-3}$)	Calc. (g.cm.$^{-3}$)			
1:2-4:5-tetrachloro-benzene	α		See text								? to 188 °K.(5)
	β	9·731 ±0·005	10·631 ±0·005	3·855 ±0·005	103° 28′(1) ±5′	$P2_1/a$	1·858(2)	1·848	2	Needles elongated along [001] and showing {110}	188 °K. to at least 373 °K
1:2-4:5-tetrabromo-benzene	β	10·323 ±0·001	10·705 ±0·001	4·018 ±0·004	102° 22′ ±6′	$P2_1/a$	3·027(2)	3·014	2	Needles elongated along [001] and showing {110}	? to 319·5 °K.(4)
	γ(5)	12·08 ±0·01	9·71 ±0·01	4·07 ±0·02	112° 14′ ±20′	$P2_1/a$	—	2·956	2	Needles elongated along [001] and showing {110}	319·5 °K. to at least 393 °K.
Chloranil		8·72 ±0·01	5·785 ±0·005	17·04 ±0·01	103° 24′(6)	$P2_1/a$	1·933	1·954	4	Plates	
Hexabromobenzene		15·39 ±0·02	4·01 ±0·01	8·39 ±0·01	93 ±1°	$P2_1/n$	—	3·543	2	Needles elongated along [010]	
1:4:5:8-tetrachloro-naphthalene		9·45 ±0·02	15·20 ±0·01	7·07 ±0·02	—	$Pccn$	1·688	1·740	4	Needles elongated along [001]	
Octachloronaphthalene		19·48 ±0·03	7·30 ±0·04	9·76 ±0·01	111° 33′ ±5′	$P2_1/a$	2·08	2·07	4	Needles elongated along [010]	

(1) From Dean *et al.* (1958).
(2) From Handbook of Chemistry and Physics (30th Edition).
(3) Monfils (1955).
(4) Johnson (1958).
(5) Photographed at 59 °C.
(6) From Groth (1919).

at 77 °K. and a singlet at 298 °K. The diffraction and resonance measurements can be reconciled if the NQR spectrum of the β-phase consists of two frequencies at low temperatures which become increasingly difficult to resolve as the temperature is raised. The $\beta \rightleftharpoons \gamma$ phase change has also been investigated by NQR methods (Johnson, 1956) and the transition temperature found to be $46{\cdot}5 \pm 0{\cdot}2$ °C. In this work only one resonance was used and no attempt appears to have been made to find any other resonances.

The system 1:2-4:5-tetrachlorobenzene, 1:2-4:5-tetrabromobenzene has been investigated by the thaw-melting method (Rheinboldt, Perrier, Giesbrecht, Levy, Cecchini & de Campos, 1951) and reported to show continuous mixed-crystal formation. This can be reconciled with our present results only if 1:2-4:5-tetrachlorobenzene shows a $\beta \rightleftharpoons \gamma$ transformation between 100 °C. and the melting point at 138 °C. No information is available to test this.

(*c*) *Chloranil*

The crystallographic data were determined from oscillation and Weissenberg photographs about [100] (see Table 1). The results are in good agreement with those given by Chorghade (1939). It is not intended to continue work on this compound.

(*d*) *Hexabromobenzene**

This compound was obtained from Dr Th. J. de Boer (University of Amsterdam) and recrystallized from toluene. As the data in the literature (Plummer, 1925) are rather old, it was considered desirable to check them. Good agreement was obtained after re-orienting the cell chosen by Plummer to match our results. It is not intended to determine the crystal structure of this compound.

3. Compounds in Group IV

Crystallographic data have been reported for 1:8-dichloronaphthalene (Goldar, Zhdanov, Umanskii & Glushkova, 1952). In order to take advantage of any possible crystallographic symmetry, it was decided to investigate 1:4-5:8-tetrachloronaphthalene and octachloronaphthalene.

1:4-5:8-tetrachloronaphthalene was obtained from Dr E. Clar (University of Glasgow) (Clar & Marschalk, 1950) and recrystallized from a mixture of acetic acid and toluene. Octachloronaphthalene was obtained from Dr W. L. Mosby (American Cyanamid Co.) (Mosby, 1955) and further purified by recrystallization from cyclohexane. The crystallographic data are given in Table 1.

Although there are obvious resemblances between the unit cells and crystal symmetries (or pseudo-symmetries) of the three compounds 1:4-5:8-tetrachloronaphthalene, octachloronaphthalene and octamethylnaphthalene (Donaldson & Robertson, 1953) these resemblances are deceptive in that they do not reflect similarities in crystal structures. A crystal-structure analysis of 1:4-5:8 tetrachloronaphthalene, to be reported later, shows that, although both this compound and octamethylnaphthalene are layer structures, the arrangement of the molecules in the two crystals is quite different. Preliminary measurements indicate that octachloronaphthalene is not a layer structure.

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