688. *Electronic Levels in Pyrimidines: The Crystal Spectrum of 2-Amino-4-chloro-6-methylpyrimidine.*

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The polarised crystal absorption spectrum of 2-amino-4-chloro-6-methylpyrimidine is reported for frequencies up to 40,000 cm.$^{-1}$. By means of a first-order Davydov splitting calculation, the lowest-energy system in the absorption spectrum of the crystal is assigned to the allowed molecular transition $B_2 \leftarrow A_1$.

If the pyrimidine molecule is considered as derived from benzene by the replacement of two CH groups by nitrogen atoms in the *meta*-position, then the electronic properties of pyrimidine can be correlated with those of benzene, the molecular symmetry being reduced from group $\mathscr{D}_{6h}$ of the hydrocarbon to $\mathscr{C}_{2v}$ of the diazine.

The ultraviolet singlet–singlet absorption spectra of pyrimidines above 2000 Å usually contain three distinct band systems,[1] I, II, and III. The system I, which lies at longest wavelengths, has [2] a molar extinction coefficient of about 300 and the band maxima undergo blue shifts when the dielectric constant of the solvent is increased. System I is exceedingly sharp in pyrimidine vapour [3] and a rotational analysis of this electronic transition has been reported.[4] As a consequence, system I has been assigned [5] to the $n \rightarrow \pi^*$ transition originating from the promotion of an electron from a non-bonding orbital of the nitrogen atoms to an antibonding π orbital.[6] Systems II and III have been assigned [5,7,8] by analogy with benzene to $\pi \rightarrow \pi^*$ transitions.

A powerful method for identifying molecular transitions in pyrimidines is the study of the spectra of molecular crystals in which the molecular units are held in fixed positions. By means of Davydov's [9] exciton [10] theory it has been possible to explain the spectra of many molecular crystals.[11,12] However, few studies [8,13] of crystal spectra of pyrimidines

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[1] Andrisano and Modena, *Gazzetta*, 1951, **81**, 405.

[2] Heyroth and Loofbourow, *J. Amer. Chem. Soc.*, 1934, **67**, 60.

[3] Uber, *J. Chem. Phys.*, 1941, **9**, 777.

[4] Innes, Merritt, Tincher, and Tilford, *Nature*, 1960, **187**, 500.

[5] Halverson and Hirt, *J. Chem. Phys.*, 1949, **17**, 1165; 1951, **19**, 711.

[6] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.

[7] Ito, Shimada, Kuraishi, and Mizushima, *J. Chem. Phys.*, 1957, **26**, 1508.

[8] Lyons, *J. Chem. Phys.*, 1952, **20**, 1814; Ph.D. Thesis, London University, 1952.

[9] Davydov, *Zhur. eksp. teor. Fiz.*, 1948, **18**, 210.

[10] Frenkel, *Phys. Z. Sowjetunion*, 1936, **9**, 158.

[11] Fox and Schnepp, *J. Chem. Phys.*, 1955, **23**, 767; McClure, *J. Chem. Phys.*, 1956, **25**, 481; Craig and Walsh, *J.*, 1958, 1613; Lyons, *J.*, 1958, 1347.

[12] Craig and Hobbins, *J.*, 1955, 539.

[13] Seeds, *Discuss. Faraday Soc.*, 1950, **9**, 394.

have been made. Lyons[8] studied the crystal spectra of 2-amino-4-chloro-6-methylpyrimidine and 2-chloro-4,6-dimethylpyrimidine. In the former, conjugative substitution of the amino-group shifts the first $\pi\rightarrow\pi^*$ molecular transition, II, to lower energy, so that the less intense $n\rightarrow\pi^*$ transition, I, is hidden. System I is, however, observable in the dimethyl compound. The crystal spectrum of the amino-compound was reported[8] only for frequencies less than 30,000 cm.$^{-1}$. The present work extends the experimental observation to ~40,000 cm.$^{-1}$ and also gives the results of a first-order Davydov splitting calculation for the crystal. The results are used in discussing the assignment of energy levels in pyrimidines.

EXPERIMENTAL

2-Amino-4-chloro-6-methylpyrimidine crystallises as very thin laths with lengths parallel to the *b* crystallographic axis.[14] Lyons[8] concluded from a study of sublimation laths that, if α, β, and γ are the three refractive indices of the crystal in increasing order of magnitude, then α lay along the *b* axis.

The amine was purified by recrystallisation from ethanol, and crystals were grown by sublimation. This process generally produced elongated lath-shaped crystals which did not transmit frequencies of more than 30,000 cm.$^{-1}$. It was possible, however, to select very small crystals which were sufficiently thin to permit absorption studies to be made.

The small size of crystals ($\sim 2 \times 10^{-2} \times 10^{-4}$ mm.^{3}) necessitated the use of a microscopic technique to obtain the spectrum. The crystal was mounted on to the stage of a microscope with reflecting objectives. The light source was an Osram XBO 150 high-pressure xenon lamp, and its focused image was observed by fitting an eye-piece to the microscope. The microscope stage was then adjusted so that the crystal completely covered the image of the source. The crystal image so formed was then focused on to the slit of a Hilger Medium quartz spectrograph. A Wollaston prism was interposed between spectrograph and microscope and served to polarise the light both parallel and perpendicular to the *b* axis (length) of the crystal.

Spectra were photographed on Kodak orthochromatic contrast process plates. Exposures of up to 3 hr. were required to penetrate band maxima. Relative plate-blackening measurements were made on a Leeds and Northrop microdensitometer. Solution spectra were obtained on a Cary model 14 recording spectrophotometer. Transition oscillator strengths, *f*, were measured by graphical integration of the expression,[15]

$$f = 4{\cdot}317 \times 10^{-9}\int\varepsilon d\nu,$$

where ε is the molar extinction coefficient and ν is the frequency in cm.$^{-1}$.

RESULTS

A microphotometer tracing of a plate of the spectrum of a 2-amino-4-chloro-6-methylpyrimidine crystal between 30,000 and 40,000 cm.$^{-1}$ is shown in Fig. 1. The component polarised parallel to the *b* axis of the crystal is seen to lie at higher energy than the oppositely polarised component. Maximum absorption of the $\perp b$ component occurred at 36,060 cm.$^{-1}$. Onset of strong absorption in the component $\| b$ took place at 39,100 cm.$^{-1}$. The splitting between the two components is at least 3000 cm.$^{-1}$. Several thicker crystals were also studied. In every case the $\perp b$ component commenced to absorb at lower frequencies than the $\| b$ component.

The solution spectrum of 2-amino-4-chloro-6-methylpyrimidine in 95% ethanol is shown in Fig. 1. The maximum extinction coefficient of this transition was found to be 4540 ± 50 at a frequency of 33,800 ± 50 cm.$^{-1}$. A mean oscillator strength of $7{\cdot}90 \pm 0{\cdot}09 \times 10^{-2}$ was calculated from these values. From the relation[15]

$$f = 3{\cdot}24 \times 10^{-5} B\, \Delta E . M^2,$$

where ΔE is the transition energy in cm.$^{-1}$, M is the transition moment in Å, and B is a geometrical factor which averages in vapour and solution to $\frac{1}{3}$, the transition moment was calculated to be $M = 0{\cdot}465 \pm 0{\cdot}005$ Å.

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[14] Clews and Cochran, *Acta Cryst.*, 1948, **1**, 4.

[15] Mulliken and Rieke, *Reports Progr. Phys.*, 1941, **8**, 231.

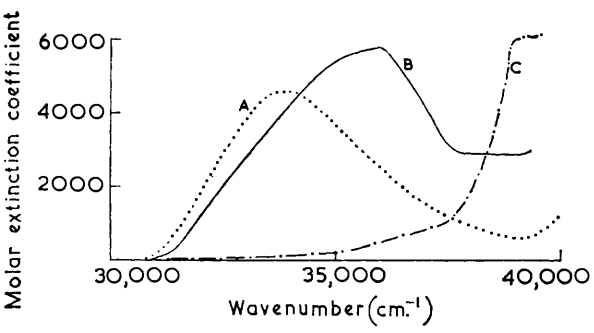

FIG. 1. Absorption spectra of 2-amino-4-chloro-6-methylpyrimidine. (A) Solution in 95% ethanol. (B) $\perp b$ Crystal spectrum with electric vector of light perpendicular to *b* crystal axis. (C) $\parallel b$ Crystal spectrum; electric vector parallel to *b* axis. The ordinate scale refers to the solution spectrum only. Absorption by the crystal is in relative units.

THEORETICAL

2-Amino-4-chloro-6-methylpyrimidine crystals are monoclinic,[14] of space group $P2_1/a$ (C_{2h}). Crystals are isomorphous with those of 2-amino-4,6-dichloropyrimidine Cell dimensions are:[14]

Pyrimidine	*a* (Å)	*b* (Å)	*c* (Å)	*β*
2-Amino-4-chloro-6-methyl	16·426	$4{\cdot}00_0$	10·313	109° 8′
2-Amino-4,6-dimethyl	16·447	$3{\cdot}84_5$	10·283	107° 58′

Replacement of a chlorine atom by methyl does not alter the apparent symmetry from the molecular point group $\mathscr{C}_{2v}$ to which the 4,6-dichloro-compound belongs. In the present work, the 2-amino-4-chloro-6-methyl and the 2-amino-4,6-dimethyl compound are regarded as crystallographically identical and calculations on the former to be reported below were actually carried out by using Clews and Cochran's[14] atomic co-ordinates for the latter.

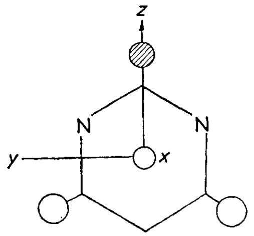

FIG. 2. Axes in 2-amino-4-chloro-6-methylpyrimidine. Open circles chlorine or methyl. Shaded circle NH_2.

Following the recommendations of the Joint Commission for Spectroscopy,[16] we assign axes in the 2-amino-compound as in Fig. 2. Thus, the *z* axis is perpendicular to the line joining the two nitrogen atoms (N–N line) and is the two-fold axis of symmetry. The *x* axis is perpendicular to the ring plane and is directed downwards into the plane of the paper.

The mean centre of the reference molecule (I) in the lattice was calculated to lie at $x' = 4{\cdot}740$, $y' = 0{\cdot}702$, and $z' = 2{\cdot}888$ Å with respect to the centre of symmetry of the unit cell as origin. (x', y', and z') are a set of Cartesian axes erected at the origin. The axes lie along ($\boldsymbol{a} + \boldsymbol{c}\cos\beta$, $\boldsymbol{b}$, $\boldsymbol{c}\sin\beta$) respectively, where $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ are the vectors defining the unit cell.* The remaining molecules, II, III, and IV, in the unit cell can be generated from I by

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* The recommended choice of axes differs from that of previous authors (*e.g.*, Sponer and Stucklen [17]) for $\mathscr{C}_{2v}$ symmetry. In the past, authors have chosen the *x* axis to be perpendicular to the ring and the *y* axis as the symmetry axis.

[16] Joint Commission for Spectroscopy, *J. Chem. Phys.*, 1955, **23**, 1997.

[17] Sponer and Stucklen, *J. Chem. Phys.*, 1946, **14**, 101.

the following symmetry operations: (i) $C_2(b)$ = two-fold rotation about the b axis, (ii) $\sigma(ac)$ = reflection in the ac plane, (iii) i = inversion through the centre of symmetry. Molecule, II, III, and IV are generated according to Table 1.

TABLE 1.

Generation of molecules for crystal species C_{2h}.

E	$C_2(b)$	$\sigma(ac)$	i
I ↔ I, etc.	I ↔ II	I ↔ III	I ↔ IV
	III ↔ IV	II ↔ IV	II ↔ III

We now follow the procedure of Craig and Hobbins.[12] Unit-cell wave functions, ξ, which are defined in terms of simple product wave-functions, ϕ, are chosen. The functions ϕ correspond to individual excitation of the four molecules of the unit cell. We shall take linear combinations of the functions ϕ; the combinations must transform as irreducible representations of the unit-cell group. Denoting the combination functions by the subscripts, α, β, γ, and δ, then for the fth excited state,

$$\begin{aligned}\xi^f_\alpha &= \tfrac{1}{2}(\phi^f_{\text{I}} + \phi^f_{\text{II}} + \phi^f_{\text{III}} + \phi^f_{\text{IV}});\\ \xi^f_\beta &= \tfrac{1}{2}(\phi^f_{\text{I}} + \phi^f_{\text{II}} - \phi^f_{\text{III}} - \phi^f_{\text{IV}});\\ \xi^f_\gamma &= \tfrac{1}{2}(\phi^f_{\text{I}} - \phi^f_{\text{II}} - \phi^f_{\text{III}} + \phi^f_{\text{IV}});\\ \xi^f_\delta &= \tfrac{1}{2}(\phi^f_{\text{I}} - \phi^f_{\text{II}} + \phi^f_{\text{III}} - \phi^f_{\text{IV}}). \qquad (1)\end{aligned}$$

Wave-functions which have the symmetry of the three-dimensional space group must now be chosen. These will be functions of the type (1) multiplied by exp $(2\pi i\boldsymbol{K}.\boldsymbol{r})$, where $\boldsymbol{K}$ is the wave vector and $\boldsymbol{r}$ is a lattice translation vector. Crystal wave functions will be

$$\Phi^f_{\alpha,\beta,\gamma,\delta}\,(K_a,K_b,K_c) = \frac{2}{N^{\frac{1}{2}}} \sum_{\lambda_1,\lambda_2,\lambda_3} \exp\,[2\pi i(\lambda_1 aK_a + \lambda_2 bK_b + \lambda_3 cK_c)]\xi^f_{\alpha,\beta,\gamma,\delta} \quad . \quad (2)$$

λ_1, λ_2, λ_3 number the unit cells, which total $N/4$.

The crystal excitation energies for $K_a = K_b = K_c = 0$ are, to first-order approximation,

$$\Delta E^f_{\alpha,\beta,\gamma,\delta} = \Delta w^f + D + \sum_p I^{ff}_{kp} + \left(\begin{smallmatrix}+\\+\end{smallmatrix}\sum_q I^{ff}_{kq} \begin{smallmatrix}+\\ \\+\end{smallmatrix}\sum_r I^{ff}_{kr} \begin{smallmatrix}\pm\\\mp\end{smallmatrix}\sum_s I^{ff}_{ks}\right). \quad . \quad . \quad (3)$$

Δw^f is the energy of the corresponding transition in the isolated molecule. D is the energy of displacement upon going from the vapour to crystal (see ref. 12). The remaining terms are intermolecular resonance integrals. p runs over all molecules equivalent to the kth molecule I; q, r, and s run over molecular types II, III, and IV, respectively. α, β, γ, and δ refer to the last three terms in equation (3); α denotes the set shown on the top line in equation (3); β, the next line, etc.

We must now correlate the symmetry of the molecular states with that of the crystal energy states defined in (3). This may be effected from the unit-cell character table and the table of group $\mathscr{C}_{2v}$. In Table 2, a correlation is made between the symmetry of molecular wave-functions and that of unit-cell functions.

Table 2 shows that each molecular energy level will be split in the crystal into four

TABLE 2.

Correlation between molecular wave-function symmetry and unit-cell function symmetry.

$\mathscr{C}_{2v}$ Molecular wave function symmetry	C_{2h} Unit-cell function and symmetry			
	α	β	γ	δ
A_1	A_g	A_u	B_g	B_u
A_2	B_g	B_u	A_g	A_u
B_1	A_u	A_g	B_u	B_g
B_2	B_u	B_g	A_u	A_g

seperate levels. Dipole transitions to two of these states, A_u and B_u, will be allowed by symmetry. Only those molecular transitions having a non-vanishing transition moment will be allowed and these will be for $\pi \rightarrow \pi^*$ transitions,

$$A_1 \leftarrow A_1, \text{ polarised } \perp \text{ N–N line;}$$
$$B_2 \leftarrow A_1, \text{ polarised } \parallel \text{ N–N line.}$$

The transition $B_1 \leftarrow A_1$ is also allowed on grounds of symmetry but will be polarised perpendicularly to the ring plane. It would be allowed for $n \rightarrow \pi^*$ transitions. The summations in (3) were calculated by means of the Ewald–Kornfeld method,[18] and crystal energy levels and their polarisations thus obtained are shown in Table 3 for allowed molecular transitions.

TABLE 3.

Energy levels in cm.$^{-1}$ Å^{-2} to first-order in 2-amino-4-chloro-6-methylpyrimidine.

Molecular transition	ΔE_α	ΔE_β	ΔE_γ	ΔE_δ
$A_1 \leftarrow A_1$ ($\perp$ N–N line)	378	376 ($A_u : \parallel b$)	1036	1118 ($B_u : \perp b$)
$B_2 \leftarrow A_1$ ($\parallel$ N–N line)	−1459 ($B_u : \perp b$)	1653	3807 ($A_u : \parallel b$)	−733
$B_1 \leftarrow A_1$ ($\perp$ Ring plane)	2377 ($A_u : \parallel b$)	2361	3135 ($B_u : \perp b$)	3155

TABLE 4.

First-order splittings in 2-amino-4-chloro-6-methylpyrimidine.

	Molecular transition	
	$A_1 \leftarrow A_1$	$B_2 \leftarrow A_1$
$[\Delta E(A_u) - \Delta E(B_u)]/M^2$ (cm.$^{-1}$ Å^{-2})	−742	5266
$[\Delta E(A_u) - \Delta E(B_u)]$ (cm.$^{-1}$)	−160	1140
Experimental splitting (cm.$^{-1}$)	3000	

Splittings between the oppositely polarised components, $[\Delta E(A_u) - \Delta E(B_u)]$, were calculated for the energy levels of Table 3 and are given in Table 4.

DISCUSSION

If we accept the conventional assignment [19,20] of benzene states, these will be successively, A_{1g}, B_{2u}, B_{1u}, E_{1u}, E_{2g}. In pyrimidines of $\mathscr{C}_{2v}$ symmetry, system II, derived from the benzene B_{2u} state, should correspond to the allowed $B_2 \leftarrow A_1$ transition. If the benzene B_{1u} state is accepted, system III of pyrimidines would be assigned to the allowed $A_1 \leftarrow A_1$ transition. Should the states E_{2g} and B_{1u} be interchanged,[21,22] the former state would become split into A_1 and B_2 components in pyrimidine. The calculated splitting between these levels is quite small [23] and mixing would be expected. If the upper state of III were solely B_2, then B_{1u} could not be a possible assignment for the 2000 Å system of benzene.

Rotational analyses [4,24] have confirmed unambiguously that transition I of azines is definitely an $n \rightarrow \pi^*$ transition polarised perpendicular to the plane of the molecule. Thus system I of pyrimidines can be assigned with certainty to the allowed $B_1 \leftarrow A_1$ transition. By means of the first-order weak coupling theory we are also able to make an unambiguous assignment of system II in 2-amino-4-chloro-6-methylpyrimidine. First-order calculations for the crystal lead to a splitting of 1140 cm.$^{-1}$ between components with the $\parallel b$ at the higher energy for the $B_2 \leftarrow A_1$ transition. The experimental splitting of 3000 cm.$^{-1}$ is in

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[18] Fox and Yatsiv, *Phys. Rev.*, 1957, **108**, 938.
[19] Goodman and Shull, *J. Chem. Phys.*, 1957, **27**, 1388.
[20] El-Sayed, *J. Chem. Phys.*, 1962, **36**, 553.
[21] Parr, Craig, and Ross, *J. Chem. Phys.*, 1950, **18**, 1561.
[22] Dunn and Ingold, *Nature*, 1955, **176**, 65.
[23] McWeeny, *Proc. Phys. Soc.*, 1957, **70***A*, 593.
[24] Mason, *J.*, 1959, 1269.

the same sense and is in semi-quantitative agreement with theory. Crystals of this compound exhibit hydrogen bonding.[14] Neglect of possible changes in hydrogen bond energies as a consequence of dipole transitions may lead to quantitative discrepancies between theoretical and experimental splittings. An $A_1 \leftarrow A_1$ assignment is unacceptable, since a splitting of -160 cm.$^{-1}$ would be expected.

Large splittings between oppositely polarised components are not altogether unexpected for crystals of pyrimidines. A splitting of about 2300 cm.$^{-1}$ has been observed for system II in crystals of 2-aminopyrimidine.[25] Although the crystal structure of this substance is unknown, it seems probable that the lowest-energy transition in 2-aminopyrimidine is also $B_2 \leftarrow A_1$.

Lyons[8] showed that system III of 2-chloro-4,6-dimethylpyrimidine was polarised differently from II. On this basis, system III should be assigned to the allowed $A_1 \leftarrow A_1$ transition.

Thus, from a comparison of experimental studies of pyrimidines, the order of energy levels in pyrimidine itself is predicted to be, with increasing energy, A_1 (ground state), B_1, B_2, A_1 in the recommended notation.[16]

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[25] Bree and Lyons, unpublished work.