NEAR INFRARED STUDY OF HYDROGEN BONDING IN *p*-NITROANILINE SINGLE CRYSTALS. THE EFFECT OF TEMPERATURE ON BAND POSITIONS AND DICHROIC RATIOS

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The spectra of single-crystalline platelets of *p*-nitroaniline (*p*-NA) have been measured in polarized light at three different temperatures (81°K, 187°K and room) in the 6400 to 7200 cm^{-1} range. The analysis of these spectra dealt with the effect of temperature on the distances between bands, integral intensities and the dichroism of four bands which arise due to vibrations of the $-NH_2$ group. The trend in changes of the distances between the examined bands has been elucidated by assuming that as temperature drops the share of interactions of the hydrogen bond type increases, thereby entailing various change in the anharmonicity of the individual bands. The sundry effect of temperature on band dichroism, depending on the symmetry of the relevant absorption transition, has been explained by the rotation of molecules due to anisotropic concentration of the crystal lattice. On the basis of the spectral data and reasoning it is presumed that such rotation proceeds in a way which promotes hydrogen bonding.

1. Introduction

In our earlier studies [1–3] on intermolecular interactions in *p*-NA crystals we had paid little attention to the problem of the hydrogen bond. In the fundamental frequency range the positions of most bands and their directions of polarization could be interpreted by accepting the oriented gas model with account taken of intramolecular charge transfer [2]. The rather strong shift of frequencies in the crystal relative to the frequencies in a CCl_4 solution of several of the bands, namely, the bands assigned to the $\nu^s_{NH_2}$, $\nu^{as}_{NH_2}$ and $\delta^s_{NH_2}$ vibrations, indicated the existance of intermolecular interactions of the hydrogen bond type in the crystal.

The possibility of hydrogen bonding appearing in crystalline *p*-NA had been discussed in papers [4, 5, 6] treating the correlation between the frequency shift $\Delta\nu_{NH_2}$ of the stret-

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ching vibrations of the $-NH_2$ group and the distance R_{X-Y} in the X−H...Y hydrogen bridge in the crystal. On the basis of research by Schroeder and Lippincott [6] and the observed frequency shift the mean energy of the hydrogen bond in *p*-NA can be estimated to be approximately 1.7 kcal/mol, while later data of Bellamy and collaborators give about 1 kcal/mol [7, 8].

As shown by research on the crystal structure of *p*-NA [9], there are two hydrogen bridges with $R_{N...O}$ distances of 3.07 and 3.14 Å. However, on the basis of spectroscopic studies of a group of seven aliphatic and aromatic amines Zhukova and Shman'ko suppose that in crystalline *p*-NA there are dimers linked by a single hydrogen bond. It must be stressed that in their work they analyzed the spectrum of crystalline *p*-NA only as suspension and only in the 3100 to 3600 cm^{-1} range.

The goal of this work is to attempt to explain the occurence of hydrogen bonding in single-crystalline *p*-NA by investigating the effect of temperature on its spectrum in polarized light.

2. Experimental procedure and results of measurements

The spectra were measured in the 6400–7200 cm^{-1} range in polarized light at temperatures of 81°K and 187°K with the use of the set-up described in Ref. [3]. To achieve temperatures higher than room temperature use was made of an electrically-heated sample holder. Temperature was measured with a copper-constantan thermocouple. The changes

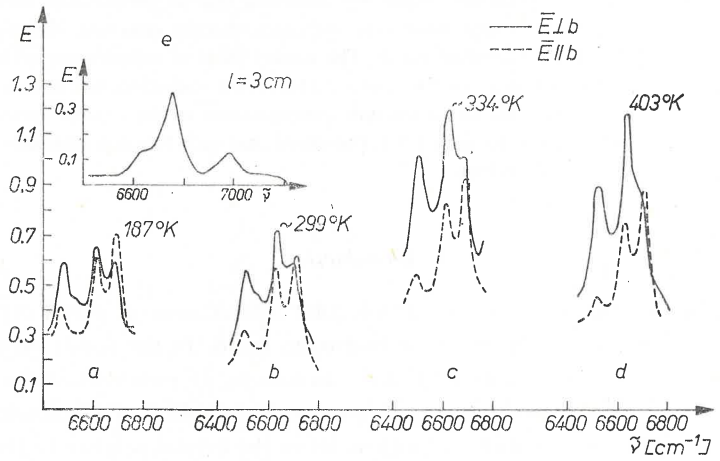


Fig. 1. a–d. Spectrum of *p*–NA single crystal in polarized light at various temperatures; e. Spectrum of saturated solution of *p*–NA in $CHCl_3$

in the spectra observed when the temperature changed, being the basis of qualitative deliberations concerning the distances between bands, are illustrated in Fig. 1.

Owing to the lack of a device for thermostating the temperature of the LiF prism in the monochromator of the spectrophotometric set-up, the absolute positions of the bands are not known precisely. In our quantitative considerations, therefore, the distances be-

tween the bands were used which are reproducible and much better known. The spectra were measured with the directions of the electromagnetic wave's vector $\boldsymbol{E}$ parallel to the crystallographic axis b and perpendicular to it, lying in the (101) cleavage plane of the sample. Results of measurements for five different samples at three different temperatures are presented in Fig. 2 and arranged in Tables I and II.

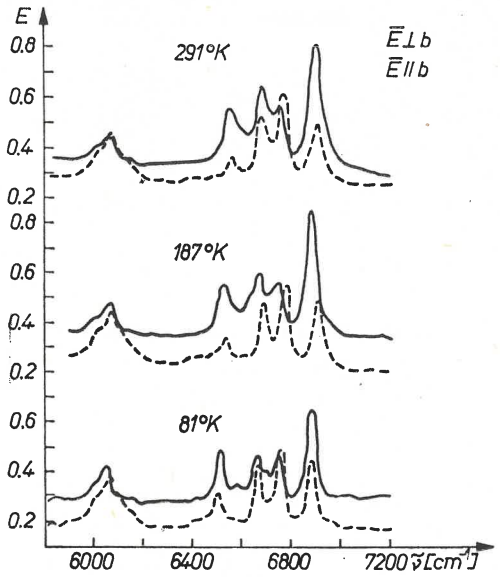


Fig. 2. Spectrum of p–NA single crystal in polarized light at various temperatures

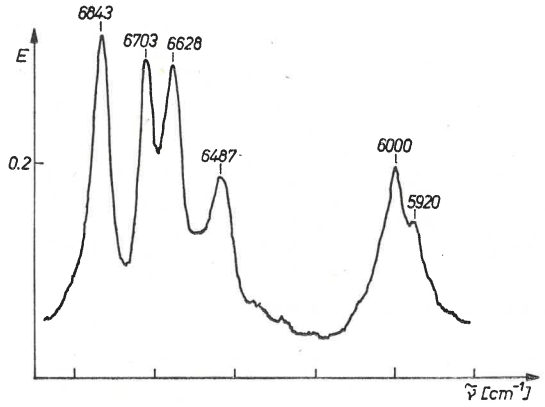


Fig. 3. Spectrum of p–NA single crystal in ordinary light

The tables have the following notation of bands (Fig. 3):

$$1-2\nu^{as}_{NH_2} = 6843 \text{ cm}^{-1},$$
$$2-\nu^{s}+\nu^{as} = 6703 \text{ cm}^{-1},$$
$$3-2\nu^{s}_{NH_2} = 6628 \text{ cm}^{-1},$$
$$4-2\delta^{s}+\nu^{s} = 6847 \text{ cm}^{-1}.$$

TABLE I

Effect of temperature on spacing between bands in *p*-NA single crystals [cm^{-1}]

Polarization direction	Temp. °K	$\Delta\nu_{1-2}$	$\Delta\nu_{1-3}$	$\Delta\nu_{1-4}$	$\Delta\nu_{2-3}$	$\Delta\nu_{2-4}$	$\Delta\nu_{3-4}$
$\perp b$	81	132	218	376	86	243	158
	187	136	217	360	83	226	141
	294	141	212	341	72	201	130
$\parallel b$	81	128	216	375	88	244	159
	187	130	216	365	87	236	149
	294	135	218	350	85	218	132

The data of Table I may be presented briefly in the following way, convenient for subsequent discussions:

$$T\downarrow\ \Delta\nu_{1-2}\downarrow\ \Delta\nu_{1-3}\ \overset{\uparrow}{\downarrow}\ \Delta\nu_{1-4}\uparrow\ \Delta\nu_{2-3}\uparrow\ \Delta\nu_{2-4}\uparrow\ \Delta\nu_{3-4}\uparrow .$$

An upwardly directed arrow stands for an increase in the value of the quantity left of it.

The analytical resolution of the absorption curve into the various bands was accomplished with the use of the Cauchy-Gauss product function [11] of the type:

$$B(\nu) = a_1[1+a_2^2(\nu-a_3)^2]^{-1}\exp\,[-a_4^2(\nu-a_3)^2] \qquad (1)$$

where $B(\nu)$ is the shape function of the absorption curve, a_1 is extinction at the band's maximum (at ν_0), a_3 is the frequency at the centre of the band (ν_0), and a_2, a_4 are form factors characterizing the share of the Gauss and Cauchy profiles.

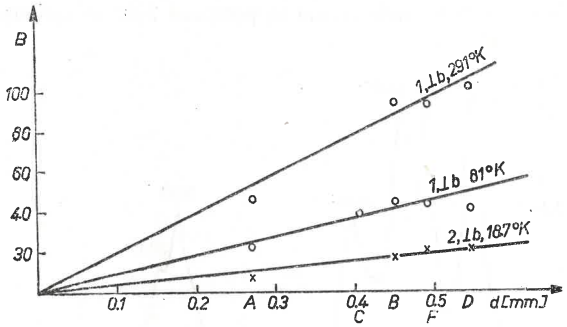


Fig. 4. Dependence of integral intensity of bands on platelet thickness

Reduced integral intensities (B/d) and dichroic ratios ($R_{a'/b}$)

Band	1. $2\nu^{as}-A_1$			2. $(\nu^{as}+\nu^{s})-B_1$		
Temp. °K	$\left(\frac{B}{d}\right)_{\perp b}$	$\left(\frac{B}{d}\right)_{\parallel b}$	$R^{exp}_{a'/b}$	$\left(\frac{B}{d}\right)_{\perp b}$	$\left(\frac{B}{d}\right)_{\parallel b}$	$R^{exp}_{a'/b}$
81	89±4	61±5	1.45±0.12	36±6	59±4	0.61±0.11
187	142±10	84±8	1.70±0.20	38±3	107±7	0.35±0.04
294	192±8	76±4	2.52±0.17	58±6	99±6	0.59±0.08

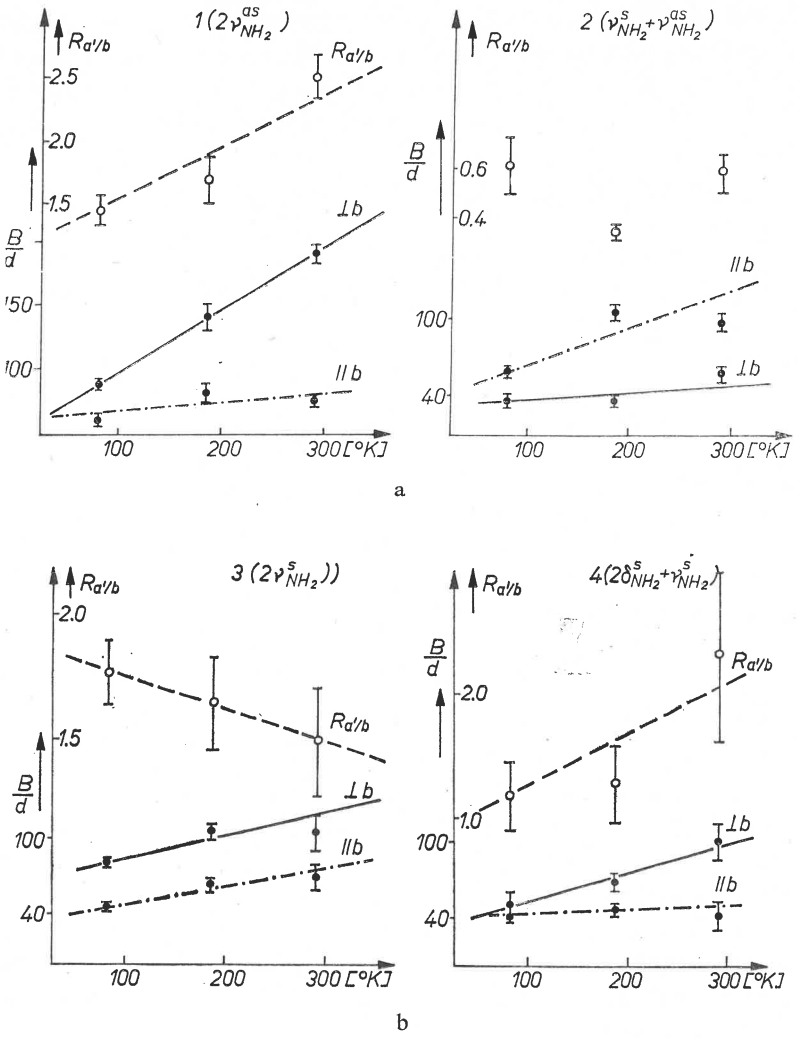


Fig. 5. Temperature-dependence of reduced integral intensity (B/d) and band dichroic ratios $R_{a'/b}$

TABLE II

of bands of *p*-NA crystals for different temperatures

3. $2\nu^s - A_1$			4. $(2\delta^s + \nu^s) - A_1$		
$\left(\frac{B}{d}\right)_{\perp b}$	$\left(\frac{B}{d}\right)_{\parallel b}$	$R^{exp}_{a'/b}$	$\left(\frac{B}{d}\right)_{\perp b}$	$\left(\frac{B}{d}\right)_{\parallel b}$	$R^{exp}_{a'/b}$
80± 1	45± 3	1.77±0.13	50∓11	42± 4	1.18±0.28
107± 7	65± 7	1.65±0.19	69± 8	53±11	1.29±0.31
107±14	71±10	1.50±0.22	102±15	43±12	2.34±0.72

After making the division, numerical integration was carried out over a region equalling ten half-widths of the given band. In order to account for the absorption at the wings of the bands beyond this region, a correction as proposed by Ramsay [12] was added to the computet area under the curve. This correction was 14.4%. Computations were carried out on an Elliott 803 computer.

The dependence of the integral intensity of several bands on platelet thickness is illustrated in Fig. 4.

Table II gives mean values of integral intensities of bands for crystal thickness equal 1 mm (B/d) and the dichroic ratio $R_{a'/b}$ as a function of temperature. The data of Table II are illustrated by the curves in Fig. 5.

3. The effect of temperature on band positions

The results gathered in Table I show that a change of temperature affects the positions of different bands in various ways. Two of the examined bands are due to overtones of $-NH_2$ group stretching vibrations (bands 1 and 3) of considerable mechanical anharmonicity. This anharmonicity is strongly effected by hydrogen bonds.

According to Sandorfy and collaborators [13, 14], the presence of hydrogen bonding causes an increase in mechanical anharmonicity, expressed as $\nu_{01}-\frac{\nu_{02}}{2}$, and the fulfilment of the inequality $\nu_{01}-\frac{\nu_{02}}{2} \neq \frac{\nu_{02}}{2}-\frac{\nu_{03}}{3}$, where ν_{01}, ν_{02} and ν_{03} denote the observed frequencies of the fundamental and the first and second overtones, respectively. The extensive studies of Couzi and Huong [15] also indicate that the mechanical anharmonicity of the X–H oscilator participating in a typical hydrogen bond is large. To answer this question for the *p*-NA crystal it seems useful to compare the frequency of the fundamental and first overtone in the crystal and in a solution with the least active solvent possible, since the frequencies in the gaseous phase are unknown. As a basis for calculations we accepted the frequencies in a cyclohexane solution quoted in Ref. [16] and the frequencies from the spectrum of a single crystal in ordinary light (overtones, Fig. 3) or in polarized light as the average frequencies for split bands [2]. These data are given in Table III, while Table IV holds data required for checking the above-given inequality of Asselin, Belanger and Sandorfy [14] for the frequencies $\nu^{s}_{NH_2}$, $\nu^{as}_{NH_2}$ and $\delta^{s}_{NH_2}$.

TABLE III

Anharmonicity of vibrations of $-NH_2$ group in *p*-NA $X = \nu_{02}-2\nu_{01}$ [cm^{-1}]

	$\nu^{s}_{NH_2}$	$2\nu^{s}_{NH_2}$	X^{s}	$\nu^{as}_{NH_2}$	$2\nu^{as}_{NH_2}$	X^{as}	$(\nu^{s}+\nu^{as})_{calc}$	$(\nu^{s}+\nu^{as})_{obs}$	X
C_6H_{12} solution [22]	3424	6752	−96	3519	6974	−64	6943	6800	−143
crystal	3371	6628	−114	3484	6843	−125	6855	6703	−152

TABLE IV

Vibration	ν_{01}	ν_{02}	ν_{03}	$\frac{\nu_{02}}{2}$	$\frac{\nu_{03}}{3}$	$\nu_{01}-\frac{\nu_{02}}{2}$	$\frac{\nu_{02}}{2}-\frac{\nu_{03}}{3}$
$\nu^{s}_{NH_2}$	3371	6628	9787	3314	3262	57	52
$\nu^{as}_{NH_2}$	3484	6843	10120	3422	3373	62	49
$\delta^{s}_{NH_2}$	1638	3245	4800	1623	1600	15	23

As is seen from Table III, vibration anharmonicity increases when passing from the solution to the crystal, and the greatest change is in the anharmonicity of the antisymmetric vibration overtone, the smallest being in the $(\nu^{s}+\nu^{as})$ combination. A similar regularity has been found by Lady and Whetsel [16], who in their study on the overtones of $-NH_2$ group vibrations in aniline derivatives observed an increase in the $(2\nu^{obs}-2\nu^{cal})$ anharmonicity of symmetric and antisymmetric stretching vibrations of $-NH_2$, and a decrease in the anharmonicity of the combination vibration. They assigned these changes to the formation of hydrogen bonds.

The data of Table IV indicate that the inequality $\nu_{01}-\frac{\nu_{02}}{2} \neq \frac{\nu_{02}}{2}-\frac{\nu_{03}}{3}$ is satisfied. However, in the case of *p*-NA the successive differences usually decrease for the stretching vibrations, whereas for phenol they increase [14].

The spectroscopic data in Tables III and IV seem to corroborate the crystallographic data on the existence of hydrogen bonding in *p*-NA. It may be expected that a drop in temperature is followed by an increased share of hydrogen bonding, hence, the effect

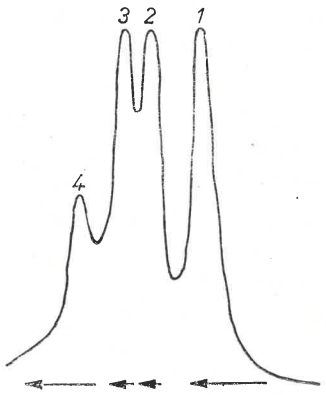


Fig. 6. Changes in anharmonicity of bands in *p*-NA caused by a lowering of temperature

corresponding to the transition from inactive solvent to the crystal. On this basis it is possible to attempt to explain the change in the distance between the bands caused by a lowering of temperature, remembering that the different directions of the anharmonicity changes of the various vibrations must be accounted for. Figure 6 shows the *p*-NA spectrum in the examined region, wherein the arrows mark out the deduced direction of band

frequency changes at descreasing temperature. The length of the vectors are proportional to the changes in anharmonicity. The changes in the distances between the bands predicted on the basis of Fig. 6 are as follows:

$$T\downarrow \ \Delta\nu_{1-2}\downarrow \ \Delta\nu_{1-3}\downarrow \ \Delta\nu_{1-4}\uparrow \ \Delta\nu_{2-3}\uparrow \ \Delta\nu_{2-4}\uparrow \ \Delta\nu_{3-4}\uparrow .$$

A comparison of these results and the data of Table I shows that there is good agreement between the directions of changes observed and those which stem from considerations of the anharmonicity differences assuming there is enhanced interaction of the hydrogen bond type when the temperature drops.

In this way it is possible to explain the increased overlapping of bands 2 and 3 at the higher temperatures, as seen in Fig. 1. This conclusion is also upheld by the spectrum of *p*-NA in $CHCl_3$, presented for the sake of comparison. In this solution there is weak interaction between the *p*-NA molecules and the $CHCl_3$ molecules, indeed, they are weaker than those in the *p*-NA crystal near 400 °K. Hence, the spacing between bands 2 and 3 is smaller than the half-widths of these bands, and they overlap.

4. Effect of temperature on band dichroism

As follows from the data in Table II and Fig. 5, with an increase in the integral intensity with increasing temperature of the bands is observed — a strong one for $\boldsymbol{E}\perp b$ and a slight one for $\boldsymbol{E}\parallel b$. Although in Fig. 5 straight lines are led through all of the points, a curvilinear character of the dependence of integral intensities and dichroic ratios on temperature cannot be excluded. In particular, it is feasible that there is an extremum of these quantities in the vicinity of 187 °K.

At least three important factors should be taken into account in order to interpret the changes in band intensities due to a change in temperature.

1. The effect of temperature on the hydrogen bond energy. According to Pimentel and McClellan [17], an increase in temperature weakens the hydrogen bond, this being reflected by the more intense bands of overtones of the oscillators engaged in the hydrogen bonding, that is, the same kind of effect that occurs in *p*-NA.

2. The coupling of lattice vibrations with internal vibrations. The considerations of Hornig [18] have proved that a rise in temperature may cause such couplings to appear, which entails an increase in the integral intensity of the internal vibration bands. According to the theory of Strizhevski [19, 20], when the existence of couplings is taken into account, band intensity may also drop with an increase in temperature.

3. The effect of finite slit width. Anderson and Person [21] and Hollenberg and Dows [22] have found that when the instrumental resolving power is poor there is an apparent increase in band intensity with a rise in temperature. The *p*–NA spectra in the 6400–7200 cm^{-1} range were measured with the use of wide spectral slits and, therefore, this factor may bear some influence on the examined temperature dependence.

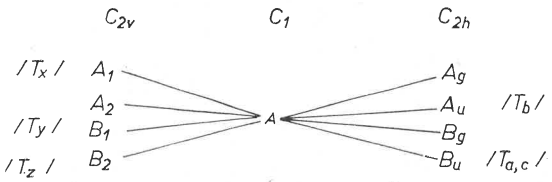
As it is impossible at this stage to determine quantitatively the shares of these three factors in the examined effect, we shall confine ourselves to an attempt of interpreting only the changes in the dichroic ratio with temperature. It was ascertained in Ref. [21]

that the ratio of band intensities in the same spectrum is independent of instrumental resolving power. It is expected, therefore, that the ratio of band intensities measured for different light polarization directions under unaltered measuring conditions should also be independent of instrumental resolving power.

In order to compare experimental results with theory the dichroic ratios of the bands of the $-NH_2$ group have been calculated on the basis of structural data [9].

p–NA crystallizes in the monoclinic system, the symmetry of the crystal belonging to the $C_{2h}^5 (P2_{1/n})$ space group, with four molecules in the unit cell. As an appriximation the C_{2v} group can be taken as the point group of symmetry of the molecule's. The numeration of atoms and the system of coordinate axes of the molecule are given in Fig. 7b. Figure 7a presents schematically the distribution of molecules in the unit cell by means of unit vectors $\vec{e}_i$ parallel to the long molecular axis (C_1C_4) in projection onto the cleavage plane *ba'* (101). This is the plane in which both directions of measurement lie, $\perp b$ and $\| b$. At the same time, this diagram illustrates the distribution of the transition moments of vibrations of molecular symmetry A_1.

The point group of the unit cell, equivalent in this case to the interchange group [23], is C_{2h}. Therefore, the correlation diagram for the *p*–NA crystal is



As ascertained in an earlier study [2], *p*–NA is described to a large extent by the oriented gas model. Therefore, the dichroic ratios of the bands may be calculated on the basis of the orientations of the *x*, *y* and *z* axes of the molecule. The direction cosines of the molecular axes with respect to the orthogonalized system of crystallographic axes *a*bc* and the orthogonal system *a'bc'* associated with the cleavage plane of *p*–NA are given is Table V.

TABLE V

Direction cosines of the system of molecular axes *x*, *y*, *z* relative to the system *a**, *b*, *c*, and *a'*, *b*, *c'*

a)	*x*	*y*	*z*	b)	$x(A_1)$	$y(B_1)$	$z(B_2)$
a*	0.7503	−0.0719	0.6563	*a'*	0.9005	−0.4060	0.1604
b	−0.4333	−0.8013	0.4077	*b*	−0.4332	−0.8013	0.4077
c	−0.4993	0.5940	0.6348	*c'*	0.0344	0.4395	0.8988

These data permit calculation of the dichroic ratios of C–C and C–H vibrational bands, for which the transition moments lie along the *x*, *y* or *z* axis. For groups of atoms whose vibrations are but weakly dependent on the remaining part of the framework, such as the $-NH_2$ group in which we are primarily interested here, the direction of the

transition moment of symmetry A_1 can be calculated with the help of the sum of –N–H vectors, whereas that of the transition of symmetry B_1 with the help of their difference.

The values of theoretical dichroic ratio were calculated with the use of the formula given by Rohleder and Luty [24], which in the case of *p*–NA takes the form

$$R^{M}_{a'/b} = \frac{N_b}{N_{a'} \cos \xi} \frac{[\cos \xi \cos (\vec{M}, a') + \sin \xi \cos (\vec{M}, c')]^2}{\cos^2 (\vec{M}, b)} \tag{2}$$

where $(\vec{M}, a')$ stands for the angle between the transition moment vector $\vec{M}_i$ of the given vibration and the electric vector $\vec{E}_{a'}$ of the electromagnetic wave polarized along the direction a' in the crystal, while $N_{a'}$ and N_b are the refractive indices along the directions a' and b respectively. In the calculations use was made of the values of refractive indices given by Tanaka [25]:

$$N_{X'} = 1.556, \; N_Y = 1.777 \text{ and } N_{Z'} = 2.005,$$

$$\text{with } N_b = N_Y \text{ and } \frac{1}{N_{a'}} = \left(\frac{1}{N^2_{Z'}} \cos^2 \varphi + \frac{1}{N^2_{X'}} \sin^2 \varphi \right)^{\frac{1}{2}}$$

the values of the angles being $\xi = 1°$ and $\varphi = 1°$, after [24].

The dichroic ratios for the bands of $-NH_2$ group vibrations calculated according to formula (2) are given in Table VI. As a comparison of the data in Tables II and VI shows

TABLE VI

Dichroic ratios of vibration bands of $-NH_2$ group in *p*-NA

Vibration mode	Symmetry type	$R^{\text{theor}}_{a'/b}$
ν_{NH_2}, δ_{NH_2}	A_1	2.61
ν_{NH_2}	B_1	0.336
γ_{NH_2}	B_2	0.033

the dichroic ratios of the bands 1 and 4 of symmetry A_1 are in agreement at room temperature with the respective values predicted by theory, within experimental error limits. On the other hand, the dichroic ratio values of the bands 2 and 3 do not agree with predicted values. With a lowering of temprature the dichroic ratios of bands 1 and 4 decrease, whereas those of band's 3 increase.

Because dichroism of a band is associated with the geometrical orientation of a molecule in the unit cell, it seems probable that changes in the values of dichroic ratio arise due to changes in this alignment brought about by changes in temperature. Krishna Murti [26] presumes that in the *p*–NA crystal at 90 °K there are strong interactions which may cause a rotation of the molecules in the unit cell. The feasibility of a similar rotation in anthracene is proved by the studies of Mason [27] concerning the structure of this crystal at 95 °K and 290 °K. It follows from Mason's data that between these two temperatures the anthracene molecule becomes rotated through an angle of about 2.5° around the axis perpendicular to the moleculear plane.

To get an idea of the extent to which molecular rotation may bear an effect on the value of dichroic ratio, calculations were performed for various hypothetical alignments of *p*–NA molecules in the unit cell. The rotation of the molecules was assumed to be in succession about the *x*, *y* and *z* axes and also about the *a**, *b* and *c* crystallographic

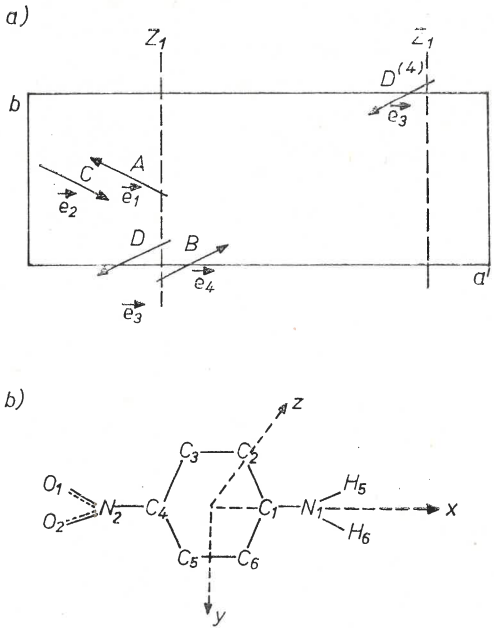


Fig. 7. a) Projection of vectors of $-A_1(C_1C_4)$ type transition moments on cleavage plane; b) Numeration of atoms and system of coordinates in *p*–NA molecule

axes. To preserve the space group symmetry, molecules *A* and *C* were assumed to rotate in the opposite direction relative to molecules *B* and *D* (Fig. 7). Notwithstanding, Rakov [28] holds the view that in a crystal reorientation may proceed only about the symmetry axes of the molecule, for it is only then that rotations do not violate the basic lattice symmetry. But this seems to be an unnecessary limitation, for other atom displacements which are in keeping with the symmetry elements of the crystal's space group are also possible. Calculations were carried out for $-NH_2$ group vibrations of symmetry A_1; the results are gathered in Tables VIIa and VIIb.

The experimental dichroism which conforms best with that predicted from structure is exhibited by the $2\nu^{as}_{NH_2}$ band (*cf.* Tables II and III). Therefore, the behaviour of this band with temperature may be accepted as a basis for comparison with the results of calculations in Tables VIIa and VIIb.

The comparison shows that the rotation of the molecule about the *z*-axis or the crystallographic *c*-axis deserves the most attention, as in these cases the changes in dichroic ratio are largest ones. A rotation about either of these axes by 6° brings about a change in dichroic ratio similar to cooling to a temperature of 187°K, whereas by 9° like cooling to 81°K.

TABLE VII

Changes of dichroic ratio of $-NH_2$ wibrations of type A_1

a) due to rotation about molecular axes x, y, z passing through molecule's center of mass

Rotation by an angle of	Rotation about axis		
	x	y	z
[°]	$R_{a'/b}$	$R_{a'/b}$	$R_{a'/b}$
0	2.63	2.63	2.63
−3	2.57	2.41	
−6	2.54	2.14	
3	2.59	2.93	2.12
6		3.26	1.66
9			1.42

b) due to rotation of molecule about crystallographic axes a^*, b, c with coordinate system origin beyond molecule

Rotation by an angle of	Rotation about axis		
	a^*	b	c
[°]	$R_{a'/b}$	$R_{a'/b}$	$R_{a'/b}$
0	2.62	2.62	2.62
3	2.3		2.13
6		2.5	1.76
9	1.9	2.4	1.45

It is interesting to see what hypothetical rotations of *p*-NA molecules in the crystal lattice may affect the hydrogen bond parameters. The distances $H_5...O'_1$ and $H_6...O'_2$ are taken as the basis for deliberations, because the N−H...O distance is a measure of the hydrogen bond force; at these temperatures the alterations of the N–H bond length are negligible ($kT \ll h\nu_{X-H}$). As a second parameter characterizing the hydrogen bond we accept the N−H...O angle; the larger the deviation of this angle from 180°, the weaker the hydrogen bond.

These calculations show that simple rotations of molecules in the lattice (Tables VIIa and VIIIa) may indeed cause changes in dichroic ratio, but do not lead to the described changes in band positons which may be explained by an increased participation of hydrogen bonding. One might arrive at the presumption that another important factor in the temperature-dependence of spectra is present, namely, strong anisotropy of the *p*-NA crystal's thermal expansion [29]. The influence of this property on crystal spectra had been considered by Colombo [30] and Lisitsa and Tsyashchenko [31] when dealing with Davydov splitting.

TABLE VIII

Changes in H...O distances and NH...O angles due to hypothetical rotations of *p*-NA molecules:

a) about the *z*-axis passing throug the molecule's center of mass

Rotation angle (in degree) α	$d_{H_5...O_1'}$	$\sphericalangle N_1-H_5...O'_1$	$d_{H_6...O''_2}$	$\sphericalangle N_1-H_6...O''_2$
0	2.35	140	2.34	164
6	2.69	128	2.73	160
9	2.82	123	2.94	157

b) about the *z*-axis passing origin common for all molecules

0	2.35	140	2.34	164
6	2.61	103	3.37	138
9	2.92	144	3.62	122

c) about the *c*-axis passing through origin common for all molecules

0	2.35	140	2.34	164
6	1.63	109	3.99	90
9	2.25	141	5.16	129

Anisotropic contraction of the lattice when temperature is lowered may cause the molecules in the lattice to simultaneously rotate and translate, the latter being different for each different direction.

It may be expected that such behaviour of molecules is similar to that assumed in calculations, the results of which are arranged in Tables VIIIb and c. Moreover, the results of Table VIIIc indicate that there may be such a direction of rotation which together with translation improve the conditions of formation of hydrogen bonding. As is seen, rotation about the *c*-axis strongly shortens one H...O bond and elongates another. The results of Table VIII c are illustrated in Fig. 8.

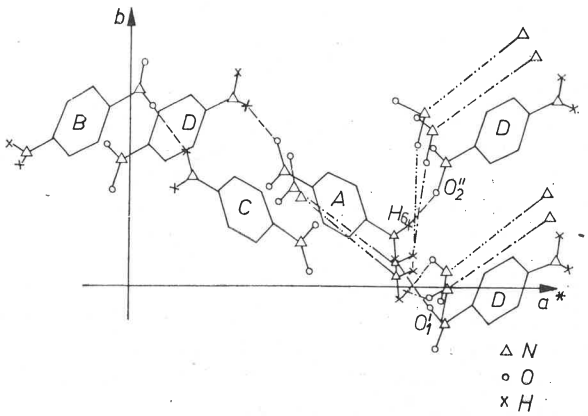


Fig. 8. Projection of *p*–NA structure on *ba** plane and an illustration of probable rotations about *c*-axis: – · – · – · – · · rotation by 6°, – ·· – ·· – ·· – ·· – rotation by 9°

For these reasons it is preasumed that anisotropic contraction of the crystal lattice of *p*–NA when temperature is lowered makes molecules to rotate in the direction which facilitates the formation of hydrogen bonding. This conclusion is in agreement with the considerations of Kitaigorodskii [32], who forwards the opinion that in crystals with hydrogen bonding the tendency to become closely packed manifests itself in the realization of all hydrogen bonds, even at the cost of their deviation from linearity.

The discrepancy between the observed and expected dichroic ratios may be the outcome of the depolarizing effect of coupling of internal vibrations with lattice vibrations, which becomes enhanced at higher temperatures. This effect has been scrutinized by Davydov and Myasnikov [33], but not in the infrared. It seems that some light on this problem may be cast by research on the behaviour of dichroism as a function of temperature, yet to be performed.

The deviation of the observed dichroic ratios from the expected values for *p*–NA may also be due to thermal vibrations of atoms in the crystal [9]. Namely, the $-NO_2$ group performs torsional motions of a average amplitude of $\sim 14°$, while the nitrogen atom in the amine group carries out oscillatory motion in a direction perpendicular to the $-NH_2$ plane of an average amplitude of 0.32 Å. In the examined spectral region the motion of the nitrogen atom in the amine group deserves the most attention, for it may cause the position of the transition moment to become obscured somewhat, especially in the case of the $-NH_2$ symmetric stretching vibration.

On the basis of analyses of *p*–NA spectra in the entire accessible spectral region it is presumed that crystals of this substance constitute the border line between the group of molecular crystals and the group of crystals with typical hydrogen bonding.

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