ular H-bonds, formed apparently in preference to possible much stronger intermolecular bonds. One answer to this question is, of course, contained in the comparison of the entropy changes associated with the formation of the two types of H-bonds.

There seems to be a further reason, however, in steric effects. Consider the H-bonded form of *o*-chlorophenol. There is no reason to believe that both the O atom and the Cl atom could not serve as electron donors for H-bonds with as many as two solvent molecules each (the H-bond O-H—Cl is probably so weak that, at equilibrium, not many molecules would be that highly solvated). In the non-bonded form, sufficient electron pairs are available so that the molecule could act as donor for five, and as acceptor for one further H-bond. For steric reasons such an extensive solvation of the substituted region of the molecule seems out of the question; it appears quite likely that steric hindrance would prevent solvation beyond four solvent molecules in this region, and thus leave both the H-bonded and the non-bonded forms approximately equally solvated. Hence the intramolecular H-bonding provides additional energy over the solvation.

Acknowledgment.—The author is indebted to Dr. Robert J. Good for several interesting discussions concerned with this work.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Polarized Electronic Absorption Spectrum of Amides with Assignments of Transitions[1]

BY DON L. PETERSON[2] AND WILLIAM T. SIMPSON

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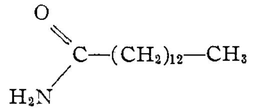
The polarized electronic spectrum of myristamide is obtained to 1600 Å. It is analyzed into n-π; NV_1; Rydberg (2p, 3s) and NV_2 transitions. Emphasis is on obtaining and interpreting the NV_1 transition moment direction.

Introduction

In this investigation the polarized electronic spectrum of myristamide



in the region between 2300 and 1600 Å. was obtained. Starting from the long wave length end there are characterized n-π and NV_1 transitions, a first member of a Rydberg series, and part of the NV_2 transition.

The main result of the paper is considered to be the determination of the direction of polarization of the NV_1 transition, appearing at 1850 Å. In the work on myristamide this direction could not be determined uniquely owing to unfavorable crystal symmetry.[3] Two possible orientations were obtained: one inclined away from the nitrogen–oxygen axis 9.1°, toward the carbon–nitrogen axis; and the other 26.7°, toward the carbon–oxygen axis.[4]

Several methods were employed in an attempt to select the correct direction. The work of Ward on N-acetylglycine was considered first.[5] In addition, an attempt was made to use the results of a π-electron calculation with full configurational interaction in the framework of the ASMO method. During the final stages of this research the crystal structure of N,N′-diacetylhexamethylenediamine was found reported in the literature.[6] This substance has only one molecule per unit cell, a circumstance which made it possible unambiguously to determine the correct polarization direction The 9.1° value proves to be the correct one, which, gratifyingly was the value selected by the theoretical calculation, and also turns out to be allowed by Ward's experiments.[7]

The theoretical work in this paper is based on calculations described in a collateral paper on the allyl system, particularly allyl anion.[8] Much of the interpretation of the experiments depends on results described in a paper on the nature of resonance force transfer of excitation energy in molecular crystals.[9] Use will also be made of earlier research in which the spectrum of amides in the gas phase down to *ca.* 1300 Å. has been recorded.[10]

I. Experimental

The instrument used in these studies is the same as described elsewhere[11] except for a sliding vane valve situated between the slit compartment and tank.[12]

The calculation of the optical densities of the sample at the various wave lengths was complicated by the fact that there was marked reciprocity failure. Time sensitometry, using numbers of flashes as abscissas, gave characteristic curves which had the usual straight line portion, but with a definite decrease in slope when the intensity was reduced. It was found possible, after a certain amount of trial and error, to assign every density, D, at a given number of flashes, n, an effective gamma determined empirically,

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[1] This research was supported in part by The Air Research and Development Command under Contract No. AF 18(600)-375.

[2] National Science Foundation Predoctoral Fellow, 1954–1955.

[3] The crystal structure was determined by J. D. Turner and E. C. Lingafelter, *Acta Cryst.*, **8**, 549 (1955), and refined by R. F. Adamsky and E. C. Lingafelter, private communication.

[4] These possibilities were briefly reported in a Communication to the Editor, D. L. Peterson and W. T. Simpson, THIS JOURNAL, **77**, 3929 (1955).

[5] J. C. Ward, *Proc. Roy. Soc.* (*London*), **A228**, 205 (1955).

[6] M. Bailey, *Acta Cryst.*, **8**, 575 (1955).

[7] Our first interpretation of Ward's results, given in ref. 4, proved to be incorrect.

[8] H. D. Hunt, D. L. Peterson and W. T. Simpson, *J. Chem. Phys.*, in press.

[9] W. T. Simpson and D. L. Peterson, *ibid.*, in press.

[10] H. D. Hunt and W. T. Simpson, THIS JOURNAL, **75**, 4540 (1953).

[11] R. C. Nelson and W. T. Simpson, *J. Chem. Phys.*, **23**, 1146 (1955).

[12] D. L. Peterson, Thesis, University of Washington, 1956.

$\gamma(D,n)$;[12] whereupon all optical densities expressing absorptivity were determined from the difference, referring to blank, B, and sample, S

$$\frac{D_B}{\gamma_B(D,n)} - \frac{D_S}{\gamma_S(D,n)}$$

Before using this procedure spectra of thick crystals had apparently different shapes than for thin crystals, though with the correction the expected Beer–Lambert behavior was found. The uncertainty in the empirically determined γ's imposes an estimated 5% error in optical densities.

Measurements on Myristamide.—Purified myristamide was obtained from Dr. J. D. Turner.[8] Single crystals were grown by sublimation in shallow, covered petri dishes. Suitable crystals had well developed 001 faces and displayed uniform interference colors in reflected light. The thinnest crystals were colored steel-grey in crossed polaroids.

In preparing a sample for an exposure a crystal was mounted between optically flat, fused quartz cover slips held under slight pressure. The orientation of the crystal was determined either by observation of edges or by location of extinctions under a polarizing microscope. The *a*- and *b*-axes were distinguished by a cleavage running parallel to *b*, and this was confirmed by a zero level X-ray precession photograph of the mounted crystal.[13]

A mounted crystal was placed in the spectrograph with its *a*- and *b*-axes aligned with the polarization directions of the Wollaston prism. An exposure consisted of between 50 and 200 12-kilovolt discharges through a Lyman tube. Each exposure was accompanied on the same plate (to minimize errors due to irregularities in the fluorescent overlay on the plates) by a blank exposure taken under identical conditions including exposure duration, discharge voltage and capillary diameter.

The *a*- and *b*-polarized myristamide spectra below 2100 Å. (Fig. 1) are the averages of separate spectra taken with three crystals of varying thickness. The thicknesses were estimated by converting to an expected vapor spectrum and comparing with that observed for dimethylformamide. They were found to range from 0.3 to 0.5 micron. Above 2100 Å. each spectrum is a composite of spectra for four crystals with estimated thicknesses ranging from 2 to 50 μ. The curves as obtained directly from the spectrograms appeared similar to the wavy curve of Fig. 4 and with this exception have all been smoothed.

The absorption curves for light polarized along the *a*- and *b*-axes are given in Fig. 1. The broken portions signify uncertainty: in the region of the maximum of the D_a curve because the crystals were all too thick for the absorption to occur near the usable portion of the plate characteristic, even for exposures of many flashes; and in the region below 1630 Å. mainly because of anticipated trouble from reflection from the interfaces in the holder assembly. The curves above 2100 Å. are magnified tenfold.

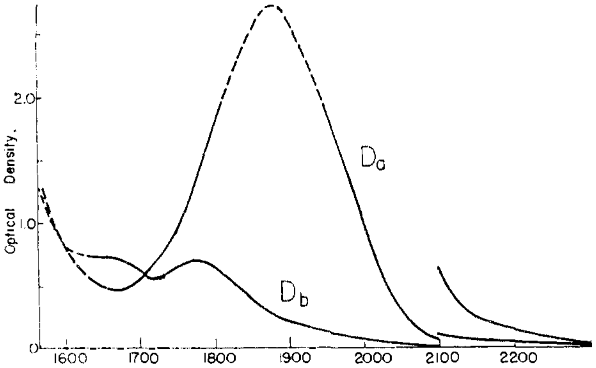

Fig. 1.—Polarized spectra of myristamide. Broken lines denote uncertainty. The curves above 2100 Å. are magnified tenfold.

In Fig. 2 the function log D_a/D_b is plotted against the same abscissa as in Fig. 1 (heavy curve). The expected vapor absorption is also included. It was obtained by introducing artificial random orientation trigonometrically.

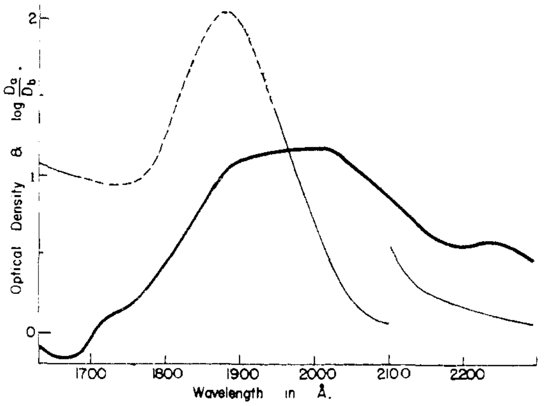

Fig. 2.—Variation of log D_a/D_b with wave length (heavy curve) and predicted vapor spectrum with region of greatest uncertainty distinguished by a broken curve. The spectrum is magnified tenfold above 2100 Å.

Measurements on N,N′-Diacetylhexamethylenediamine.—The compound was prepared by acetylation[14] of Distillation Products Inc. commercial grade (72%) hexamethylenediamine which was first purified by fractional crystallization. The product was recrystallized from 95% ethanol. In preparing specimens a thin layer of pulverized crystals was enclosed between fused quartz cover slips previously conditioned by immersion in 12 *N* NaOH. Crystallization occurred through controlled cooling of the melt.[15] The crystals so obtained were shown to have their (100) faces in contact with the cover slip surfaces by the identification of the angle "a" in crystal faces parallel to these surfaces.[6] The orientation was found by observation of extinction directions under the polarizing microscope. The extinction direction, *X*, corresponding to the larger refractive index for visible light, was found to be at an angle of 19 ± 2° with the *c*-axis (see Fig. 3). All the molecules are oriented the same way in this material, so that the principal directions are determined by the amide transition moment directly, in the 1900 Å. region.

Only seldom were sufficiently large monocrystalline sections found. The absorption measurements were made on two such sections, the area and thickness of which were estimated to be about 1 mm.^{2} and 0.1 μ. Spectra were recorded for various orientations of the crystals in light polarized in each of the two fixed perpendicular directions of the Wollaston prism. When the orientation was such that the polarization direction of one component of the light was approximately aligned with the projected transition moment direction in the 100 plane, $\overrightarrow{m'}$, complete absorption set in below 2100 Å. The crystal may then be regarded as a piece of Polaroid. The angle which $\overrightarrow{m'}$ makes with the polarization direction of the other of the two beams could then be obtained easily. Measured from the *X* direction the resulting angle is 5 ± 3° (Fig. 3).

Effect of Varying Polarization of Incident Light.—Crystal spectra must be understood as involving absorption of energy out of two independent beams along the principal directions, or, equivalently, as requiring that the light be represented as a statistical ensemble having parts polarized along the two principal directions. The weights of the two streams of photons, oppositely polarized, are given by the cosine squared law. It is believed that this phenomenon is an example of a disturbance due to the possibility of there having been a "measurement" (absorption of a photon by a crystal oscillator) thus leading to the reduction of the wave function of the light. This point has been considered in

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[13] The authors gratefully acknowledge the help of Dr. J. R. Brathovde, Dr. J. D. Brazeale and Professor E. C. Lingafelter in matters having to do with the crystallography.

[14] T. Curtius and H. Clemm, *J. prakt. Chem.*, **62**, 189 (1900).

[15] The apparatus for controlled cooling was constructed by Mr. E. E. Barnes of this Laboratory.

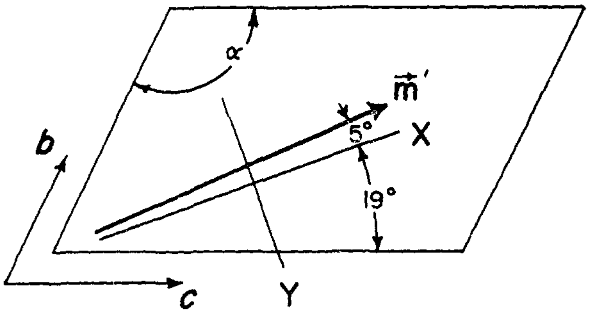

Fig. 3.—The 100 face of the N,N′-diacetylhexamethylenediamine unit cell showing the orientation of the extinction direction, X, and transition moment, m'.

previous work[11,16] and receives a practical verification from the curves in Fig. 4. The dashed curve is obtained by concluding that since the light is polarized in incidence with an angle of 45° to one of the principal directions, it exists with the same polarization inside the crystal. For this situation we project the crystal absorbers onto the electric vector of the light. The D_a and D_b curves from Fig. 1 are thus projected onto this polarization direction, giving for log I/I_0 the average

$$\cos^2 45°\, D_a + \sin^2 45°\, D_b$$

The solid curve is obtained by assuming the polarization of half the beam to be along the a-axis and, in this connection, by using the D_a data from Fig. 1. This gives an intensity I_a' emerging with polarization along the a direction according to

$$\log \frac{I_a'}{I_0/2} = D_a$$

or

$$I_a' = \frac{I_0}{2}\, 10^{Da}$$

Similarly the intensity emerging in the b direction is given by

$$I_b' = \frac{I_0}{2}\, 10^{Db}$$

whence the total intensity emerging is the sum

$$I = \frac{I_0}{2}\,(10^{Da} + 10^{Db})$$

from which the solid curve is calculated as log I/I_0. The spectrum actually obtained with the light polarized at 45° to the principal directions is the wavy curve, in agreement with the solid curve.

II. The NV$_1$ Transition

Looking at Figs. 1 and 2 we can see a region from 2050 to 1700 Å. where the absorption is strong, though not with a constant D_a/D_b ratio. This region is interpreted as the crystal absorption associated with the NV$_1$ electronic band of an isolated myristamide molecule, *e.g.*, as found in the gas phase at low pressures.

It is believed that the long wave length shoulder consists of *vibronic* transitions only weakly split by the resonance force interaction in the myristamide crystal (a situation described as weak coupling). In this region the D_a and D_b curves should be proportional, at low resolution. The ordinates would not be equal because the projection of the transition moment of a typical molecule is unequal on the two principal directions.

When the electronic band half-width, $2V$, for an ideal non-vibrating crystal much exceeds the half-width of the absorption band for isolated molecules, Δ, a situation called strong coupling is expected.[9] In this case the D_a and D_b curves would lose their resemblance to one another and to the gas phase spectrum. The separation of the peaks of the two curves would give the crystal splitting of the entire *electronic* transition, just as if vibrations could be disregarded. The separation in Fig. 1 is considered to be an example of this effect though the ratio $2V/\Delta$ is a little less than unity (0.6, see below). It is thought that the middle of the band must be treated as involving strong coupling, even though the wings of the band show weak coupling.

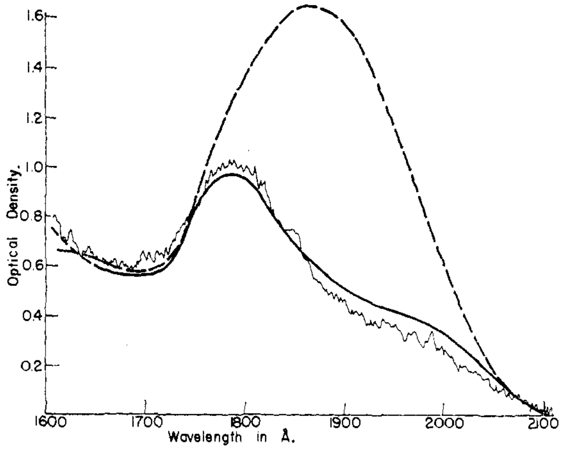

Fig. 4.—Erroneously (broken curve) and properly (heavy curve) calculated myristamide crystal spectrum for light polarized at 45° with the a-axis. The wavy curve is observed.

Crystal Spectrum with Strong Coupling.—For strong coupling we assume that the nuclei are fixed and calculate the allowed resonance force spectrum[17] based on the absorption for a single molecule. This requires a knowledge of the strength and direction of the total electronic transition moment. Before the ambiguity about the direction of the NV$_1$ transition moment was resolved, it was considered that the calculation might aid in the determination, so calculations for all plausible directions were carried out.

Looking at the 001 face of myristamide there will be allowed crystal transitions along the a and b crystallographic axes. Thus only two excited state crystal wave functions need be considered, where the phases for single molecule transitions are picked to reinforce along the respective directions. The upper state functions for a crystal of n molecules are of the form

$$\frac{1}{\sqrt{n}} \sum_{i=1}^{n} \psi_1\psi_1 \ldots \psi_i{}^{\dagger} \ldots \psi_n$$

where the dagger signifies that the ith molecule is in the V_1 state and the coefficients are approximated as all equal in absolute value (infinite wave length of the light). The expectation value of the interaction operator for an infinite crystal reduces to

$$\int (\psi_1\psi_2 \ldots \psi_i{}^{\dagger} \ldots \psi_n)^* H_{\text{int}} \sum_{j=1}^{n} \psi_1\psi_2 \ldots \psi_j{}^{\dagger} \ldots \psi_n d\tau$$

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(16) A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **23**, 1480 (**1955**).

(17) A. S. Davydov, *J. Exptl. Theoret. Phys.* (*U.S.S.R.*), **18**, 210 (**1948**).

Using the dipole approximation for the interaction, the calculation thus involves summing over all neighbors, j, of the ith molecule terms of the form

$$f_{ij}\frac{|\vec{m}|^2}{R^3}$$

where f_{ij} is a trigonometric factor, $\vec{m}$ is a single molecule transition moment, and R is the intermolecular distance. The trigonometric factors can be systematized using the symmetry of the unit cell, which was done.[12] The calculation was carried out for all neighbors within 10 Å. of a given molecule, and the splitting of a-axis and b-axis absorptions was found to vary from 1 to 1.5 e.v. for every Å.^{2} in the expression involving the transition moment squared, with the a-axis part always to the red.

With the transition moment direction 9.1° away from the oxygen–nitrogen line (the value finally found experimentally) and assuming that the transition moment squared is given by[10]

$$|\vec{m}|^2/e^2 = 0.44 \text{ Å.}^2$$

the a-axis absorption is calculated to lie toward the red of the single molecule absorption at 0.11 e.v., while the b-axis absorption should lie to the blue a distance of 0.53 e.v. The calculated splitting is thus 0.64 e.v. or 5.2×10^3 cm.$^{-1}$, with the a-axis part to the red. It is believed that the calculated value is in reasonable agreement with the experimental value (estimated as 0.4 e.v.) when it is considered that the position of the peak of the a-axis absorption is uncertain, and that not all of the single-molecule intensity contributes to the observed crystal splitting, owing to the intervention of the single-molecule vibrations spoiling the resonance.[9]

It has been suggested[9] that the electronic band width parameter for a crystal should be calculated as for a dimer with its molecules disposed according to the strongest interaction in the actual crystal. With the 9.1° angle for the transition moment this calculation leads to

$$2V = 0.4 \text{ e.v.}$$

The single-molecule band width, which is also needed to give the fraction $2V/\Delta$ which determines the nature of the coupling, was taken to be 0.7 e.v.[10] It is the ratio 0.4/0.7 which was used above in this connection.

Direction of the Transition Moment.—Let us consider once again that all the nuclei in the crystal are fixed. The transition moment along either principal direction (provisionally, the a and b crystallographic axes) is then calculated to be a sum of individual molecular moments projected on that direction

$$\frac{1}{\sqrt{n}}\sum_{i=1}^{n}\vec{m}_i\cdot\vec{a}$$

($\vec{a}$ and $\vec{b}$ are unit vectors along the principal directions). Owing to the molecular arrangement in the unit cell, all the terms are the same for an allowed transition in myristamide, so the intensity for strong coupling is given by

$$n|\vec{m}\cdot\vec{a}|^2$$

along the a-direction, and

$$n|\vec{m}\cdot\vec{b}|^2$$

along the b-direction.

It can be shown that the integrated intensity of an electronic band consisting of vibronic transitions is essentially equal to the intensity calculated with the assumption of a pure electronic transition, as above,[18] and this should be true for a crystal as well as for a molecule.

This gives us the result that whether we have strong or weak coupling, we can arrive at the orientation of the transition moment through the ratio of areas of the curves. If there is borrowing, or if the region where one band stops and another starts is ill-defined, this ratio of areas is very likely not going to give an accurate value for the direction. The situation is improved, however, by the fact that with weak coupling the D_a and D_b curves should be proportional in low resolution, so that we have the result

$$\frac{\int D_a d\lambda}{\int D_b d\lambda} = \frac{D_a}{D_b}$$

where the "dichroic ratio" D_a/D_b is independent of wave length. The situation encountered in the case of myristamide is intermediate, but it can be seen that there is a wide region on the long wave length side of the absorption where D_a/D_b is constant, at *ca.* 14.6 (see Figs. 1 and 2, particularly from 2020 to 1890). This region is considered to be the weak coupling part of the NV_1 band (see Fig. 2d of ref. 9). The dichroic ratio for the region gives two possible directions for the orientation of the moment with respect to the amide group: 9.1 and 26.7° with the N–O line, toward the C–N and C–O lines, respectively.[19]

The ambiguity in the work on myristamide has been resolved using the measurements on N,N′-diacetylhexamethylenediamine, and with a new interpretation of the work on N-acetylglycine.[5] In the former compound the direction of $\vec{m}'$ (Fig. 3) is equivalent to a transition moment direction 18 ± 5° away from the N–O line toward the C–N line. This selects the 9.1° value for myristamide.

Unexpectedly, confirmation is provided by working up the results on N-acetylglycine paying attention to the fact that, as with myristamide, there are two values for the polarization, one extraneous. The dichroic ratio was found by Ward to be $D_c/D_b = 20$ to 60 at 2100 Å. for the 100 face,[5] which gives as the correct one of the two possibilities the angle 15° from the N–O line toward the N–C line.

The various angles are all given in Fig. 5, together with arcs indicating estimated experimental uncertainties. It will be noted that the angle for myristamide is more nearly along the N–O line, perhaps outside of experimental uncertainty. (The directions for amides in different environments might well be somewhat different.)

Theoretical Significance of the Polarization.—We take as a starting point a representation of the NV_1 transition for the formate ion, using struc-

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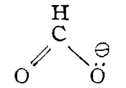
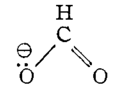
[18] H. Sponer and E. Teller, *Revs. Mod. Phys.*, **13**, 75 (1941).

[19] Explanation of the trigonometric formalism used will be deferred to Part III.

tures. The two states, N and V_1, may be depicted as involving wave functions corresponding to


(1)

and


(2)

with the normal state represented as

$$\psi_N = 2^{-1/2}\,(\psi^1 + \psi^2)$$

and the first excited state as[8]

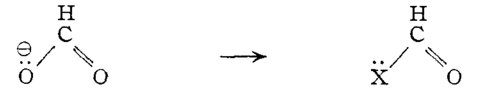
$$\psi_{V_1} = 2^{-1/2}\,(\psi^1 - \psi^2)$$

(Superscripts refer to structures.) The transition moment is

$$e\int\psi_N\vec{q}\,\psi_{V_1}d\tau = \frac{e}{2}\left[\int\psi^1\vec{q}\,\psi^1d\tau - \int\psi^2\vec{q}\,\psi^2d\tau\right]$$

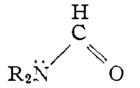
which is just one-half the difference in moments of the structures. This difference is a vector along the O–O line with the length (factor) predicted to be equal to the O–O distance.[20] The transition moment length thus is estimated to be of the order of 1.1 Å., while the value found is *ca.* 0.7 Å.[10]

If the electronegativity of one of the oxygen atoms could be successively increased we should have a *series* of compounds going through the acid all the way, say, to the acid halide, and beyond.



At the furthest extreme the NV_1 transition would be the same as the NV_1 transition for a carbonyl group and so would be polarized along the C–O line. Amides are in or just outside the series, the nitrogen having comparable electronegativity to that of an oxygen with a formal negative charge. It might be expected that the transition moment direction would change monotonically from the O–O to C–O lines in such a series, so that the direction of the moment could be used very simply to characterize the various members.

It is certainly a matter of interest to locate amides in the series. In fact this may be taken as the central question concerning the electronic structure of amides. The question is very closely related to the one regarding the relative contributions to the ground state of the two structures



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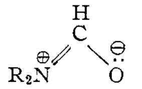


It can be partially answered through consideration of the dipole moment,[21] infrared intensity,[22] carbonyl force constant,[23] and even the position of the n-π band.[24] It is felt that one of the best approaches is through the Brooker deviation. Brooker in his work on the merocyanine dyes has been able to show convincingly that for vinylogous amides the energy of the charged and uncharged structures must be nearly equal; for some dyes he has found conditions under which true equality of energy may be demonstrated.[25] The Brooker deviation of a very simple vinylogous amide

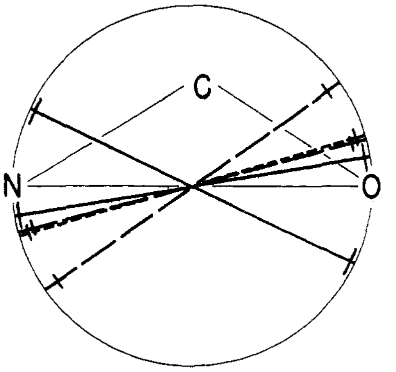


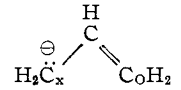
Fig. 5.—The two possible orientations of the NV_1 transition moment for myristamide (solid lines) and N-acetylglycine (broken lines), and the single orientation for N,N′-diacetylhexamethylenediamine (dashed line) as referred to the plane of the amide group. Uncertainties are indicated by the lengths of arcs through the lines.

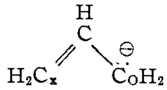
$$Me_2\ddot{N}—CH{=}CH—CH{=}CH—CH{=}O$$

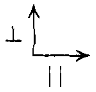
has been found to be zero in water, and the color shifts monotonically toward the blue as methanol is added. In pure methanol the deviation is 40 mμ.[26] This positive or normal deviation means that the uncharged structure is the more stable, even in the relatively polar water–methanol environment. That the same conclusion may apply to the amides themselves is easy to imagine, and is borne out by considering the question in detail.

If we now look at the experimental values of the polarizations (Fig. 5) we see that the direction is toward the N–C line, which is surprising considering our expectation for the series. Thus either the amides in their crystalline environment are outside the series, or else the theoretical polarization direction for the series does not vary monotonically between the O–O and the C–O lines. The second alternative is favored by much evidence, including the following calculation.

Theoretical Calculation of the Polarization.—In view of the discussion in the last section, short of having the wave functions for amides themselves, it would be desirable to have good functions for formate ion and apply perturbation theory. We had obtained, in another connection, a set of state wave functions after configurational for allyl anion[8]







We shall use these wave functions as a substitute for the formate functions to represent the start of the series. (The subscripts x and o will be used below to distinguish positions affected differently by a particular perturbation.) The first singlet-singlet transition, NV_1, for the allyl anion is polarized along a line joining the terminal carbons (||) and the

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(20) W. H. Zachariasen, *Phys. Rev.*, **53**, 917 (1938).

(21) For a recent discussion see A. Kotera, S. Shibata and K. Sone, THIS JOURNAL, **77**, 6183 (1956).

(22) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

(23) C. G. Cannon, *Mikrochim. Acta*, **2–3**, 555 (1955); *J. Chem. Phys.*, **24**, 491 (1956); and H. Letaw, Jr., and A. H. Gropp, *ibid.*, **21**, 1621 (1953).

(24) S. Nagakura, *Bull. Chem. Soc. Japan*, **25**, 164 (1952).

(25) See the series of articles in THIS JOURNAL, beginning with **73**, 5326 (1951).

(26) W. T. Simpson, unpublished research.

second, NV_2, is perpendicular to this line (⊥). The next higher V states are, according to calculation, not close at all to the V_2 state.[8] There is a Rydberg transition to a state found experimentally to be fairly close to the V_2 state (see Part III) but quite weakly absorbing. It is considered that the magnitude of the rotation of the NV_1 transition moment under an infinitesimal perturbation should thus depend mainly on mixing with the V_2 state. It follows that the sense of the rotation would be given correctly by a calculation involving wave functions for just the N and the first two V states. Moreover, even though the π-electron wave functions are not accurate in any fundamental way, they are known empirically to represent positions and intensities of π-electron transitions quite well provided that configurational interaction has been introduced. Perhaps it is not being unrealistic, therefore, to expect the calculation here to provide the correct sense of the rotation. Probably the greatest uncertainty stems from using allyl anion functions for formate ion functions.

What was done was to obtain the abbreviated first-order perturbed wave functions

$$\psi_N = \psi_N{}^0 - \frac{H'_{NV_1}}{W_{V_1} - W_N}\,\psi_{V_1}{}^0 - \frac{H'_{NV_2}}{W_{V_2} - W_N}\psi_{V_2}{}^0$$

$$\psi_{V_1} = \psi_{V_1}{}^0 - \frac{H'_{V_2V_1}}{W_{V_2} - W_{V_1}}\,\psi_{V_2}{}^0 - \frac{H'_{NV_1}}{W_N - W_{V_1}}\,\psi_N{}^0$$

under a perturbation at one of the terminal carbons (labeled C_x, referring to the allyl anion structures above) such that the Coulomb integral for that carbon decreases infinitesimally. This change represents the first increase in electronegativity of x as the series develops, away from formate ion. The functions are found to be

$$\psi_N - \psi_N{}^0 - 0.0903\epsilon\psi_{V_1}{}^0 - 0.0318\epsilon\psi_{V_2}{}^0$$

$$\psi_{V_1} = \psi_{V_1}{}^0 + 0.0903\epsilon\psi_N{}^0 - 0.1303\epsilon\psi_{V_2}{}^0$$

where for atom C_x

$$\int(2p)H'(2p)d\tau = \epsilon < 0$$

The various state moments and transition moments for the unperturbed state functions have to be evaluated paying careful attention to consistency in the selection of phases. They are given in Table I. The NV_1 transition moment after the perturbation is a function of these moments and the mixing coefficients. To the first order in ϵ, the direction of $\vec{m}$ is $0.0605\ \epsilon\,\vec{j} + (-1.2994 + 0.0145\ \epsilon)\,\vec{i}$. The $\vec{i}$ vector is parallel (||) and the $\vec{j}$ vector perpendicular (⊥), with senses as given above in connection with the structures for allyl anion. With $\epsilon < 0$ this gives a twisting away from the parallel direction toward the bond connecting C_x with the center carbon, as found experimentally. Similarly, the NV_2 transition moment is found to twist from ⊥ toward the $C–C_0$ line.

TABLE I

THEORETICAL ELECTRIC MOMENT LENGTHS FOR ALLYL ANION IN Å.

	N	V_1	V_2	NV_1	NV_2	V_1V_2
||	0	0	0	−1.2994	0	−0.4362
⊥	0.8161	0.7418	1.0439	0	−0.4127	0

We may conclude that notwithstanding the observed NV_1 polarizations, amides can still be in the series, with the nitrogen being effectively more electronegative than the oxide ion of formate ion. The polarizations found in this research are a long way from lying along the C–O axis of the carbonyl group, a fact which is in harmony with the customary qualitative understanding of amides in organic chemistry.

III. Absorptions at 2200 and 1660 Å.

Returning again to the consideration of Figs. 1 and 2 we find from the behavior of the polarization that the long wave length tail of the NV_1 absorption may be interpreted as containing a separate electronic transition, which is assigned as n-π[10,27] and called the 2200 Å. band. The region around 1660 Å. is qualitatively different from the NV_1 part and is believed to be the first member of the Rydberg series previously found.[10] It is tentatively assigned as involving a jump of a non-bonding 2p electron on the oxygen to an orbital which is an in-phase linear combination of 3s atomic orbitals. There is a polarization change below 1600, which, however, is in a region where the experimental error is likely to be great. There is an NV_2 transition expected on quite general theoretical grounds in this region, so the tentative assignment of the absorption below 1600 as NV_2 is made. The most important conclusion with regard to the high energy absorption is that the 1660 Å. band is not NV_2.

In this third part the n-π and Rydberg transitions will each be discussed, though first it is convenient to introduce a somewhat formal trigonometric theory connecting the crystal-fixed and molecule-fixed polarization directions.

Trigonometric Analysis of the Dichroic Ratio.—With the assumption of weak coupling one has the following relationships connecting absorption densities along molecule-fixed (x,y,z) and crystal-fixed (**a**,**b**,**c**) axes.[16]

$$\begin{pmatrix} D_x \\ D_y \\ D_z \end{pmatrix} = \mathbf{M}\begin{pmatrix} D_a \\ D_b \\ D_c \end{pmatrix} \text{ or } \begin{pmatrix} D_a \\ D_b \\ D_c \end{pmatrix} = \mathbf{M}^{-1}\begin{pmatrix} D_x \\ D_y \\ D_z \end{pmatrix}$$

In practice the matrix **M** is derived from its inverse, a matrix with elements equal to the squared projections of molecule-fixed unit vectors on the **a**, **b** and **c** directions in the crystal. The **a**-, **b**- and **c**-axes have to be the eigen-directions of a section of the indicatrix in order properly to take into account the splitting of the light into two independent beams, as discussed in Part I. Myristamide is monoclinic, so for light incident normal to the 001 face the principal directions are parallel to the a and b crystallographic axes. For light polarized along the a-axis the E vector inside the crystal is not required by symmetry to lie in a plane containing the 001 face. However considering the orientations of the NV_1 transition moments it is believed that to assume this particular orientation is a good approximation—so that the **c**-axis is defined here as effectively normal to the 001 plane, and the **a**- and **b**-axes as coinciding with the crystallographic a- and b-axes.[28]

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[27] J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **20**, 335 (1952).

[28] Detailed consideration of the error introduced by this assumption gives the result that if the correct c-axis were inclined by the unlikely amount of 30° away from the 001 plane the final deter-

As a simple example of the formal use of the above relationships consider the weak coupling region of the NV_1 band. The z-axis is taken as perpendicular to the plane of the molecule and the x direction is the as yet unknown direction of the transition moment, which is, however, assumed to be in-plane. The inverse equation simplifies to

$$\begin{pmatrix} D_a \\ D_b \\ D_c \end{pmatrix} = \mathbf{M}^{-1} \begin{pmatrix} D_x \\ 0 \\ 0 \end{pmatrix}$$

resulting in an equation for the polarization direction

$$D_a/D_b = M_{11}^{-1}/M_{21}^{-1}$$

It was the observed dichroic ratio combined with this ratio of $\mathbf{M}^{-1}$ elements which led to the angles given in Fig. 5. The fact that the matrix elements are projections squared is to be connected with the fact that the dichroic ratio is always positive, and is of course responsible for the ambiguity.

The n-π Transition.—What is known with certainty about the n-π transition is that a simple orbital approach to the system of 4 π electrons in 3 π orbitals makes the highest filled level non-bonding, so the n-π transition should have approximately the same frequency as the first π-π transition. The 2200 Å. band may then be provisionally assigned as n-π because it is in about the right place and because the analysis of the dichroic ratio is consistent with the expected polarization.

The predicted allowed polarization is out-of-plane, or z, but with a strength depending on the extent to which the lobes of the non-bonding 2p orbital on the oxygen are put out of balance by interaction with the nitrogen, which is long-range. It would therefore be anticipated that except for the zero-zero region there would be a comparatively strong formally forbidden part, polarized like the neighboring NV_1 transition.[5] The z molecular axis does not have an appreciable projection on the a crystal axis in myristamide so the test of the degree of forbiddenness is the deviation of D_a/D_b from zero. Actually D_a/D_b is around 3.6 at 2200, becoming understandably smaller at the long wave length edge.

The expression for the crystal fixed densities with x the NV_1 polarization direction, becomes

$$\begin{pmatrix} D_a \\ D_b \\ D_c \end{pmatrix} = \mathbf{M}^{-1} \begin{pmatrix} D_x \\ 0 \\ D_z \end{pmatrix}$$

giving

$$D_a = M_{11}^{-1}D_x + M_{13}^{-1}D_z$$
$$D_b = M_{21}^{-1}D_x + M_{23}^{-1}D_z$$

The required $\mathbf{M}^{-1}$ elements are known from the work on the NV_1 transition and from the orientation of the molecular plane, so that the ratio of "allowed" to "forbidden" absorption can be computed. It turns out to be

$$D_z/D_x \approx {}^1/_2$$

The Rydberg Transition.—There is a Rydberg series in formamide corresponding to the formula[10]

$$\nu = 82{,}566 - \frac{R}{(n - 0.639)^2} \qquad n = 3, 4, 5, \ldots$$

The first member should be at 1610 Å. and is identified with the 1660 Å. absorption of myristamide.

The formula is written differently than originally[10] following a scheme by which it is expected that the low energy termination point may be predicted.[11] Briefly the plan is to write the formula with an appreciable negative quantum defect. Only then are the quantum numbers presumed to give a correct description of the nodal characteristics of the orbitals. For example, having $n = 3$ as the first member is connected with the fact that there are no unfilled molecular orbitals for amides which have $n = 2$ when considered as "fused," as for a united atom approach. (The fused atomic orbital description of the π orbitals is illustrated in Fig. 6.) We go on now to make a tentative assignment of the Rydberg transition guided by the above considerations.

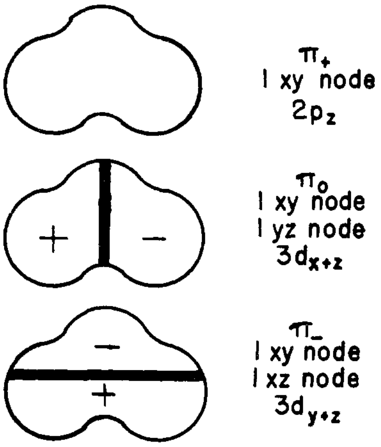

Fig. 6.—Illustration of the fused atomic orbital description for allylic π orbitals.

There are two $n = 3$ empty orbitals, either one of which might be reached in the first transition. One is the anti-bonding $2p_\pi$ orbital, π_-, which is 3d with respect to nodal behavior and the other is a bonding linear combination of 3s AO's which is 3s. These orbitals could well have comparable energies, the anti-bonding character of the π orbital balancing the promotion involved in going to the molecular orbital made up of 3s AO's.

This leaves the question of the originating orbital. It could not be the highest filled or non-bonding π orbital, $\pi\sigma$, because this would lead to the possibilities (fused AO description in parentheses)

$$\pi_0(3d) \longrightarrow \pi_-(3d)$$
$$\pi_0(3d) \longrightarrow 3s(3s)$$

The former is the NV_1 transition and the latter is forbidden provided that amides are considered as having allylic symmetry. The two most plausible possibilities for the originating orbital are considered to be the bonding π orbital, π_+, and the non-bonding oxygen 2p orbital, $2p_y$. The first member of the Rydberg series would then be

$$\left.\begin{matrix} \pi_+(2p) \\ 2p_y(2p) \end{matrix}\right\} \longrightarrow \left.\begin{matrix} \pi_-(3d) \\ 3s(3s) \end{matrix}\right\}$$

Of the four possibilities the one

$$2p_y(2p) \longrightarrow 3s(3s)$$

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mination of the angle of the NV_1 polarization direction would be only 5° in error.

seems to be the most plausible. The $2p_y \rightarrow \pi_-$ transition is the n-π transition assigned to the 2200 Å. region. (It would appear that the experimental results for the 1660 band, polarization and nearness to the NV_1 transition, make it possible to assign the band as n-π; however the allowed intensity is too high. The formally allowed intensity for the n-π transition must, it should be remembered, be quite small.) The $\pi_+ \rightarrow \pi_-$ transition is also the NV_2 transition and on the most general theoretical grounds would not be expected to lie so close to the NV_1 transition. (This closeness is most acutely demonstrated in the spectrum of formamide itself[10] where the absorption around 1600 A. is not even resolved, but shows up as a broadening of the NV_1 band relative to the band in dimethylformamide.) The $\pi_+ \rightarrow 3s$ transition would be at shorter wave lengths than the $2p_y \rightarrow 3s$ transition, so unless there is yet another Rydberg band at longer wave lengths the $2p_y \rightarrow 3s$ assignment is to be preferred.

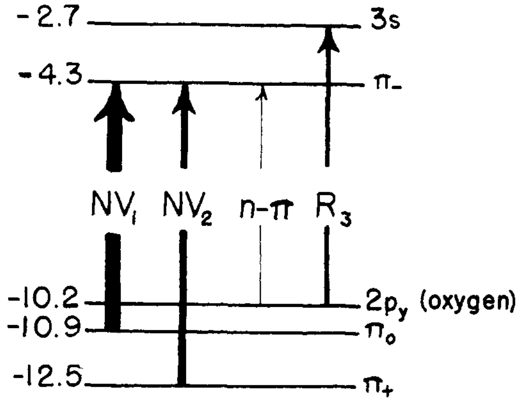

Fig. 7.—Orbital energy diagram for myristamide: (e.v.) intensities are depicted by varying widths of the arrows representing the various transitions.

The picture of the orbital reached in the transition is a linear combination of 3s orbitals, all in phase, with perhaps the greatest amplitude on the oxygen, though the higher Rydberg members gradually become more and more like atomic orbitals. The structure in the 1600 Å. region of formamide,[10] with a spacing of 1600 cm.$^{-1}$, may then be interpreted as vibrational intervals corresponding to a carbonyl stretching motion in the upper state (the ground state stretching frequency is 1740 cm.$^{-1}$).[29]

Examination of Fig. 1 shows that the absorption in the 1660 Å. region is likely to be partly from the *b*-axis component of the NV_1 transition (considered from the strong coupling point of view) and partly from the long wave length part of the band below 1600 Å. Nevertheless the qualitative result

$$D_b > D_a$$

is believed to be a characteristic of the Rydberg member itself. It is found using the trigonometric methods illustrated in the foregoing that this result is consistent with the polarizations expected for all four possibilities considered above, in particular for the possibility which is considered the most likely

$$2p_y \longrightarrow 3s$$

If we adopt this latter process we can, by considering various combinations, represent all the transitions found in this research for myristamide by means of an orbital energy diagram. This is done in Fig. 7. The effective orbital energy of the π_+ orbital is obtained by adopting for the NV_2 absorption a value of 1520 Å. This is estimated by assuming for myristamide an NV_1/NV_2 energy ratio intermediate between the ratio for formamide and dimethylformamide.[10] The zero of energy is taken as the ionization limit for the observed Rydberg series.

(29) J. C. Evans, *J. Chem. Phys.*, **22**, 1228 (1954).

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[Contribution from the Department of Chemistry, The Johns Hopkins University, and Chemical Warfare Laboratories]

Nuclear Magnetic Resonance Study of the B_2D_6–B_5H_9 Exchange Reaction[1]

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The exchange of deuterium between diborane and pentaborane was investigated by nuclear magnetic resonance. It was found that the exchange proceeded preferentially in the terminal hydrogen positions in pentaborane. The rate of exchange of the apex hydrogen appeared to be within ±10% the same as the exchange rate of the base terminal hydrogen. Under the experimental conditions the bridge hydrogens in pentaborane did not participate in the exchange.

Introduction

Recently we have had occasion to investigate the exchange of deuterium between diborane and pentaborane and we have found that the reaction proceeds through borane, derived from the dissociation of diborane, as an intermediate. By means of a mass spectroscopic study[2] we were able to disentangle the exchange from a complicating reaction due to the pyrolysis of diborane to form pentaborane, and by an infrared study[3] to show that only the five terminal hydrogens participated in the exchange reaction. The bridge hydrogens

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(2) W. S. Koski, Joyce J. Kaufman, L. Friedman and A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).

(3) Joyce J. Kaufman and W. S. Koski, *ibid.*, **24**, 403 (1956).