

# ANISOTROPY OF THE DIAMAGNETIC SUSCEPTIBILITY IN $\alpha$ AND $\beta$ *p*-NITROPHENOL CRYSTALS

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(Received August 17, 1968)

The  $\alpha$ -form of nitrophenol which is stable below 63°C, becomes coloured when illuminated with sunlight while the  $\beta$ -form, stable above 63° does not exhibit this property. To check the hypothesis that the reason for the difference in the properties of the two forms is a different distribution of the molecules in the unit cell, the diamagnetic anisotropy of the crystal has been measured, and the principal susceptibilities of the *p*-nitrophenol molecule, calculated from this anisotropy have been compared.

## 1. Introduction

Crystalline *p*-nitrophenol occurs in two phase forms. The crystals of these two forms are built up of infinitely long chains in which the molecules are connected with hydrogen bonds of the type OH...O. According to Winchell [1] the form which is stable below 63°C is the  $\alpha$ -form called stable, while above this temperature the stable form is  $\beta$ , — called meta-stable.

The  $\alpha$ -form has the property of being coloured on the surface under the influence of illumination with sunlight [2, 3]. The illuminated surface of the crystal changes its colour from bright-yellow to bright-red and after being illuminated for several days it becomes dark-red. The  $\beta$ -form does not change its colour.

Detailed X-ray studies of the structure of  $\beta$ -*p* nitrophenol have been made by Tous-saint [4] and of both forms by Coppens [3, 5]. Coppens has given the parameters of the structure and atom sites, also for the temperature of 90°K. Both structures differ in the distribution of the molecules in the unit cell which in both cases shows the symmetry of the monoclinic system.

In particular in the  $\beta$ -form, which does not change the colour, the oxygen atoms of the —NO<sub>2</sub> groups are located more symmetrically with respect to the proton of the — OH

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group of the preceding molecule, whereas in the  $\alpha$ -form one of the oxygen atom lies slightly closer to the — OH group than the other one. According to the considerations presented in Ref. [2] this fact considerably decreases the potential barrier for the transition of the proton from the — OH group to the — NO<sub>2</sub> group of the next molecule in the  $\alpha$ -*p*-nitrophenol crystal which results in the formation of quinoid structure and colouration of the crystal.

According to the above hypothesis only the distribution of the molecules in the unit cell is the decisive factor with regard to the photo-chromic properties of the  $\alpha$ -*p*-nitrophenol crystals. To check this viewpoint studies of the anisotropy of the magnetic susceptibility of the crystals of both forms have been made. It is well-known that the magnetic susceptibility of the crystal is chiefly dependent on the anisotropy of the susceptibility of the molecule which in both cases is the same, and on the distribution of the molecules in the unit cell which is known for both forms. One should expect that the principal susceptibilities of the molecule calculated from the results of measurements of the anisotropy of the crystals should be equal in both forms within the limits of experimental error.

## 2. Sample preparation

Pure *p*-nitrophenol (manufactured by POCH-Gliwice) was first purified by twofold recrystallization from toluene. Next, the substance was subjected to recrystallization from its vapour in a flask under the pressure of 30 Tr. In these conditions only single crystals of the  $\alpha$ -form grow on the walls of the flask in the form of big needles or sometimes plates. The purity of *p*-nitrophenol after such processing is sufficient for diamagnetic anisotropy measurements.

During the search for a suitable method of crystal growth several observations were made concerning the crystallization of *p*-nitrophenol in different physical conditions. It turned out that during the crystallization of the substance from vapour state under the pressure of 30 Tr only  $\alpha$ -crystals are formed whereas under the pressure of several torrs mostly  $\beta$ -crystals are obtained with only a comparatively small number of  $\alpha$ -crystals.

We did not succeed in growing  $\beta$ -crystals by crystallization from toluene or benzene although this crystallization was performed at temperatures above 63°C. Big single crystals of  $\alpha$ -*p*-nitrophenol grow even at 87°C when toluene is slowly evaporated from the solution. The  $\beta$ -crystals in the form of needles can be obtained only from aqueous solution at room temperature.

To grow bigger crystals of the  $\beta$ -form aqueous solution a Necken apparatus [6] was used. The crystals grown in this way had the shape of long prisms with the thickness of several millimeters.

## 3. Methods of diamagnetic anisotropy measurements

The diamagnetic anisotropy has been measured by well-known methods devised by Krishnan [7, 8]. The measurements by means of the dynamical method in which the period of torsional vibrations of the single crystal plate is measured in a uniform magnetic field,

has been described in a previous paper [9]. In this method the difference between the lengths of the principal axes of the susceptibility ellipse which lies in a plane perpendicular to the direction of suspension is given by:

$$\Delta\chi = \frac{4\pi^2}{M} \frac{1}{H^2} \left( \frac{1}{T^2} - \frac{1}{T_0^2} \right), \quad (1)$$

where  $\Delta\chi = \chi' - \chi''$ , and  $\chi'$ ,  $\chi''$  are the greatest and smallest susceptibility in the plane perpendicular to the suspension direction, respectively;  $I$ —the moment of inertia of the crystal,  $M$ —mass of the crystal in moles,  $H$ —magnetic field strength,  $T$ ,  $T_0$ —the periods of torsional vibrations in the magnetic field  $H$  and zero field, respectively.

In some cases the measurement of  $\Delta\chi$  can be easier made by means of the statical method. When the crystals are small, having thus a small moment of inertia with respect to the axis of suspension, the accuracy of this method is better. The difference between the statical method and the dynamical method consists only in the fact that the quantity measured is the angle  $\alpha_c$  of the rotation of the suspension head which is necessary to rotate the crystal by 45 degrees from equilibrium position in magnetic field (instead of the period in the dynamical method). In practice the measurement of  $\alpha_c$  is carried out by careful rotation of the head until the 45°-position is attained by the crystal. An even very small further rotation of the head gives rise to a sudden and fast rotation of the crystal. The so-called critical angle  $\alpha_c$  is read on an angular scale attached to the head. To obtain a sufficient accuracy the magnetic field strength and the diameter of the suspending fibre were chosen so that the critical angle was several times greater than the perigon. The expression for  $\Delta\chi$  in the statical method has the form

$$\Delta\chi = \frac{8\pi^2 I}{MT_0^3 H^2} \left( \alpha_c - \frac{1}{4} \pi \right). \quad (2)$$

The angle  $\theta$  made by the plane of the single crystal plate (or its normal) and the direction of  $H$  was measured according to the method described in Refs [9] and [10].

All measurements were made on crystals with masses between 3 and 20 mg for three magnetic field strengths. The position of the crystal was observed by means of a reading telescope.

#### 4. Principal susceptibilities of the $\alpha$ *p*-nitrophenol crystal

The orientations of the crystallographic axes with respect to the single crystal plate were determined by means of the rotating crystal method. It was found that these plates are (010) elongated in the direction  $[10\bar{1}]$ . The principal susceptibility of the crystal  $\chi_2$  is perpendicular to the plane of the plate while  $\chi_1$  and  $\chi_3$  lie in it. The orientation of  $\chi_1$  with respect to the  $a$  axis was found from the orientation of the crystal which was suspended in the magnetic field parallel to  $\chi_2$  ( $\chi_2 \parallel b$ ):

$$\varphi_\alpha = -40^\circ 00' \pm 50'$$

where  $\varphi_\alpha$  is the angle between  $\chi_1$  and  $a$ , and the minus sign means that  $\chi_1$  lies in the acute angle made by the crystallographic axes  $a$  and  $c$ .

The differences in the susceptibilities  $\Delta^I\chi$  and  $\Delta^{II}\chi$  have been measured for two different suspensions in the plane of the plate ZI and ZII shown in Fig. 1.

The directions I and II were chosen parallel to the extinction directions observed in the polarization microscope. For these suspensions the plate locates itself parallel or perpen-

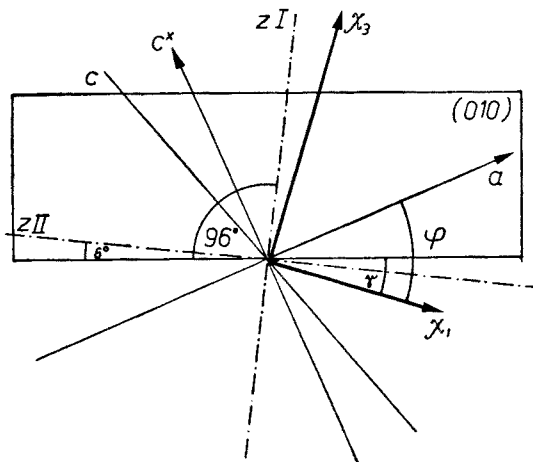


Fig. 1. Orientation of the suspensions of the  $\alpha$ -form crystal. zI and zII are the suspensions directions

pendicular to the magnetic field. From the measurements of  $\Delta^I\chi$ ,  $\Delta^{II}\chi$  and the mean susceptibility of the powdered sample,  $\bar{\chi}$ , it is possible to calculate the principal susceptibilities of the crystal  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$  by making use of the equations

$$\begin{aligned}\chi_1 \cos^2 \gamma + \chi_3 \sin^2 \gamma - \chi_2 &= \Delta^I\chi, \\ -\chi_1 \sin^2 \gamma - \chi_3 \cos^2 \gamma + \chi_2 &= \Delta^{II}\chi, \\ \chi_1 + \chi_2 + \chi_3 &= 3\bar{\chi},\end{aligned}\quad (3)$$

where  $\gamma = 10^\circ 30'$  designates the angle between  $\chi_1$  and the direction of the greatest susceptibility perpendicular to the suspension axis I and lying in the plane of the plate,  $\Delta^I\chi = (17.5 \pm 0.1) \times 10^{-6}$  cgs emu/mole is the difference between the susceptibilities measured for the suspension I,

$\Delta^{II}\chi = (14.33 \pm 0.05) \times 10^{-6}$  cgs emu/mole is the difference between the susceptibilities measured for the suspension II,

$\bar{\chi} = -65.66 \times 10^{-6}$  cgs emu/mole is the mean susceptibility of powdered *p*-nitrophenol according to Ref. [11].

As the result of these calculations we obtained:

$$\begin{aligned}\chi_1 &= (-48.1 \pm 0.4) \cdot 10^{-6} \text{ cgs emu/mole} \\ \chi_2 &= (-66.7 \pm 0.1) \cdot 10^{-6} \text{ cgs emu/mole} \\ \chi_3 &= (-82.2 \pm 0.4) \cdot 10^{-6} \text{ cgs emu/mole.}\end{aligned}$$

5. Principal susceptibilities of the  $\beta$ -*p*-nitrophenol crystal

The prisms of the  $\beta$ -monocrystals had two well-developed crystallographic planes. Measurements by means of the rotating crystal method have shown that these are the planes  $(\bar{1}10)$  and  $(110)$ , i.e. that the  $c$ -axis is parallel to the lateral edge of the prism (Fig. 2).

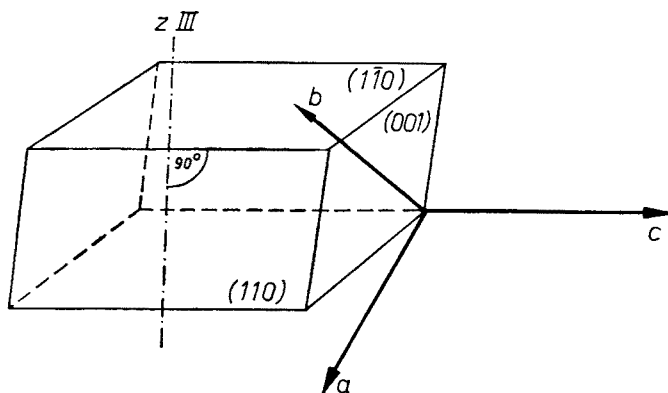


Fig. 2. Orientation of the crystallographic axes in the  $\beta$ -form crystal of *p*-nitrophenol.  $z_{III}$  is the suspension direction in the  $(110)$ -plane

For such orientation of the single crystal there is no possibility of direct measurement of the angle  $\varphi$ . Thus it was necessary to measure three susceptibility differences for three suspensions, out of which only two may lie in the same plane (Fig. 3). In addition, for each suspension it was necessary to measure the angle between the direction of the maximum

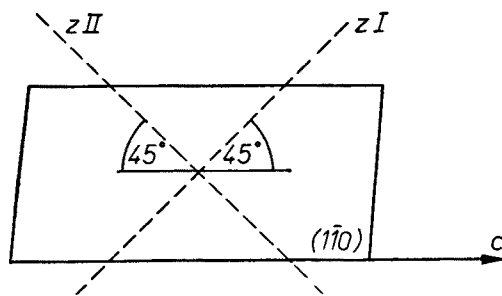


Fig. 3. Orientation of the suspensions of the  $\beta$ -form crystal of *p*-nitrophenol in the  $(110)$ -plane

susceptibility and the suspension plane, and to find the orientation of this direction with respect to the crystallographic axes system. The relations between the measured quantities,  $\Delta^{(k)}\chi$  and  $\bar{\chi}$ , and the calculated ones,  $\chi_i$  and  $\varphi$ , are

$$\begin{aligned} & \chi_1[(a_{1i}^{(k)} \cdot b_{1i})^2 - (a_{2i}^{(k)} \cdot b_{1i})^2] + \chi_2[(a_{1i}^{(k)} \cdot b_{2i})^2 - (a_{2i}^{(k)} \cdot b_{2i})^2] + \\ & + \chi_3[(a_{1i}^{(k)} \cdot b_{3i})^2 - (a_{2i}^{(k)} \cdot b_{3i})^2] = \Delta^{(k)}\chi, \quad (i, k = 1, 2, 3), \quad (4) \\ & \chi_1 + \chi_2 + \chi_3 = 3\bar{\chi}, \end{aligned}$$

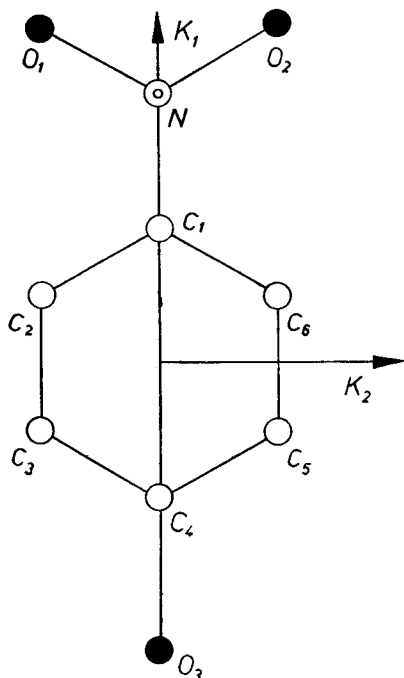


Fig. 4. Direction of the principal molecular susceptibilities  $K_i$  in the *p*-nitrophenol molecule.  $K_3$  is perpendicular to the molecule plane

where:  $b_{ji}$  are the direction cosines of  $\chi_j$  in the orthogonal system of crystallographic axes  $a^*$ ,  $b$ ,  $c$ ,

$a_{1i}^{(k)}$  are the direction cosines of the maximum susceptibility in the direction perpendicular to the suspension  $k$ ,

$a_{2i}^{(k)}$  are the direction cosines of the minimum susceptibility in the direction perpendicular to the suspension  $k$ ,

$\Delta^{(k)}\chi$  is the susceptibility difference measured for this suspension.

In the coordinate system accepted, the direction cosines of  $\chi_i$  are the following:

	$a^*$	$b$	$c$
$\chi_1$	$\cos \delta$	0	$\sin \delta$
$\chi_2$	0	1	0
$\chi_3$	$\sin \delta$	0	$-\cos \delta$

where  $\delta = \varphi - 17^\circ 04'$ .

The values of the measured susceptibility differences  $\Delta^{(k)}\chi$  are:

$$\Delta^{\text{I}} \chi = (12.0 \pm 0.2) \times 10^{-6} \text{ cgs emu/mole,}$$

$$\Delta^{\text{II}} \chi = (37.6 \pm 0.5) \times 10^{-6} \text{ cgs emu/mole,}$$

$$\Delta^{\text{III}} \chi = (42.9 \pm 0.6) \times 10^{-6} \text{ cgs emu/mole.}$$

The solution of the system of equations (4) with regard to the angle  $\varphi$  is

$$\varphi = -5^{\circ}09'$$

and with regard to the principal susceptibilities of the crystals

$$\begin{aligned}\chi_1 &= (-49.4 \pm 0.6) \times 10^{-6} \text{ cgs emu/mole,} \\ \chi_2 &= (-50.4 \pm 0.5) \times 10^{-6} \text{ cgs emu/mole.} \\ \chi_3 &= (-97.2 \pm 0.9) \times 10^{-6} \text{ cgs emu/mole.}\end{aligned}$$

### 6. Principal susceptibilities of the *p*-nitrophenol molecule

The results of detailed X-ray investigations of both forms of *p*-nitrophenol have been given by Coppens [3, 5]. The parameters of the unit cell of both forms are summarized according to these data in Table I. For the  $\alpha$ -form the coordinates of the atoms have been determined by Coppens at the temperature of 90°K, while for the  $\beta$ -form at room temperature. Since no data on the atomic coordinates of the  $\alpha$ -form at room temperature have been found in the literature available, the direction cosines  $K_i$  for this form were calculated from the data of Coppens for 90°K. Thus the  $K_i$ -values calculated from the principal susceptibilities of the  $\alpha$ -crystal are not accurate. One should expect, however, that the error due to this procedure does not exceed the experimental error of  $\chi_i$ .

TABLE I

Form	$\alpha$		$\beta$	
	Room temp. [4]	90°K [3]	Room temp. [3]	90°K [3]
<i>a</i>	11.8 Å	11.66	15.403	15.21
<i>b</i>	8.9	8.78	11.117	11.04
<i>c</i>	6.17	6.098	3.785	3.662
$\beta$	106°52'	107°32'	107°04'	106°49'
Space group	$P2_1/n$	$P2_1/n$	$P2_1/a$	$P2_1/a$

TABLE II

	Form $\alpha$	Form $\beta$
$K_1$	-49.5	-49.9
$K_2$	-44.6	-46.8
$K_3$	-103.0	-100.3
Anisotropy — $\frac{K_3}{K_1}$	2.08	2.01
$\varphi_{\text{calc.}}$	44°10'	-4°02'
$\varphi_{\text{calc.}} - \varphi_{\text{meas.}}$	-4°10'	1°07'

The results of the calculations are given in Table II. As it is known the value of the difference  $\varphi_{\text{calc.}} - \varphi_{\text{meas.}}$  can be regarded as a check of the accuracy of the measurements.

For  $\beta$  *p*-nitrophenol this difference equals to  $1^{\circ}07'$ , a result which can be regarded as quite good, bearing in mind the difficult measurement conditions. For the  $\alpha$ -form of the compound this value is much greater. This result may be at least partly, explained in terms of the discrepancies between the values of the direction cosines accepted in the calculations and their actual values. In the papers on anisotropy published so far, the values of this difference vary between several minutes and degrees, depending on the substance.

On the basis of the above results one can state that the calculated  $K_i$ -values of both polymorphic forms are indeed equal within the experimental error limits.

## APPENDIX

Measured values and direction cosine matrices used in the calculation of  $\beta$  *p*-nitrophenol anisotropy.

1. The components of the unit vectors normal to the suspension planes in  $a^*$ ,  $b$ ,  $c$  coordinate system:

$$(1\bar{1}0) - A_1^{I,II} = 0.6025, A_2^{I,II} = -0.7981, A_3^{I,II} = 0,$$

$$(110) - A_1^{III} = 0.6025, A_2^{III} = 0.7981, A_3^{III} = 0.$$

2. The components of the unit vectors parallel to the suspension directions in the  $a^*$ ,  $b$ ,  $c$  coordinate system ( $a_{mj}$  is the  $j$ -th component of the vector parallel to the suspension  $m$ ):

$$a_{11} = 0.5643, a_{111} = 0.5643, a_{1111} = 0.7981$$

$$a_{12} = 0.4261, a_{112} = 0.4261, a_{1112} = -0.6025$$

$$a_{13} = 0.7071, a_{113} = -0.7071, a_{1113} = 0.$$

3. Measured values of the angle  $\theta_1^j$  between the direction of the greatest susceptibility perpendicular to the suspension  $j$  and the normal to this suspension plane

$$\theta_1^I = 32^{\circ}40' \pm 1^{\circ}00', \theta_1^{II} = 12^{\circ}10' \pm 0^{\circ}40', \theta_1^{III} = 13^{\circ}50' \pm 0^{\circ}40'.$$

4. The system of equations for the calculation of the components of the unit vectors parallel to the maximum susceptibility direction for the suspension  $k$ :

$$\sum_i a_{1i}^{(k)} \cdot A_i^{(k)} = \cos \theta_1^{(k)},$$

$$\sum_i a_{1i}^{(k)} a_{ki} = 0,$$

$$\sum_i (a_{1i}^{(k)})^2 = 1.$$

The vectors  $\mathbf{a}_2^{(k)}$  are equal to the cross product of the vectors:

$$\mathbf{a}_2^{(k)} = [\mathbf{a}_1^{(k)} \times \mathbf{a}_k].$$



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