CRYSTAL STRUCTURE OF PARAOXYACETOPHENONE

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Abstract

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CRYSTAL STRUCTURE OF PARAOXYACETOPHENONE

DETERMINATION OF THE STRUCTURE MODEL

The investigation of the structure of paraoxyacetophenone crystals was undertaken by us following the determination of the structure of benzophenone ([1,2]). Both crystals belong to the class of aromatic ketones with space group $P2_{12_{12}}1$ and have a non-centrosymmetric molecular structure. At the same time, benzophenone is a known piezoelectric, whereas paraoxyacetophenone crystals do not exhibit noticeable piezoelectric properties.

Experimental part. Paraoxyacetophenone crystals are elongated prisms of yellowish color, stable in air.

The dimensions of the unit cell of the crystals were determined from rotation photographs and Weissenberg photographs and were found to be: $a = 9.48$ Å, $b = 22.51$ Å, $c = 6.07$ Å. On layer-line nets $hk0$, $0kl$, $h0l$, systematic absences of the type $h00$, $0k0$, $00l$ with odd h, k, l were observed, which unambiguously indicated the space group $P2_{12_{12}}1$.

The density of the crystals was determined by the flotation method in a mixture of bromoform ($d = 1.499$ g/cm^3) and xylene ($d = 0.861$ g/cm^3) and is 1.26 g/cm^3. According to this density, the number of molecules in the unit cell is 8, i.e., twice the multiplicity of the general position of the group $P2_{12_{12}}1$. This indicates that the molecules in the crystal occupy two regular systems of points. The presence of carbonyl and hydroxyl groups in the paraoxyacetophenone molecule points to the possibility of the existence of associates in the structure due to hydrogen bonds.

A three-dimensional set of intensities from the crystal was obtained by the equi-inclination Weissenberg method with copper radiation. Nets of 6 layer lines ($l = 0 \div 5$) were recorded. The intensities of 750 reflections were estimated visually from blackening standards. After introducing the polarization and Lorentz factors, the squares of the moduli of the structure amplitudes were first re-

Fig. 1. Molecular model for the search

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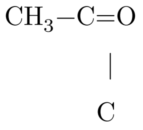
duced to a common scale and then to an absolute scale by Wilson' s method. Simultaneously, the value of the isotropic temperature factor was determined: $B = 4.0$ Å^2.

Determination of the structure model. To find the structure model, the method of nonlocal search for the minimum of a function of many variables—the "ravine" method (^{3})—was used. By this method a number of structures of molecular crystals have been solved. In all previously solved structures, one molecule fell within the independent part of the cell.

The problem of finding the structure of paraoxyacetophenone was of definite methodological interest, owing to the presence of two symmetrically independent systems of molecules in the unit cell of the crystal. The number of principal parameters of the minimized function in this case doubles, since the search variables are already two sets of coordinates of the molecular centers and two sets of Euler angles. The rotation of the groups



$$\begin{array}{c} CH_3{-}\overset{}{C}{=}O \\ | \\ C \end{array}$$

about the aliphatic bonds C—C of both molecules was determined by additional parameters v_1 and v_2. The total number of parameters of the minimized function was 14.

The molecular model for searching for the minimum of the R-function was specified with standard bond lengths and values of the valence angles in the benzene ring and in the ketone group (Fig. 1).

Fig. 1. Molecular model for the search

The following functions were used in the search:

$$\tilde{R} = \sum_{hkl} \left(|F_{hkl}|^{\text{exp}} - |F_{hkl}|^{\text{theor}} \right)^2$$

and

$$D = \begin{cases} \sum_{ij} \left(r_{ij} - (r_i + r_j) \right)^4, & \text{for } r_{ij} < r_i + r_j, \\ 0, & \text{for } r_{ij} \geqslant r_i + r_j, \end{cases}$$

Fig. 2. Projection of the electron density $\rho(x, y)$ of the structure at a false minimum

Figure 2: Fig. 2. Projection of the electron density $\rho(x, y)$ of the structure at a false minimum

where r_i and r_j are the intermolecular radii of the atoms, and r_{ij} is the distance between the i-th and j-th atoms of different molecules.

Unlike what was described in (3), in the course of searching for the structure of paraoxyacetophenone, from each "starting" point a local descent was first carried out by the least-squares method for the function $D(x_1, y_1, z_1, x_2, y_2, z_2, \dots, v_1, v_2)$ until D became smaller than a certain prescribed constant (for example, 1.0). The function D was calculated taking into account the hydrogen atoms in the benzene rings. Then the function $G = \tilde{R} + \alpha D$ was minimized, where α is a certain multiplier (usually $\alpha = 1$).

A search using the 50 strongest reflections, constituting 50% of the total sum of intensities, gave several points with a low R-factor (18–22%). However, when the number of reflections was increased to 130, the R-factor in them rose to 30%. The lowest point was studied in detail; on 200 reflections (80% of the total sum of intensities) it gave an R-factor of 28%. The "ravine" led to this point twice, and it seemed to be the solution of the structure.

Fig. 2. Projection of the electron density $\rho(x, y)$ of the structure at a false minimum

From the coordinates of this point, a projection of the electron density onto the $[x, y]$ plane was constructed (Fig. 2). The synthesis contained only one low "false" peak; the ratio of the peak heights partly did not correspond to the ratio of the atomic numbers of the atoms entering into the molecule. In the three-dimensional synthesis, however, along with the prescribed peaks several "extra" peaks appeared, with heights 1/3 of the principal ones, and the R-factor was 50%. The minimum value—

The decrease in the R-factor during least-squares refinement over F_{hkl} was 37%.

Next, a synthesis $\rho(x, y)$ was considered (Fig. 3), calculated from the data of the minimization function constructed by the graphical method for the projection of the structure along the c axis. Comparison of this synthesis with that shown in Fig. 2 indicated that some of the peaks in the syntheses are located in the same region—in the region of molecule II. This fact, as well as the relatively low value of the R_{hkl}-factor, indicated that the positions of some atoms, namely the atoms of molecule II, had been determined correctly.

A further search for the structure by the "enemy" method, carried out with the position of molecule II fixed, led to a point which, for 220 reflections, had an R_{hkl}-factor of 25%. The structure at this point differed from that considered earlier by an approximately 180° rotation of molecule I about an axis perpendicular to the plane of the molecule, and by a certain displacement of it along the long axis. The position of molecule II, as expected, did not in fact differ from that found earlier (see Figs. 2, 4). The atomic coordinates of the preliminary model are given in Table 1. From the coordinates of this point, a three-dimensional synthesis of the electron density $\rho(x, y, z)$ was constructed. The synthesis no longer contained extraneous peaks, and the distribution of their heights was correct.

Fig. 3. Fourier synthesis $\rho(x, y)$ from the data of the minimization function

As expected, the crystal structure is based on a saturated system of hydrogen bonds OH…O between molecules of "different kinds." These bonds (length 2.60 Å) unite the molecules into zigzag chains along the *b* axis. The individual chains, in turn, are compactly packed into a three-dimensional framework and are connected with one another by van der Waals forces.

Fig. 4. Projection of the electron density onto the $[x, y]$ plane at the true minimum

In calculating this structure, various methodological investigations were carried out. It is obvious that the time required to calculate the structure by the "enemy" method is reduced if it is possible to reduce the region in which the minimum is sought, or if it is possible to choose a function with the smallest possible number of local minima. Thus, if a molecule has an almost symmetrical geometrical shape (for example, almost an axis of symmetry), it is advisable to carry out the calculation for a molecule of symmetrical shape.

In the model of the *p*-hydroxyacetophenone molecule, the CH_3 group can be replaced by an O atom, with a corresponding change in the length of the C—C valence bond. With such a replacement, the *R*-factor calculated from 200 reflections changes practically not at all.

In analyzing the already solved structure of paraoxyacetophenone, it turned out that for the calculation it was possible to adopt a simplified geometrical model of the molecule consisting of 12 atoms (see Fig. 1). In this model the CH_3 groups and the atom O_{10} were omitted from the molecule, and the atom C_8 was replaced by an O atom. The *R*-factor calculated for 200 reflexions using this model was found to be 30% at the minimum point. It follows from the foregoing that the entire calculation of the preliminary model of the structure could have been carried out for the simplified geometrical model described above, additionally investigating all local minima of the *R*-factor below 35% for 200 reflexions.

Table 1

Relative coordinates of the atoms of the preliminary structural model of paraoxyacetophenone (without hydrogen atoms)

Atoms	Molecule I	Molecule I	Molecule I	Atoms	Molecule II	Molecule II	Molecule II
	x/a	y/b	z/c		x/a	y/b	z/c
O_1	0.3385	0.4107	1.3270	O_{11}	0.1401	0.8326	0.6626
C_2	0.3514	0.3682	1.1667	C_{12}	0.2399	0.8765	0.6507
C_3	0.4535	0.3236	1.1866	C_{13}	0.3240	0.8893	0.8343
C_4	0.4667	0.2802	1.0227	C_{14}	0.4259	0.9342	0.8221
C_5	0.3777	0.2814	0.8387	C_{15}	0.4437	0.9663	0.6265
C_6	0.2756	0.3261	0.8188	C_{16}	0.3595	0.9535	0.4430
C_7	0.2624	0.3694	0.9825	C_{17}	0.2576	0.9087	0.4552
C_8	0.3918	0.2350	0.6631	C_{18}	0.5528	1.0144	0.6135
C_9	0.5207	0.1963	0.6552	C_{19}	0.5848	1.0435	0.3967
O_{10}	0.2964	0.2284	0.5234	O_{20}	0.6171	1.0303	0.7829

Let us note that the calculation of the structure of paraoxyacetophenone was carried out with van der Waals radii increased by 0.1 Å; the function D calculated in this way has fewer local minima.

The main difficulty in searching for complex molecular organic structures is due to the fact that they consist of atoms with the same, or very nearly the same, low scattering power, and, moreover, the molecules making up the crystals are often in themselves sufficiently symmetrical. In this case, for selecting structures the R-function becomes insufficiently discriminating. As was already noted, in our case the R-factor in the search was 28% for 200 reflexions for an incorrect structure and 24% for the correct one. The relatively low values of the discrepancy factors for incorrect structures of this kind are due to the fact that some of the atoms in them inevitably prove to be determined correctly.

A similar situation was encountered in determining the structure of *l*-proline (^{4}), where the transition from a false minimum to the true one required displacement of the molecule along the a axis by 0.25. The number of low false minima increases as the structure becomes more complicated.

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Note: Figure translations are in progress. See original paper for figures.