The Electronic Spectra of Aromatic Molecular Crystals. I. Substitued Benzene Molecules

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(Received February 11, 1963)

Considerable progress has recently been made in the interpretation of the electronic spectra of benzene and the polyacenes[1]. The effect of substituents on the spectrum of benzene has been studied by Nagakura and Tanaka[2], Longuet-Higgins and Murrell[3] and many others[4]. The best way of confirming the theoretical assignments is to measure the polarization of the single crystal absorption band. One such investigation is the study of *p*-dimethoxybenzene by Albrecht and Simpson[5]. They measured the polarization of crystalline absorption and showed that the 280 mμ band of the molecule is polarized perpendicular to the two-fold symmetry axis; hence, the symmetry of the excited level corresponding to the 260 mμ band of benzene is confirmed to be $^1B_{2u}$. In general, monosubstituted benzene molecules have an absorption band corresponding to the 260 mμ band of benzene. When electron-donating substituent groups (such as amino, hydroxyl, methyl and others) are introduced, the 260 mμ band of benzene shifts to the red and increases in intensity. When electron-accepting groups (such as nitro, carbonyl and carboxyl) are substituted, a conspicuous strong, new absorption band appears in the region of 230∼360 mμ; this has been interpreted as an intramolecular charge transfer band on the basis of relative energy level locations of benzene and substituent[2]. The direction of the transition moment (polarization) of the latter type of band should be quite different from the former; it may lie on the line connecting the center of the benzene ring and the substituent group.

The primary purpose of this paper is to present a sound basis for the intramolecular charge transfer theory of the spectra of monosubstituted benzenes by measuring the polarization of bands with single crystals. The crystal structures of durene, *p*-nitroaniline, benzoic acid, acetanilide and *trans*-cinnamic acid are known, so the directions of the transition moments can be determined easily by measuring the crystal spectra on the assumption that an oriented gas model is applicable. Owing to a mixing of different excited states and an electron exchange interaction between neighboring molecules, some crystals show noticeable deviations from an oriented gas model, but the crystals of the present investigation show little of this. For this reason it is safe to deduce the direction of the transition moment from the polarization measurement. The possibility of Davydov splitting and of intermolecular charge transfer bands in the crystal has also to be taken into account[6-10].

Experimental

The Spectra of Solutions.—Ultraviolet absorption spectra measurements have been made with a Cary recording spectrophotometer model 14. The spectrophotometer was flushed with dry nitrogen for recording between 220∼185 mμ.

Ultraviolet Microspectrophotometer. — For the transmission measurement of aromatic molecular crystals, very thin crystals less than one micron thick are needed because the molar extinction coefficients are 10^4 to 10^5. An ultraviolet microspectrophotometer was used for measuring the spectra of very thin and small crystals.

A schematic diagram of the apparatus is shown in Fig. 1. A double monochromator of the Olympus Optical Co. (A), equipped with synthetic silica prisms and a hydrogen discharge lamp or tungsten lamp (L), has been used. The small diaphragm (B) is set to eliminate the stray light at the exit slit. The light beam is reflected by a mirror (C), is polarized by a Rochon-type polarizer (D) made of natural quartz, and is condensed by

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[1] M. G. Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938); R. Pariser and R. G. Parr, ibid., **21**, 466, 767 (1953); M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.*, **A67**, 795 (1954); R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956); **25**, 1112 (1957).

[2] S. Nagakura and J. Tanaka, ibid., **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955); J. Tanaka, S. Nagakura and M. Kobayashi, ibid., **24**, 311 (1956); J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).

[3] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrel, ibid., **A68**, 969 (1955).

[4] A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939); ibid., **10**, 135 (1942); F. A. Matsen. *J. Am. Chem. Soc.*, **72**, 5243 (1950); J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); L. Goodman, I. G. Ross and E. Shull, ibid., **26**, 474 (1957).

[5] A. C. Albrecht and W. T. Simpson, ibid., **23**, 1480 (1955).

[6] D. P. Craig, *Rev. Pure and Appl. Chem.* (*Australia*), **3**, 207 (1953).

[7] D. S. McClure, *Solid State Physics*, **8**, 1 (1958).

[8] H. C. Wolf, ibid., **9**, 1 (1959).

[9] J. Tanaka, *Prog. Theoret. Physics* (*Kyoto*), Suppl. **12**, 183 (1959).

[10] K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952).

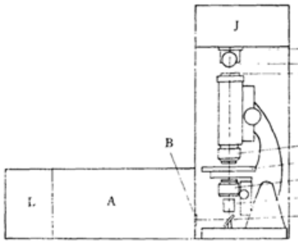

Fig. 1. Ultraviolet microspectrophotometer.

a lens (E) onto the sample. The lenses (E and G) are of Grey's Bausch and Lomb reflecting-refracting type. The numerical aperture of the lens is 0.20∼0.72, and the magnification is ×53. The condenser lens (E) is used to collimate the monochromatic light onto the crystal, thereby eliminating the Schwarzschild-Villiger effect[12]. The crystal to be measured is placed between a quartz objective slide 1.0 mm. thick and a 0.18 mm-thick cover glass, and settled on the rotatable table (F). The orientation of the crystal is adjusted, so that one of the crystalline axes is parallel to the direction of the polarization of the light, by the aid of the eyepiece (H) and the cross (I). The iris-diaphragm placed at the top of the microscope is used to cut off the flare light, which disturbs the accurate measurement of the polarization. The shutter (K) is placed in front of an RCA 1p-28 photomultiplier tube, by the use of which, along with that of a direct current amplifier (J), it is possible to measure the light intensity. The effective slit-widths are smaller than 1 mμ, which is sufficient to resolve the broad absorption band of aromatic crystals at room temperature.

The angle of the incident light normal to the plane of the crystal ranges from 12° to 46° because objective and condenser lenses have numerical apertures of 0.20 to 0.72. The polarization of the light is not altered by reflection and refraction at the lens surfaces. In addition, if the transition moments associated with each molecules are parallel to the developed crystalline surface, the intensity of the absorption bands does not depend on the angle of the incident light[13]. However, when the transition moments are vertical to the developed crystalline plane, the absorption may depend greatly on the directional angle of the incident light, and the intensity of absorption has only a qualitative significance.

The stray light of the instrument is estimated to be less than 0.5% of the total light; hence, the measured optical density is reliable up to 2.5. By the use of this microspectrophotometer, the ultraviolet absorption spectra of small single crystals, as small, for example, as $20\mu \times 20\mu \times 0.5\mu$, of aromatic molecules are easily obtained.

p-Nitroaniline

The ultraviolet absorption spectra of *p*-nitroaniline in ethanol and *n*-heptane solutions are shown in Fig. 2. A large solvent effect is observed for this molecule. The first band undergoes a shift from 320 mμ in *n*-heptane to 370 mμ in ethanol. The shift is probably due to a polar solvent effect—the stabilization of the polar-excited state in the polar solvent—or to the hydrogen bonding between the amino group and the oxygen atom of the hydroxyl group of ethanol[14]. One interpretation of this band is that its origin is the 260 mμ band of benzene shifted to the red and intensified by the substituent groups. However, according to Nagakura and Tanaka's theory of intramolecular charge transfer spectra, the 370 mμ band is interpreted by a mechanism

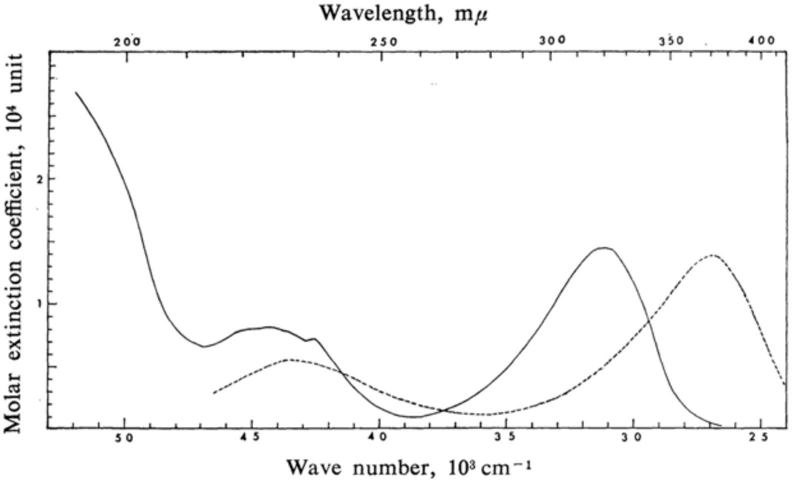

Fig. 2. Electronic absorption spectrum of *p*-nitroaniline.

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[11] D. S. Grey and P. H. Lee, *J. Opt. Soc. Am.*, **39**, 719 (1949).

[12] H. Naora, *Science*, **114**, 279 (1951).

[13] M. F. Perutz, *Acta Cryst.*, **6**, 859 (1953).

[14] S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

of charge transfer, which takes place from the highest-occupied level of the anilino group to the vacant orbital of the nitro group. Following the former interpretation, the band should be polarized along the short axis of the molecule, while the latter predicts the long axis polarization. By a polarization measurement of the crystalline spectrum, it is easy to eliminate one of these possibilities.

Calculation of the Excited State of *p*-Nitroaniline.—The author[15] has previously calculated the electron affinity of the nitro group and has shown that it behaves as an electron acceptor when conjugated with other π-electron systems, because the group has a large electron affinity. In the present treatment, *p*-nitroaniline is considered to be a composite molecule, consisting of anilino and nitro groups; the electronic interaction between those two groups is calculated by the method of Longuet-Higgins and Murrell[3].

The electronic spectrum of aniline has been studied by Platt and Klevens[16] experimentally and by Murrell[3] theoretically. According to the latter assignment, the ground state and lower excited states configurations are described by a combination of the χ_0, ψ_α, ψ_p, ψ_β, ψ_β , $\theta^{-1}\varphi_4$ and $\theta^{-1}\varphi_5$ wave functions, where χ_0, ψ_α, ψ_p, ψ_β and $\psi_{\beta'}$ are the wave functions of benzene in its ground state, $^1B_{2u}$, $^1B_{1u}$ and $^1E_{1u}$ are excited states. Functions $\theta^{-1}\varphi_4$ and $\theta^{-1}\varphi_5$ represent, respectively, charge transfer configurations in which a non-bonding electron in the amino nitrogen (denoted by θ) is transferred into the vacant φ_4 and φ_5 orbitals of benzene.

The electron affinity of the nitro group was calculated as -0.40 eV.[15], and the vacant orbital is written as

$$\varphi_w = 0.700\chi_N - 0.502(\chi_0 + \chi_{0'})$$

where χ_N, χ_0 and $\chi_{0'}$ are the $2p\pi$ atomic orbitals of nitrogen and oxygen atoms.

We restrict our attention to the two charge transfer configurations of lowest energy. The highest-occupied orbital of aniline is at -7.70 eV., and the second highest orbital is assumed to be the same as benzene. Next, the configurational interaction between the charge transfer configuration with the locally-excited configurations of aniline is taken into account. The energy of the $\varphi_2{}^{-1}\varphi_w$ and $\varphi_3{}^{-1}\varphi_w$ charge transfer configurations are calculated by the following formula;

$$H_{CT} = I_p - E_A - (\varphi_w\varphi_w \mid \varphi_D\varphi_D) + \sum \delta_{DS}$$

where E_A is the electron affinity of the nitro group, I_p is the ionization potential of the donor orbital in aniline, $(\varphi_w\varphi_w \mid \varphi_D\varphi_D)$ is the electrstatic energy between electrons in φ_w and φ_D orbitals, and the last term, $\sum \delta_{DS}$, denotes the electrostatic energy between the hole in the anilino group with the formal charges on each atom of the substituent nitro group. Taking the numerical values of $E_A = -0.40$ eV., $I_{p_2} = 7.70$ eV., $I_{p_3} = 9.24$ eV., $(\varphi_w\varphi_w \mid \varphi_{D_2}\varphi_{D_2}) = 4.60$ eV., $(\varphi_w\varphi_w \mid \varphi_{D_3}\varphi_{D_3}) = 4.13$ eV., $\sum \delta_{2S} = 0.27$ eV. and $\sum \delta_{3S} = 0.43$ eV., the levels are calculated as 3.77 eV. and 5.94 eV. for the A-type and B-type symmetry states respectively.

The off-diagonal matrix elements are calculated by taking the carbon-nitrogen atom's exchange integral β to fit the calculated value with the observed excitation energies, and the value is selected as -2.30 eV. Then the secular equations for A and B type symmetry levels are given as follows:

A-type symmetry:

$$\begin{array}{c|ccccc|} \varphi_0 & -E & 0.93 & 0 & 0 & 0 \\ \varphi_2{}^{-1}\varphi_w & 0.93 & 3.77-E & 0.21 & 0.33 & 0.73 \\ \varphi_{1A} & 0 & 0.21 & 5.27-E & 0 & 0 \\ \varphi_{2A} & 0 & 0.33 & 0 & 6.30-E & 0 \\ \varphi_{3A} & 0 & 0.73 & 0 & 0 & 7.40-E \end{array} \qquad (3)$$

B-type symmetry:

$$\begin{array}{c|cccc|} \varphi_{1B} & 4.31-E & 0.51 & 0 & 0 \\ \varphi_3{}^{-1}\varphi_w & 0.51 & 5.94-E & 0.71 & -0.40 \\ \varphi_{2B} & 0 & 0.71 & 6.30-E & 0 \\ \varphi_{3B} & 0 & -0.40 & 0 & 7.40-E \end{array} \qquad (4)$$

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[15] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1636 (1957).

[16] J. R. Platt and H. B. Klevens, *J. Am. Chem. Soc.*, **71**, 1714 (1949).

By solving these equations, the energies of the states are obtained as follows:

$$\begin{array}{lll}
\text{Energy} & \text{Wave function} & \text{Symmetry} \\
-0.22\text{ eV.} & 0.972\varphi_0+0.231\varphi_2{}^{-1}\varphi_{\mathrm{w}}-0.212\varphi_{1\mathrm{A}}-0.017\varphi_{2\mathrm{A}}-0.025\varphi_{3\mathrm{A}} & \mathrm{A} \\
+3.78\text{ eV.} & -0.232\varphi_0+0.937\varphi_2{}^{-1}\varphi_{\mathrm{w}}-0.121\varphi_{1\mathrm{A}}-0.113\varphi_{2\mathrm{A}}-0.201\varphi_{3\mathrm{A}} & \mathrm{A} \\
+5.30\text{ eV.} & 0.089\varphi_0-0.132\varphi_2{}^{-1}\varphi_{\mathrm{w}}-0.991\varphi_{1\mathrm{A}}-0.022\varphi_{2\mathrm{A}}-0.019\varphi_{3\mathrm{A}} & \mathrm{A} \\
+6.34\text{ eV.} & 0.012\varphi_0-0.123\varphi_2{}^{-1}\varphi_{\mathrm{w}}+0.040\varphi_{1\mathrm{A}}-0.990\varphi_{2\mathrm{A}}-0.053\varphi_{3\mathrm{A}} & \mathrm{A} \\
+7.55\text{ eV.} & 0.022\varphi_0-0.189\varphi_2{}^{-1}\varphi_{\mathrm{w}}+0.042\varphi_{1\mathrm{A}}+0.078\varphi_{2\mathrm{A}}-0.978\varphi_{3\mathrm{A}} & \mathrm{A}
\end{array} \tag{5}$$

$$\begin{array}{lll}
+4.15\text{ eV.} & 0.947\varphi_{1\mathrm{B}}+0.294\varphi_3{}^{-1}\varphi_{\mathrm{w}}+0.126\varphi_{2\mathrm{B}}-0.080\varphi_{3\mathrm{B}} & \mathrm{B} \\
+5.53\text{ eV.} & -0.303\varphi_{1\mathrm{B}}+0.702\varphi_3{}^{-1}\varphi_{\mathrm{w}}-0.641\varphi_{2\mathrm{B}}+0.068\varphi_{3\mathrm{B}} & \mathrm{B} \\
+6.90\text{ eV.} & 0.100\varphi_{1\mathrm{B}}-0.646\varphi_3{}^{-1}\varphi_{\mathrm{w}}-0.756\varphi_{2\mathrm{B}}-0.077\varphi_{3\mathrm{B}} & \mathrm{B} \\
+7.37\text{ eV.} & 0.029\varphi_{1\mathrm{B}}-0.051\varphi_3{}^{-1}\varphi_{\mathrm{w}}-0.037\varphi_{2\mathrm{B}}+0.998\varphi_{2\mathrm{B}} & \mathrm{B}
\end{array} \tag{6}$$

TABLE I.

Calculated energy Symmetry		Observed energy
A	B	
4.00 eV.		3.88 eV (320 mμ in *n*-heptane solution)
	4.37 eV.	4.60 eV (270 mμ in the crystal)
5.52 eV.	5.75 eV.	5.52 eV (220 mμ in *n*-heptane solution)
6.56 eV.		
	7.12 eV.	
7.77 eV.	7.59 eV.	

where φ_0, $\varphi_{1\mathrm{A}}$, $\varphi_{2\mathrm{A}}$, $\varphi_{3\mathrm{A}}$, $\varphi_{1\mathrm{B}}$, $\varphi_{2\mathrm{B}}$ and $\varphi_{3\mathrm{B}}$ denote the wave functions of aniline in the ground and excited states as calculated by Murrell, and $\varphi_2{}^{-1}\varphi_{\mathrm{w}}$ and $\varphi_3{}^{-1}\varphi_{\mathrm{w}}$ are the charge transfer configurations described above. The levels belonging to the A-type symmetry group should be active in the long axis, and the B-type symmetry levels, in the short axis of the molecule. The calculated excitation energies are tabulated in Table I, together with the observed values. The agreement between observed and calculated values is generally good, and it is shown that the first strong band at 320mμ in an *n*-heptane solution is predominantly derived from the charge transfer configuration with A-type symmetry. The polarization of this band is deduced to be long-axis, while the next band, at 270 mμ, should be short axis-polarized. The latter band is observed in the crystalline spectrum, but not in *n*-heptane and ethanol solutions, this may be because it borrows intensity from allowed transitions in the crystal. In the region below 220 mμ, there are several transitions belonging to both A- and B-type symmetries; hence, the 220 mμ absorption may consist of two bands, namely, those arising from the transititions between the ground state and the 5.30 eV. and 5.53 eV. states.

The Spectrum of *p*-Nitroaniline Crystal.—The optical properties of *p*-nitroaniline crystal are described by Groth and Winchell as follows[17,18]:

$$N_{\mathrm{X}}'=1.556,\quad N_{\mathrm{Y}}=1.777,\quad N_{\mathrm{Z}}\ ?;$$

$$\text{Optical plane } (010):\quad 2V=80^\circ(\pm\ ?)$$

The optical axis X is nearly vertical to the (101) plane, and Y=b. This work has been confirmed with the addition of $2V=-80^\circ$. By the use of these values, N_{Z} is calculated to be 2.005, and the birefringence with (101) plane is estimated to be 0.228. The crystal used for spectral measurement is made by sublimation, and it develops the (101) cleavage plane.

The crystal structure of *p*-nitroaniline has been determined by Abrahams and Robertson and by Donohue and Trueblood[19]. The crystal is monoclinic with the following unit cell dimensions: $a=12.34$, $b=6.02$, $c=8.63$ Å and $\beta=91^\circ 40'$. The space group is $\mathrm{C_{2h}{}^5-P2_1/}n$ with four molecules per unit cell. The projection of the molecules in the unit cell onto the (101) plane, which is the most easily developing face, is shown in Fig. 3(a).

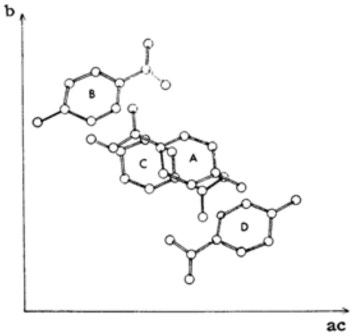

Fig. 3 (a). Projection of *p*-nitroaniline molecules onto the (101) plane.

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[17] P. Groth, "Chemische Kristallographie", W. Engelmann Leipzig (1906-1919).

[18] A. N. Winchell, "The Optical Properties of Organic Compounds", University of Wisconsin Press, Madison. Wisconsin (1943).

[19] S. C. Abrahams and J. M. Robertson, *Acta Cryst.*, **1**, 252 (1948); J. Donohue and K. N. Trueblood, ibid, **9**. 960 (1956); K. N. Trueblood, E. Goldish and J. Donohue, ibid., **14**, 1009 (1961).

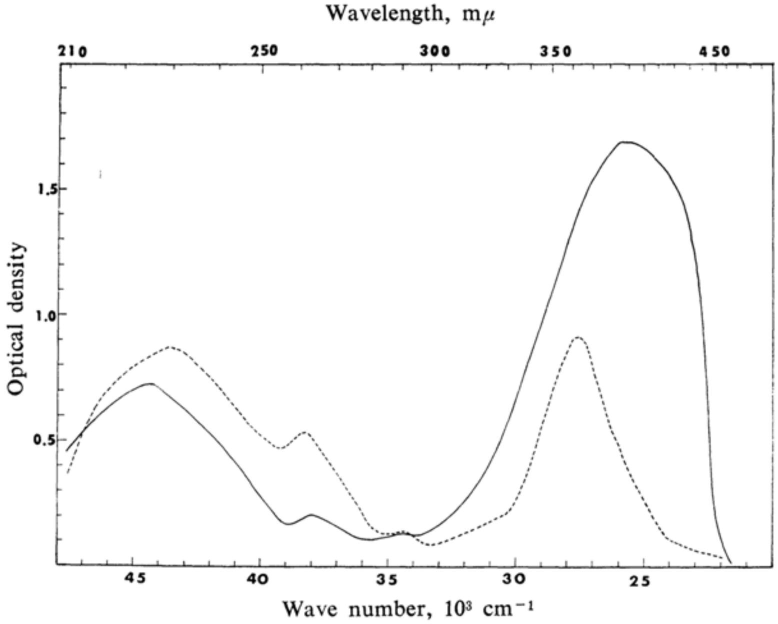

Fig. 3 (b). Polarized absorption spectrum of *p*-nitroaniline crystal.
—— The light polarized parallel to 101 dirrection
---- The light polarized parallel to b-axis

The thickness of the crystal was determined approximately by observing the interference color with a polarizing microscope and by using the relation between the retardation and birefringence; namely $R=d(n_{ac}-n_b)$, where R is the retardation and $n_{ac}-n_b$, the birefringence with the (101) plane, and d, the thickness. For more accurate measurement of crystalline thickness, the "apparent absorption band" in the visible region was measured with the polarized light. This absorption appears as a result of the interference of the beam reflected from the front surface with the beam reflected upon the rear surface[20]. For a wavelength at which the two beams interfere additively upon reflection and at which the transmission is at a maximum, the thickness, d, of the crystal is given by:

$$d=m\lambda/2n, \text{ where } m=3, 4, 5,\cdots\cdots$$

and n is the refractive index at the wavelength of measurement. For a wavelength where the transmission is at a minimum,

$$d=(2m+1)\lambda/4n, \text{ where } m=3, 4, 5,\cdots\cdots$$

In principle we can obtain the crystal thickness accurately by these means, but the dispersion of refractive index is not known, so the accuracy is limited to $\pm 0.03\mu$.

As has been mentioned before, the light falls onto the crystalline surface not at right angles but inclined about 46° to 12°. However, because of the refraction of the light at the crystalline surface, the light passes into the crystal inclined from 22° to 6° normal to the surface plane, and the optical path becomes necessarily large by about 1 to 10 per cent. This correction must be made in considering the optical path and, hence, the intensity of the crystalline absorption. As for the dichroism of the crystal, the transition moments of the molecules are nearly parallel to the (101) plane, so the dichroic ratio may be quite reliable in determining the polarization properties of molecular excited states.

The crystalline spectrum is shown in Fig. 3(b), where the spectrum with the light

TABLE II. THE OSCILLATOR STRENGTH OF THE 370 mμ BAND IN CRYSTAL

	Observed	Calculated (Oriented gas model)
$b_\perp$	0.127	0.74
$b_\parallel$	0.033	0.19

TABLE III. THE OBSERVED AND CALCULATED DICHROIC RATIOS

	Observed	Calculated	
		Long-axis polarization	Short-axis polarization
$D_{ac}:D_b$	3.90 : 1.00 (370 mμ band)	3.96 : 1.00	1.00 : 3.32
	1.00 : 3.26 (270 mμ band)		

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[20] A. Bree and L. E. Lyons, *J. Chem. Soc.*, **1956**, 2658; E. Edser and C. P. Butler, *Phil. Mag.*, **46**, 207 (1898).

polarized parallel and perpendicular to the b-axis is presented. The thickness of this crystal is estimated to be 0.36 μ. Four absorption bands are seen in the spectrum, three are fairly strong and one very weak. Each band shows a conspicuous dichroism. The observed oscillator strength and dichroic ratios for the 370 mμ and 270 mμ bands are given in Tables II and III, together with the calculated values for the oriented gas model. Comparing the calculated dichroic ratio with the observed value, it is unequivocally determined that the 370 mμ band is polarized parallel to the long axis of the molecule, while the 270 mμ band is directed to the short axis of the molecule. This result is in conformity with the above-mentioned theory, and the strong band appearing at 370 mμ (320 mμ in an *n*-heptane solution) is proved to be an intramolecular charge-transfer absorption. The fact that the 270 mμ band is not observed in solution but appears in the crystal may be explained by a perturbation of other allowed transitions or by a lowering of the symmetry of the excited state in the crystal. Anyway, this transition is shown to have the symmetry of the B type, polarized to the short axis of the molecule, while the wave function in Eq. 6 shows that the state is mainly composed of the $^1B_{2u}$ excited state of benzene. In addition to this band, another very weak absorption band is also observed at 295 mμ only in the crystalline spectrum. This band is not seen in the spectrum of the solution, but Wepster[21] had found a corresponding band in the spectrum of 4-nitro-*N*, *N*-dimethylaniline. Since a very weak transition of this kind would not be expected to appear judging from the results of the calculation of the π-electron system mentioned before, it is most probable that this is an n-π^* transition of the nitro group. The polarization of such a weak band cannot retain its own characteristic directional property of n-π^*, because the intensity mainly comes from the mixing with the allowed π-π^*. Therefore, the polarization of this band cannot be perpendicular to plane of the molecule, and the dichroism may be observed according to the mixing with nearby π-π^* transition.

The band at 220 mμ has a much larger intensity in the ac direction than in the b-axis; however, we cannot say anything conclusive about the polarization of this band, because the calculated energy levels are crowded in this region and a mixing with higher excited levels also easily takes place.

The Calculation of Davydov Splitting.—The crystal of *p*-nitroaniline belongs to a space group of $C_{2h}^5-P2_1/n$, and the molecule A in Fig. 3 (a) is transformed into B by a screw axis rotation parallel to the b-axis, into D by a glide plane vertical to the b-axis, and into C by an inversion. Combining the results of this operation with the character table of the C_{2h}^5 group, we obtain the following excited states wave functions:

$$\left.\begin{array}{ll} A_g: & \varphi_\alpha=\frac{1}{2}(\varphi_D'+\varphi_C'+\varphi_A'+\varphi_B') \\ A_u: & \varphi_\beta=\frac{1}{2}(\varphi_D'+\varphi_C'-\varphi_A'-\varphi_B') \\ B_u: & \varphi_\gamma=\frac{1}{2}(\varphi_D'-\varphi_C'+\varphi_A'-\varphi_B') \\ B_g: & \varphi_\delta=\frac{1}{2}(\varphi_D'-\varphi_C'-\varphi_A'+\varphi_B') \end{array}\right\} \quad (7)$$

where φ_A', φ_B', φ_C' and φ_D' denote the excited states wave functions of A, B, C and D site molecules respectively.

The selection rule allows a transition to the A_u excited state polarized along the b-axis and to the B_u state polarized along the a, c-axes. The energies of these levels can be shown to be:

$$\Delta E_\beta=\Delta E_m+D+\varepsilon_\beta$$
$$\Delta E_\gamma=\Delta E_m+D+\varepsilon_\gamma$$
$$\varepsilon_\beta=(\lambda_{AB}-\lambda_{AC}-\lambda_{AD})/2$$
$$\varepsilon_\gamma=(-\lambda_{AB}-\lambda_{AC}+\lambda_{AD})/2$$
$$\lambda_{AB}=\sum_B\int\psi_A{}^{*\prime}(r_1)\psi_B{}^*(r_2) \times\frac{e^2}{r_{12}}\psi_A(r_1)\psi_B'(r_2)d\tau_1 d\tau_2$$

where ΔE_m is the excitation energy for a free molecule, D is the whole shift of the center of the crystalline level from that of the free molecule, and λ_{AB} represents the interaction between an excited A molecule ψ_A' with all other excited B site molecules in the crystal.

It is the splitting of the band between b and a, c crystalline directions which is important: $\Delta E_\gamma-\Delta E_\beta$. The calculation of the integrals λ_{AB} and λ_{AD} was carried out using the dipole-dipole approximation, and the summation was taken over a 11Å radius sphere. The results are shown in Table IV. Comparing them with the experimental value of the splitting $E_b-E_{a,c}=1680\ \mathrm{cm}^{-1}$, it is evident that an assignment of the band as long axis polarized gives the better result; the agreement

TABLE IV. THE CALCULATED AND OBSERVED VALUES OF DAVYDOV SPLITTING (E_b-E_{ac})

Assumed polarization	Calculated	Observed
Long axis	1484 cm^{-1}	1680 cm^{-1}
Short axis	76 cm^{-1}	

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[21] B. M. Wepster, *Rec. trav. chim.*, 76, 357 (1959).

between the observed and the calculated values is remarkably good. The appearance of such a large splitting means that a strong coupling of resonance energy transfer takes place in the crystal of *p*-nitroaniline.

The Intensity of the Crystalline Absorption.— The intensity of the 370 mμ band decreases greatly in the crystal in both crystalline directions, namely about one-sixth of the expected value of the oriented gas model, as is seen in Table II. One of the reason for the reduction in the intensity of the crystal is that the actual electric field acting upon a molecule has a factor of $(n/\varepsilon(E_e/E))$, where n is the refractive index of the crystal, ε is the static dielectric constant, and E_e and E are the effective field and the average field respectively[22]. The numerical estimation of this factor is a difficult problem. However, an approximate values may be $\sim 1/n$. This accounts in part for the reduction of the intensity, because n is in the range of 2.0～2.5.

Recently Tinocco[23] and Rhodes[24] have presented a formula of the hypochromism of polymeric systems. However, it has not yet been established that their formula explains the results in the crystal of *p*-nitroaniline.

In some other aromatic molecular crystals such as naphthalene, McClure and Schnepp[25] and the present author[26] have found a more pronounced decrease in the intensity from the oriented gas values. This phenomenon is not explained by a simple oriented gas model, neglecting the electronic exchange interaction between neighboring molecules. In order to explain it, we must use another approach, taking into consideration the electronic exchange interaction of the electronic levels of the molecules in the crystal. On the contrary, the crystal of *p*-nitroaniline affords a good example of an appearance of the Davydov splitting; it also presents a successful use of the exciton theory of molecular crystals in explaining the features of the crystalline spectrum except for the anomalous reduction of the absorption intensity.

Abrahams and Robertson[19] have proposed the formation of a self-molecular complex of *p*-nitroaniline, but no absorption was found which could be attributed to the intermolecular charge transfer. Probably the intramolecular charge transfer process is predominant in the molecule itself, and the highest occupied orbital (the donor orbital) of aniline is stabilized by the nitro group, so that no intermolecular charge transfer occurs in the *p*-nitroaniline crystal.

Benzoic Acid

The ultraviolet absorption spectrum of benzoic acid has been measured in an *n*-heptane solution and is shown in Fig. 4. Three absorption bands appear in the region of 185～290 mμ; only the one of the longest wavelength shows some vibrational structures. A theoretical interpretation of the spectrum has been given previously[2], and that of benzaldehyde has been investigated more extensively by the present author[27]. The spectrum of benzaldehyde is very much like that of benzoic acid except that it has an n-π^* transition in the 330 mμ region. According to earlier calculations[27], the 280 mμ band of benzoic acid is assigned to the transition between the $^1A_{1g}$ ground state and the excited state, mainly

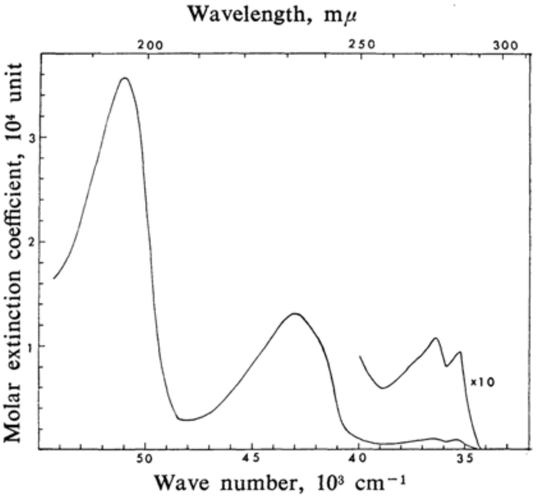

Fig. 4. Ultraviolet absorption spectrum of benzoic acid in *n*-heptane solution.

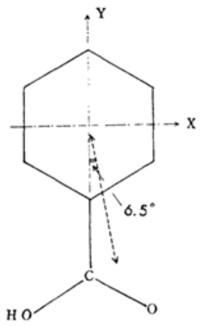

Fig. 5. Direction of the transition moment of the 230 mμ band of benzoic acid.

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[22] M. Lax, *J. Chem. Phys.*, **20**, 1752 (1952).

[23] I. Tinocco, Jr., *J. Am. Chem. Soc.*, **82**, 4785 (1960); *J. Chem. Phys.*, **33**, 1532 (1960); ibid., **34**, 1067 (1961).

[24] W. Rhodes, *J. Am. Chem. Soc.*, **83**, 3609 (1961).

[25] D. S. McClure and O. Schnepp, *J. Chem. Phys.*, **23**, 1575 (1955).

[26] J. Tanaka, unpublished result.

[27] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1114 (1958).

composed of the $^1B_{2u}$ excited level of benzene, which has the short-axis polarization. The second excited state, corresponding to the 230 mμ absorption, is assigned to a state having a large component of the intramolecular charge transfer configuration, and the direction of the polarization is calculated to be on the 6.5° line, inclined outward from the Y axis (Fig. 5) to the carbonyl group. Another interpretation of this band is to regard it as derived from the $^1B_{1u}$ excited level of benzene; then the polarization would be along the Y-axis. The measurement of the crystalline spectrum was undertaken in order to decide between the two interpretations.

Spectrum of Benzoic Acid Crystal.—The crystal structure analysis of benzoic acid as carried out by Sim, Robertson and Goodwin[28] showed that the crystal belongs to $C_{2h}^5-P2_1/c$ space group, including four molecules in a unit cell. Based on this finding the projection of molecules onto the (001) plane is pictured in Fig. 6 (a). Thin flakes of crystal are obtained by sublimation and are used for spectral measurement. The developed face is (001). The optical properties of the crystal are as described by Winchell[18], and the axes are easily determined by a polarization microscope. The thickness of the crystal is measured by the interference pattern described in a previous paragraph. The observed crystalline spectrum crystal 0.23 μ thick, is shown in Fig. 6(b). Comparing the integrated intensity of each band when the polarization of light is along the a-axis with that of along the b-axis, the dichroic ratio is estimated to be $D_a : D_b = (10\pm2) : 1$ for the 280 mμ band. In the region between 210∼230 mμ there are two bands overlapping each other, and the band near 210 mμ is much stronger along the a-axis than along the b-axis. The 230 mμ band is apparently stronger in the b-axis. In order to estimate the dichroic ratio of the 230 mμ band, we have separated these overlapping bands; the dichroic ratio of the 230 mμ band was thus found to be $D_a : D_b = 1 : (31\pm3)$.

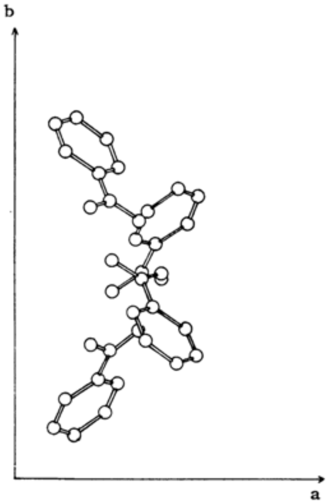

Fig. 6 (a). Projection of benzoic acid molecules onto the (001) plane.

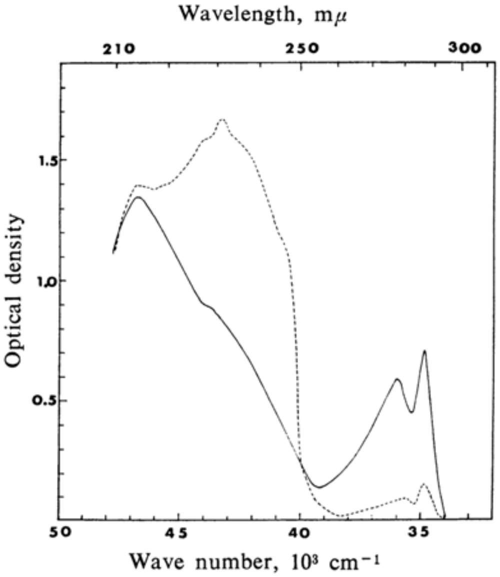

Fig. 6 (b). Polarized absorption spectrum of benzoic acid crystal.
—— The light polarized parallel to the a-axis
---- The light polarized parallel to the b-axis

According to the crystalline structure data, the dichroic ratio is calculated for the short-axis (X-axis in Fig. 5) transition as $D_a : D_b = 12 : 1$; hence, the 280 mμ band is confirmed to be polarized along the X-axis of the molecule, and to be largely a $^1B_{2u}$ transition. As for the 230 mμ band, the ratio is 1 : 30 if we take the direction of the transition moment to lie 6.5° inclined outward to the Y-axis towards the carbonyl group, but it is 1 : 11 if the direction is assumed to be on the Y-axis. Comparing the calculated value with the observed one, it is concluded that the 230 mμ band is polarized 6.5° outward to the Y-axis towards to the carbonyl group. Thus, the 230 mμ band is shown to have a characteristic polarization of an intramolecular charge transfer. The band at 210 mμ is not seen in solution; it may appear as the result of borrowing intensities from the allowed excited states situated in the shorter wavelength region. The polarization of this band seems to be

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[28] G. A. Sim, J. M. Robertson and T. H. Goodwin, *Acta Cryst.*, **8**, 157 (1955).

short-axis, but it cannot be discussed further because the absorption band is not wholly observed.

Finally, as for the intensity of the crystalline absorption bands, the observed value is compared with the calculated value in Table V. The observed intensity of the 278 mμ band is nearly equal to the calculated value, but in the case of the 230 mμ band the observed value is one half the calculated one. In this case the hypochromic effect is again observed in the crystalline spectrum.

Acetanilide

The absorption spectrum of acetanilide measured in an *n*-heptane solution is shown in Fig. 7. Three absorption bands are seen in the region of 290~190 mμ; the long wavelength one is safely regarded by analogy with other substituted benzenes to be an absorption analogous to the 260 mμ band of benzene. In the theoretical interpretation of the spectrum of acetanilide given by Baba and Suzuki[29], it has been shown that the transition moment of the second band at 230 mμ lies 20.5° inclined to the C_1N axis towards the carbonyl group. According to the X-ray crystal structure analysis made by Brown and Corbridge[30], acetanilide is not a planar molecule and the plane of the acetyl group makes an angle of 37°54′ to the plane of the anilino group. The acetyl group can accept electrons from other conjugated systems, and aniline is a good electron donor, so that it is quite probable that an electron transfer takes place from the highest occupied orbital of the anilino group to the vacant orbital of the carbonyl group. If this charge transfer configuration is predominant for the excited state, in this particular transition the polarization should be along the line connecting the center of the highest occupied orbital of the anilino group to that of the vacant orbital of the carbonyl group (the center of the highest occupied orbital is 0.58 Å from the center of the benzene ring in the direction of the amino group, according to the LCAO MO calculations). This direction makes an angle of 32.5° with the C_1C_4 axis (Fig. 8). The 230 mμ band may be considered to have the large character of the charge transfer of this type. However, in order to give an accurate description of the nature of electronic transition, the configurational interaction between the charge transfer state and the locally excited states of aniline and of the carbonyl group must be taken into account. The symmetry of the molecule is less simple than *p*-nitroaniline, and the excited states will be a more complicated mixture of several excited configurations. Anyway, the crystalline spectrum will reveal the direction of the transition moment, and it will be useful for the theoretical assignment of the absorption bands.

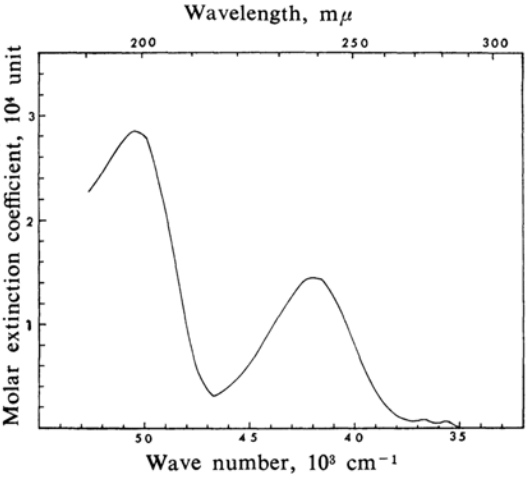

Fig. 7. Ultraviolet absorption spectrum of acetaniline in *n*-heptane solution.

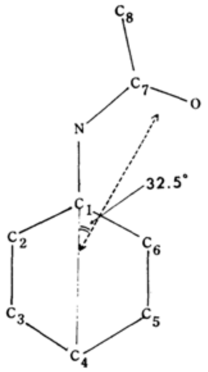

Fig. 8. Direction of the transition moment of the 230 mμ band of acetanilide.

The Spectrum of Acetaniline Crystal.—According to Brown and Corbridge[30], the crystal belongs to the space group of Pbca-D_{2h}^{15}, with the unit cell dimensions of a=19.640, b=9.483 and c=7.979 Å, and eight molecules are contained in a unit cell. The crystals for the spectral measurement were made by sublimation, and the (100) or (001) faces develop most easily. Projections of molecules onto these faces are shown in Figs. 9 (a) and 10 (a). The identification of the developed face is made by the use of X-ray rotation photography and the polarization microscope. The crystalline absorption is measured with a (100) face by a light polarized along the b and the

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[29] H. Baba and S. Suzuki, *J. Chem. Phys.*, 32, 1706 (1960).

[30] C. J. Brown and D. E. C. Corbridge, *Acta Cryst.*, 7, 711 (1954).

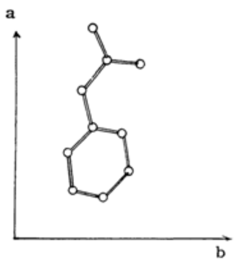

Fig. 9 (a). Projection of acetanilide molecule onto the (001) crystalline plane.

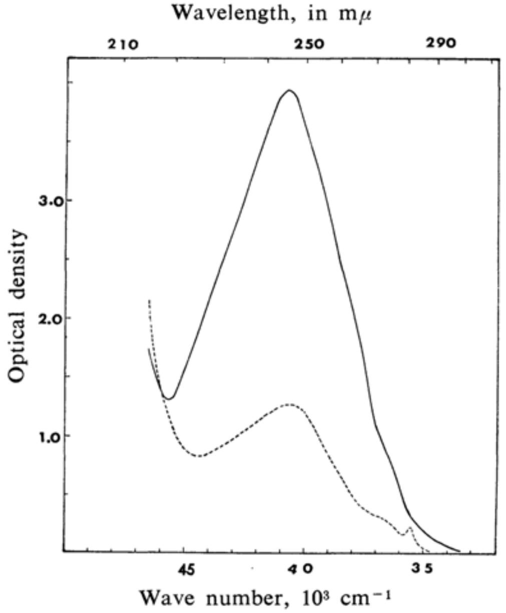

Fig. 9 (b). Polarized absorption spectrum of acetanilide crystal through the (001) plane.

—— The light polarized parallel to the a-axis

---- The light polarized parallel to the b-axis

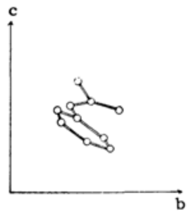

Fig. 10 (a). Projection of acetanilide molecule onto the (100) plane.

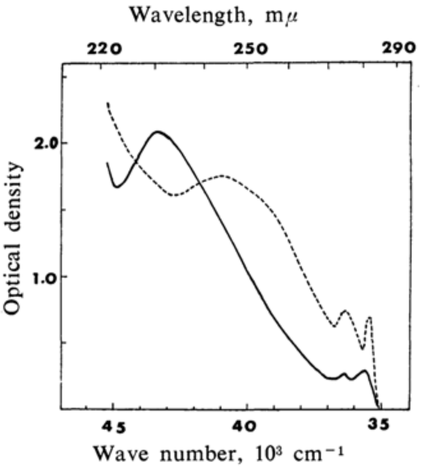

Fig. 10(b). Polarized absorption spectrum of acetanilide crystal through the (100) plane.

—— The light is polarized parallel to the c-axis

---- The light polarized parallel to the b-axis.

c axes and with a (001) face by a light polarized along the a and the b axes, are respectively. The results are shown in Figs. 9(b) and 10(b). From Fig. 10(b), the direction of the transition moment of the 284 mμ band is confirmed to be nearly perpendicular to the C_1N axis, because the observed intensity ratio, $D_b:D_c=2.90:1.0$, is almost in agreement with the calculated value of $D_b:D_c=2.76:1.0$. This result is fairly satisfactory, considering the fact that the 284 mμ band overlaps the 230 mμ band which has a much larger intensity.

The polarization of the next 230 mμ band is determined by both (100) and (001) spectra independently. From the (100) spectrum, the observed intensity ratio is $D_b:D_c=1.0:0.76$, while the calculated value is 1.0 : 0.74 if we take the direction of the transition moment on the line inclined 32.1° to the C_1C_4 axis toward the carbonyl group (36.2° to the C_1N axis) (Fig. 8). From the (001) spectrum, the observed intensity ratio $D_a:D_b$ is 4.53 : 1.0, whereas the calculated value is 4.95 : 1.0 if the direction of the transition moment is assumed along the line 33.2° inclined to the C_1C_4 axis (35.4° to the C_1N axis) outward to the carbonyl group. The agreement of these two measurements is quite satisfactory, and the polarization of the 230 mμ band is determined to be along the direction of 32.5±0.5° inclined to the C_1C_4 axis (35.6° to the C_1N axis) outward to the carbonyl group. This direction is the same as the direction of the charge transfer from the highest occupied orbital of the anilino group to the vacant orbital of the carbonyl group, but this coincidence cannot be stressed too much, because the exact description of the excited state must be given by the configurational interaction calculations.

The Davydov splitting of the second absorption is obviously seen in Figs. 9(b) and

10(b); namely, it appears at 243 mμ in the a-axis, at 244 mμ in the b-axis, and at 230 mμ in the c-axis. The splitting was not found with the 282 mμ band, because the dipole-dipole interaction between the excited states is smaller than for the stronger 230 mμ band.

As for the intensity of the 230 mμ band in the crystal, the observed intensity is about one half that of the calculated value, as is shown in Table VI. The hypochromism of crystalline absorption is found again; hence, it seems a common experimental fact that the fairly strong absorption band loses some of its intensity in the crystalline spectrum.

TABLE V. THE OSCILLATOR STRENGTH OF THE CRYSTALLINE ABSORPTION OF BENZOIC ACID

	Observed	Calculated
287 mμ band (a-axis)	0.032	0.030
230 mμ band (b-axis)	0.17	0.36

TABLE VI. THE OSCILLATOR STRENGTH OF THE 230 mμ CRYSTALLINE ABSORPTION OF ACETANILIDE

	Observed	Calculated
a-axis	0.290	0.72
b-axis	0.066	0.145

trans-Cinnamic Acid

The electronic absorption spectrum of *trans*-cinnamic acid measured in an *n*-heptane solution is illustrated in Fig. 11. A weak absorption band is seen at 296 mμ as a shoulder of the stronger band at 277 mμ. Another stronger band with vibrational structure is observed near 222 mμ.

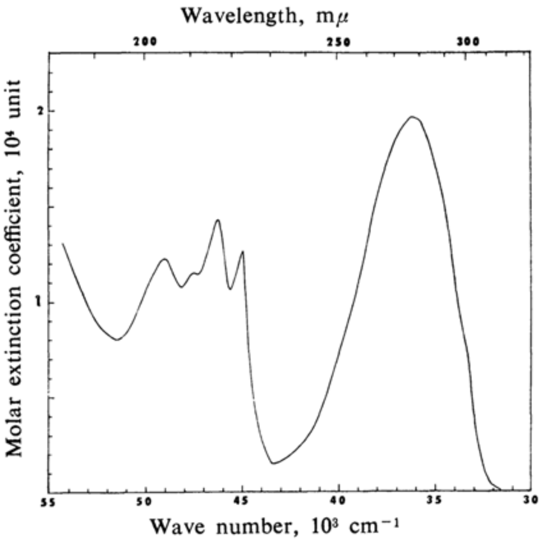

Fig. 11. Ultraviolet absorption spectrum of *trans*-cinnamic acid in *n*-heptane solution.

trans-Cinnamic acid is considered to be a composite, consisting of the electron-donating styryl group and the electron-accepting carboxyl group. The charge transfer from the highest occupied orbital of the styryl group to the vacant orbital of the carboxyl group will take place quite easily, because the ionization potential of styrene is as small as 8.86 eV.31) and the charge density of the highest occupied orbital of styrene is most dense at the terminal α-carbon atom, where the interaction between the donor and the acceptor group takes place. By this reasoning, the strong absorption band at 277 mμ is regarded as an intramolecular charge transfer band; this is confirmed by a measurement of the crystalline absorption spectrum.

The Crystalline Spectrum of *trans*-Cinnamic Acid.—The crystal structure analysis of *trans*-cinnamic acid is now being carried out by Schmidt and his coworkers32). They find two crystalline forms. The α-form belongs to the $P2_1/a$ space group and has lattice constants as follows: $a=8.94$, $b=17.56$, $c=5.51$ Å and $\beta=58°40'$ and $n=4$; the β is found to have cell dimensions of $a=6.05$, $b=4.04$, $c=31.3$ Å, $\beta=90.3°$ and $n=4$. By sublimation, both α and β forms are obtainable, and the α-form develops a (010) face and the β develops a (001) plane. These crystalline faces are confirmed by X-ray rotation photographs. According to the unpublished results of Schmidt et al.32) the projection of molecules of the α crystal onto a (010) face is shown in Fig. 12(a). The crystalline ultraviolet absorption of the *a*-form as measured through the (010) plane by a light polarized parallel and perpendicular to a-axis is shown in Fig. 12(b). With the β-form, spectrum is taken through the (001) face; the result is shown in Fig. 13. Comparing the spectrum of Fig. 12 (b) with the projections of molecules in Fig. 12 (a), it is easily found that the 270 mμ absorption band

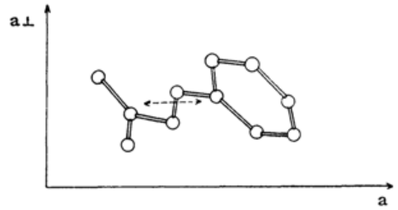

Fig. 12(a). Projection of *trans*-cinnamic acid molecule onto the (010) plane of α-form.

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31) J. D. Morrisson and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1221 (1952).

32) G. M. J. Schmidt, private communication based on the work by J. Ladell, T. R. R. McDonald and G. M. J. Schmidt, *Acta Cryst.*, **9**, 195 (1956).

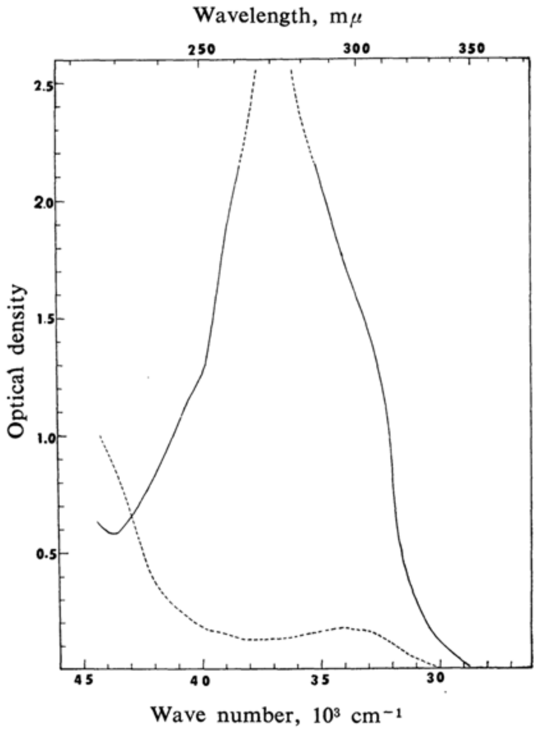

Fig. 12 (b). Polarized absorption spectrum of *trans*-cinnamic acid α-form through the (010) plane.
—— The light polarized parallel to the a-axis
---- The light polarized perpendicular to the a-axis

has a polarization nearly parallel to the a-crystalline axis. The direction of the transition moment is on the line expected from the charge transfer from the styryl group to the vacant orbital of the carboxyl group. In the crystalline spectrum, particularly in the β-form as seen in Fig. 13, the band which is at 277 mμ in an *n*-heptane solution shifts to about 255 mμ. The *trans*-cinnamic acid molecules are supposed to be aligned in pairs by a hydrogen bonding in the crystal. In this situation the transition moments of the pair of molecules are parallel to each other but are in oposite directions, and by a dipole-dipole interaction the excited states split into two, one allowed at a higher energy and the other forbidden at a lower energy. Therefore, the observable band should move to a shorter wavelength region. As a result of this blue shift, the weak absorption band which appears as a little shoulder in a solution at about 296 mμ becomes more evident in the crystalline spectrum. As is seen in Fig. 12 (a), if this absorption corresponds to the 260 mμ band of benzene, it should be observed in directions both parallel and perpendicular to the a-axis because the polarization should be short-axis. In Fig. 12 (b), the 295 mμ band appears both parallel and perpendicular to the a-axis so it is established that the band is derived from the $^1B_{2u}$ excited state of benzene. We cannot discusss further the spectrum shown in Fig. 13 because the crystal structure has not yet been fully analyzed.

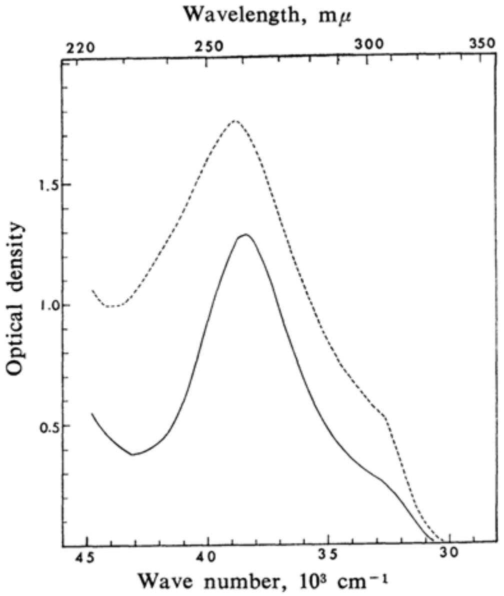

Fig. 13. Polarized absorption spectrum of *trans*-cinnamic acid β-form through the (001) plane.
—— The light polarized parallel to the a-axis
---- The light polarized parallel to the b-axis

Durene

The electronic absorption spectrum of durene is quite similar to that of benzene, and the spectrum in *n*-heptane is illustrated in Fig. 15.

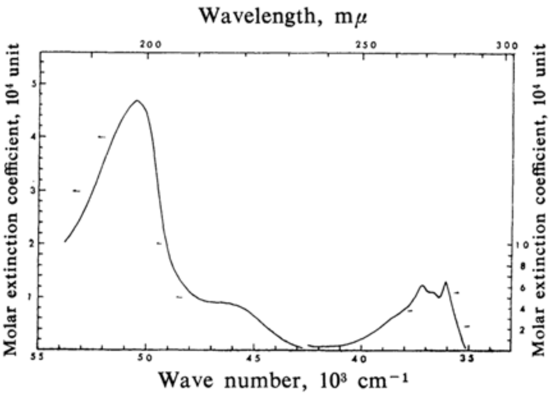

Fig. 14. Ultraviolet absorption spectrum of durene in *n*-heptane solution.

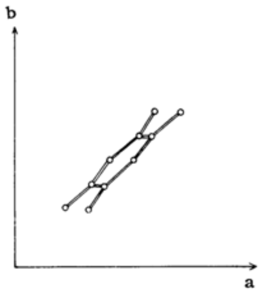

Fig. 15 (a). Projection of durene molecule onto the (001) plane.

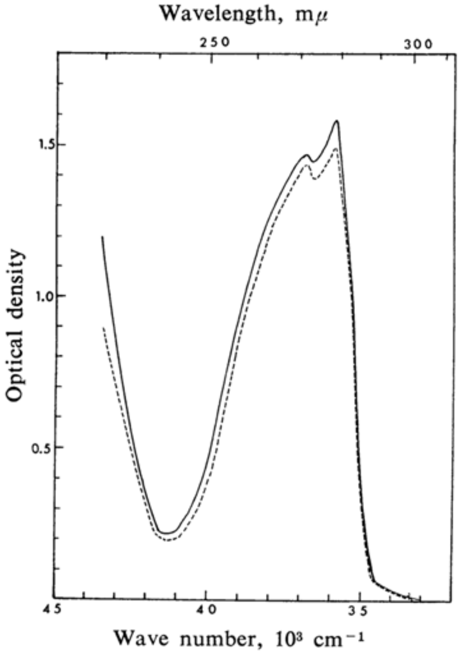

Fig. 15 (b). Polarized absorption spectrum of durene crystal.
—— The light polarized parallel to the a-axis
---- The light polarized parallel to the b-axis

The band near 278 mμ corresponds to the 260 mμ band of benzene ($^1A_{1g} \rightarrow {}^1B_{2u}$), the band around 217 mμ is correlated with 205 mμ band ($^1A_{1g} \rightarrow {}^1B_{1u}$) of benzene, and the strongest one, at 198 mμ, corresponds to the 185 mμ band ($^1A_{1g} \rightarrow {}^1E_{1u}$) of benzene. Following the theory of the spectrum of benzene[1], the first singlet excited state, $^1B_{2u}$, was shown to be polarized perpendicular to the two-fold symmetry axis of the molecule; hence, the polarization of the first band of durene should be perpendicular to the line connecting the two carbon atoms not substituted by methyl groups.

The crystalline absorption spectrum of durene has been studied by Schnepp and McClure[33]. The crystal structure of durene was determined by Robertson[34], and its optical properties were described by Groth[17]. Using Robertson's results, the molecules are projected onto the (001) plane in Fig. 15(a). The crystals measured are obtained by sublimation, and the developed face is easily confirmed as (001) by the aid of a polarization microscope. From Fig. 15(a) it is easy to see that the absorption band should have the same intensity in the a and b axes if the transition moment is parallel to the long axis of the molecule, while it should be stronger along the a-axis than along the b-axis if it is parallel to the short axis. The observed absorption spectrum is shown in Fig. 15 (b). As compared with the results of Schnepp and McClure, the present spectrum is broad and diffuse, because the measuement is made at room temperature. However, the general features of bands are in accordance with their results, and it is confirmed that the intensity ratio of the 280 mμ band is nearly equal in the directions of the a and b crystalline axes. The results show that the polarization of the 278 mμ band is parallel to the long axis of the molecule; hence, the excited level is confirmed to correspond exactly to the $^1B_{2u}$ excited state of benzene. The observed intensity ratio is rather small compared with the oriented gas ratio of $D_a : D_b = 1.0 : 1.3$; this deviation must be explained by the mixing of the $^1B_{2u}$ excited state of a particular molecule with the $^1B_{1u}$ excited state of neighboring molecules[35]. As compared with other substituent groups mentioned before, methyl groups have rather a small influence on the spectrum of benzene, and the polarization of durene's band is in accordance with that of benzene.

Conclusion

The electronic absorption spectra of substituted benzenes are in some way modifications of that of benzene itself. When the substituent group has rather a small influence as in, for instance, the methyl, hydroxyl or chloro groups, the pattern of the benzene spectrum is retained, the absorption peaks being shifted to red and the intensity of the 260 mμ band being strengthened to some extent[4]. A substitution by an amino, *N, N*-dimethylamino or ionized hydroxyl group causes the appearance of an additional excited level next to the $^1B_{2u}$

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33) O. Schnepp and D. S. McClure, *J. Chem. Phys.*, **30**, 874 (1960).

34) J. M. Robertson, *Proc. Roy. Soc.*, **A141**, 594,; **A142**, 659 (1933).

35) D. P. Craig and J. R. Walsh, *J. Chem. Soc.*, **1958**, 1613.

level of benzene, since a charge transfer takes place in this region because the non-bonding electrons of these groups have relatively low ionization energies(3). Two charge transfer states are possible, one from the substituent to the vacant orbital symmetrical to the two-fold axis, and the other to the antisymmetrical orbital. The former interacts with the $^1B_{1u}$ state, and the latter mixes with the $^1B_{2u}$ state. However, upon a substitution of the electron-donating groups, there are no serious changes in the polarization properties of each band, because the symmetrical properties of the excited states are not altered in sequence. The $^1B_{2u}$ excited state is the lowest singlet excited state in these substituted benzenes even if the electron-donating power of the substituent is so strong that the lowest state has a large percentage of charge transfer; hence, the longest absorption band is always polarized perpendicular to the two-fold symmetry axis of the molecule. Both the $^1B_{1u}$ excited state and the symmetrical charge transfer state have a polarization parallel to the two-fold axis, so the next band has this polarization in all cases. The results of durene and *p*-dimethoxybenzene(5) confirm the above statement, and such other molecules as aniline and phenol can be treated similarly.

In other substituted benzene molecules, in which the substituents have an electron-accepting property, a different situation arises. Electrophilic substituent groups have vacant orbitals which accept electrons from the benzene ring; as a result of this, new absorption bands often appear in addition to benzen's intrinsic transition(2,19,27). The 370 mμ band of *p*-nitroaniline, which is the longest absorption band of this molecule, is not an analogous band to the 260 mμ band of benzene but a charge transfer band, and it is polarized along the two-fold symmetry axis of the molecule. In the case of benzoic acid, acetanilide and *trans*-cinnamic acid, charge transfer bands are observed next to the band derived from the $^1B_{2u}$ excited level of benzene. In these molecules, there are also other charge transfer states which interact with the $^1B_{2u}$ state of benzene. In fact, the longest absorption band of nitrosobenzene includes fairly large amounts of this type of charge transfer, together with the $^1B_{2u}$ state of benzene(27). The sequence of these levels has been determined by the order of the energy levels of the initial states prior to configuration interaction.

Such electrophilic substituent groups as nitro, carbonyl, carboxyl, azo, nitroso are classified by Witt's classical theory as " chromophores "(36). These groups are characterized by low-lying vacant orbitals which can receive electrons by resonance interaction. When an unsaturated hydrocarbon, which has electronic absorptions in the visible or near-ultraviolet region, is substituted by an electrophilic group, a new strong absorption band is often observed in the visible or the near-ultraviolet region arising from a new charge transfer state in which an electron is transferred from the parent hydrocarbon to the vacant orbital of the substituent. This is a quantum-chemical explanation of Witt's chromophore theory. Witt's "auxochrome" (such substituents as NH_2, NMe_2, OH, OMe, and Cl) may be understood in two ways; it produces bathochromic shifts in the transitions of the parent molecule, and it facilitates the transfer of electrons from the parent system to the electrophilic substituent by decreasing the ionization potential of the parent molecule.

The crystalline ultraviolet absorption spectral measurements are very useful in confirming this theory, because they give information about the directions of the transition moments of the bands and confirm the symmetry properties of excited levels. Moveover, some hidden and ambiguous bands in solution become evident in the crystalline spectra; they are very instructive in ascertaining what kinds of electronic interactions are prevalent in molecular crystals. It turns out that the dipole-dipole interactions of the exciton type are predominant in the case of the crystals studied here.

Summary

The electronic absorption spectra of some substituted benzene molecules *p*-nitroaniline, benzoic acid, acetanilide, *trans*-cinnamic acid, and durene have been measured in ethanol or *n*-heptane solutions and as single crystals, using polarized light. The measurement of the crystalline spectra reveals in many respects the properties of the transitions of substituted benzene molecules. The 277 mμ of durene, which is reasonably regarded as a band analogous to the 260 mμ of benzene, is shown to be polarized perpendicular to the two-fold symmetrical axis of the molecule. Bands of the same type occur at 264 mμ in *p*-nitroaniline (crystal), at 284 mμ in benzoic acid, at 282 mμ in acetanilide and at 299 mμ in *trans*-cinnamic acid. In addition, those molecules in which the benzene ring is substituted by the electron-accepting groups, show a strong band, associated with intramolecular charge transfer, in the near ultraviolet region. The 370 mμ band of *p*-nitroaniline is shown to be

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36) A. E. Gilam and E. S. Stern, " Electronic Absorption Spectroscopy ", Edward Arnold, Ltd., London (1958).

polarized parallel to the long axis of the molecule, and the 230 mμ band of benzoic acid has a polarization parallel to the line connecting the centers of the benzene ring and the carbonyl group. The directions of the transition moments of the 240 mμ band of acetanilide and the 276 mμ band of *trans*-cinnamic acid are also shown to be on the line connecting the substituents and the benzene ring. Davydov splitting is observed in the crystal of *p*-nitroaniline; this splitting is in good agreement with the values calculated by the exciton theory.

The author thanks Professor Saburo Nagakura for his continued encouragement and Professor Zyun Koana for lending him Bausch and Lomb's lenses. The author's gratitude is also due Dr. G. M. J. Schmidt for his kind communication of his unpublished findings on *trans*-cinnamic acid and also Dr. J. N. Murrell for his valuable discussion and kind hospitality during the author's stay in Sheffield, where some parts of this paper were written.

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