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Thermal Expansion of *p*-Nitroaniline and *p*-Dinitrobenzene

By P. J. A. McKeown, A. R. Ubbelohde and (Miss) I. Woodward

Department of Chemistry, Queen's University, Belfast, Northern Ireland

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Measurements on the thermal expansion of single crystals of *p*-nitroaniline have been made over the range 90–293° K. by X-ray methods. Mean values of the principal axes of the expansion ellipsoid are

$$\alpha_{11} = 150{\cdot}3 \times 10^{-6}, \quad \alpha_{22} = 7{\cdot}5 \times 10^{-6}, \quad \alpha_{33} = 24 \times 10^{-6}.$$

As the crystal is monoclinic α_{22} coincides with the *b* crystal axis; α_{11} makes an angle $\psi = 40° \, 2'$ with the *a* axis.

The very large α_{11} expansion of the crystal coincides within 6° with the projection on the (010) plane of the short 'polarization bonds' (2·66 A.) in *p*-nitroaniline. These bonds link the aromatic C atom *ortho* to the NH_2 group of one molecule and the O atom of an NO_2 group from an adjacent molecule.

It is suggested that the marked anisotropic expansion of the crystal is due to anomalously large thermal expansion of the polarization bond, and that there is some tilting of the molecules in the crystal as the temperature changes, so as to maintain the polarization bond normal to the plane of the benzene rings. At 90° K. the polarization bond has a length 2·44 A. and (by extrapolation) a length around 2·40 A. at 0° K. This distance of approach implies some form of valency interaction such as an electron transfer from the aromatic ring to the O of the NO_2. This interaction reaches a maximum at 0° K. and becomes rapidly less as the temperature rises. The very large thermal expansion must be due to a very unsymmetrical potential-energy curve, and the forces acting in the polarization bond cannot be wholly accounted for on the basis of normal intermolecular forces. Resonance effects between alternative bond structures may lead to an overlap of potential-energy curves and a consequent large anharmonicity of bond vibrations.

Introduction

Much discussion has centred around the nature of the 'bonding' between nitro compounds, quinones, etc., and aromatic hydrocarbons, amines, or phenols. One extreme view regards these bonds as involving a kind of salt formation (Weiss, 1942, 1943) with a transfer of an electron from the 'donor' aromatic molecule (phenol etc.) to the acceptor molecule (e.g. NO_2 group). To some extent the optical absorption of complexes may be correlated with the effect of an incipient oxidation–reduction reaction (Gibson & Loeffler, 1940). However, the 'heats of bonding' in solution are only of the same order as for hydrogen bonds (Hammick & Yule, 1940). Crystal compounds whose structure has been determined generally fail to show any close approach between the donor and acceptor molecules (cf. Rapson, Saunder & Stewart (1946) for earlier references). This must mean that in such crystals any intermolecular bonding is extremely weak. To avoid introducing special hypotheses, the attraction between such molecules is conveniently termed a polarization bond.

Crystalline *p*-nitroaniline appears to provide an extreme case of a polarization bond. An unusually close approach at room temperature has recently been discovered (Abrahams & Robertson, 1948) between an aromatic C atom of one molecule *ortho* to the NH_2 and one of the atoms of an NO_2 group from an adjacent molecule. The present investigation initiates a study of the thermal properties associated with this 'bond'.

By analogy with hydrogen bonds in crystals (cf. Ubbelohde, 1949) abnormal force fields might be expected to correspond with abnormal thermal expansions. As shown in the results detailed below, the contraction of crystalline *p*-nitroaniline approximately in the direction of the polarization bond is so large on cooling that the interaction appears to undergo substantial increase.

Experimental

Measurements on the thermal expansion of single crystals of *p*-nitroaniline follow, with a few modifications, previously described procedure.

Crystals

'Analar' *p*-nitroaniline was purified by recrystallization from chloroform. Crystals were grown by allowing a solution in chloroform saturated at about 35° C. to cool slowly to 15° C. This gave plates up to 1 mm. thick, elongated along the *b* axis, which could be split into needles by gentle pressing between filter paper. The lower end of a selected needle was mounted on a pyrex fibre by means of cellulose acetate/acetone. A narrow protecting thimble of cellulose acetate was then slipped over the crystal, and was sealed off with more cellulose acetate top and bottom.

Temperature control

Many exposures were made alternately at room temperature, and at 90° K. by allowing a drip of liquid oxygen to flow over the crystal and evaporate. For exposures at 153° K. a slight modification of the 'boiling oxygen' thermostat (Ubbelohde & Woodward, 1946) was used.

X-ray reflexions

Records were made on a multiple-exposure camera (Ubbelohde, 1939). Planes giving reflexions of sufficiently large Bragg angle with Cu $K\alpha$ radiation were:

Plane	Angle with *a* axis	Bragg angle
10.0.6	+41° 36′	56½°
14.0.4	+23° 38′	73°
$15.0.\bar{1}$	− 3° 47′	70°
$10.0.\bar{8}$	−48° 7′	70°
$9.0.\bar{9}$	−54° 29′	77°

In a crystal with monoclinic symmetry, the deformation ellipsoid has one axis coincident with the b axis of the crystal lattice. The other two may be in any mutually perpendicular direction in the (010) plane, and, in general, if α is the expansion in a direction making an angle ξ with the a axis (cf. Wooster, 1938),

$$\alpha = A + B \cos 2\xi + C \sin 2\xi, \qquad (1)$$

where the inclination of the axis α_{11} of the ellipsoid to the a axis is given by

$$\psi = \tfrac{1}{2} \tan^{-1} (C/B)$$

and

$$\alpha_{11} = A + B/\cos 2\psi,$$

$$\alpha_{33} = A - B/\cos 2\psi.$$

From observations on the planes listed above, α_{11} and α_{33} were calculated over the temperature range from 293 to 90° K. to give the line of closest fit of the experimental data with equation (1). This work involved about 28 independent records. α_{22} was calculated from the 'best' values of α_{11} and α_{33} in conjunction with the measured change in spacing of the $47\bar{4}$ plane at 25° 38′ to the b axis (Bragg angle 83°) using four independent records.

This gave as *mean* expansion coefficients per degree over the range from 293 to 90° K.

$\alpha_{11} = (150{\cdot}3 \pm 3) \times 10^{-6}$ (at $\psi = 40° \, 2' \pm 45'$ to a axis),

$\alpha_{22} = (7{\cdot}5 \pm 0{\cdot}5) \times 10^{-6}$ (along b axis),

$\alpha_{33} = (24 \pm 2) \times 10^{-6}$ (normal to α_{11} and α_{22}).

The number of records was insufficient to apply strict probability theory. The uncertainties quoted above are estimates which include possible systematic errors. In view of the very large mean value of α_{11} over the whole range of temperatures, an attempt was made to evaluate the temperature coefficient of α_{11} so as to estimate more accurately the length of the polarization bond at 0° K. Temperatures below 90° K. were not available, and in view of the labour involved it was necessary to restrict the determination of the slope of the expansion curve around 90° K. to calculations based on the spacing of the 14.0.4 plane at room temperature, 153° K. and 90° K. The change of spacing of this plane at the different temperatures is plotted in Fig. 1.

It was desirable to verify whether the large expansion might be related to a structural or polymorphic transition of some kind in the crystal. Although no completely detailed study of all possible reflexions was made for the purpose of the present investigation, no evidence of any transition was found from the reflexions used. Cooling in liquid oxygen and reheating gave no signs of break-up of the crystals, such as might have occurred if a major structural change took place on cooling.

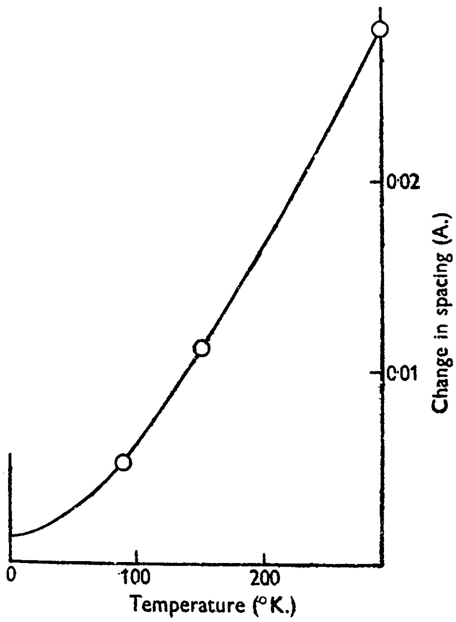


Fig. 1. Change of spacing of (14.0.4) plane of *p*-nitroaniline with temperature. Curve used for extrapolation $d = 0{\cdot}780 + 5{\cdot}43 \times 10^{-7}\, t^2 - 8{\cdot}01 \times 10^{-10}\, t^3$.

Effect of temperature on lattice vibrations

Calculations of the characteristic temperature from visual comparisons of the ratio of intensities of Bragg reflexions at 290° K. and 90° K. were made from reflexions from five different planes. Only very approximate values could be obtained since the experiments on thermal expansion were not designed to give the best conditions for comparing intensities. The average value of $\sqrt{(\overline{u^2_{293}} - \overline{u^2_{90}})}$ normal to the 14.0.4 plane was 0·13 A. A characteristic temperature of about 340° K. would account for these variations of intensity. Crystals of *p*-nitroaniline showed marked 'diffuse reflexions' at room temperature, but not at 90° K.

Thermal contraction of p-*dinitrobenzene*

In order to have a norm for the interpretation of the very anisotropic contraction of *p*-nitroaniline on cooling, measurements were sought on related crystals. Completely determined structures of single crystals with analogous forces are at present very limited in number.

p-Dinitrobenzene was finally selected as the nearest structure containing nitro groups but no very short polarization bonds (Llewellyn, 1947; Abrahams, 1950). The approximate expansion of this was determined as for *p*-nitroaniline. Results were:

$$\alpha_{11} = 93 \times 10^{-6} \quad (\text{at } \psi = -6^\circ \text{ to } a \text{ axis}),$$

$$\alpha_{22} = 74 \times 10^{-6} \quad (\text{along } b \text{ axis}),$$

$$\alpha_{33} = 11 \times 10^{-6} \quad (\text{normal to } \alpha_{11} \text{ and } \alpha_{22}).$$

Discussion

The numerical magnitude of the thermal expansion of *p*-nitroaniline may be compared with a number of other crystals with intermolecular or van der Waals bonds (Table 1).

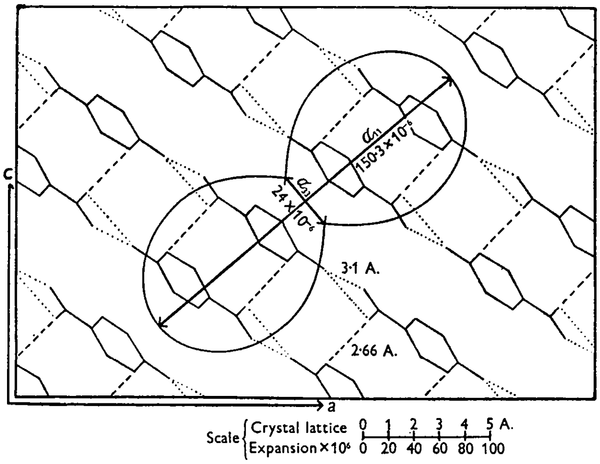


Fig. 2. Projection of *p*-nitroaniline on the (010) plane showing expansion in relation to molecular positions.

Contraction of the polarization bond in relation to crystal structure

The general relation of the thermal expansion of *p*-nitroaniline to its crystal structure can be seen from Figs. 2 and 3. Fig. 2 shows that the direction of maximum anomalous expansion coincides within 6° (in a preliminary calculation (McKeown, Ubbelohde & Woodward, 1950) the value estimated was 11°) with that of the projections of the polarization bonds. The only other special feature in this direction in the crystal is the 'open-layer structure' with comparatively large (about 4 A.) van der Waals separations. It is not possible at present to exclude entirely the possibility that such layers account for part of the anomalously high expansion; in *p*-dinitrobenzene, however, layers more closely packed (3·24 A.) have only a small expansion (cf. Fig. 4). Only complete intensity data for all possible reflexions at the different temperatures could give a rigorous proof that the large contraction α_{11} of the lattice on cooling is in fact due to the contribution of the polarization bond. However, as in other anomalous expansions studied, the correlation between the direction of maximum expansion and the direction of the polarization 'bond' is close. As a reasonable working hypothesis the total contraction *of the bond* may be calculated by the formula

$$\frac{\text{Total contraction in direction } \alpha_{11} - \text{mean contraction in all directions}}{\text{Number of polarization bonds per unit cell in direction } \alpha_{11}},$$

which refers to the unit cell.

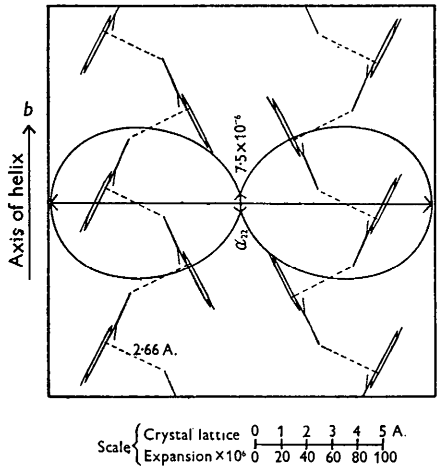


Fig. 3. Sectional projection of two helices of *p*-nitroaniline on to a plane containing the polarization bonds. (Benzene rings have been opened out diagrammatically.)

A further refinement may be noted. In the structure at 293° K., which is fully known, the polarization bond is normal to the plane of the benzene ring, probably because this secures a maximum overlap of a π orbital of the benzene ring with an orbital of the O atom. On cooling, the contraction of the crystal is such that if the plane of the benzene rings relative to the crystal axes remained unchanged the polarization bond would be bent about 2° away from the normal. If it is supposed that these bonds in fact remain normal to the rings,

Table 1

Crystal	Maximum linear expansion coefficient × 10^6	Mean linear expansion × 10^6	Length of polarization or hydrogen bond at room temperature (A.)
p-Nitroaniline	150·3	61	2·66
p-Dinitrobenzene	93	59	3·24
Oxalic acid dihydrate	55	—	2·52
Rochelle salt	82	64	2·56
Potassium dihydrogen phosphate	34	26	2·54
α-Resorcinol	91	—	2·66
H-Phthalocyanine	65	—	van der Waals forces only

it is necessary to tilt the plane of the rings through a small angle (about 4°) which is smallest when the tilt takes place about an axis in the 010 plane normal to the projection of the short bond. This would leave α_{33} practically unaffected by the change of tilt.

Comparatively small changes in van der Waals energy appear to be associated with such changes of tilt (cf. Ubbelohde & Woodward, 1943, for another example). On this basis, the polarization bond has the length 2·44 A. at 90° K. This length is not sensitive to the tilt assumed for the molecules. Using a plot of the change in spacing of the 14.0.4 plane at the three temperatures measured (Fig. 1) and simple power series for extrapolation, the bond length at 0° K. is estimated to be 2·40 A.

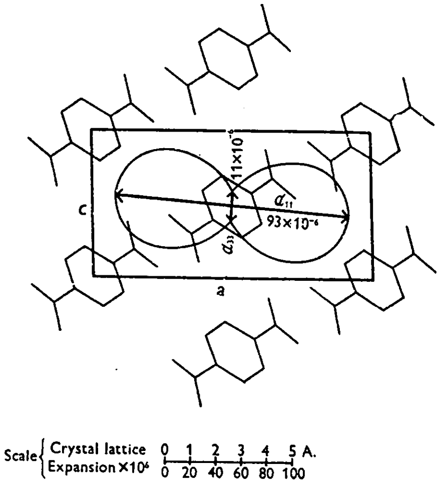


Fig. 4. Projection of p-dinitrobenzene on (010) plane showing expansion in relation to molecular positions.

This interpretation leads to the conclusion that, particularly at low temperatures, the polarization bond is so short in p-nitroaniline that some form of valency interaction must become quite important. In this connexion, it is useful to note that the thermal expansion of the crystal corresponds with the exertion of quite high internal pressures due to the lattice vibrations. To estimate the order of magnitude of these internal pressures the compressibility of p-nitroaniline would be required. It has not been measured but is likely to be comparable with the value for p-amino-benzoic acid (Bridgman, 1945). A thermal contraction of 3% in axial length of p-nitroaniline from 293 to 90° K. corresponds to the application of a pressure of about 12,000 atm. to p-amino-benzoic acid. Corresponding thermal pressures in p-nitroaniline and in other crystal compounds involving polarization bonds would force the molecules apart at ordinary temperatures. Cooling provides a simpler way of promoting more extensive overlap of the π electrons with the field of the NO_2 groups than the application of high external pressures, as used by Gibson & Loeffler (1940). Other investigations on this point are in hand.

In the present state of our knowledge the generalization which follows is only tentative. It applies both to intermolecular hydrogen bonds and to polarization bonds. Closer consideration shows that the exceptionally large expansion of the *shortest* intermolecular distance in a crystal is specially remarkable. Though the vibrational energy content differs in different crystals, the thermal expansion should show a general dependence on the shape of the potential-energy curves as the molecules are separated.

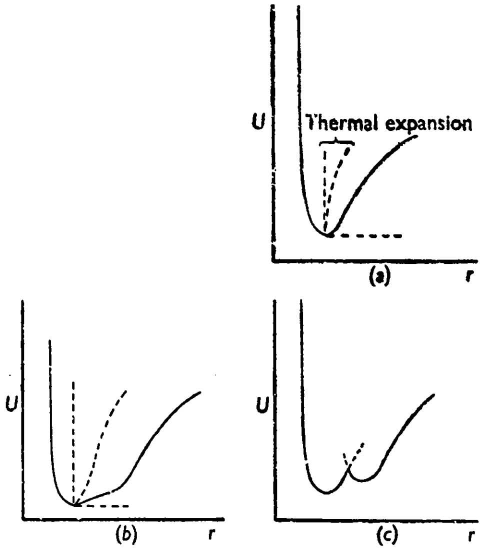


Fig. 5. Possible form of potential-energy curve to explain large thermal expansion for strong intermolecular binding. (a) Normal intermolecular forces. (b) Suggested form of curve for p-nitroaniline. (c) Possible origin of curve (b).

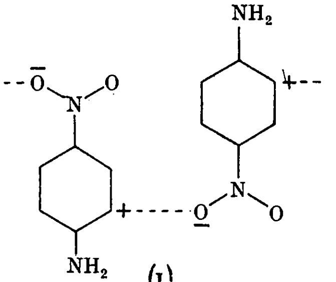
An approximate expression for the expansion α in any direction is

$$\alpha = +\frac{6a}{r_0}\frac{\partial(1/f)}{\partial r},$$

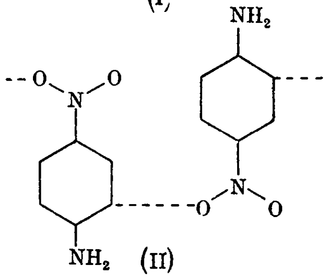
where a is the number of the order unity, f is the force for unit expansion, and r_0 is the bond length at equilibrium (Ubbelohde, 1949). Fig. 5 illustrates qualitatively the difference to be expected between molecules with different attractive potentials. The direction of the strongest intermolecular bonding can also be the direction of largest thermal expansion if the potential-energy curve has an exceptionally large $\partial(1/f)/\partial r$ near the bottom as illustrated in Fig. 5 (b). Such a shape of curve can combine a high coefficient of expansion with a high energy of bonding.

A potential-energy curve of this peculiar shape can be attributed to the overlapping of two potential-energy curves with closely adjacent minima. Such curves have, in fact, been proposed on the basis of somewhat different evidence to explain the isotope effect in oxalic acid dihydrate and other short hydrogen bonds (Robertson & Ubbelohde, 1939; Dickson & Ubbelohde, 1950), and have been discussed in some detail in an explanation of the piezo-electric properties of Rochelle salt (Ubbelohde

& Woodward, 1946; Ubbelohde, 1949). Overlapping of this kind arises when two alternative bond arrangements are possible in the crystal with only small shifts of certain atoms. In Rochelle salt and in oxalic acid dihydrate, as in *p*-nitroaniline, anomalous thermal expansion is, in fact, a prominent feature of the thermal behaviour.



(I)



(II)

In the case of *p*-nitroaniline, the short polarization bonds join the molecules in rectangular left-hand and right-hand helices, with the axes of the helices parallel to the *b* axis. The molecules and short intermolecular bonds form a kind of screw thread in each helix. Though it is not possible to do more than suggest what two bond arrangements give overlapping potential-energy curves, the short approach, 2·40 A. at 0° K., gives a clue. The ionic contact radius attributable to O in a nitrite ion is taken to be 1·45 A. from crystallographic data. This suggests (I) as a possible bond arrangement involving actual electron transfer. The positively charged carbon would have an ion contact radius at 0° K. of the order $2\cdot40-1\cdot45=0\cdot95$ A., which seems quite reasonable and compares with $r_{\mathrm{Na}^+}=0\cdot98$ A. The bond arrangement (II) in resonance with (I) merely involves normal molecules without electron transfer.

An important point is that resonance between states (I) and (II) is not confined to pairs of molecules, but extends right along each spiral through the crystal. In this respect the case is analogous to that postulated in oxalic acid dihydrate (Robertson & Ubbelohde, 1939). The intermolecular resonance is *long-range* and this may explain why the intermolecular contraction is unusually large.

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