

## The Crystal Structure of $\alpha$ -1,2,4,5-Tetrachlorobenzene Based on Spectroscopic Evidence and Packing and Lattice Frequency Calculations

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The crystal structure of  $\alpha$ -1,2,4,5-tetrachlorobenzene has been investigated by spectroscopic methods and packing calculations. With the existing unit-cell parameters, the crystal has been found to belong to space group  $P\bar{1}$  with two unrelated molecules located at (0,0,0) and  $(\frac{1}{2}, \frac{1}{2}, 0)$ . Atomic positions are given. The structure is closely related to that of the monoclinic  $\beta$  phase. Calculated lattice vibration frequencies are in good agreement with experiment.

### Introduction

Solid 1,2,4,5-tetrachlorobenzene has two known crystalline phases:  $\alpha$ , stable below 188 K, and  $\beta$ , stable between 188 K and the melting point. The structure of the  $\beta$  phase has been solved: the bimolecular unit cell is monoclinic, space group  $P2_1/a$ , with molecules lying on inversion centres. The  $\alpha$ -phase crystals grow twinned, and while the parameters of the bimolecular unit cell are known, the space group is not (Herbstein, 1964).

The cell parameters for both phases are shown in Table 1. The cells are similar, the  $\alpha$  cell being somewhat contracted, with **b** no longer perpendicular to the *ac* plane. In view of this, it would seem that the structures are closely related, and the molecules in the  $\alpha$  cell should be slightly rotated from their  $\beta$ -cell position. However, there is some evidence which makes this straightforward conclusion questionable, at least without further research. First, the phase transition is very sharp, and neither phase can be trapped in the temperature range corresponding to the other. Secondly, the Raman spectrum changes drastically with the phase transition (D'Alessio & Bonadeo, 1973), a fact that could correspond to a major molecular reordering.

In those cases where a direct determination of some structural data is difficult, or impossible, additional considerations based on other physico-chemical properties can be useful, and give at least approximate answers to the problem.

In particular, spectroscopic data in conjunction with symmetry considerations may yield information on the space group, and packing considerations reveal approximate positions of atoms in molecular crystals of rigid or quasi-rigid molecules. In those cases where a suitable intermolecular potential is available, calculations reproduce molecular equilibrium positions within a few degrees or tenths of an angström, for molecular rotations and centre of mass positions respectively. Furthermore, the values of the crystal energies for different equilibrium positions make a choice between these configurations possible (Mirsky, 1976).

The intermolecular potential considering non-bonded atom-atom interactions is the most widely used for packing calculations, and has been shown to reproduce well vibrational frequencies, especially in the lattice mode region (Dows, 1972; Bonadeo & D'Alessio, 1973). It assumes that atoms belonging to different molecules interact according to the nature of the pair involved, and that the corresponding energies depend on the interaction distance only. The most used potentials are of the 6-exp, Buckingham, form, or the 12-6, Lennard-Jones, form. The potential parameters are obtained empirically from static, and in some cases static and dynamic, properties of a series of related crystals.

The problem of the crystal structure of  $\alpha$ -1,2,4,5- $C_6H_2Cl_4$  seems to be particularly suitable for the kind of treatment discussed above. Firstly, only two space groups,  $P1$  and  $P\bar{1}$  are compatible with the X-ray data, and the problem is considerably simplified. Secondly, spectroscopic data from different sources are available. Finally, suitable potential parameters have been obtained by fitting simultaneously static and dynamic properties of a series of chlorinated benzene crystals

Table 1. Unit-cell parameters of the  $\alpha$  and  $\beta$  phases of 1,2,4,5- $C_6H_2Cl_4$  (Herbstein, 1964)

	Triclinic ( $\alpha$ ) at ~150 K	Monoclinic ( $\beta$ ) at ~300 K
<i>a</i>	9.60 Å	9.73 Å
<i>b</i>	10.59	10.63
<i>c</i>	3.76	3.86
$\alpha$	95°	90°
$\beta$	102.5	103.5
$\gamma$	92.5	90
<i>V</i>	371 Å <sup>3</sup>	388 Å <sup>3</sup>

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(Bonadeo & D'Alessio, 1973), and have been used with success for the calculation of crystal vibrations of  $\beta$ -1,2,4,5- $C_6H_2Cl_4$  which was not included in the fitting.

In the present work we study the crystal structure of  $\alpha$ -1,2,4,5- $C_6H_2Cl_4$  correlating X-ray evidence, spectroscopic data, calculated packing energies and calculated lattice mode frequencies.

### Symmetry properties and selection rules

Isolated molecules of 1,2,4,5- $C_6H_2Cl_4$  possess  $D_{2h}$  point symmetry. Of all the operations of the point group, we will be most interested in the inversion, since it is the only one compatible with a triclinic structure. There are 30 internal vibrational modes, 15 corresponding to  $g$  modes (Raman active, IR inactive) and 15 to  $u$  modes (IR active, Raman inactive). If the crystal site occupied by the molecule preserves the inversion centre, this exclusion rule holds in the crystalline spectrum. Furthermore, lattice vibrations are separated into Raman-active librational modes and IR-active translational modes. This is the case for the  $\beta$  phase, where the two molecules occupy  $\bar{1}$  sites, and are related by a glide plane and a screw axis.

If, instead, the inversion centre is lost and the molecules occupy general positions all internal vibrations become IR and Raman active, and lattice modes are built up from mixed librational and translational motions. In all cases the presence of two molecules in the unit cell makes the internal bands split into two components (correlation splitting), and there are nine optical lattice modes.

From the spectroscopic point of view, there are three distinct possibilities for the crystal structure of  $\alpha$ -1,2,4,5- $C_6H_2Cl_4$ . (1) Space group  $P1$ : the two molecules in the unit cell are in unrelated general positions; all internal modes are IR and Raman active; and both components appear in all spectra. The nine lattice modes are IR and Raman active. (2) Space group  $P\bar{1}$ : here there are two possibilities. (a) The two molecules occupy general positions, related by an inversion centre. All internal modes are IR and Raman active, one of the components of the doublet appearing in the IR and the other in the Raman spectrum. There are six Raman and three IR active libration-translation lattice modes. (b) The two molecules each occupy sites

with inversion symmetry. Raman and IR activities of internal modes are unchanged from the isolated molecule, and doublets appear in both spectra. There are six Raman-active librational lattice modes, and three IR-active translational lattice modes. This structure is closely related to that of the  $\beta$  phase.

### Spectroscopic evidence

NQR spectra of the crystal (Monfils, 1955) show only four distinct peaks corresponding to independent Cl atoms. This is consistent with the presence of an inversion centre (2a and 2b). On the other hand, Raman spectra in the lattice mode region show only five bands, pointing again to the  $P\bar{1}$  structure which predicts six Raman-active bands, against the  $P1$  structure which predicts nine such bands. These two experiments, however, do not distinguish between 2(a) and 2(b).

In order to obtain additional evidence, we have recorded IR spectra in the internal mode region. For 2(a) the bands should be singlets, and isolated molecule  $g$  bands should become active. For 2(b), on the other hand, only doublets corresponding to  $u$  modes should appear. The monoclinic  $\beta$  phase, which follows the same selection rules as 2(b) provides an adequate blank spectrum for the experiment. Since the presence of the two isotopic species of Cl obscures the observation of the Davidov splittings, we have focused our attention on the possible appearance of forbidden bands.

The spectra were recorded with a Beckman IR12 spectrophotometer, with a standard low-temperature cell cooled to liquid nitrogen temperature. The resolution was about  $0.8 \text{ cm}^{-1}$  to allow the observation of weak and narrow bands. For the same reason, the sample was about 1 mm thick, one or two orders of magnitude thicker than those used in common IR experiments.

In spite of these rather extreme conditions, no new bands appeared upon cooling the sample through the  $\beta$ - $\alpha$  transition down to 78 K. As discussed before, the absence of new bands points to 2(b).

In itself, none of these experiments is conclusive since they give only negative evidence. The observation of four NQR bands does not exclude the existence of four other bands, the observation of only five

Table 2. Potential parameters for the atom-atom interactions in 1,2,4,5- $C_6H_2Cl_4$

Interaction	BD* parameters			RKW† parameters		
	A (kcal $\text{\AA}^6$ )	B (kcal)	C ( $\text{\AA}^{-1}$ )	A (kcal $\text{\AA}^6$ )	B (kcal)	C ( $\text{\AA}^{-1}$ )
H-H	27.3	2654	3.740	27.3	2654	3.740
H-C	125	8766	3.670	125	8766	3.670
C-C	568	83630	3.600	568	83630	3.600
C-Cl	-631	44200	3.653	1140	180000	3.620
H-Cl	1005	33300	3.623	250	18000	3.700
Cl-Cl	3650	263000	3.510	2300	426000	3.650

\* Bonadeo & D'Alessio (1973).

† Reynolds, Kjems & White (1974).

Raman lines does not necessarily mean that only six are active and possible activated IR bands might be extremely weak. However, when all these facts are put together, there is strong evidence pointing to space group  $P\bar{1}$ , and we may reasonably favour 2(b).

### Packing calculations

If entropy contributions are neglected, the equilibrium position of the molecules in the cell, corresponding to the lowest crystal energy, is coincident with the minimum free energy which gives the actual position of the molecules in the crystal.

In the atom-atom model, the intermolecular energy is written as

$$2V = \sum_{\alpha\beta} \sum_{\mu\nu} \sum_{ij} V_{\alpha\mu i}^{\beta\nu j}(r_{ij}).$$

We have used functions of the Buckingham form:

$$V_{\alpha\mu i}^{\beta\nu j}(r_{ij}) = -Ar_{ij}^{-6} + B \exp(-Cr_{ij})$$

where  $\alpha, \beta$  label unit cells;  $\mu, \nu$  molecules in the unit cell;  $ij$  atoms in the different molecules;  $r_{ij}$  is the interatomic distance and the parameters  $A, B$  and  $C$  depend on the nature of atoms  $i$  and  $j$ .

The analysis has been performed with William's *PACK* 3 crystallographic packing program. This program calculates the crystal energy for a given configuration, and iteratively modifies this configuration towards minimum energy by a steepest-descent method. The input data include the available structural parameters, together with a specification of the degrees of freedom compatible with the crystal symmetry, the molecular geometry, and a suitable set of potential parameters.

We have analysed the packing properties of the three possible structures. The molecular geometry was assumed to be the same as in the  $\beta$  phase, with a C-H distance of 1.08 Å. Two different sets of potential parameters, those obtained by BD (Bonadeo & D'Alessio, 1973) and those obtained by RKW (Reynolds, Kjems & White, 1974), were used, and are reproduced in Table 2. All interactions involving interatomic distances larger than 6 Å have been neglected; the equilibrium positions are negligibly modified by adding more interactions, and the crystal energy can be adequately extrapolated (Burgos, Bonadeo & D'Alessio, 1977a).

For case 1, there are nine degrees of freedom, three rotations for each molecule, and three translations for one of the molecules (allowing both molecules to move would be translating the whole crystal). We have found that the refinement shifts the molecule to the inversion centre, thus giving 2(b), which confirms the spectroscopic data.

For 2(a), there are six degrees of freedom, three rotations and three translations of one molecule: the position of the other is fixed through the inversion operation connecting them.

For 2(b), the six degrees of freedom are the rotations of both molecules about their inversion centres. For steric reasons these must be at (0,0,0) and  $(\frac{1}{2}, \frac{1}{2}, 0)$ , as for the monoclinic structure.

Table 3 shows the crystal energies for the minimum energy packings of 2(a) and 2(b), calculated with the parameters of BD and of RKW. It can be seen that with both sets, the calculated packing energy for 2(b) is lower, by almost a factor of two, than that of 2(a). This difference is very drastic, and from the point of view of packing considerations it constitutes strong evidence for 2(b).

Table 3. *Calculated crystal energies for the minimum energy packings of structures 2(a) and 2(b)*

	$E$ (kcal mol <sup>-1</sup> )	
	2(a)	2(b)
BD*	-21.89	-37.63
RKW†	-34.24	-48.94

\* Potential parameters of Bonadeo & D'Alessio (1973).

† Potential parameters of Reynolds, Kjems & White (1974).

Although the packing energies obtained with the two potential parameter sets are quite different, the equilibrium positions are indistinguishable within the accuracy of the calculations. In Table 4 we report the atomic positions obtained with the parameters of BD. In Fig. 1 we show projections in the  $ab$  and  $ac$  planes of the corresponding unit cell, together with the  $\beta$ -phase unit cell: the two structures are very similar.

Table 4. *Fractional atomic coordinates ( $\times 10^4$ ) corresponding to the minimum packing energy structure for the  $\alpha$  phase of 1,2,4,5-C<sub>6</sub>H<sub>2</sub>Cl<sub>4</sub>*

	$x$	$y$	$z$
Molecule 1			
C(1)	425	1267	201
C(2)	1407	322	1761
C(3)	882	-906	1710
Cl(1)	993	2848	11
Cl(2)	3187	763	4070
H(3)	1606	-1571	2976
Molecule 2			
C(1)	4593	6240	-460
C(2)	3661	5242	-1824
C(3)	4175	4042	-1497
Cl(1)	4030	7792	-637
Cl(2)	1972	5580	-4212
H(3)	3492	3336	-2614

### Lattice mode calculations

The detailed knowledge of the crystal structure of a molecular crystal and of the intermolecular potential allows a further extension of the calculations, since for rigid molecules these factors completely determine the lattice vibration frequencies. It was mentioned before that the Raman spectrum in the lattice mode region changes drastically from the  $\beta$  to the  $\alpha$  phase.

Table 5. Observed and calculated frequencies of the Raman-active lattice vibrations of 1,2,4,5- $C_6H_2Cl_4$ 

$\beta$ phase			$\alpha$ phase		
Symmetry	Observed frequency*	Calculated frequency*	Symmetry	Observed frequency*	Calculated frequency
	( $cm^{-1}$ )	( $cm^{-1}$ )			( $cm^{-1}$ )
$A_g$	58	61	$g$	—	2(a) 157
	46	54		68	88
	35	35		55	115
$B_g$	—	69	48	86	62
	49	48	43	72	46
	21	19	33	47	38
				24	33

\* D'Alessio &amp; Bonadeo (1973).

D'Alessio & Bonadeo (1973) have calculated the corresponding frequencies for the  $\beta$  phase, which show good agreement with experiment (Table 5). We have calculated the lattice mode frequencies for the  $\alpha$  phase (2a and 2b) with BD parameters, and the positions obtained in the packing calculations. The calculation method employed here is discussed in detail by Taddei, Bonadeo, Marzocchi & Califano (1973), and

has been extended to cover the case of molecules occupying different sites (Burgos, D'Alessio & Bonadeo, 1977b); it will not be described here. The results are shown in Table 5. Once more, comparison with experiment favours 2(b), where the agreement is good.

It can be seen that although the structures of the  $\beta$  and  $\alpha$  phases are closely related, the calculated frequencies are widely different. This apparent contradiction is explained as follows: in the monoclinic phase, the in-phase ( $A_g$ ) and out-of-phase ( $B_g$ ) normal modes are symmetry separated, and therefore do not interact; since in the triclinic phase the molecules are independent, this restriction is lifted and, according to our calculated eigenvectors, they mix strongly, and none of the modes can be even approximately classified as symmetric or antisymmetric. A thermodynamic study of the compound, which will be published elsewhere, based on these calculated frequencies, also predicts a sharp  $\alpha$ - $\beta$  phase transition.

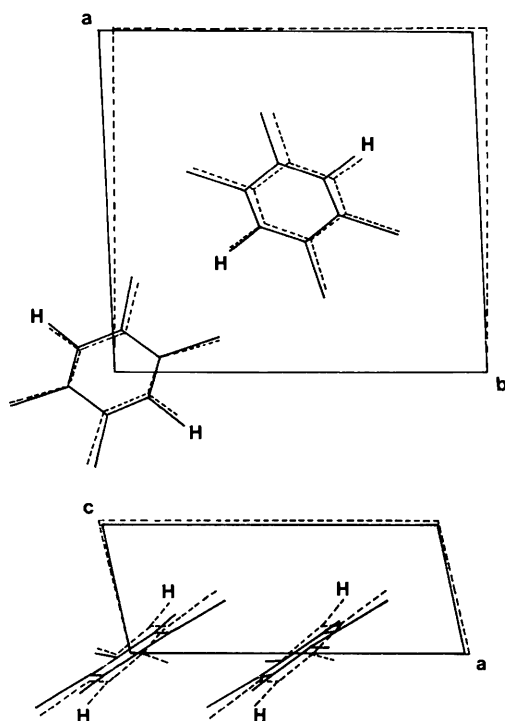


Fig. 1. Projections on the  $ab$  and  $ac$  planes of the unit cells of  $\alpha$  and  $\beta$ -1,2,4,5- $C_6H_2Cl_4$ . —  $\alpha$  phase, ---  $\beta$  phase.

### References

- BONADEO, H. & D'ALESSIO, E. A. (1973). *Chem. Phys. Lett.* **19**, 117-119.  
 BURGOS, E. M., BONADEO, H. & D'ALESSIO, E. A. (1977a). *J. Chem. Phys.* In the press.  
 BURGOS, E. M., D'ALESSIO, E. A. & BONADEO, H. (1977b). *J. Chem. Phys.* In the press.  
 D'ALESSIO, E. A. & BONADEO, H. (1973). *Chem. Phys. Lett.* **22**, 559-561.  
 DOWS, D. A. (1972). *Rend. Sc. Int. Fis. 'Enrico Fermi'*, pp. 55-62.  
 HERBSTEIN, F. H. (1964). *Acta Cryst.* **18**, 997-1000.  
 MIRSKY, K. (1976). *Acta Cryst.* A **32**, 199-207 and references therein.  
 MONFILS, A. (1955). *C.R. Acad. Sci. Paris*, **241**, 561-562.  
 REYNOLDS, P. A., KJEMS, J. K. & WHITE, J. W. (1974). *J. Chem. Phys.* **60**, 824-834.  
 TADDEI, G., BONADEO, H., MARZOCCHI, M. P. & CALIFANO, S. (1973). *J. Chem. Phys.* **58**, 966-978.