THERMAL EXPANSION OF *p*-NITROANILINE IN THE TEMPERATURE INTERVAL OF 290 TO 380°K

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An *X*-ray and dilatometric study has been carried out of the thermal expansion of p-nitroaniline single crystals in the temperature range 290 to 380°K. By means of the first method two sections of the expansion tensor were evaluated with the following results for the principal axes:

$$\alpha_{11} = 246.0, \alpha_{22} = 13.2, \alpha_{33} = 14.5, \text{all in } 10^{-6} \text{ deg}^{-1},$$

and for the angle between α_{11} and a-axis a value of 32.2°. Dilatometric measurement carried out on the cleavage plane in the directions [010] and $[\bar{1}01]$ indicate that α_{22} is temperature dependent and that the results for both directions are higher than the corresponding values from *X*-ray measurements. The differences are discussed in terms of crystal deffects.

1. *Introduction*

In due course of a spectrophotometric study of single crystals of *p*-nitroaniline in the near infrared region it has been found that a marked change with temperature occurs of the intensity of certain absorption bands when measured with polarized radiation [1]. One of possible explanations to this fact involves the assumption that the orientation of the molecules in the unit cell may depend on temperature. However, there are no structural informations available to confirm this point of view, and it is believed that the knowledge of thermal expansion coefficients may be of some help in deducing the possible amount of reorientation.

The measurement of the thermal expansion of this compound have already been carried out by means of *X*-rays method by McKeown and collaborators between —180°C and the room temperature [2], basing on structural data given by Abrahams and Robertson[3]. However, it is well known that the thermal expansion coefficients depend on temperature exhibiting rapid decrease as the temperature is lowered in the neighbourhood of Debye temperature. For this reason new measurements were deemed worthwhile to be carried out at some higher temperatures, for which the spectral changes were also observed [1]. The structural data in this study were taken from paper of Trueblood and others [4].

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2. Experimental

Single crystals of p-nitroaniline, which was purified very carefully by means of several methods [1], were grown either from the melt according to Bridgman's method or from a saturated solution in chloroform. Two kinds of samples were used: rods cleaved from the plates grown from solution were elongated along the b axis. The other samples were cut by means of a razor blade perpendicular to both the cleavage plane and b axis, and were then elongated along $[10\bar{1}]$. The samples mounted on a head of a Weissenberg goniometer were kept at a constant temperature in a stream of heated air. A sealed off glass capillary tube prevented the sample from evaporation. The temperature was controlled by means of a copper-constantan thermocouple and a Philips recording unit within the limits of ± 1.5°C. The zero-layer Weissenberg patterns were recorded photographically on the same film at two temperatures: the room temperature, about 20°C, and the higher temperature, about 107°C. The distance within a pair of spots was measured on a Zeiss'photometer with an accuracy of about 0.003 mm. Therefore, nearly all spots including those for small diffraction angles could be used to estimate the shape and dimensions of the particular section of the expansion tensor. The results were evaluated on two samples for each orientation.

The dilatometric study was made by means of a microscopic method described earlier [5].

3. Results and discussion

A section of the tensor of thermal expansion with (010) plane was obtained from the temperature shift of the $h0l$ reflection spots when the b axis of the crystal was taken as the rotation axis. The observed spots together with calculated expansion coefficients, α_{ij}, and corresponding directions of normals to the reflecting planes on (010), φ_i, are given in Table I. The figures in the fifth column, w_i, are the "statistical weights", and give the number of observations made for particular $h0l$ on all recordings. This type of section of any second rank tensor in a monoclinic crystal will contain two principal axes, α_{11} and α_{33}, with an arbitrary orientation which has to be determined experimentally. Let us choose, following McKeown [2], the a axis as reference axis and denote by ψ_1 the angle between α_{11} and the a axis. Therefore, the (010) section of the tensor can be described by means of the following function:

$$\alpha = A_1 + B_1 \cos 2\varphi + C_1 \sin 2\varphi, \tag{1}$$

where α is the expansion coefficient in a direction on (010) making an angle φ with the reference axis, and A_1, B_1 and C_1 are constants:

$$A_1 = \tfrac{1}{2}(\alpha_{11}+\alpha_{33}),\ B_1 = \tfrac{1}{2}(\alpha_{11}-\alpha_{33}) \cos 2\psi_1,\ C_1 = \tfrac{1}{2}(\alpha_{11}-\alpha_{33}) \sin 2\psi_1. \tag{2}$$

From the observed 21 (φ_i, α_{ij}) points the "best and weighted" curve can be calculated by means of least squares method. The results are shown together with McKeown's in Fig. 1. The constants A_1, B_1 and C_1, as calculated by the least squares method, have the following values:

$$A_1 = 130.2,\ B_1 = 49.8,\ \text{and}\ C_1 = 104.4 \times 10^{-6}\ \text{deg}^{-1}.$$

The principal axes, α_{11} and α_{33}, and their orientation, ψ_1, are given in Table III.

TABLE I

Thermal expansion on (010) plane

No	Spot indices $h0l$*	φ**	$\bar{\alpha}_{exp}\times10^6$ deg^{-1}	Statistical weight w_i***	$\alpha_{calc}\times10^6$ deg^{-1}
1	200	1.45	186.6±5.7	13	185.3
2	901	10.5	196.0±2.2	2	214.2
3	701	12.6	208.7	1	219.8
4	501	17.9	230.8±2.4	5	231.8
5	301	26.8	148.4±24.6	4	243.9
6	503	41.6	249.5	1	239.9
7	101	55.6	215.4±5.6	7	209.6
8	305	67.3	179.9	1	169.6
9	103	77.0	129.0±2.0	2	131.2
10	105	82.1	115.5±1.1	2	110.7
11	002	90.0	67.0±13.7	6	80.4
12	$\bar{1}05$	98.0	60.1±6.5	3	53.6
13	$\bar{1}03$	103.5	14.4±5.9	2	38.4
14	$\bar{5}07$	116.7	25.4±1.0	3	16.7
15	$\bar{1}01$	125.3	25.7±1.4	4	15.2
16	$\bar{8}06$	133.5	28.0	1	23.3
17	$\bar{7}05$	135.0	31.2±3.2	3	25.8
18	$\bar{5}03$	140.1	43.2±10.4	2	36.3
19	$\bar{3}01$	155.6	82.0±7.7	9	84.5
20	$\bar{5}01$	165.3	114.0±10.2	4	122.4
21	$\bar{7}01$	169.8	144.2±3.3	4	140.6

* Including multiples of $h0l$

** Angle between normal to $h0l$ and the a axis

*** Number of spots measured

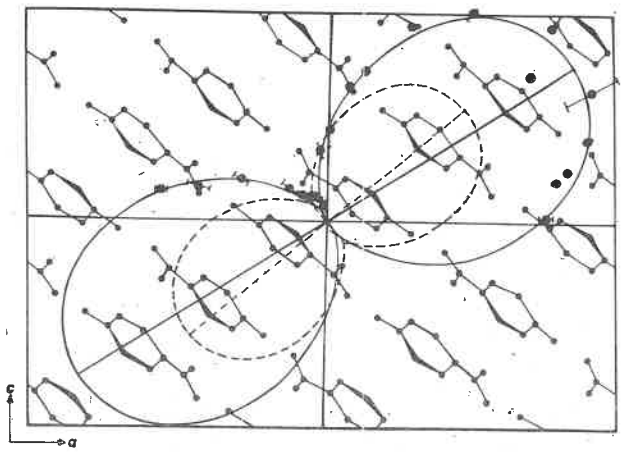

Fig. 1. A view along b axis on thermal expansion of p-nitroaniline on (010). Full line—calculated section of the tensor by least squares method, broken line — section calculated according to McKeown's results [2]

The section of the tensor in a plane perpendicular to (010) was evaluated from the *hkh* reflection spots by making the [10$\bar{1}$] direction the rotation axis. In this orientation only one axis of the figure is parallel to the principal axis of the tensor, $\alpha_{22} \| b$, which we take as the reference axis, and the other has the meaning of expansion coefficient along the [101] direction. Owing to this orientation, $\psi_2 = 0$, by definition, and we can use a more simple relation:

$$\alpha = A_2 + B_2 \cos 2\varphi \tag{3}$$

where $A_2 = \frac{1}{2}(\alpha_{22} + \alpha_{[101]})$, $B_2 = \frac{1}{2}(\alpha_{22} - \alpha_{[101]})$, and $C_2 = 0$. The results are given in Table II and are shown in Fig. 2. The constants A_2, B_2 as calculated by the least squares method, have the following values:

$$A_2 = 108.2, \; B_2 = -95.0 \times 10^{-6} \text{ deg}^{-1}.$$

TABLE II

Thermal expansion on ($\bar{1}$01) plane

No	Spot indices *hkh*	φ	$\bar{\alpha}_{exp} \times 10^6$ deg^{-1}	Statistical weight w_i	$\alpha_{calc} \times 10^6$ deg^{-1}
1	020	0	32.3±5.1	4	13.2
2	121	23.5	43.4±3.1	2	43.4
3	111	41.0	85.9±8.4	10	95.0
4	212, $\bar{2}1\bar{2}$	60.2	140.4±11.1	6	156.2
5	414, $\bar{4}1\bar{4}$	106.0	189.2±5.7	5	188.8
6	202	90.0	218.9±8.2	7	203.3

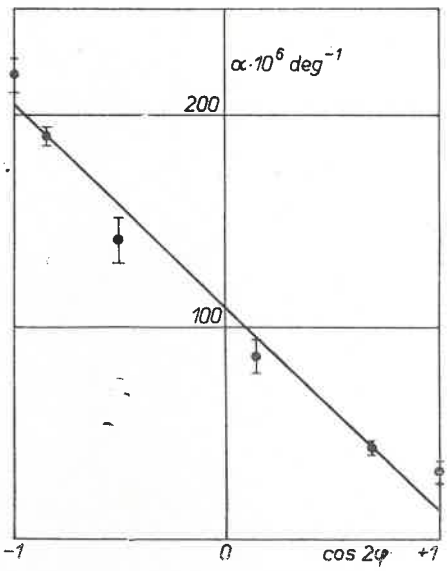

Fig. 2. Thermal expansion coefficients measured on ($\bar{1}$01) plane

The tensor axis, α_{22}, is given in Table III, and $\alpha_{[101]}$ amounts to:

$$\alpha_{[101]} = 203.3 \times 10^{-6} \text{ deg}^{-1}.$$

TABLE III

The principal axes of the thermal expansion tensor in p-nitroaniline, in 10^{-6} deg^{-1} units

Temperature range	α_{11}	α_{22}	α_{33}	ψ_1	Reference
290 to 380°K	246.0	13.2	14.5	32.2°	this work
90 to 293°K	150.3	7.5	24.0	40.03	McKeown [2]

A glance at Table I row 7 shows that both values obtained for $\alpha_{[101]}$ from the two independent sections agree quite well. The mutual relations of the investigated sections are shown schematically in Fig. 3.

It can be seen from Table III that, in comparison to McKeown's results, the values of α_{11} and α_{22} are both greater for the range of higher temperatures. Additionally, the α_{11}

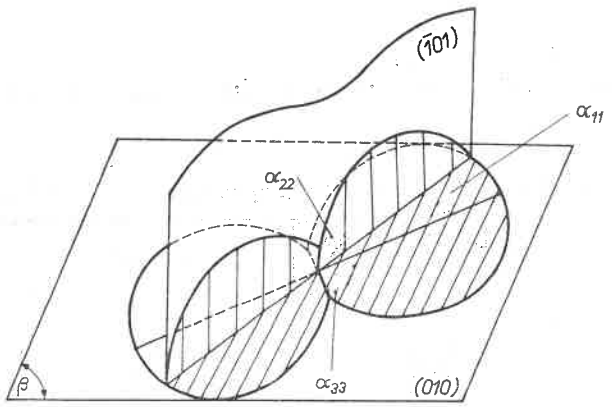

Fig. 3. Mutual orientation of the two investigated sections of the thermal expansion tensor (schematic)

axis is shifted on (010) toward the a axis by an angle of 7.8°. Such differencies are commonly observed because the thermal expansion coefficient for a given direction is a function of temperature. For example, α_{33} in biphenyl crystal at 257°K is three times that at 148.5°K and α_{22} is even eight times greater at the higher temperature, as it is found by Kozhin and Mirskaya [6]. The most rapid changes of α_i occur in the neighbourhood of the Debye temperature. We believe that this behaviour of α_i is most probably due to a temperature dependence of the mean square amplitudes of the atomic vibrations which can influence both the length of the α_i axes as well as their orientation. Of course, the changes of orientation of the tensor axes can only occur in those cases where some "degree of freedom" exists, as is the case f.e. in a monoclinic crystal. However, a more rigorous correlation between tensors of the thermal expansion and mean square amplitudes of vibrations will be discussed later in another paper.

The results of dilatometric measurements carried out in the two mutually perpendicular directions on (101), *i.e.* [010] and [$\bar{1}$01], are shown in Fig. 4. The length of the sample at a temperature t, l_t, depends linearly on t in the [$\bar{1}$01] direction, but a small non-linearity is found for measurements along the b axis. This clearly indicates a weak dependence of α_{22} on temperature. Using a linear approximation in the first case and a parabolic in the second one, least squares method leads to values of thermal expansion coefficients given in Table IV.

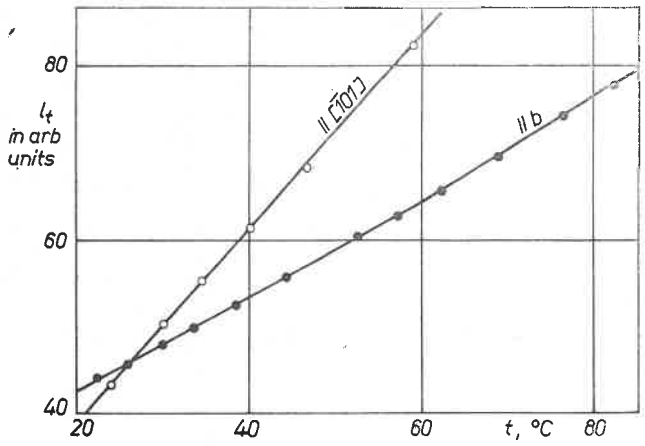

Fig. 4. Increase of length of samples of p-nitroaniline crystals with temperature, observed by dilatometric method

TABLE IV

Results of dilatometric measurements of α_i on (101) plane in p-nitroaniline

Sample number	Direction of measurements	$a \times 10^6$	$\beta \times 10^9$
1	[010]	16.6_2	29.3
2	[010]	15.8_6	47.9
3	[010]	16.5_7	32.1
4	[$\bar{1}$01]	54.4	—
		50.0	—
5	[$\bar{1}$01]	58.2	—
6	[$\bar{1}$01]	56.7	—
		53.4	

$\alpha_{[010]} = \alpha_{22} = [(16.4 \pm 0.2) + (36.4 \pm 6.3) \times 10^{-3}\, t] \times 10^{-6}\ \mathrm{deg}^{-1}$
$\alpha_{[\bar{1}01]} = (54.5 \pm 1.4) \times 10^{-6}\ \mathrm{deg}^{-1}$

The mean values of $\alpha_{[010]}$ and $\alpha_{[101]}$ for a temperature range 20° to 107°C are compared with X-ray results in Table V. As it is seen, the dilatometric values are greater for both directions than the X-ray values, and the cause of these discrepancies is not quite clear at present. They may possibly be due to the difference by which the lattice variation with temperature is "seen" by different experimental methods. In a real crystal there is

TABLE V

Comparison between α_i's measured in two directions on (101) by X-ray and dilatometric methods

in 10^{-6} deg^{-1} units	X-ray method	Dilatometric method
$\alpha_{[010]}$	13.2	18.7
$\alpha_{[\bar{1}01]}$	25.7	54.5

always a small amount of irregularities, f.e. molecules in improper orientation, whose concentration increases with the increase of temperature. This effect is of great influence on dilatometric results and can show its own anisotropy. However, for a X-ray study the departure from ideal periodicity of the lattice is too small to be observed. Whatever the cause may be we feel that a further study of the thermal expansion is nesessary in particular on such an organic solid, in which a great concentration of defects can be anticipated.

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