THE ABSORPTION SPECTRUM OF p-NITROANILINE SINGLE CRYSTALS IN POLARIZED LIGHT IN THE FUNDAMENTAL FREQUENCY RANGE

By M. Szostak and J. W. Rohleder

Laboratory of Chemical Physics, Institute of Organic and Physical Chemistry, Technical University, Wrocław*

The absorption spectrum of single crystal plates of p-nitroaniline in polarized light has been studied in the range from 600 to 3600 cm^{-1}. On the basis of the determined frequencies and polarization directions the assignments of the particular bands to normal vibrations have been revised. An attempt has been made to make a qualitative explanation of the observed splittings of the bands and other differences between the spectrum of the crystal and that of the solution, on the basis of the theory of molecular crystals which describes the deviations from the oriented gas model by means of perturbation methods. In order to describe the spectrum of crystalline p-nitroaniline, except a few bands, it is sufficient to assume only first-order perturbation, *i. e.*, dipole-dipole interactions.

Introduction

The infrared absorption spectrum of p-nitroaniline (p-NA) in the fundamental frequency range has been investigated by many authors, either in the case of comparative studies of a number of para-disubstituted benzene derivatives [1—7], or in the case of studies of the vibrations of the functional groups: $-NH_2$ [8—23], $-NO_2$ [22—30] and $-CN$ [31, 32].

The authors of two of the above-mentioned papers, [4] and [5], give the spectrum of p-NA in solutions and in a KBr-pellet in the whole fundamental frequency range (400—3600 cm^{-1}). In addition, Ref. [5] gives a comparison of the experimental frequencies with values calculated by means of a computer on the basis of model which treats the substituents as mass points and neglects the coupling between the vibrations of the substituents and the vibrations of the ring.

The aim of the present paper was a revision of the assignments in the fundamental frequency range and an attempt of giving an answer to the question which interactions from among those occurring in crystalline p-NA are reflected in the investigated region of the spectrum. The intermolecular interactions in the p-NA crystal are appreciable owing to the

---

* Address: Instytut Chemii Organicznej i Fizycznej, Politechnika Wrocławska, Wrocław, Wybrzeże Wyspiańskiego 27, Polska.

considerable static dipole moment of the molecule and to the characteristic arrangement of the molecules in the elementary cell [33]. The program of the studies comprised the determination of the spectra of single-crystal plates of p-NA (101) in polarized light and, for the sake of comparison, the spectra of solutions (CCl_4, $CHCl_3$), the spectra of powders (suspension in paraffin, hexachlorobutadiene, KBr pellet), and partially oriented, fused layers.

I. The spectroscopy of the crystalline state

According to the data of Winchell [34] and Trueblood et al. [35] p-NA crystallizes in the monoclinic system, the symmetry of the crystal belonging to the $C_{2h}^5(P2_1/n)$ space group. The unit cell contains four molecules. A free molecule has the symmetry of the C_{2v} point group. In a crystal the molecule is subject to deformation: the plane of the $-NO_2$ group is twisted by about 2° while the plane of the $-NH_2$ group is twisted by 16° with respect to the plane of the benzene ring. In spite of these deviations from the coplanarity one can assume, as a first approximation, that the molecule retains its C_{2v} symmetry also in the crystal.

Interactions of excited dipoles in the unit cell lead to characteristic differences between the spectra of the crystal and of the solution. According to the theory of Davydov [36] each molecular term is split in the crystal field into few components whose number equals the number of molecules in unit cell. The selection rules for the unit cell give which transitions are allowed in the infrared region. A detailed consideration of the distribution of the molecules in the unit cell of p-NA implies that each band, which corresponds to vibrations of a free molecule, should be split into two components: one with the polarization parallel to the crystallographic axis b and the other with the polarization perpendicular to the direction of the b-axis [37].

The arrangment of molecules in unit cell permits the existence of molecular pairs forming dimers with C_i symmetry to be assumed. This opinion has also been given in Ref. [20].

The coupling within the dimer implies that the phases of vibrations in both molecules cannot be arbitrary: the vibrations of both molecules which form the dimer can only be either symmetric or antisymmetric with respect to the centre of inversion.

A glance at the correlation diagram between the point-group of the dimer symmetry, the site group and the factor-group:

Point group of the dimer C_i	Point group of the site C_i	Factor group C_{2h}	Activity	Polarization
A_u ————	A_u <	A_u	IR	$\|b$
		B_u	IR	$\perp b$
A_g ————	A_g <	A_g	R	
		B_g	R	

shows that the same result is obtained as that on the basis of the theory of Davidov. Vibrations which are active in infrared region will be those of A_u-symmetry with polarization

parallel to the direction of the b-axis of the crystal, and those of B_u-symmetry with polarization perpendicular to b-axis.

Although the correlation between the types of symmetry of the free molecule (C_{2v}) and the symmetry species of the factor group in case of the existence of dimers can only be indirect, the use of such correlation is convenient and therefore this correlation has been used in the preparation of Table I.
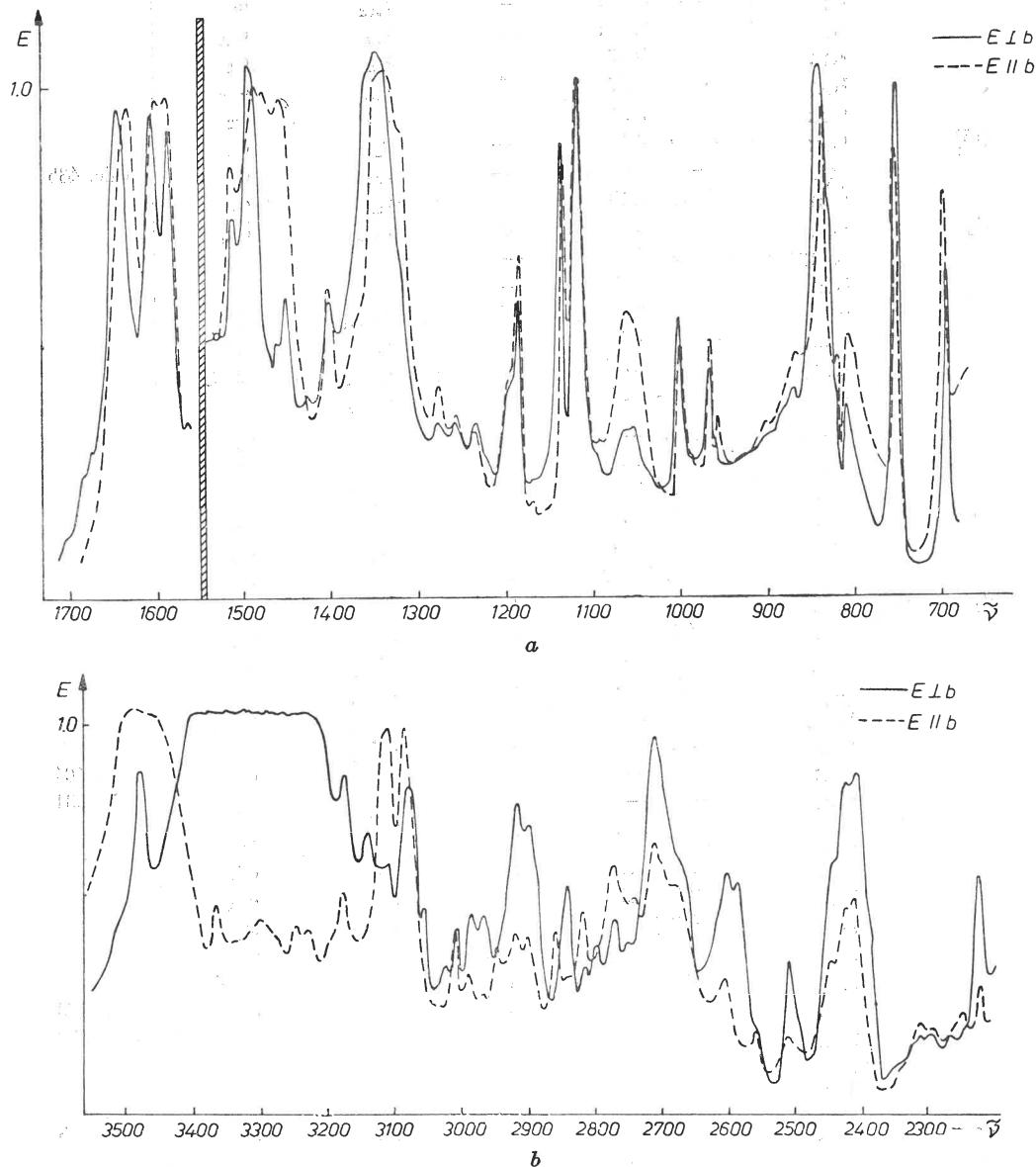

Fig. 1a, b. The spectrum of a crystal plate of p-nitroaniline in polarized light. Solid line — spectrum for $E \perp b$. Dashed line — spectrum for $E \parallel b$

TABLE I

Frequencies of normal vibrations in p-nitroaniline single crystals

Molecular symmetry type of vibration	Mode of vibration	Crystal frequency observed		Crystal splitting cm^{-1}	Notation according to Wilson [4]	Notation according to Brandmüller [5]	Remarks
		A_u	B_u				
	ν_{CH}	—	3078?	—	ν_{20a}	ω_1	
	ν_{CH}	—	3112?	—	ν_{7a}	ω_{18}	
	ν_{CC}	1601	1607	6	ν_{8a}	ω_2	
	ν_{CC}	1480	1487	7	ν_{19a}	ω_{19}	
	δ_{CC}	1120	1121	1	ν_{12}	ω_3	
(15)	δ_{CC}	~ 840	~840	—	ν_1	ω_5	
	δ_{CC}	—	—	—	ν_{6a}	ω_6	calc. 435
	δ_{CH}	1135	1140	5	ν_{9a}	ω_4	
A_1	δ_{CH}	1002	1005	3	ν_{18a}	ω_{21}	
	$\nu_{CN(H_2)}$	~1340	~1340	—			
	$\nu_{CN(O_2)}$	~840	~840	—			
	δ_{NH_2}	1632	1645	13	$\delta^s_{NH_2}$	δ_{NH_2}	
	δ_{NO_2}	~660	671	~11	$\delta^s_{NO_2}$	δ_{NO_2}	
	ν_{NH_2}	3365	3377	12	$\nu^s_{NH_2}$	ν_{NH_2}	
	ν_{NO_2}	~1340	~1340	—	$\nu^s_{NO_2}$	ν_{NO_2}	
	ν_{CH}	3082?	—	—	ν_{7b}	ω_9	
	ν_{CH}	3108?	—	—	ν_{20b}	ω_{26}	
(14)	ν_{CC}	1588	1588	0	ν_{8b}	ω_{10}	
	ν_{CC}	1450	1450	0	$\nu_{19}b$	ω_{27}	
	δ_{CH}	1188	1189	1	ν_{15}	ω_{29}	
	δ_{CH}	1318?	1318?	—	ν_3	ω_{11}	
B_1	δ_{CC}	1400	1400	0	ν_{14}	ω_{28}	
	δ_{CC}	(632)		—	ν_{6b}	ω_{12}	
	ν_{NH_2}	3481	—	—	$\nu^{as}_{NH_2}$	ν_{NH_2}	
	ν_{NO_2}	1509	1509	0	$\nu^{as}_{NO_2}$	ν_{NO_2}	
	δ_{NH_2}	1055	1062	7	$\delta^{as}_{NH_2}$	ϱ_{NH_2}	
	δ_{NO_2}	(535)		—	$\delta^{as}_{NO_2}$	ϱ_{NO_3}	
	δ_{CN}	—	—	—		ω_{13}	calc. 404
	δ_{CN}	—	—	—		ω_{30}	calc. 331
	γ_{CH}	968	970	2	ν_5	ω_{23}	
	γ_{CH}	870	872	2	ν_{11}	ω_{14}	
(8)	γ_{CC}	697	700	3	ν_4	ω_{24}	
	γ_{CC}	(490)		—	ν_{16b}	ω_{15}	
B_2	γ_{NH_2}	808	811	3		γ_{NH_2}	
	γ_{NO_2}	752	752	0		γ_{NO_2}	
	γ_{CN}	—	—	—	ν_{10b}	ω_{16}	calc. 173
	γ_{CN}	—	—	—	ν_{17b}	ω_{25}	calc. 372
	γ_{CH}	958	—	—	ν_{17a}	ω_7	
	γ_{CH}	820	—	—	ν_{10a}	ω_{17}	
(5)	γ_{CC}	—	—	—	ν_{16a}	ω_8	calc. 405
A_2	γ_{NH_2}	—	—	—		τ_{NH_2}	
	γ_{NO_2}	—	—	—		τ_{NO_2}	

The frequencies given in parentheses correspond to those found in the spectrum of solution.

II. Discussion of the assignments

1. Frequencies of stretching vibrations, ν_{CH}

It follows from detailed consideration of the character table of the C_{2v} point-group and internal coordinates of the molecule that in case of the p-NA molecule there should be four types of stretching vibrations of C—H bonds, including two of symmetry A_1 and two of symmetry B_1.

The following frequencies of these vibrations have been calculated by Brandmüller et al. [5]: 3044 cm^{-1} ($\omega_9 - B_1$), 3063 cm^{-1} ($\omega_1 - A_1$), 3071 cm^{-1} ($\omega_{18} - A_1$) and 3079 cm^{-1} ($\omega_{26} - B_1$). All frequencies found by these authors in the spectrum lie at about 3100 cm^{-1}.

Garrigou-Lagrange [4] reports about three frequencies found in the spectrum of the solution as corresponding to the vibrations ν_{CH}: 3052 cm^{-1}, 3078 cm^{-1} and 3109 cm^{-1}. For other para-disubstituted derivatives of benzene the following frequencies are reported: for p-fluoronitrobenzene 3089 cm^{-1}, 3103 cm^{-1}, 3130 cm^{-1} [38]; for p-chloronitrobenzene 3034 cm^{-1}, 3079 cm^{-1}, 3105 cm^{-1} [39]; for p-chloroaniline 3040 cm^{-1} and 3059 cm^{-1} [40].

In the spectrum of p-NA single crystals the situation is not quite clear. In the 3050—3150 cm^{-1} range there are four bands with polarization $\perp b$ and two of very high intensity with polarization $\|b$. Two of the four above-mentioned bands are probably not due to fundamental vibrations because of their extreme position in the discussed region (3057 cm^{-1} and 3140 cm^{-1}) and very low intensity. In the spectrum of a partially oriented p-NA layer fused between NaCl plates one can notice that each of the two very intensive bands in the vicinity of 3100 cm^{-1} consists of two bands with the following frequencies: 3078 cm^{-1}, 3082 cm^{-1} and 3108 cm^{-1}, 3112 cm^{-1}. On the basis of direction of their polarization it seems that the frequencies: 3078 cm^{-1} and 3112 cm^{-1} can be assigned to the C—H vibrations of symmetry A_1, while the frequencies 3082 cm^{-1} and 3108 cm^{-1} to the C—H vibrations of symmetry B_1. These assignments, however, may be regarded as tentative at present.

2. Frequencies of in-plane deformation vibrations, δ_{CH}

There are four in-plane C—H deformation vibrations in the molecule, two of symmetry A_1 and two of symmetry B_1. The frequencies calculated in Ref. [5] are the following: 1022 cm^{-1} ($\omega_{21} - A_1$), 1081 cm^{-1} ($\omega_{29} - B_1$), 1145 cm^{-1} ($\omega_4 - A_1$), and 1289 cm^{-1} ($\omega_{11} - B_1$) and those found experimentally are 998, (1112), 1181 (1302) cm^{-1}, respectively.

Garrigou-Lagrange [4] gives the frequencies: 1015 cm^{-1} ($\nu_{18a} - A_1$), 1112 cm^{-1} ($\omega_{15} - B_1$), 1178 cm^{-1} ($\omega_{9a} - A_1$), and 1326 cm^{-1} ($\omega_3 - B_1$), while Mooney [39] reports about the frequencies 1013 cm^{-1} (B_1), 1109 cm^{-1} (B_1), 1170 cm^{-1} (A_1), and 1309 cm^{-1} (B_1) as corresponding to in-plane C—H deformation vibrations of the p-chloronitrobenzene molecule. In p-chloroaniline [40] these frequencies are: 1004 cm^{-1} (A_1), 1089 cm^{-1} (A_1), 1118 (B_1), and 1380 (B_1).

The frequencies quoted above are rather consistent with one another, bearing in mind the fact that they correspond to different compounds. There are, however, some discrepancies with regard to the assignment of the particular types of symmetry. In particular the assignments of Mooney, who mentions three vibrations of type B_1 and one of type A_1 is inconsistent with the predictions of group theory. Our considerations were based on symmetry types given in Refs [4] and [5].

In the spectrum of p-NA single crystals four bands have been found at the frequencies 1002/1005 cm^{-1}, 1188/1189 cm^{-1}, 1135/1140 cm^{-1}, and $\sim$1318 cm^{-1}, the first three bands being doublets. The first of the two numbers given denotes the frequency of the doublet component with polarization $||b$, and the other $\perp b$. The experimental definition of the dichroic ratio of these bands, as estimated neglecting the splitting effects, is $R_{b/a} = E_{||b}/E_{\perp b}$, where $E_{||b}$ is the extinction measured with the electric vector $\vec{E}$ parallel to b. On the basis of the geometrical distribution of the molecules in the unit cell of p-NA [33] and the theory of dichroism [41] one can predict that for vibrations of the type A_1 the value of the ratio $R_{b/a}$ should be less than unity. These predictions are in agreement with observed polarization and the experimental values of dichroic ratio. On this basis, the bands 1002/1005 and 1135/1140 cm^{-1} have been assigned to vibrations of type A_1, while the bands 1188/1189 and 1318 cm^{-1} to vibrations of B_1 symmetry species.

The band with the frequency $\sim$1318 cm^{-1} is a component of the band group 1300—1380 cm^{-1} which is difficult to be separated into single components as its intensity is too high. On the other hand this group of bands is well separated in the spectrum of powdered p-NA suspension in hexachlorobutadiene and in paraffin. It is possible to distinguish at least three bands of frequencies about 1304 cm^{-1}, 1330 cm^{-1} and 1340 cm^{-1}. When comparing the spectrum of the powder with that of a single crystal one can notice the following differences in this region: _1°_ a change in the intensity distribution: in the powder spectrum the strongest band is that at 1304 cm^{-1} whereas in the case of a crystal the strongest band is that at 1340 cm^{-1}; _2°_ a shift of frequencies: in the crystal the lowest frequency in the group of bands under consideration appears at 1318 cm^{-1} and is marked only as a shoulder of the 1340 cm^{-1} band whereas in the powder spectrum this frequency occurs at 1304 cm^{-1}.

3. _Frequencies of out-of-plane deformation vibrations,_ γ_{CH}

There are also four out-of-plane deformation vibrations in the molecule, namely $2A_2$ and $2B_2$. The frequencies of the vibrations of type A_2, which are forbidden in the IR spectrum of a free molecule, have been calculated by Brandmüller _et al._ [5] who obtained the values 848 cm^{-1} and 979 cm^{-1}. In the spectrum of the single crystal there occur two bands, similar to each other, of low intensity and polarization parallel to b-axis. These bands are not observed in the spectra of solutions. Their frequencies are close to those calculated by Brandmüller _et al._ and amount to 820 cm^{-1} and 958 cm^{-1}. It seems that these frequencies can be assigned to vibrations of type A_2.

For vibrations of type B_2 the calculated frequencies given by Brandmüller _et al._ [5] are 839 cm^{-1} and 949 cm^{-1}, while those observed are 842 cm^{-1} and 960 cm^{-1}, respectively. Evans [42] assigns the following frequencies to out-of-plane deformation CH vibrations in the spectrum of aniline: 826 cm^{-1}, 880 cm^{-1}, 959 cm^{-1} and 970 cm^{-1}. On this basis and because of the agreement between the observed value of the dichroic ratio with that predicted for the B_2 type, we have assigned the doublet 968/970 in the spectrum of single crystal to the vibration of type B_2. The remaining vibration of type B_2 probably corresponds to the doublet 870/872 rather than the frequency 840 cm^{-1} which is closer to the calculated frequency.

4. Frequencies of in-plane vibrations of the carbon skeleton, ν_C

There are four ν_{C-C} vibrations: two of symmetry A_1 and two of symmetry B_1. The calculated frequencies are: 1583 cm^{-1}($\omega_{10}-B_1$), 1614 cm^{-1}($\omega_{27}-B_1$), 1705 cm^{-1}($\omega_{19}-A_1$), and 1778 (ω_2-A_1). The respective frequencies observed are: 1589 cm^{-1}, 1250 cm^{-1}?, 1503 cm^{-1}, and 1599 cm^{-1} [5].

The frequencies given by Garrigou-Lagrange [4] are 1394 cm^{-1} ($\nu_{19b}-B_1$), 1480 cm^{-1} ($\nu_{19a}-A_1$), and 1595 cm^{-1} ($\nu_{8a}-A_1$). In Ref. [1] the following frequencies are assigned to C—C stretching vibrations for a number of para-disubstituted derivatives of benzene: 1450 cm^{-1} (19b), 1490 cm^{-1} (19a), 1570 cm^{-1} (8b), and 1590 cm^{-1} (8a).

In the spectrum of a single crystal the component of symmetry B_u of the 1599 cm^{-1} band lies at 1607 cm^{-1} while that of symmetry A_u at 1601 cm^{-1}; the component B_u of the 1503 cm^{-1} at 1487 cm^{-1} and A_u at 1480 cm^{-1}. Similar intensities of the components of these bands, similar spacings and frequencies close to those observed in the above--mentioned papers permit these components to be assigned to molecule vibrations of symmetry A_1 denoted by 8a and 19a (ω_2, ω_{19}), respectively. At the frequencies 1588 cm^{-1} and 1450 cm^{-1} there are two bands which are not split at all and their dichroic ratios are greater than unity. Therefore, we shall assign them to vibrations of symmetry B_1, denoted by 8b and 19b (ω_{10}, ω_{27}), respectively.

5. Frequencies of in-plane deformation vibrations of the carbon ring, δ_{C-C}

There are five in-plane deformation vibrations of this mode: $3A_1+2B_1$. The calculated frequencies are: 435 cm^{-1} (ω_6-A_1), 660 cm^{-1} ($\omega_{12}-B_1$), 848 cm^{-1} (ω_5-A_1), 1368 cm^{-1} ($\omega_{28}-B_1$), 1410 cm^{-1} (ω_3-A_1) and the observed frequencies are: — ,653 cm^{-1}, 858 cm^{-1}, 1393 cm^{-1} and 1112 cm^{-1}, respectively [5].

In the spectrum of a single crystal there is one band at 1120 cm^{-1} whose polarization corresponds to vibration of type A_1. Since the frequency observed is close to that observed in Ref. [5] we assign it to ω_3 vibration. The second band, which corresponds to the frequency ω_5, appears in the band group 830—850 cm^{-1} which is difficult to be separated into components. In the direction $\perp b$ there are three bands visible while in the direction $\|b$ we can distinguish only one band, indeed an asymmetric one. The band which corresponds to the third vibration of symmetry A_1 (ω_6) appears outside the measured range and is probably situated at an even lower frequency than that calculated in Ref. [5], since in the spectrum of the p-NA solution in CHCl$_3$ no bands are observed in the range between 400 cm^{-1} and 480 cm^{-1}.

Bands corresponding to symmetry B_1 have been found at 1400 cm^{-1} ($R_{b/a} > 1$) and at 630 (625) cm^{-1}, the latter only in the spectrum of the solution (KBr pellet).

6. Frequencies of out-of-plane vibrations of the carbon ring, γ_{CC}

There are three out-of-plane deformation vibrations: A_2+2B_2. The frequencies calculated in Ref. [5] are: 405 cm^{-1} (ω_8-A_2), 522 cm^{-1} ($\omega_{15}-B_2$) and 735 cm^{-1} ($\omega_{24}-B_2$). The experimental frequencies of vibrations of type B_2 are the following: 491 cm^{-1}, (ω_{15}) and 698 (ω_{24}). In the spectrum of single crystal only one band was found which corresponded

to the ω_{24} vibration (ν_4) at the frequency of 697/700 cm^{-1}. Its dichroic ratio, however, was in disagreement with that predicted theoretically.

A frequency corresponding to the vibration ω_{15} (ν_{16b}) was found in the spectrum of the solution in chloroform at 490 cm^{-1}, and in the spectrum of powder (suspension in paraffin) at 484 cm^{-1}.

7. C—N vibrations

The vibrations of the C–N bonds in p-NA are not characteristic vibrations. Coupling between these vibrations occurs both with ring vibrations and vibrations of the substituents. Therefore a distinction of the frequencies corresponding to vibrations of C–N bonds in p-NA encounters considerable difficulties.

It follows from group-theoretical analysis that there are six C–N vibrations: two stretching vibrations of symmetry A_1, two in-plane deformation vibrations of symmetry B_1 and two out-of-plane deformation vibrations of symmetry B_2.

For reasons discussed in the preceding text Brandmüller *et al.* do not distinguish these vibrations. One should make a search for them among the vibrations of the ring which are sensitive to the substituent (ω_x). The frequencies of such vibrations of type A_1, calculated in Ref. [5] are the following: 435 cm^{-1} (ω_6), 722 cm^{-1} (ω_{22}), 1372 cm^{-1} (ω_{20}), and 1410 cm^{-1} (ω_3).

The authors of Ref. [1] define the C–NO$_2$ vibrations as those which are responsible for the bands at 850 cm^{-1} in nitro derivatives of benzene, and in Ref. [42] the frequency 1303 cm^{-1} in aniline is assigned to the C–NH$_2$ vibration. These vibrations are probably those which we denote as ν_{CN}.

On the other hand Krüger [31] and Ritschl [32] have studied the frequencies of vibrations regarded as stretching vibrations of C–N in the solutions of p-NA and of other para-disubstituted anilines in tetrahydrofurane. In the case of p-NA they give only one frequency: 1319 cm^{-1}.

In the spectrum of a single crystal the frequency $\sim$1340 cm^{-1} which lies in the band group 1300–1380 cm^{-1} has been assigned to the ν_{C-NH_2} vibration. One of the bands belonging to this group has already been previously assigned to vibration δ_{C-H}.

The vibration ν_{C-NO_2} has been assigned to the frequency $\sim$840 cm^{-1} in the band group 830–850 cm^{-1}.

The frequencies calculated in Ref. [5] corresponding to vibrations δ_{CN} (ω_{13}, ω_{30}) amount to 404 cm^{-1} and 331 cm^{-1} and are thus outside the measured range. The same remark applies to γ_{CN} vibrations whose calculated frequencies ω_{16} and ω_{25} are 188 cm^{-1} and 384 cm^{-1}, respectively.

8. Vibrations of substituents

a) Amine — group

The vibrations of the —NH$_2$ group are classified as characteristic vibrations. Their number is six: $2A_1$, $2B_1$, A_2 and B_2. The assignments of valence vibrations made by the particular authors quoted above are in agreement. Garrigou-Lagrange [4] gives the following

values in CCl_4 solution: 3417 $(\nu^s_{NH_2})$, 3510 $(\nu^{as}_{NH_2})$, 1049 (r_{NH_2}) and in KBr pellet: 1629 cm^{-1} $(\delta^s_{NH_2})$. Brandmüller *et al.* [5] have been found the following frequencies: 3350 cm^{-1} $(\nu_{NH_2}-A_1)$, 3470 cm^{-1} $(\nu_{NH_2}-B_1)$, 1629 cm^{-1} $(\delta_{NH_2}-A_1)$, 1050 cm^{-1} $(\delta_{NH_2}-B_1)$ and 810 cm^{-1} $(\gamma_{NH_2}-B_2)$.

In a single crystal of p-NA the symmetric $-NH_2$ vibration has been assigned to the frequencies 3365 cm^{-1} (A_u) and 3377 cm^{-1} (B_u), while the antisymmetric vibration to 3484 cm^{-1} (A_u) and 3484 cm^{-1} (B_u).

The symmetric vibration, $\delta^s_{NH_2}$ has been assigned to the frequency 1632 cm^{-1} (A_u) and to 1645 cm^{-1} (B_u), while the antisymmetric vibration $\delta^{as}_{NH_2}$ to 1062 cm^{-1} (A_u) and 1055 cm^{-1} (B_u).

The out-of-plane deformation vibration of symmetry B_2 has been assigned to the frequencies 808 cm^{-1} (A_u) and 811 cm^{-1} (B_u). The vibration of symmetry A_2 is forbidden for free molecule and in crystal, if any, it should be situated below 400 cm^{-1} [5].

b) Nitro-group

The vibrations of the $-NO_2$ group are not fully characteristic vibrations [27]. According to group theory there are six such vibrations: $2A_1$, $2B_1$, A_2 and B_2.

Garrigou-Lagrange [4] assigns to symmetric and antisymmetric stretching vibrations the following two frequencies: 1334 cm^{-1} and 1503 cm^{-1}, respectively.

In Ref. [5] the frequencies observed in powder spectrum and assigned to symmetric vibrations are 1335 cm^{-1} and 1302 cm^{-1}, as well as two frequencies in the CCl_4 solution: 1335 cm^{-1} and 1300 cm^{-1}. The reason for this "splitting" given in that paper is a partial association of p-NA molecules to dimers. Two frequencies, 1470 cm^{-1} and 1481 cm^{-1} have also been given in Ref. [5] as assigned to antisymmetric vibration $\nu^{as}_{NO_2}$, however, without any further explanation of this fact.

Assignments analogous to Ref. [4] have been given by Brown [28] and Garrigou-Lagrange *et al.* [29].

It seems that one should assign the frequency $\sim$ 1340 cm^{-1} in single crystal to the $\nu^s_{NO_2}$ vibration, while the band at 1509 cm^{-1}, whose dichroic ratio is grater than unity, to the $\nu^{as}_{NO_2}$ vibration. The frequencies mentioned in Ref. [5] (1470 cm^{-1} and 1481 cm^{-1}) correspond probably to the strong 1480/1487 cm^{-1} band which has been assigned in the present work to ν_{CC} vibration of symmetry A_1 and to the 1460/1467 cm^{-1} band which is probably due to combination. The latter statement will be discussed later.

Ref. [5] also gives the frequencies of $\delta^{as}_{NO_2}$ vibrations at 535 cm^{-1} and $\gamma_{NO_2}(B_2)$ at 745 cm^{-1}. On the other hand Ref. [4], reports that the frequencies 537 cm^{-1} in the powder spectrum and 741 cm^{-1} in the spectrum of the solution correspond to $\delta^s_{NO_2}$. In a later paper [29], however, the authors have some doubt with regard to such an assignment of both frequencies and mention that the $\sim$860 cm^{-1} frequency may also come from ν_{CN} vibration coupled with the aromatic nucleus. Medhi [43] assigns the band of medium intensity at 674 cm^{-1} in p-chloronitrobenzene to deformation vibration of symmetry A_1. Brown [28] also locates the band corresponding to the deformation of NO_2 nitroparaffins at 15.24 μ(654 cm^{-1}).

As a result we have assigned to the $\delta^s_{NO_2}$ vibration the $\sim$660/671 cm^{-1} band in single

crystal whose dichroic ratio $(R_{b/a}<1)$ is consistent with the predicted value. The frequency corresponding to the $\delta^{as}_{NO_2}$ vibration occurs in the solution spectrum at 535 cm^{-1}.

The frequency 752 cm^{-1} in the single crystal spectrum has been assigned to the out-of-plane deformation vibration of symmetry B_2. The dichroic ratio of this band is, however, in disagreement with that predicted by theory.

III. Discussion

In the investigated range of the absorption spectrum of p-nitroaniline single crystals we have observed the following regular features:

1. The frequencies observed in the crystal do not differ much from those in CCl$_4$ solution given in literature as well as from the frequencies observed in the present work in CHCl$_3$ solution. This supports the validity of the oriented gas model in the case of p-NA crystals. Exceptions are the frequencies assigned to the vibrations $\nu^s_{NH_2}$, $\nu^{as}_{NH_2}$ and $\delta^s_{NH_2}$.

The large difference between the frequencies corresponding to $\nu^s_{NH_2}$ vibration observed in p-NA crystals and in solution is explained in Ref. [20] by the existence of a hydrogen bond in which one of the hydrogen atoms of the amino group is participating. It seems, however, that the distances between the O and H atoms and the direction of N—H and N—O bonds in p-NA do not provide favourable conditions for the formation of a hydrogen bond in the crystal. On the other hand it is well known that even very weak intermolecular interactions, much weaker than for a typical hydrogen bond is expected, give rise to significant perturbations of the frequency of a X—H oscillator. No doubt that such a weak interactions occur in p-NA crystal between the —NH$_2$ and —NO$_2$ groups of two adjacent molecules.

2. Fourteen out of the thirty two bands assigned to normal vibrations in the crystal split into two components. The splitting varies between 1 and 13 cm^{-1}. The observed splitting values are comparable with those found in the infrared spectra of other crystalline compounds. Califano [44] has observed splitting of the order of 10 cm^{-1} of several bands in anthracene and deuterized anthracene. Bottger and Eggers [46] have also observed splitting of the order of 10 cm^{-1} in the spectra of polycrystalline layers of acetylene. Fox and Hexter [45] have observed splitting varying from 3 to 35 cm^{-1} in the spectra of N$_2$O, CO, CO$_2$ and CH$_4$. Kharchenko [48] and Lisica and Kharchenko [50] have found splitting values between 15 and 18 cm^{-1} in the spectra of frozen solutions of chloroform and dichloro-ethylene. In the paper of Tomczak [49] it is also possible to estimate the splitting of the 480 cm^{-1} band in 2.3-dimethylnaphthalene as about 10 cm^{-1}. The values of Rich and Dows [51] of the splitting of bands of naphthalene vary between 1 and 16 cm^{-1}.

3. The experimental values of the dichroic ratio of the majority of bands, are in qualitative agreement with those predicted on the basis of the oriented gas model, even for those bands which are subject to splitting. Exceptions are those bands whose dichroic ratio is difficult to be estimated either owing to large splitting (e.g. the 1601/1607, 1480/1487, 1632/1645 cm^{-1} bands) or because of the overlap of adjacent intensive bands (e.g. in the band groups $\sim$840 cm^{-1} and $\sim$1340 cm^{-1}). In the case of the 697/700 and 752 cm^{-1} bands which have been assigned to γ_{CC} and γ_{NO_2} vibrations of molecular symmetry B_2, the sign of the dichroic ratio is opposite to that predicted by the model. This discrepancy is

probably due to the occurence of second order perturbations. A possible argument may be the hypothesis of Kübler quoted in Ref. [5], namely that interactions between those vibrations may change the predicted ratio of intensities.

4. Among the bands subject to splitting the greatest splitting effect appears to occur in those assigned to vibrations of molecular symmetry A_1. This is connected with the fact that these bands are in general the most intensive. The high intensity of these bands can be probably explained in terms of the hypothesis proposed by Brown [28]. The latter author assumes a considerable contribution of the resonance structure:

in which the charge is displaced along the C_2 axis of the molecule. This gives rise to an increase in the intensity of those bands whose transition moments are parallel to the direction of charge displacement. The intramolecular charge displacement along the long axis of the molecule in crystalline p-NA is also discussed by Tanaka [54].

The influence of electronic structure of $-NH_2$ group on the infrared spectrum of aliphatic and aromatic amines is also discussed by Orville-Thomas et al. [53]. The contributions of the dipole moment of the free electron pair of the nitrogen atom belonging to the amine group exerts in the stretching vibration a greater influence on the intensity of the ν^s band than ν^{as}.

The effects mentioned in 1 through 4 are in qualitative agreement with the theory of Davydov which has been later developed by other authors. This theory has been applied, among others by Craig and Hobbins [4] to the electronic spectra of anthracene and by Hexter [52] and Fox and Hexter [46] to infrared spectra.

According to this theory the energy levels and intensities of absorption bands in crystals can be explained on the basis of the oriented gas model and the deviations from the model can be described by perturbation methods. It is assumed that first order perturbations are the interactions between induced dipole moments. In this approximation both the intensities of the bands and the amount of splitting are proportional to the square of the transition moment, and thus splitting is greater in case of bands of higher intensity. As it was found the first-order perturbation method gives a good description of such transitions only, for which transitions other than dipole-dipole may be neglected — i.e. only of strong transitions. Second order perturbations additionally influence the magnitude of splitting and can converse the ratio of intensities resulting from the oriented gas model.

5. In the case of p-NA crystal vibrations of A_2 symmetry appear with only the A_u component. The appearence of these vibrations can be explained in terms of the correlation diagram. The occurence of a component in only one polarization direction is probably due to the rather low intensity of the band.

6. In the group of bands 1300–1350 cm^{-1} we observe an inversion of the intensity distribution as compared to the spectrum of powder.

7. In the spectrum of crystal there occur some intensive bands or groups of bands

which are difficult to be assigned, namely the groups of bands at ~ 3100 cm^{-1}, ~ 1340 cm^{-1}, ~ 840 cm^{-1} and the 1470 cm^{-1} band.

What concerns the assignment the ~ 3100 cm^{-1} region there are so far no detailed data available in literature while in the case of the group of bands 1300–1350 cm^{-1} the situation is not quite clear and is discussed already for a long time. The papers of Iogansen and Liotvchenko [26], Shorygin and Lopatina [27] and Bobovich [24] discuss various reasons for the occurence of two bands in p-NA solution at frequencies ~ 1340 cm^{-1} and ~ 1323 cm^{-1}.

The following possibilities are taken into account: *a*) the existence of association, *b*) formation of a hydrogen bond in which the $-NO_2$ group is participating, *c*) resonance interaction between two different vibrations of the same symmetry (Fermi resonance), *d*) the existence of donor-acceptor interactions with the solvent.

It seems that in the case of crystal the most probable explanation is *c*), because that both $\nu_{NO_2}^s$ and ν_{C-NH_2} have similar frequencies and the same symmetry and, therefore, satisfy all conditions which are necessary for the occurence of the Fermi resonance. The view is confirmed by the considerable intensity of the group of bands dicussed which makes impossible an accurate reading the position of maximum. Owing to the fact that in this region of the spectrum of powder three maxima occur, we have located in this group of frequencies also in-plane deformation vibration of the ring, of symmetry $B_1(\delta_{CH})$.

Resonance interactions seem also probable in the group of bands ~ 840 cm^{-1}, between the δ_{CC} and ν_{C-NO_2} vibrations which are both of symmetry A_1. Such interaction also implies an increase in intensity.

In the band group 1450–1500 cm^{-1} there occurs a very strong band at the frequency of 1460–1467 cm^{-1} which is not assigned to any normal vibration. It is possible that this band corresponds to the combination vibration $\delta_{CC}(\nu_{C-NO_2}) + \delta_{NO_2}$ and its intensity is increased by the occurence of a Fermi resonance with the ν_{CC} (A_1) vibration of similiar frequency.

IV. Experimental

The measurements were made with a Unicam SP-100 spectrometer equipped with a diffraction grating [49]. The resolution of the apparatus was 2 cm^{-1}, 1 cm^{-1} and 2 cm^{-1} for the ranges 375–650 cm^{-1}, 650–2150 cm^{-1}, 2150–3651 cm^{-1}, respectively.

The slit width was programmed and changed automatically with the wavelength so that the amount of incident energy in the channel I_0 would be constant for the entire range of the spectrum. The radiation was polarized by means of a Perkin–Elmer polarizer.

REFERENCES

[1] C. Garrigou-Lagrange, J. M. Lebas, M. L. Josien, *Spectrochim. Acta*, **12**, 305 (1958).
[2] J. M. Lebas, C. Garrigou-Lagrange, M. L. Josien, *Spectrochim. Acta*, **15**, 225 (1959).
[3] A. R. Katritzky, P. Simmons, *J. Chem. Soc.*, 2051 (1959).
[4] C. Garrigou-Lagrange, *Thesis*, Bordeaux 1962.

[5] J. Brandmüller, E. W. Schmid, H. W. Schrötter, G. Nonnenmacher, *Spectrochim. Acta*, **17**, 523 (1961).

[6] H. W. Schrötter, *Z. Electrochem.*, **64**, 853 (1960).

[7] I. D. Rae, *Spectrochim. Acta*, **21**, 1857 (1965).

[8] L. J. Bellamy, R. L. Wiliams, *Spectrochim. Acta*, **9**, 341 (1957).

[9] Yu. S. Varshavskii, *Optika i Spektrosk.*, **11**, 686 (1962).

[10] A. I. Finkelstein, *Optika i Spektrosk.*, **12**, 801 (1962).

[11] I. I. Shmanko, A. I. Finkelstein, *Optika i Spektrosk.*, **23**, 506 (1967).

[12] M. R. Yagudaev, Yu. N. Sheinker, *Izv. Akad. Nauk SSSR, Ser. Chim.*, **00**, 2230 (1963).

[13] M. R. Yagudaev, E. M. Popov, J. P. Yakovlev, Yu. N. Sheinker, *Izv. Akad. Nauk SSSR, Ser. Chim.*, **00**, 1189 (1964).

[14] J. H. Lady, K. B. Whetsel, *Spectrochim. Acta*, **21**, 1669 (1965).

[15] P. J. Krüger, *Nature*, **194**, 1077 (1962).

[16] P. J. Krüger, *Canad. J. Chem.*, **41**, 363 (1963).

[17] P. J. Krüger, *Z. Naturforsch.*, **18a**, 1239 (1963).

[18] P. J. Krüger, *Canad. J. Chem.*, **40**, 2300 (1962).

[19] K. C. Medhi, G. S. Kastha, *Indian J. Phys.*, **37**, 275 (1961).

[20] E. L. Zhukova, I. I. Shmanko, *Optika i Spektrosk.*, **25**, 500 (1968).

[21] A. G. Moritz, *Spectrochim. Acta*, **16**, 1176 (1960).

[22] Z. A. Shmakova, *Doklady Mezhvuz. Nauch. Konf. po Spektrosk. i Spektr. Analizu, Tomsk Univ.*, **141**, (1960) in Russian.

[23] K. Semba, *Bull. Chem. Soc. Japan*, **33**, 1640 (1960).

[24] Ya. S. Bobovich, *Optika i Spektrosk.*, **19**, 886 (1965).

[25] A. V. Iogansen, G. D. Litovchenko, *Optika i Spektrosk.*, **16**, 700 (1964).

[26] A. V. Iogansen, G. D. Litovchenko, *Zh. Priklad. Spektrosk.* (USSR), **3**, 538 (1965).

[27] P. P. Shorygin, B. W. Lopatin, *Zh. Fiz. Chimii*, **39**, 2868 (1965).

[28] J. F. Brown, *J. Amer. Chem. Soc.*, **77**, 6341 (1955).

[29] C. Garrigou-Lagrange, M. Chehata, G. Sourisseau, *J. Chim. Phys.*, **62**, 261 (1965).

[30] P. P. Shorygin, B. V. Lopatin, *Zh. Fiz. Chimii*, **42**, 450 (1968).

[31] F. Ritschl, *Z. Chem.*, **9**, 285 (1961).

[32] P. J. Krüger, *Z. Naturforsch.*, **17a**, 692 (1962).

[33] J. W. Rohleder, M. Szostak, *Acta Phys. Polon.*, **30**, 187 (1966).

[34] A. N. Winchell, *The Optical Properties of Organic Compounds*, Sec. Ed., Acad. Press Inc., New York 1954.

[35] K. N. Trueblood, E. Goldish, J. Donohue, *Acta Cryst.*, **14**, 1009 (1961).

[36] A. S. Davydov, *Zh. Eksper. Teor. Fiz.* (USSR), **18**, 210 (1948).

[37] J. W. Rohleder, M. Szostak, to be published.

[38] K. C. Medhi, *Spectrochim. Acta*, **20**, 675 (1964).

[39] E. F. Mooney, *Spectrochim. Acta*, **20**, 1021 (1964).

[40] V. B. Singh, R. N. Singh, J. S. Singh, *Spectrochim. Acta*, **22**, 927 (1966).

[41] J. W. Rohleder, T. Luty, *Molecular. Cryst.*, **5**, 145 (1968).

[42] J. C. Evans, *Spectrochim. Acta*, **16**, 428 (1960).

[43] K. C. Medhi, *Indian. J. Phys.*, **39**, 390 (1965).

[44] S. Califano, *J. Chem. Phys.*, **36**, 903 (1962).

[45] D. Fox, R. M. Hexter, *J. Chem. Phys.*, **41**, 1125 (1964).

[46] G. L. Bottger, D. F. Eggers, *J. Chem. Phys.*, **40**, 2010 (1964).

[47] D. P. Craig, P. C. Hobbins, *J. Chem. Soc.*, 539 (1955).

[48] N. P. Kharchenko, *Optika i Spektrosk.*, **3**, 21 (1967).

[49] Z. Tomczak, *Thesis*, Warszawa 1967.

[50] M. P. Lisica, N. P. Kharchenko, *Zh. Priklad. Spektrosk.* (USSR), **8**, 667 (1968).

[51] N. Rich, D. A. Dows, *Molecular Cryst.*, **5**, 111 (1968).

[52] R. M. Hexter, *J. Chem. Phys.*, **33**, 1833 (1960).

[53] W. J. Orville-Thomas, A. E. Parsons, C. P. Ogden, *J. Chem. Soc.*, **195**, 1047 (1958).

[54] J. Tanaka, *Bull. Chem. Soc. Japan*, **36**, 833 (1963).