Cyclic Imides. XII (1). Absorption and Fluorescence Spectra of 3-Benzamidophthalimides

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The ultraviolet absorption, fluorescence, and infrared absorption spectra of fifteen 3-benzamidophthalimides are described. In general, the nature or position of the substituents on the benzamide moiety has little effect on the ultraviolet absorption and fluorescence spectra of these compounds. The absorption band at 271 nm is more sensitive to substituent variations than the other two bands (at 227 nm and 341 nm), indicating this band is a composite of bands observed in the spectra of 3-aminophthalimide and the substituted benzamide. The fluorescence of 3-aminophthalimide and the 3-benzamidophthalimides is due to the same transitions. The infrared absorption wavenumbers for the amide and imide vibrations of the 3-benzamidophthalimides are characterized.

3-Aminophthalimide (I) is brilliant yellow in color, and intensely fluorescent (2). Its fluorescence is sufficiently well known that it has been recommended as one of a set of reference compounds for determining the correction factors for the emission units of spectrofluorometers (3). The visible color and fluorescence are both suppressed by acylation of the amino group. If we assume that the color and fluorescence are properties related to the transfer of nonbonding electrons from the primary amino group to an imide carbonyl (2), then acylation would suppress these properties by placing the acyl group carbonyl in competition with the imide moiety for the unshared pair. The net effect would be enhancement of the excitation energy and a shift of the absorption and emission bands into the ultraviolet. On the other hand, a sufficiently bulky *ortho*-substituent on a 3-benzamidophthalimide might sterically partially inhibit the withdrawal of the unshared pair to the acyl carbonyl by warping the amide group out of coplanarity, and at least partially restore the interaction of the unshared pair with the phthalimide moiety.

Only seven examples of 3-benzamidophthalimides (II) have been described in the literature. The parent member of the series (II, X = H) has been described both as cream-colored (4) and as colorless (5). The remaining examples, with the exception of the light-yellow *p*-nitro derivative (II, X = 4-NO₂), have also been described as colorless (5). No examples with *ortho*-substituents on the benzoyl group have been described.

In order to extend the knowledge of 3-benzamido-

phthalimides and, in particular, to examine the spectral behavior of these compounds, we have synthesized fifteen examples, including five *ortho*-substituted compounds, and six of the compounds which have been previously described. These compounds were synthesized by the method used by Arcoria and Scarlata (5), in which 3-aminophthalimide was acylated by an acid chloride in pyridine solution. All of the products were obtained as white, crystalline powders after four to six recrystallizations. We suspect that the "cream" and "light-yellow" colors described previously may be due to residual traces of 3-aminophthalimide (6). The results of these syntheses are summarized in Table I. 3-Acetamidophthalimide (III) was also prepared (7) to provide for comparison an example of a 3-amidophthalimide with an aliphatic acyl group. This product was also without color after several recrystallizations.

Arcoria and Scarlata (5) measured the ultraviolet absorption spectra of their 3-benzamidophthalimides in ethanol solutions. The extremely low solubilities of two of these compounds (II, X = 3-NO₂ and X = 4-NO₂) in ethanol necessitated determining their spectra with saturated solutions, and thus prevented determination of their molar absorptivity values. We have measured both the absorption and fluorescence spectra of 3-aminophthalimide (I), our fifteen 3-benzamidophthalimides (II), and 3-acetamidophthalimide (III) for solutions in dioxane, in which II are somewhat more soluble. Table II gives the wavelength λ max in nanometers, the wavenumber ν̄ max in kilokaysers, and the molar absorptivity ε max for each of the three absorption bands displayed by these compounds, together with the fluorescence excitation and emission wavelengths and wavenumbers, and the Stokes' shift, ν̄ (excitation)-ν̄ (emission).

The most remarkable thing about the ultraviolet absorption spectra of the 3-benzamidophthalimides is their sameness. Contrary to expectation, these spectra do not appear

I   III   II
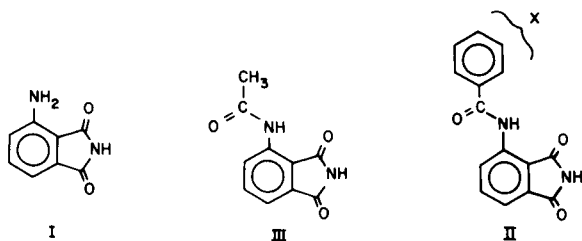
Table I
3-Benzamidophthalimides

Compound II, X =	Yield, %	Recrystallization Solvent	Melting Point, °C Found (b)	Reported (c)	Molecular Formula	Analyses (a) %C Calcd.	Found	%H Calcd.	Found	%N Calcd.	Found
H	84	Ethanol	253-254	248-249	$C_{15}H_{10}N_2O_2$						
2-Cl	59	Ethanol	246-247		$C_{15}H_9ClN_2O_2$	59.91	59.87	3.02	3.04	9.32	9.53
3-Cl	94	Ethanol	292.5-293		$C_{15}H_9ClN_2O_2$	59.91	60.04	3.02	3.07	9.32	9.34
4-Cl	70	Methanol	301-302		$C_{15}H_9ClN_2O_2$	59.91	59.95	3.02	3.04	9.32	9.35
2-F	58	Hexane	274.5-275		$C_{15}H_9FN_2O_2$	63.38	63.22	3.19	3.27	9.86	9.75
3-F	71	Hexane	289-290		$C_{15}H_9FN_2O_2$	63.38	63.21	3.19	3.28	9.86	9.75
4-F	71	Ethanol	305-306		$C_{15}H_9FN_2O_2$	63.38	63.36	3.19	3.23	9.86	9.78
2-NO2	54	Ethanol	274-275		$C_{15}H_9N_3O_4$	57.88	57.87	2.91	2.94	13.50	13.42
3-NO2	71	Ethanol	337-339	330	$C_{15}H_9N_3O_4$	57.88	57.73	2.91	2.95	13.50	13.49
4-NO2	80	Ethanol	296-298	295	$C_{15}H_9N_3O_4$	57.88	57.93	2.91	2.94	13.50	13.49
2-CH3	59	Methanol	264.5-265		$C_{16}H_{12}N_2O_2$	68.57	68.53	4.32	4.34	9.99	9.87
3-CH3	93	Benzene	262-263	260-261	$C_{16}H_{12}N_2O_2$	68.57	68.38	4.32	4.37	9.99	9.81
4-CH3	57	Methanol	291-292	285	$C_{16}H_{12}N_2O_2$	68.57	68.38	4.32	4.39	9.99	9.86
2-CH3O	77	DMF	302-303		$C_{16}H_{12}N_2O_3$	64.86	64.88	4.08	4.02	9.45	9.44
4-CH3O	28	DMF	277	270-271	$C_{16}H_{12}N_2O_3$	64.86	64.71	4.08	4.00	9.45	9.35

(a) Microanalyses by Atlantic Microlab, Inc., Atlanta, Georgia. (b) Electrothermal apparatus. (c) Reference 5.

Table II
Absorption and Fluorescence Spectra of 3-Amidophthalimides in Dioxane Solution

Compound	λ max, nm	$\bar{\nu}$ max, kK	ε max ×10⁻³	λ max, nm	$\bar{\nu}$ max, kK	ε max ×10⁻³	λ max, nm	$\bar{\nu}$ max, kK	ε max ×10⁻³	λ Ex, nm	$\bar{\nu}$ Ex, kK	λ Em, nm	$\bar{\nu}$ Em, kK	$\bar{\nu}$Ex-$\bar{\nu}$Em, kK
I	223.5 / 235	44.7 / 42.6	19.5 / 16.6	256	39.1	6.61	378	26.5	4.17	378	26.5	441	22.7	3.8
II, X = 2-CH₃O	224	44.6	36.3	271.5 / 280.5	36.8 / 35.6	19.5 / 17.8	344	29.1	6.31	346	28.9	399	25.1	3.8
II, X = 4-CH₃O	225	44.4	35.5	281.5	35.5	31.6	346	28.9	5.89	350	28.6	402	24.9	3.7
II, X = 2-F	230.5	43.4	33.9	271	36.9	18.2	338	29.6	5.13	338	29.6	390	25.6	4.0
II, X = 3-F	231.5	43.2	32.4	270.5	37.0	18.2	341.5	29.3	5.01	345	29.0	398	25.1	3.9
II, X = 4-F	229	43.7	31.6	269	37.2	17.4	342.5	29.2	4.90	348	28.7	400	25.0	3.7
II, X = 2-Cl	226	44.2	58.9	261	38.3	20.9	339	29.5	6.17	344	29.1	404	24.8	4.3
II, X = 3-Cl	225	44.4	61.7	270	37.0	29.5	341	29.3	9.12	346	28.9	400	25.0	3.9
II, X = 4-Cl	229.5	43.6	44.7	272	36.8	28.2	341.5	29.3	6.76	345	29.0	398	25.1	3.9
II, X = 2-CH₃	228.5	43.8	36.3	264	37.9	20.4	342	29.2	5.62	346	28.9	398	25.1	3.8
II, X = 3-CH₃	221	45.2	33.9	269.5	37.1	20.4	343.5	29.1	5.50	346	28.6	400	25.0	3.6
II, X = 4-CH₃	229	43.7	36.3	272	36.8	25.7	344	29.1	5.89	350	28.7	400	25.0	3.7
II, X = H	229.5	43.6	32.4	270.5	37.0	17.8	343.5	29.1	4.90	348	28.7	399	25.1	3.6
II, X = 2-NO₂	227	44.1	39.8	255	39.2	24.5	334	29.2	5.01	(a)				
II, X = 3-NO₂	225	44.4	46.8	264	37.9	22.9	339	29.5	6.31	346	28.9	429	23.3	5.6
II, X = 4-NO₂	225	43.7	34.7	290	34.5	14.4	336	29.8	7.59	(a)				
III	225 / 232(b)	44.5 / 43.1	31.6 / 27.	252	39.7	14.4	341.5	29.3	4.57	345	29.0	395	25.3	3.7

(a) Not fluorescent. (b) Shoulder.

Table III

Comparison of Absorption Spectra of Solutions in Alcohol and in Dioxane

Compound	Solvent	λ max, nm	$\bar{\nu}$ max, kK	ϵ max, $\times 10^{-3}$	λ max, nm	$\bar{\nu}$ max, kK	ϵ max, $\times 10^{-3}$	λ max, nm	$\bar{\nu}$ max, kK	ϵ max, $\times 10^{-3}$	λ max, nm	$\bar{\nu}$ max, kK	ϵ max, $\times 10^{-3}$
I	Ethanol	224	44.7	22.3	235.5	42.5	19.4	257.5	38.9	7.67	388.5	25.7	5.14
	Dioxane	223.5	44.7	23.5	235	42.6	20.9	256	39.1	8.94	378	26.5	5.66
II	Ethanol(a)	227	44.1	34	236(b)	42.3	26	273	37	21	340	29.4	5.0
		±3	±0.5	±3	±1	±0.1	±2	±8	±1	±4	±4	±0.3	±0.3
	Dioxane(c)	227	43.9	40				271	37	22	341	29.3	6
		±3	±0.5	±9				±8	±1	±5	±3	±0.2	±1
III	Ethanol(d)	226	44.2	32.4	232(b)	43.1	29.5	253	39.5	13.2	342	29.2	3.98
	Dioxane	225	44.5	31.6	232(b)	43.1	27	252	39.7	14.4	341.5	29.3	4.57
Phthalimide	Ethanol	219	45.7	42.2	229.5	43.6	16.1	237.5	42.1	10.4	291.5	34.3	1.87
	Dioxane	215.5	46.4	40.2	229(b)	43.7	15.2	236.7	42.2	9.88	290	34.5	1.68
Benzamide	Methanol(e)	224	44.6	12.0	263	38.0	0.79	265(b)	37.7	0.56	278(b)	36.0	0.36
	Dioxane	224	44.6	11.8				269.5	37.1	0.79	276.5	36.2	0.56

(a) The λ max and $\bar{\nu}$ max values are averages for seven compounds, and the ϵ values are averages for five compounds(5). (b) Shoulder. (c) Averages for the fifteen compounds in Table II. (d) Reference 5. (e) Reference 8.

to be influenced in any major way by either the nature or the position of the substituent on the benzamide moiety. It is, in fact, quite convenient to average the spectral data to obtain a single set of data points descriptive of the spectra of the entire set of II. These average points, with their standard deviations, are presented in Table III, along with the average points for the published spectra of alcohol solutions (5) and for comparison, the spectra of 3-aminophthalimide (I), 3-acetamidophthalimide (III), phthalimide and benzamide (8), in alcoholic and dioxane solutions. The positioning in Table III of the bands of phthalimide and benzamide is one of convenience and is not intended to imply an exact correspondence of the bonds of these spectra with those of the spectra of I, II and III.

The spectra of III and of phthalimide are nearly independent of solvent. The spectra of II differ among the solvents only in the enhancement of the 227-nanometer band, resulting in the submersion of the shoulder at 236 nanometers, for dioxane solutions. 3-Aminophthalimide, on the other hand, shows a significant solvent effect with the longest wavelength band, which is red-shifted by ethanol. The spectrum of benzamide in methanol (8) shows two weak shoulders, which become resolved in dioxane into three equally spaced peaks averaging 37.1 kilokaysers (269.5 nanometers).

The average value for the λ max of the middle peak in the spectra of II has a standard deviation at least twice as great as the standard deviations of the other two peaks. This must indicate that this peak is significantly more sensitive to variations in the substituent, and position of substitution, on the benzamido group. This 271-nanometer band is therefore a composite of the 256-nanometer band of 3-aminophthalimide and the band of the substituted benzamide corresponding to the 269.5-nanometer cluster of benzamide. A complete analysis of this composite band would have to take into account not only the excitation of the π-electrons of both aromatic rings, but also the transfer of charge from the amide nitrogen to both the amide carbonyl oxygen and to the aromatic ring of the phthalimide moiety, and the transfer of charge to the amide oxygen from the aromatic ring of the benzamide moiety.

The absorption spectra of dioxane solutions of fourteen monosubstituted benzamides were also measured. Most of these spectra resembled that of benzamide, but with considerably more variation of the absorption maxima than was observed with the 3-benzamidophthalimides. For most of the benzamides the molar absorptivity was in the vicinity of 1000. The absorption band of 2-methoxybenzamide at 286 nanometers (35.0 kilokaysers), on the other hand, was unusually strong, with an ϵ max of 25,100. The extra peak at 280.5 nm in the absorption spectrum

of 3-(2-methoxybenzamido)phthalimide (II, X = 2-CH₃O) doubtless corresponds to this peak and provides a case where the benzamide transition is resolved from the aminophthalimide transition at 271 nm. The molar absorptivity of 2-fluorobenzamide, 17,000, was also unusually strong, but since its absorption band was at 275 nm (36.4 kK), the two bands were not resolvable in the spectrum of 3-(2-fluorobenzamido)phthalimide (II, X = 2-F). The enhancement of the benzamide transition in the cases of the *ortho*-methoxy and *ortho*-fluoro compounds may be due to hydrogen-bonding of the amide proton to the atom at the *ortho*-position. Contrary to the idea suggested in the first paragraph, such an interaction would enhance coplanarity instead of inhibiting it.

The lowest energy band, with an average wavenumber of 29.3 kK, was nearly identical for all of the 3-amidophthalimides II and III, and corresponds to the 26.5 kK band of 3-aminophthalimide. The principal factor in this transition is the transfer of charge from the nitrogen atom on the aromatic ring to an oxygen of the imide moiety (2). This band is blue-shifted by acylation as the result of the introduction of competition for this charge by the acyl carbonyl. It is from this band that the fluorescence

excitation occurs.

All of the 3-amidophthalimides except the 2- and 4-nitro derivatives exhibited fluorescence (9), but the intensity of the fluorescence was much weaker than that of 3-aminophthalimide. Very similar fluorescence characteristics were observed for all of the 3-amidophthalimides except the three nitro compounds. For II, the average excitation wavenumber was 28.9 ± 0.3 kK, the average emission wavenumber was 25.1 ± 0.2 kK, and the average Stokes'shift was 3.8 ± 0.2 kK (10). The fact that 3-aminophthalinide displays the same Stokes'shift leaves no doubt that the same transitions are involved in the fluorescence of all of these compounds.

For those examples of II for which X = H, CH₃, CH₃O, 2-F or 3-F, fluorescence was alos excited at a frequency slightly below that of the middle absorption band. The average wavenumber for this excitation was 35.2 ± 0.4 kK (284 ± 3 nm). Since none of the corresponding benzamides exhibited fluorescence in dioxane solutions (11), it must be concluded that this excitation derives from the aminophthalimide component of the middle absorption band. This conclusion is also supported by the fact that both excitations lead to the same emission, a result which

Table IV

Infrared Absorption Spectra of 3-Benzamidophthalimides and Related Compounds

Compound	Amide Bands				Imide Bands		
	$\bar{\nu}$ NH, K		$\bar{\nu}$ CO, K	$\bar{\nu}$ CNH, K	$\bar{\nu}$ NH, K	$\bar{\nu}$ CO, K	
	stretch	wag				sym	asym
I	(a)				3293	1745	1709
II, X = H	3354	690	1688	1546	3195	1768(b)	1734
II, X = 2-CH₃O	(c)	738	1658	1550	(c)	1763	1730
II, X = 4-CH₃O	3365	703	1663	1540	3210	1762	1728
II, X = 2-F	3350	721	1684	1550	3205	1767(b)	1734(b)
II, X = 3-F	3315	692	1678	1547	3215	1758	1726
II, X = 4-F	3309	695	1678	1550	3210	1762	1728
II, X = 2-Cl	3350	671	1685	1532	3190	1766	1732
II, X = 3-Cl	3305	689	1676	1540	3210	1762	1728
II, X = 4-Cl	3310	683	1679	1538	3200	1758	1723
II, X = 2-CH₃	3334	696	1690	1530	3209	1766(b)	1730
II, X = 3-CH₃	3320	681	1674	1539	3192	1759	1722
II, X = 4-CH₃	3372	704	1684	1542	3205	1767(b)	1725(b)
II, X = 2-NO₂	3340	694	1664	(d)	3190	1766	1722
II, X = 3-NO₂	3304	686	1673	(d)	3218	1754	1721
II, X = 4-NO₂	3364	710	1690	(d)	3208	1762	1724(b)
II, average	3340	700	1680	1542	3204	1763	1727
	±20	±20	±10	±7	±9	±4	±4
III	3318		1680	1512	3250	1752	1707
Phthalimide					3201	1768(b)	1738
Benzamide	(e)		1645				

(a) Asymmetric NH₂ stretch, 3471 K; symmetric NH₂ stretch, 3343 K. (b) Midpoint of a doublet. (c) Single broad, strong NH band at 3270 K. (d) Submerged by the stronger asymmetric NO₂ stretch at ~1530 K. (e) Asymmetric NH₂ stretch, 3363 K; symmetric NH₂ stretch, 3158 K.

could occur only if both of the initial excited states can decay to the same state from which the fluorescent de-excitation occurs. It is probable that the 284-nm excitation involves a π^* orbital of the benzene ring of the phthalimide moiety, while the 346-nm excitation reaches an antibonding orbital of an imide oxygen.

The characterization of II was completed by measurement of the infrared spectra for II in KBr pellets. The absorption wavenumbers, in Kaysers, for the amide and imide vibrations of II are reported in Table IV, along with the average values and standard deviations for these bands, and the corresponding bands for I, III, phthalimide and benzamide. As expected, all of the 3-amidophthalimides showed three carbonyl bands. The lowest of these bands in frequency was characteristic of secondary amides, but it is found at the high end of the frequency range for these compounds, showing that the phthalimide moiety is strongly electron-attracting (12). The remaining two carbonyl bands are the lower-frequency, higher-intensity asymmetric stretching of the pair of carbonyls of the imide moiety, and the higher-frequency, lower-intensity symmetric stretching of the same pair (13).

The NH stretching frequencies of the two NH groups were also readily distinguishable. The NH stretch of the secondary amide group was a very sharp band of variable intensity. The average wavenumber of 3340 K is within the range characteristic of an acyclic, trans-amide with hydrogen-bonding of the NH (12,14). The imide NH showed a strong, very broad band in the vicinity of 3200 K. This band was almost always stronger than that of the amide. The low frequency of this band indicates that it also involves a hydrogen-bonded NH. With the two possible exceptions discussed earlier, the hydrogen-bonding of the amide and imide protons must be intermolecular rather than intramolecular.

The two remaining bands which were identified were the NH out-of-plane wagging and the CNH composite of the amide. The NH wagging band is one of several medium bands in the vicinity of 700 K. It is distinguishable from the other bands in this region by its comparative broadness. With nearly all of the compounds in this study, it also had a skewed shape, rather than a symmetrical one. The CNH band in the vicinity of 1540 K is a strong band. In the cases of the three nitro compounds, however, it was submerged by the even stronger NO_2 asymmetric vibration at 1530 K.

The imide vibrations of II showed little variation among the individual members of the fifteen examples. This lack of variation is to be expected, since the imide moiety is remote from the part of the molecule in which the individual variations occur.

We should expect the amide carbonyl frequency to show sensitivity to the nature and position of the sub-

stituents on the benzamide moiety. In fact, this frequency shows little variation for the four meta-substituted examples, and their sequence $F > Cl > CH_3 > NO_2$ is not the sequence of the inductive effects of these substituents. On the other hand, the sequence $NO_2 > CH_3 > Cl > F > CH_3O$ observed for the para-substituted examples is the same as the sequence of σ_R values for these groups. The same sequence is observed for the ortho-substituted examples, with the exception that the carbonyl frequency for the nitro compound is shifted from the highest in the series to the second lowest. This change is doubtless the result of a steric interaction between the ortho-nitro group and the carbonyl. The small size of the sample does not justify the effort of seeking a quantitative statistical correlation of the $\sigma\rho$ type for these carbonyl bands. (15).

Although the amide NH out-of-plane wagging frequency shows the largest variation of any of the bands summarized in Table IV, there appears to be no relationship between the values of this frequency and the electronic effects of the substituents. This band does occur at unusually high frequencies in the cases of the two compounds for which the ultraviolet absorption spectra indicated intramolecular hydrogen-bonding between the amide proton and the ortho-atom, namely 3-(2-methoxybenzamido)phthalimide and 3-(2-fluorobenzamido)phthalimide. We believe that the high frequencies of the NH wag for these two cases supports the conclusion that they are intramolecularly bonded. The "freezing" of the structure into coplanarity required by this effect would raise the energy, and therefore the frequency, of the NH out-of-plane vibration.

The amide CNH frequency showed the least variation of the amide frequencies. There may be some significance, however, in both extremes of its values. The highest wavenumber, 1550 K, observed for this vibration occurred for the o-fluoro and o-methoxy compounds; but since the p-fluoro compound (II, X = 4-F) also gave this value, the factors involved in determining it must be electronic ones operating through the benzoyl moiety as well as those due to hydrogen-bonding. On the other hand, the two lowest values for the CNH vibration, 1530 K for 3-(2-methylbenzamido)phthalimide (II, X = 2-CH_3) and 1532 K for 3-(2-chlorobenzamido)phthalimide (II, X = 2-Cl), involve two ortho-substituents whose only electronic characteristic in common is the unlikelihood of their forming hydrogen bonds. These two cases may represent a lowering of the CNH frequency through steric effects.

The amide NH stretching vibration averaged 3344 K for both ortho- and para-substituted benzamide groups but only 3311 K for the meta-substituted groups. The variation among the values in the para-series was some four times greater than the variation for either the ortho- or meta-series. An unusual effect was observed in the NH region of the spectrum of the intramolecularly hydrogen-

bonded 3-(2-methoxybenzamido)phthalimide. For this compound we were unable to obtain a spectrum in which the amide and imide NH frequencies were resolved from each other. There was instead a single very broad NH band with a peak intensity at 3270 K, about midway between the average values of the two bands.

EXPERIMENTAL

3-Benzamidophthalimides.

3-Aminophthalimide (I) was benzoylated according to the procedure described by Arcoria and Scarlata (5). A mixture of 1.40 g. (0.01 mole) I, 0.01 mole of the benzoyl chloride, and 20 ml. of pyridine was refluxed four hours with stirring, cooled to room temperature, and poured into 100 ml. of ice-cold water to precipitate the product. The precipitate was collected by suction filtration, dried and recrystallized several times. The results of these syntheses are summarized in Table I.

Measurement of spectra.

The ultraviolet absorption spectra were measured with a Cary Model 15 absorption spectrophotometer, using 1-cm cylindrical cells. The absorption peaks reported in Table II were measured to the nearest 0.5 nanometer. The fluorescence spectra were determined with a Perkin-Elmer SPF-2A fluorescence spectrophotometer, using 10^{-5} to 10^{-4} molar solutions and a sensitivity of 4 or 5. For the excitation spectra, the excitation slit width was 2 nanometers and the emission slit width was 12 nanometers; for measurement of the emission spectra, these slit widths were reversed. The fluorescence spectra in Table II are therefore measured to the nearest 2 nm.

The infrared absorption spectra were measured with a Perkin-Elmer 225 infrared spectrophotometer, using potassium bromide pellets. The spectrum of each compound was measured at least twice, each time by a different operator, and the values reported in Table IV are averages of these measurements.

Acknowledgments.

REFERENCES AND NOTES

(1) Previous paper in this series: L. R. Caswell, P. Palacios, S. J. Schmidt, R. Anvar and A. Garcia, J. Heterocyclic Chem., 15, 33 (1978).

(2) L. R. Caswell and P. C. Atkinson, J. Org. Chem., 29, 3151 (1964).

(3) C. E. White and R. J. Argauer, "Fluorescence Analysis: A Practical Approach," Marcel Dekker, Inc., New York, N. Y., 1970, pp. 48-51.

(4) H.D. K. Drew and F. H. Pearman, J. Chem. Soc., 26 (1937).

(5) A. Arcoria and G. Scarlata. Boll. Sed. Accad. Gioenia Sci. Nat. Catania IV, 8, 58 (1964). This paper was not abstracted by Chemical Abstracts. A reprint was obtained through private correspondence with the senior author.

(6) K. A. McDowell of our laboratory has found that visible color may be imparted to colorless compounds by traces of 3-aminophthalimide (which is readily identifiable by its fluorescence spectrum) so small that the contaminated materials give acceptable microanalyses.

(7) M. T. Bogert and F. L. Jouard, J. Am. Chem. Soc., 31, 488 (1909).

(8a) H. Ley and H. Specker, Ber., 72, 192 (1939); (b) Sadtler Standard Spectra, Standard Ultraviolet Spectrum 744.

(9) All of our preparations of 3-(2-nitrobenzamido)phthalimide showed an extremely weak fluorescence. This was at first interpreted as an example of the steric effect predicted in the first paragraph of this paper. Later it was found that the intensity varied from one preparation to another, and declined with repeated recrystallization. Since the excitation and emission wavelengths turned out to be identical with those of 3-aminophthalimide, the fluorescence of the o-nitro compound must therefore be be due to unremoved traces of this compound (6).

(10) The fluorescence data for 3-(3-nitrobenzamido)phthalimide were not used in computing these averages.

(11) 2-Methoxybenzamide is fluorescent in hydroxylic solvents: S. J. Powell, Ph.D. Dissertation, The Texas Woman's University, 1969.

(12) N. B. Colthup, L. H. Daly and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy." Academic Press, New York, N. Y., 1964, pp. 263-267.

(13) Although this assignment is quite familiar for the very similar pair of carbonyl bands in cyclic anhydrides (cf. reference 12, p. 256), the first published applications of it to the carbonyl bands of cyclic imides appear to be those of C. Fayat and A. Foucaud, Bull. Soc. Chim. France, 4491, 4501 (1970). Earlier discussions of the two carbonyl bands of cyclic imides have used other interpretations or, at least, other terminology.

(14) K. Nakanishi and P. H. Solomon, "Infrared Absorption Spectroscopy," 2nd Edition, Holden-Day, Inc., San Francisco, CA, 1977, p. 42.

(15) We question the theoretical justification for such an effort even for a set of sufficiently large size to be statistically justifiable, as long as the spectra are measured for the solid state. In this state the molecules of the different compounds are not in completely identical environments, and the spectra are therefore comparable only on a qualitative basis. Quantitative comparisons, including attempts at op correlations, should be based on spectra measured for conditions in which the molecules are sufficiently separated from each other that intermolecular hydrogen-bonding cannot occur.