915. *Spectrophotometry in the Far Ultraviolet Region. Absorption Spectra of Some Amides and Cyclic Imides.*

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The spectra of nine simple cyclic imides in the 1750—2000 Å region in aprotic solvents are described, together with those of related amides. The effect on intensity of progressive C_α-alkyl substitution is noted; a shift to longer wavelengths in glutarimide is ascribed to steric strain.

A double-beam spectrophotometer with photon counter for solution studies in the vacuum ultraviolet region is described.

THOUGH some investigations have been made upon the far ultraviolet spectra of vapours of simple amides and their *N*-alkyl derivatives [1] and upon aqueous and ethanolic solutions of simple peptides,[2,3] no systematic quantitative examination of the spectra of more complex *C*-alkylated amides in aprotic solvents, or of cyclic imides, has been reported. An experimental difficulty lies in the low volatility and low solubility in aprotic solvents which must result from a high degree of intermolecular hydrogen bonding. Hydroxylic solvents, apart from having transmission limits not far below 1900 Å in a thin cell, are unsuitable when hydrogen bonding might directly affect the chromophore under consideration.

Many amides and imides are sufficiently soluble in aliphatic nitriles, and in hydrocarbon–nitrile mixtures, for spectroscopy. For the most polar compounds acetonitrile was used; it transmitted to 1800 Å ($E_{0\cdot02\text{cm.}} = 1\cdot0$) if carefully purified (see Experimental section). In other cases, however, specially purified *n*-hexane (cf. Potts [4]) containing

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[1] Hunt and Simpson, *J. Amer. Chem. Soc.*, 1953, **75**, 4540.

[2] Ham and Platt, *J. Chem. Phys.*, 1952, **20**, 335.

[3] Saidel, *J. Amer. Chem. Soc.*, 1955, **77**, 3892.

[4] Potts, *J. Chem. Phys.*, 1952, **20**, 809.

1—10% of propionitrile or valeronitrile had adequate solvent power and permitted measurements at 1740 Å ($E_{0\cdot02} = 1\cdot0$). No specific solvent effects were noticed; where solubility permitted, the same material was studied in more than one solvent mixture. The resultant spectra (see Fig. 1) were identical within experimental error.

All the succinimide derivatives have an absorption maximum at 51,300 cm.$^{-1}$ (1910 Å) independent of the nature or position of the substituents. The shift to longer wavelengths of 70 Å shown by glutarimide could be attributed to non-coplanarity of the imide group, in particular to a twist about the CO·NH bonds. The construction of models indicates that this twist may be as much as 40°, though the loss of resonance stabilisation which this would imply would probably result in the deformation's being partly taken up by C–C bonds of the ring. Since the twist increases the energy of the ground state relative to that of the excited state, the latter should involve an antibonding π orbital whose energy function has a minimum 90° from the planar configuration. This transition in the imides could thus be described as $N \longrightarrow V$, analogous to the longer-wavelength bands in formamide (1717 Å) and *NN*-dimethylformamide (1974 Å) vapours described by Hunt and Simpson.[1]

Peterson and Simpson [5] measured the direction of the transition-moment vector of the 1850 Å band of crystalline myristamide, finding alternative directions of either nearly parallel to the C–O bond or in the general direction of the C–N bond. If the above analogy is correct, sensitivity of the position of the 1910 Å imide band to twist about the C–N bond would favour the latter direction (also supported by theoretical calculations [5]). I hope to investigate further the quantitative effects of non-planarity on spectra in strained amides and imides.

The presence of alkyl substituents at C_α in both amides and imides results in a progressive decrease in intensity of the 1910 Å band (*ca.* 1750 Å in the amides) and in a series of similar symmetry (*e.g.*, 1; 2, 3; 4) the reduction is roughly proportional to the number of methyl groups introduced (a behaviour closely similar to that of the 1910 Å band in methyl ketones in the vapour state [6] and in hexane solution [7]). Comparison of the spectra of imides with amides having formally the same degree of C_α-substitution (numbers 2 or 3 with 11, 1 with 10 in Fig. 1) shows the $\varepsilon_{\text{max.}}$ values to be in the ratio 2 : 1 within the limits of experimental error, as expected if the two halves of the imide group behave as independent amide chromophores.

EXPERIMENTAL

The Spectrophotometer.—A double-beam photoelectric vacuum instrument with fluorite optics was used, allowing greater precision in intensity measurements than usual in this region.

The double-beam section, inserted between the light source (a low-pressure, water-cooled hydrogen discharge operating at 0·2 A) and the entrance slit of a small prism spectroscope, contained a chopping wheel which interrupted each beam alternately 5 times per sec., and bore on its shaft a commutator. In the " sample " beam was placed the sample cell composed of two fluorite plates (0·5 in. diam.) separated by a 0·204 mm. brass spacer, in a brass surround, the seal being made on the edges of the plates by Araldite bonding resin. Entrance and exit ports entered the bottom and top of the cell tangentially in opposite directions. Oscillation of the flowing solution in the cell by means of an external pump produced vigorous stirring, thus, preventing the formation of stagnant regions in the cell in which products of photolysis otherwise accumulated.

In the " reference " beam, the cell was replaced by an accurately adjustable slit by which the cell absorption could be balanced. The recombined beams, after dispersion by a conventional 60° prism spectrograph, passed through an exit slit (0·002 in., equivalent to $\sim$100 cm.$^{-1}$) behind which was a photon counter; the whole assembly of slit, counter, and associated head amplifier could be moved along the focal plane by a lead screw operated by a servo-motor. Impulses from the counter, after amplification ($\times$ *ca.* 2×10^4) and shaping (to square pulses,

[5] Peterson and Simpson, *J. Amer. Chem. Soc.*, 1955, **77**, 3929.

[6] Duncan, *J. Chem. Phys.*, 1940, **8**, 444.

[7] Turner, unpublished work.

duration 20 μsec.), were divided into two channels (corresponding to sample and reference beams) by the chopping wheel commutator, and fed to conventional diode rate-meter circuits. The ratio of the potentials developed was recorded continuously on paper scaled in optical density. Linearity between rate-meter output and count-rate was checked with a high-speed scaler, and circuit parameters were adjusted to allow a maximum deviation from linearity of 2%. At the count-rates used (~1000 counts/sec.) an integrating time constant of 2 sec. gave deviations of E from the mean of 5%. Graphical interpolation on the chart enabled the error to be reduced to at most ±2%. The solvent absorption curve was recorded frequently, generally immediately after that of each sample.

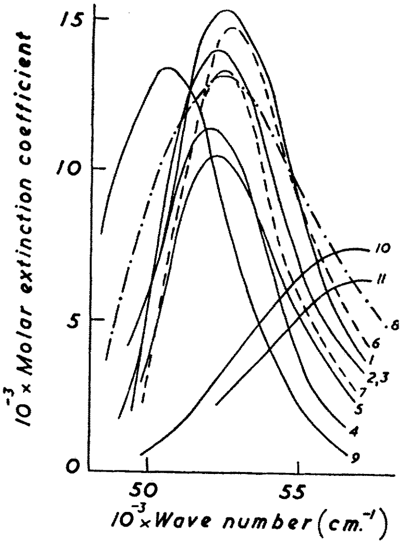
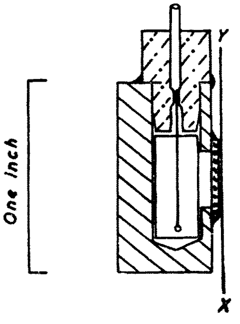


FIG. 1.

Compound, with solvent in parentheses.—1, Succinimide (A, E); 2, (±)-dimethylsuccinimide (A); 3, *meso*-dimethylsuccinimide (A); 4, tetramethylsuccinimide (F); 5, *cis*-hexahydrophthalimide (F); 6, *gem.*-dimethylsuccinimide (D); 7, methylsuccinimide (F); 8, *cyclo*hexyl*spirocyclo*propylsuccinimide (C, D); 9, glutarimide (A); 10, propionamide (F); 11, *iso*butyramide (A, F).

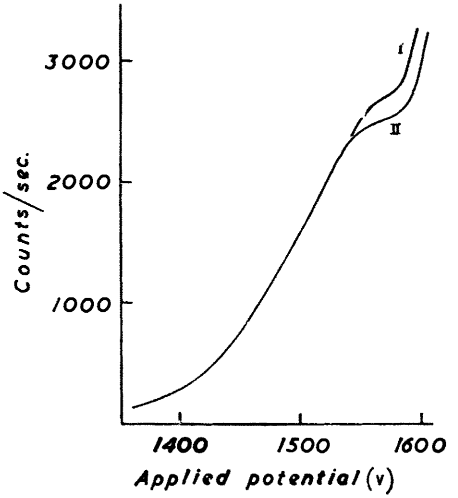
Solvents.—A, Acetonitrile; B, *n*-hexane (90%)–valeronitrile (10%); C, *n*-hexane (95%)–valeronitrile (5%); D, *n*-hexane (99%)–valeronitrile (1%); E, *n*-hexane (95%)–propionitrile (5%); F, *n*-hexane (98%)–propionitrile (2%).

FIG. 2. *The photon counter.*



XY, Plane of exit slit.

FIG. 3. *Counter operating characteristic.*



Scaler paralysis time: (I) 5 μsec.; (II) 50 μsec.

The Photon Counter.—This was constructed of brass (Fig. 2) with a copper iodide [8,9] (on copper foil) photoemissive surface, and had a 0·003 in. tungsten wire anode. It was filled with methane, and operated as a proportional counter at 1560 v (Fig. 3).

[8] Lormean, *Compt. rend.*, 1947, **225**, 453, 865; 1948, **227**, 274.

[9] Turner, *Nature*, in the press.

The photoemissive surface was prepared by treatment of the cleaned and degreased copper foil cylinder with a dilute solution of iodine in carbon tetrachloride until a visible film of iodide had formed; the treated foil was then thoroughly washed with carbon tetrachloride and dried at room temperature before insertion in the counter. After assembly, the counter was evacuated to 10^{-4} mm. for 2 hr., flushed with pure methane, filled to 10 cm. pressure, and sealed.

Sensitivity.—A larger (0·5 in. diam.) experimental counter with a magnetically movable photocathode allowed the photosensitivity of this surface to be compared with that of clean copper (photoelectric yield at 2000 Å *ca.* 10^{-4}) under the same conditions. A ratio of $\nless 10^3 : 1$ was found for the wavelength range 2300 Å (photothreshold)—1850 Å (air cut-off).

The high order of the quantum efficiency of the copper iodide surface in this region was confirmed by direct measurement by use of an electrically heated platinium strip whose temperature (1500° c) was measured by an optical pyrometer. Conditions of black-body radiation being assumed, the lower level of quantum efficiency was 10^{-2} count per incident quantum. No marked change in sensitivity was apparent between 1900 Å and 1450 Å, the limit of the fluorite spectrograph.

Linearity.—Strict proportionality between count rate and light intensity over a range of $\nless 10^3$ was confirmed with a fast scaler (paralysis time, 3 μsec.) for count rates up to ·20,000 counts/sec.

Solvents.—*n*-Hexane was purified[4] by treatment with chlorosulphuric acid followed by washing with water, drying, and distillation from sodium. Activated silica gel finally removed traces of aromatic impurities. The pure solvent was stored over freshly cut sodium under nitrogen.

Acetonitrile, propionitrile, and valeronitrile were repeatedly distilled from phosphoric oxide, the first 10% each time being rejected. For acetonitrile, which was used undiluted (being immiscible with *n*-hexane), five such distillations were required before absorption by an unidentified impurity fell to acceptable levels (*i.e.*, $E_{0.02} \ngtr 0{\cdot}3$ at 1900 Å).

Preparation of Solutions.—Since the materials studied were all only slightly soluble in the solvent mixtures used, the sample (2—4 mg. ±0·02 mg.) was dissolved initially in the nitrile (0·1—1·0 ml. depending on the final solvent proportion desired), and diluted with *n*-hexane to 10 ml., the mixture being stirred by a stream of nitrogen bubbles to remove all oxygen before admission to the cell.

Cyclic Imides.—These were analytical samples presented by Dr. J. A. Elvidge, Dr. M. Whalley, Miss P. M. Brown, and Mr. A. L. Bull (who are thanked), and used without further purification. M. p.s were as follows: Succinimide, m. p. 125—126°; (±)-dimethylsuccinimide,[9a] m. p. 125—127°; *meso*-dimethylsuccinimide,[9a] m. p. 45—47°; tetramethylsuccinimide, m. p. 87°; *cis*-hexahydrophthalimide,[10] m. p. 136—137°; *gem.*-dimethylsuccinimide, m. p. 105—106° (Sircar[11] gives m. p. 105—106°); methylsuccinimide, m. p. 62° (cf. Arppe[12]); *cyclo*-hexyl*spirocyclo*propylsuccinimide, m. p. 161°; glutarimide, m. p. 154—155° (Wolffenstein[13] gives m. p. 154—155°).

Propionamide.—Ammonia was led into refluxing propionic acid (20 g.) (air condenser) at such a rate that only the water produced was removed from the top of the condenser. After 4 hr. the product was distilled (b. p. 150°/20 mm.) and crystallised from benzene to yield propionamide (7·8 g., yield 40%), m. p. 81° (Found: N, 19·0. Calc. for C_3H_7ON: N, 19·2%). Mitchell and Reid[14] give m. p. 81·3°.

iso*Butyramide.*—A commercial specimen, recrystallised from chloroform, had m. p. 129° (Hofmann[15] gives m. p. 128—129°) (Found: N, 15·96. Calc. for $C_4H_9O_2N$: N, 16·08%).

I thank Dr. J. A. Elvidge for bringing to my attention the lack of ultraviolet data for imides, and record my debt to the late Dr. E. A. Braude, at whose instance far ultraviolet investigations were started here.

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[9a] Linstead and Whalley, *J.*, 1954, 3722.
[10] Ficken, France, and Linstead, *J.*, 1954, 3730.
[11] Sircar, *J.*, 1927, 1255.
[12] Arppe, *Annalen*, 1853, **87**, 230.
[13] Wolffenstein, *Ber.*, 1892, **25**, 2777.
[14] Mitchell and Reid, *J. Amer. Chem. Soc.*, 1931, **53**, 1881.
[15] Hoffmann, *Ber.*, 1882, **15**, 982.