Aspects of Tautomerism. Part V.† Solvent, Substituent, and Steric Effects on the Ring–Chain Tautomerism of *o*-Benzoylbenzamides

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Ring-chain tautomeric equilibria of *o*-benzoylbenzamides in 95% ethanol, chloroform, dioxan, and acetonitrile have been estimated using u.v. spectroscopy. Unlike the case of acids, solvent polarity has only a small effect. In ethanol the cyclic form is favoured. Electron-withdrawing groups in the amide-bearing ring disfavour the cyclic form. Substitution of methyl, ethyl, and phenyl groups on the nitrogen atom of the amide function results in increase of the proportion of the cyclic form in the first two cases and decrease in the last.

GRAEBE and ULLMAN [1] treated the acid chloride of *o*-benzoylbenzoic acid (I) with ammonia and obtained an amide which was designated as (II). The i.r. spectrum of the amide in chloroform revealed that it exists in the cyclic form (III).[2] We have found that it exists in the open form in the solid state, but is completely in the cyclic form in solution.[3] Reaction of (I) with aniline resulted in the formation of two anilides [4] [(A), m.p. 221° (75%) and (B), m.p. 195° (12·5%)]. Compound (A) was originally assigned structures (IV) [4] or (V) [5] and (B) structure (VI).[4] On the basis of i.r. spectra (A) and (B) have now been assigned structures (VI) and (VII) respectively.[6]

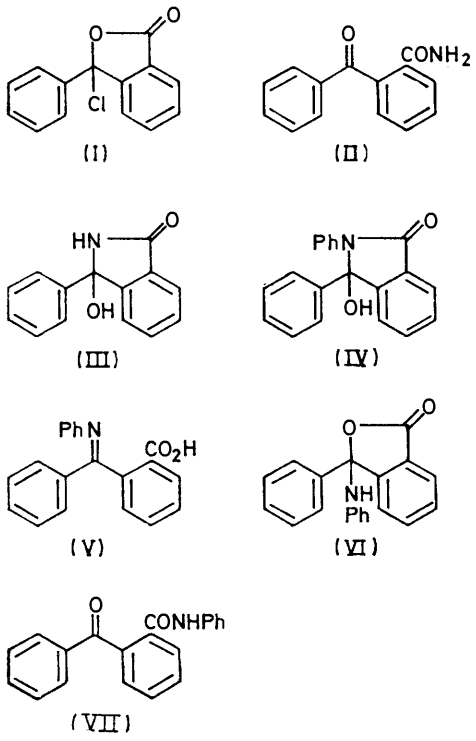
Many early reports in the literature on the structure of γ- and δ-keto-amides, based on reactivity studies or on the mode of their formation, are misleading. The use of physical methods is necessary to give dependable answers. There is no report of a systematic study on the γ-keto-amide–hydroxy-lactam equilibrium. The influence of solvents and substituents on this equilibrium has not been studied. This information may allow some conclusions to be drawn relevant to biologically important systems. It is well known that amides are more basic than the corresponding acids (pK_a of benzamide [7] is −2·0 and of benzoic acid [8] is −7·28 in concentrated sulphuric acid). Comparable data are not

† Part IV, M. V. Bhatt and M. Ravindranathan, preceeding paper.

[1] C. Graebe and F. Ullman, *Annalen*, 1896, **291**, 8.
[2] W. Graf, E. Girod, E. Schmid, and W. G. Stoll, *Helv. Chim. Acta*, 1959, **42**, 1085.
[3] M. V. Bhatt and K. M. Kamath, *J. Chem. Soc.* (*B*), 1968, 1036.
[4] H. Meyer, *Monatsh.*, 1907, **28**, 1211.
[5] S. Wawzonek, H. A. Laitinen, and S. J. Kwiatkowski, *J. Amer. Chem. Soc.*, 1944, **66**, 830.
[6] M. V. Bhatt, K. M. Kamath, and M. Ravindranathan, *J. Chem. Soc.* (*C*), 1971, 1772.
[7] J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 1957, 2000.
[8] R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, 1960, **82**, 4059.

available on equilibria in which the carbonyl group acts as a Lewis acid instead of the proton.

Part I [3] described a detailed study of the ring–chain tautomerism of *o*-benzoylbenzoic acids. It was observed

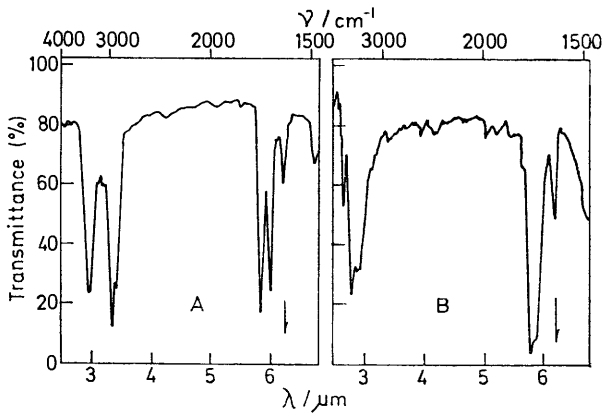


that the more polar solvents favour the cyclic form. If the analogy with acids is applicable, one could expect a similar effect of solvent polarity on the keto-amide–hydroxy-lactam equilibrium. A study of this equilibrium for *o*-benzoylbenzamides is reported here. The influence of (*a*) substituents in the rings and on the nitrogen atom and (*b*) solvents on the equilibrium has been studied.

A number of difficulties seriously limit the extent of this study. The parent compound itself exists completely in the cyclic form even in the least polar medium in which it is soluble. Electron-withdrawing groups on the benzoyl ring favour the cyclic form (see Table 1). The immediate problem was to make appropriate structural modifications to destabilize the cyclic form, and thus obtain a measurable amount of the open form at equilibrium. By analogy with the *o*-benzoylbenzoic acid equilibrium, the amide ring–chain tautomerism can be looked upon as a carbonyl addition–dissociation phenomenon. On this basis three methods were tried. (*a*) The carbonyl strength of the ketone was decreased, thus increasing the stability of the open form, by means of electron-donating groups in the benzoyl ring. (*b*) Steric hindrance at the carbonyl group was increased. (*c*) The basicity of the amide function was decreased by electron-withdrawing groups in the amide ring and on the nitrogen atom. All three methods proved helpful and were utilized.

Techniques of Measurement.—I.r. spectroscopy, which was a convenient tool in the study of acids, was not found useful because the keto and amide carbonyl bands were not sufficiently resolved to be helpful. The i.r. spectrum of *o*-benzoylbenzamide showed bands at 1660 and 1710 cm^{-1} (diaryl ketone and amide carbonyl) in the solid state (Figure A). In chloroform solution the amide showed a single band at 1710 cm^{-1} which can be assigned to the lactam carbonyl (Figure B). Considerable shifts in frequencies of these absorptions were observed in the case of other substituted amides both in the solid state and in solution (see Experimental section). The absorption due to the amide carbonyl is susceptible to substitution on the nitrogen. Moreover, some *o*-benzoylbenzamides gave a single absorption in the carbonyl region, resulting from unresolved diaryl ketone and amide carbonyl groups. Because of the difficulty of obtaining a general criterion for the estimation of the equilibria of different substituted *o*-benzoylbenzamides and the problems caused by the overlapping absorption bands in the carbonyl region, i.r. spectroscopy was not used.

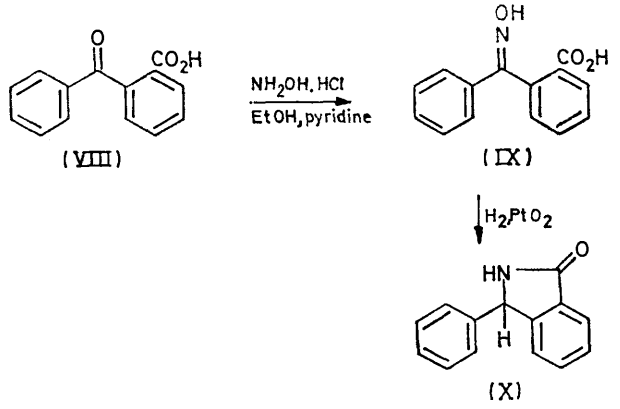
The method employed for the estimation of tautomeric compositions was based on u.v. spectroscopy. *o*-Benzoyl-*NN*-dimethylbenzamide and methyl *o*-benzoylbenzoate which are known to exist exclusively in the open form were taken as standards for the open form of the amide. This assumption is not unreasonable, because substitution on the nitrogen atom by hydrogen or methyl may not be expected significantly to influence the u.v. spectrum of the diaryl ketone chromophore.



I. r. spectra of *o*-benzoylbenzamide in A, Nujol and B, chloroform

Moreover, as expected, the normal ester and the *NN*-dimethylamide have an absorption maximum at *ca.* 250 nm with similar extinction coefficients (16,240 and 16,120 respectively in ethanol). The pseudo-ester of *o*-benzoylbenzoic acid and the lactam (X) were taken as standards for the hydroxy-lactam form of the amide. $\varepsilon_{max.}$ at 250 nm for these compounds was 157 and 102 respectively, <1% of the absorption of the diaryl ketone chromophore. The extinction coefficient of any equilibrium mixture was used to compute the fraction of the

open form. The rest was taken as the cyclic form. Similarly when the estimation was made using the

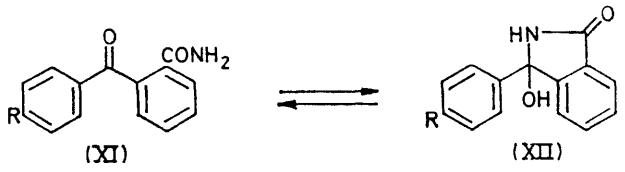


350 nm band, it was found that the cyclic isomer absorbed by <1% of the open tautomer in this region.

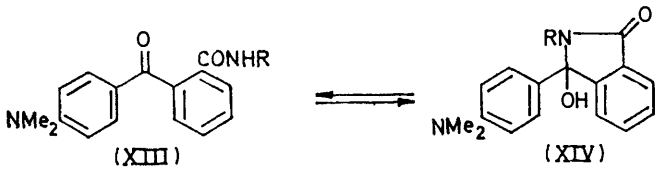
RESULTS AND DISCUSSION

The u.v. spectral data of seven *o*-benzoylbenzamides (XIa—g) with substituents in the *para*-position of the benzoyl ring are tabulated in Table 1. It can be seen that all the amides except (XIf) and (XIg) exist exclusively in the cyclic form. 2-(4-Dimethylaminobenzoyl)benzamide (XIg) exists more (38%) in the open form than the corresponding *p*-amino-amide (8%). This is a consequence of the greater electron-donating capacity of the dimethylamino- (σ −0·83) than the amino-group (σ −0·66). The absorption maximum at 250 nm characteristic of the diaryl ketone chromophore was shifted to 350 and 334 nm respectively by *p*-dimethylamino- and *p*-amino-substituents.

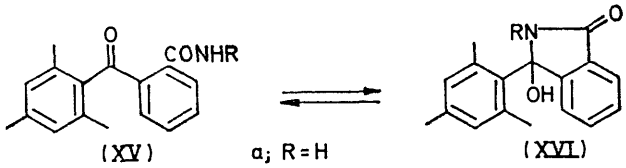
The amides generally exist in substantially greater extent in the cyclic form than do the corresponding acids. The example of *o*-benzoylbenzoic acid and its amide presents an interesting contrast. The former is completely open in methanol solution whereas the latter is completely cyclic in 95% ethanol (Table 1). This



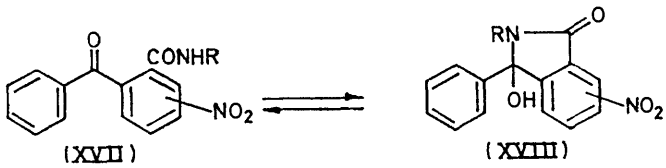
a; R = H
b; R = Me
c; R = Cl
d; R = Br
e; R = NO_2
f; R = NH_2
g; R = NMe_2



a; R = H
b; R = Me
c; R = Et
d; R = Ph



a; R = H
b; R = Me
c; R = Ph



a; 6 - NO_2, R = H
b; 6 - NO_2, R = Me
c; 5 - NO_2, R = H
d; 5 - NO_2, R = Me
e; 4 - NO_2, R = H
f; 4 - NO_2, R = Me
g; 3 - NO_2, R = H
h; 3 - NO_2, R = Me

difference is a direct consequence of greater basicity of the amide function compared to the carboxylic acid function.

TABLE 1

U.v. absorption and approximate equilibrium composition of 4′-substituted *o*-benzoylbenzamides in 95% ethanol

4′-Substituent	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Approximate equilibrium composition (%) Cyclic	Open
H	224	14·4	100	
Me	224	18·5	100	
Cl	226	19·4	100	
Br	226	19·5	100	
NO_2	226	19·7	100	
NH_2	224	19·2		
	242	8·57	92 [a]	8 [a]
	334	1·64		
NMe_2	210	26·2		
	262	15·1		
	352	9·09	62·5 [b]	37·5 [b]

[a] Determined by comparing with the $\varepsilon_{max.}$ of the normal ester at 330—340 nm. [b] Determined by comparing with the $\varepsilon_{max.}$ of *NN*-dimethylamide at 340—355 nm.

TABLE 2

U.v. absorption and approximate equilibrium composition of *o*-mesitoylbenzamides in 95% ethanol

Amide	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Equilibrium composition (%) [a] Cyclic	Open
(XVa)	214	28·2		
	244	10·4	4	96
(XVb)	214	27·8		
	246	9·44	9	91
(XVc)	214	29·4		
	247	18·9 [b]		

[a] By comparing with $\lambda_{max.}$ (EtOH) 248 nm (ε 10,480) of *NN*-dimethylamide. [b] High $\varepsilon_{max.}$ is due to the absorption by the anilino-chromophore in this region.

TABLE 3

U.v. absorption and approximate position of ring–chain equilibria of amide ring nitro-substituted *o*-benzoylbenzamides in 95% ethanol

Amide	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Equilibrium composition (%) [a] Cyclic	Open
(XVIIa)	226	14·4	100	
(XVIIb)	226	14·5	100	
(XVIIc)	226	14·1		
	250	13·9	24	76
(XVIId)	226	14·8		
	252	12·5	31	69
(XVIIe)	226	14·1		
	252	11·7	36·5	63·5
(XVIIf)	226	14·8		
	250	9·11	52	48
(XVIIg)	224	14·2		
	250	6·31	66	34
(XVIIh)	224	14·8		
	250	5·43	71	29

[a] Determined by comparing with $\varepsilon_{max.}$ of normal esters at 250 nm.

The effects of substituents in the amide ring and on the nitrogen atom of the amide group follow a simple pattern. The electronic spectra of the amide ring nitro-substituted *o*-benzoylbenzamides are given in Table 3. The effect of this group varied with its position. When present in the 4- and 5-positions, electronic effects only may be expected to operate. In the case of compounds (XVIIe, f, and c, d), the effect of the nitro-group is to increase the open form [*cf.* unsubstituted amide (XIa) which is 100% cyclic].

TABLE 4

U.v. absorption and approximate equilibrium composition of 2-(4-dimethylaminobenzoyl)benzamides in 95% ethanol

Amide	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Equilibrium composition (%) [a] Cyclic	Open
(XIIIa)	210	26·2		
	262	15·1		
	352	9·09	62·5	37·5
(XIIIb)	211	26·2		
	262	14·9	100	
(XIIIc)	212	26·2		
	262	15·1		
	352	1·92	92	8
(XIIId)	212	32·1		
	242	19·7		
	350	16·8	31	69

[a] Equilibrium composition was determined by comparing with $\varepsilon_{max.}$ of *NN*-dimethylamide at 350—352 nm.

TABLE 5

U.v. absorption and approximate equilibrium composition of 2-(4-dimethylaminobenzoyl)benzamides in chloroform [a]

Amide	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Equilibrium composition (%) [b] Cyclic	Open
(XIIIa)	348	17·6	22·5	77·5
(XIIIb)	346	1·80	92	8
(XIIIc)	346	1·80	92	8
(XIIId)	346	19·2	15	85

[a] Absorptions below 250 nm were not recorded since chloroform was not transparent. [b] Determined by comparing with $\lambda_{max.}$ ($CHCl_3$) 348 nm (ε 22,500) of *NN*-dimethylamide.

TABLE 6

U.v. absorption and approximate equilibrium composition of 2-(4-dimethylaminobenzoyl)benzamides in dioxan

Amide	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Equilibrium composition (%) [a] Cyclic	Open
(XIIIa)	215	18·5		
	242	13·5		
	346	18·9	24·0	74·0
(XIIIb)	216	20·1		
	264	15·4		
	348	1·53	94·0	6·0
(XIIIc)	215	20·6		
	264	16·2		
	342	1·54	94	6
(XIIId)	215	21·9		
	240	20·1		
	348	21·6	15	85

[a] Determined by comparing with the $\lambda_{max.}$ (dioxan) 348 nm (ε 25,500) of *NN*-dimethylamide.

The nitro-group could be expected both to increase the carbonyl reactivity of the keto-group and decrease the basicity of the amide function. The shift in equilibrium would depend upon which of these effects plays the predominant role and which group is more susceptible to electronic influences. Apparently the decrease in

basicity more than counterbalances the increase in carbonyl reactivity and shifts the equilibrium in favour of the open form. It is also necessary to take into consideration the effect of electron withdrawal by the nitro-group on the cyclic form. Because the lactam is structurally constrained to a cisoid arrangement of the carbonyl dipole with respect to the R group (in contrast to the *trans*-arrangement found in most amides), this

TABLE 7

U.v. absorption and approximate equilibrium composition of 2-(4-dimethylaminobenzoyl)benzamides in acetonitrile

Amide	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Equilibrium composition (%) [a] Cyclic	Open
(XIIIa)	216	17·3		
	242	14·2		
	350	18·0	30	70
(XIIIb)	216	18·5		
	264	14·9		
	352	0·98	96	4
(XIIIc)	216	16·7		
	266	14·1		
	352	1·36	95	5
(XIIId)	216	18·7		
	242	18·9		
	350	20·9	18	82

[a] Determined by comparing with $\lambda_{max.}$ (MeCN) 350 nm (ε 25,500) of *NN*-dimethylamide.

group may be more affected by the destabilizing influence of the nitro-group resulting in substantial amounts of open form at equilibrium. The fact that the nitro-group in the 4-position (XVIIe) results in 64% of the open form, whereas the 5-nitro-group (XVIIc) gives 76% of the open form, instead of *vice versa*, indicates that, both the factors outlined above have to be taken into consideration.

When the nitro-groups are present in the 6- and 3-positions steric effects become operative. Newman and his co-workers [9] have observed that methyl groups in these positions lead to the formation of the cyclic tautomer because of steric effects. We find that in our case too, the steric effect of the nitro-groups plays an important role. For example, compounds (XVIIa) and (XVIIb) exist completely in the cyclic form. On the basis of electronic effects alone compounds (XVIIc, d) and (XVIIe, f) should be partially open. In the case of (XVIIa, b) the shift of the equilibrium towards the cyclic form cannot be due to its electronic effect and should be attributed to the steric effect as in the case of the 6-methyl analogues. The effect of the 3-nitro-group is similar, but the steric effect is less pronounced. This behaviour is also analogous to that observed by Newman and Muth [9] for the 3-methyl compound which shifts the equilibrium towards the cyclic form. In (XVIIg, h) the electronic effect of the nitro-group is more effective than its steric effect, with the net result of shifting the equilibrium towards the open form.

Substitution of a methyl group into the 2- and 6-positions in the benzoyl ring destabilizes the cyclic form of *o*-benzoylbenzoic acid.[9] In the case of amides similar behaviour is observed (*cf.* Table 2). Whereas the amide without the 2′- and 6′-methyl groups is totally cyclic, *o*-mesitoylbenzamide (XVa) is 96% open.

The effect on the basicity of the amide group by substitution by methyl, ethyl, and phenyl groups is predictable on the basis of the basicity of the corresponding amines. But whether an analogous order of basicity towards a carbonyl group is maintained, is not certain. Although the experimental results presented in this paper cannot hope to attain the precision of the pK values, it is possible to state definitely that the order of equilibrium constants are similar. It can be seen from Tables 4—7 that substitution of a hydrogen atom by a methyl or ethyl group increases the basicity by roughly the same extent, but the phenyl group decreases it.* We have also observed with the help of molecular models that even bulky groups like phenyl on the nitrogen atom do not introduce steric hindrance to the formation of the cyclic form, as it easily attains a staggered position with respect to the benzoyl ring.

Solvent Effects.—The equilibrium is so much in favour of the cyclic form in the case of amides that it is not sufficiently sensitive and delicately balanced always to respond to the influence of solvents. The tautomeric composition of 2-(4-dimethylaminobenzoyl)benzamides in four solvents (95% ethanol, chloroform, dioxan, and acetonitrile) are recorded in Tables 4—7. The influence of solvent polarity on the equilibrium is slight. The effect of the protic solvent, 95% ethanol, on the equilibrium is, however, more pronounced. Among the solvents studied it is more effective than any other in stabilizing the cyclic form (Tables 4—7). This is apparently caused by the more favourable hydrogen-bonding solvation of the cyclic form by ethanol.

The lack of influence of solvent polarity observed in this investigation may be contrasted with its profound influence in the case of acids.[3] In the case of acids, the cyclic form is markedly the more polar form, because of the periplanar cisoid arrangement of the lone pair on oxygen and the carbonyl dipole. In the hydroxylactam structure the lone pair on nitrogen aligns itself nearly at right angles to the carbonyl dipole and avoids the unfavourable interaction.

The keto-amides exist to a larger extent in the cyclic form than the corresponding keto-acids. This behaviour could be ascribed to the greater basicity of the amide function than the carboxylic group. A simple carbonyl addition–dissociation model (Scheme) is adequate to describe the tautomeric equilibrium and the effect of substituents. Substituents which decrease the electron deficiency on the carbonyl group shift the equilibrium to

* The pK_a values of methylamine, ethylamine, ammonia, and aniline are 10·7,[10] 10·67,[11] 9·25,[12] and 4·64 [10] respectively.

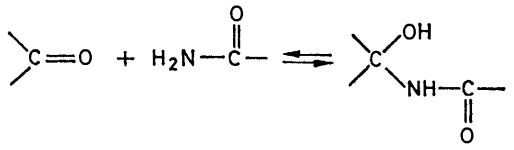
[9] M. S. Newman and C. W. Muth, *J. Amer. Chem. Soc.*, 1951, **73**, 4627.

[10] B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559.

[11] P. Damagaard-Sorensen and A. Unmack, *Z. physik. Chem.*, 1935, *A***172**, 389.

[12] H. S. Harned and B. B. Owen, *J. Amer. Chem. Soc.*, 1930, **52**, 5079.

the left. Groups which increase the basicity of the amide shift the equilibrium to the right.



SCHEME

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer model 137 Infracord or a Zeiss (Jena) double-beam model UR10 spectrophotometer. N.m.r. spectrum was taken using a Varian A60 instrument. Hexane refers to the light petroleum fraction, b.p. 40—60°. Before removal of solvents the organic extracts were washed, neutralized, and dried (Na_2SO_4). M.p.s are uncorrected.

2-(4-Substituted benzoyl)benzoic acids were prepared by literature procedures.[13-17] 2-(4-Nitrobenzoyl)benzoic acid was prepared according to the method of Bhatt and Kamath.[3] Acid chlorides were obtained by warming the acids with thionyl chloride at 50—60° for 3 h.

General Method for the Preparation of Amides.—A solution of the acid chloride (10 mmol) in chloroform (15 ml) was added with stirring to ammonia or alkylamines (20 mmol). After 2 h the mixture was diluted with water and extracted with chloroform. The solvent was evaporated and the amide was crystallized from a suitable solvent.

Oxime of o-Benzoylbenzoic Acid.—The oxime was prepared by the method described by Vogel.[18] *o*-Benzoylbenzoic acid (2 g), on reacting with hydroxylamine hydrochloride (2 g) and pyridine (2 ml) in ethanol (20 ml) for 1 h, gave the oxime (IX) (1·9 g, 88·8%), m.p. 161° (lit.,[19] 159—160°).

3-Phenylisoindolin-1-one (X).—The oxime (IX) (1·9 g) was dissolved in ethyl acetate and hydrogenated over platinum oxide. When absorption was complete, the catalyst was filtered off and the solvent was removed by distillation. Crystallization of the solid from benzene gave *crystals* of (X) (1·42 g, 92·5%), m.p. 212°, $\lambda_{max.}$ (EtOH) 223 nm (ε 12,240), $\nu_{max.}$ (Nujol) 3230 (NH) and 1705 cm^{-1} (lactam C=O), τ ($CDCl_3$) 1·8—2·8 (8H, m, ArH), 3·0br (1H, NH), and 4·3 (1H, s, ArC*H*) (Found: C, 80·5; H, 5·6; N, 7·0. $C_{14}H_{11}NO_2$ requires C, 80·4; H, 5·3; N, 6·75%).

NN-Dimethyl-2-(4-dimethylaminobenzoyl)benzamide.—Treatment of the appropriate acid chloride (2·9 g) with dimethylamine furnished the *NN-dimethylamide* (2·57 g, 82%), m.p. 142—143°, $\lambda_{max.}$ (EtOH) 214 (ε 15,100), 248 14,200), and 352 nm (24,400), $\nu_{max.}$ (Nujol) 1660 (ketone C=O) and 1625 cm^{-1} (amide C=O) (Found: C, 73·2; H, 5·9; N, 9·45. $C_{18}H_{20}N_2O_2$ requires C, 73·0; H, 6·75; N, 9·5%).

o-Mesitoylbenzoic Acid.—The procedure followed was essentially that of Newman and McCleary.[20] Mesitylene (20 ml), phthalic anhydride (15 g), and aluminium chloride (30 g) in 1,1,2,2-tetrachloroethane (75 ml) gave *o*-mesitoylbenzoic acid (24·4 g, 90%), m.p. 215° (lit.,[20] 214—216°).

o-Mesitoylbenzamide.—The acid chloride (2·8 g) dissolved in chloroform was treated with ammonia to obtain the amide (XV; R = H) (2·45 g, 91·8%), m.p. 176—177° (from benzene–hexane), $\nu_{max.}$ (Nujol) 3410 and 3150 (NH), 1700 (amide C=O), and 1670 cm^{-1} (ketone C=O).

o-Mesitoyl-N-methylbenzamide.—The acid chloride (2·8 g) in chloroform and methylamine solution gave the *N-methylamide* (XV; R = Me) (2·6 g, 92·5%), m.p. 168—169°,

TABLE 8

Amides of 4′-substituted *o*-benzoylbenzoic acids

					Analysis					
					Found (%)			Required (%)		
Amide	M.p. (*T*/°C)	Yield (%)	$\nu_{max.}$ (Nujol)/cm^{-1}	Formula	C	H	N	C	H	N
(XIb)	171—172 [a]	96	3500—3175, 1710, 1660	$C_{15}H_{13}NO_2$	75·5	5·4	5·6	75·3	5·4	5·85
(XIc)	183—184	90·5	3500—3200, 1705, 1670	$C_{14}H_{10}ClNO_2$	64·3	3·5	5·05	64·7	3·8	5·4
(XId)	193—194 [b]	95·5	3500—3200, 1705, 1670	$C_{14}H_{10}BrNO_2$	55·2	3·1	4·2	55·3	3·3	4·6
(XIe)	213—214	87	3500—3175, 1705, 1678, 1540, 1345	$C_{14}H_{10}N_2O_4$	62·0	3·45	10·3	62·2	3·7	10·4
(XIf)	137—138	95	3450—3250, 1702, 1662	$C_{14}H_{12}N_2O_2$	70·0	5·0	11·3	70·0	5·0	11·65

[a] Lit., m.p. 173—175° (D. W. Ockenden and K. Schofield, *J. Chem. Soc.*, 1953, 3914). [b] Lit., m.p. 190° (E. D. Bergmann and R. Barshai, *J. Amer. Chem. Soc.*, 1959, **81**, 5641).

TABLE 9

N-Substituted amides of 2-(4-dimethylaminobenzoyl)benzoic acids

					Analysis					
					Found (%)			Required (%)		
Amide	M.p. (*T*/°C)	Yield (%)	$\nu_{max.}$ (Nujol)/cm^{-1}	Formula	C	H	N	C	H	N
(XIIIa)	171—172	88	3450—3250, 1705, 1660	$C_{16}H_{16}N_2O_2$	71·45	5·8	10·15	71·6	6·0	10·45
(XIIIb)	176—178	92	3270, 1680	$C_{17}H_{18}N_2O_2$	73·2	6·15	9·55	72·4	6·4	9·9
(XIIIc)	195—196	90	3270, 1682	$C_{18}H_{20}N_2O_2$	72·8	6·5	9·25	73·0	6·75	9·5
(XIIId)	182—183	42 [a]	3215, 1680, 1660	$C_{22}H_{20}N_2O_2$	76·9	5·95	8·0	76·7	5·8	8·1

[a] Pseudo-anilide (50%), m.p. 202—204°, was also obtained.

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$\nu_{max.}$ (Nujol) 3378 (NH) and 1670 cm^{-1} (unresolved ketone and amide C=O) (Found: C, 77·1; H, 6·8; N, 5·2. $C_{18}H_{19}NO_2$ requires C, 76·9; H, 6·75; N, 5·0%).

o-*Mesitoyl*-N-*phenylbenzamide*.—The acid chloride (2·8 g) and aniline in chloroform solution afforded the *N*-phenylamide (XV; R = Ph) (2·85 g, 80%), m.p. 152° (from benzene), $\nu_{max.}$ (Nujol) 3333 (NH) and 1664 cm^{-1} (unresolved ketone and amide C=O).

o-*Mesitoyl*-NN-*dimethylbenzamide*.—The reaction of the appropriate acid chloride (2·8 g) with dimethylamine gave the NN-*dimethylamide* (2·42 g, 82·2%), m.p. 147—148°, $\nu_{max.}$ (Nujol) 1660 cm^{-1} (unresolved ketone and amide C=O) (Found: C, 77·1; H, 7·0; N, 4·65. $C_{19}H_{21}NO_2$ requires C, 77·3; H, 7·1; N, 4·75%).

Preparation of 3-, 4-, 5-, *and* 6-*Nitro*-2-*benzoylbenzoic Acids*.—These acids were prepared following the method of Chase and Hey.[21] Friedel–Crafts reaction of benzene (75 ml) with the acid chloride of hydrogen 2-methyl 3-nitrophthalate[22] (15 g) gave, after hydrolysis, 6-nitro-2-benzoylbenzoic acid (9 g, 43%), m.p. 162° (lit.,[21] 162·5°) and 3-nitro-2-benzoylbenzoic acid (1·9 g, 9%), m.p. 236—237° (lit.,[21] 236—238°). Similarly the acid chloride of hydrogen 1-methyl 4-nitrophthalate[23] (15 g), benzene (75 ml), and aluminium chloride (20 g) gave, after hydrolysis, 5-nitro-2-benzoylbenzoic acid (10·1 g, 48%), m.p. 213—214° (lit.,[21] 214—215°) and 4-nitro-2-benzoylbenzoic acid (1·0 g, 5%), m.p. 163—164° (lit.,[21] 163—164°).

Normal Methyl Esters of 3-, 4-, 5-, *and* 6-*Nitro*-2-*benzoylbenzoic Acids*.—The Fischer–Speier esterification of the acids in methanol[24] gave the normal esters. Table 10 summarizes the normal esters prepared.

Measurement of the U.v. Spectra.—All u.v. spectra reported in this paper were recorded on a Unicam SP-700A model ultraviolet and visible spectrophotometer at 22°. Solvents were purified according to literature methods[25] and tested for transparency in the region studied. Studies were made within 2 h of the preparation of solutions. The concentration employed was 5×10^{-5}M in all cases. The values of extinction coefficient reported are the mean of 2—4 determinations.

TABLE 10

Normal methyl esters of 6-, 5-, 4-, and 3-nitro-2-benzoylbenzoic acids

Ester	M.p. (*T*/°C)	Yield (%)	$\nu_{max.}$ (Nujol)/cm^{-1}	$\lambda_{max.}$/nm	Mean $\varepsilon_{max.}$ $\times 10^{-3}$	Analysis (%) [d] C	H	N
6-NO_2	93 [b]	92	1728, 1675, 1540, 1350	224	14·3	63·0	3·7	5·0
				250	18·3			
5-NO_2	124 [c]	94	1728, 1675, 1540, 1350	224	14·5	63·1	3·9	4·9
				250	18·5			
4-NO_2	109	93	1730, 1675, 1540, 1350	224	14·3	63·2	3·9	4·9
				250	18·9			
3-NO_2	122—123	95	1728, 1675, 1540, 1350	224	14·8	63·0	3·8	5·0
				248	18·2			

[a] All esters have the same molecular formula. $C_{15}H_{11}NO_5$ requires C, 63·2; H, 3·9; N, 4·9%. [b] Lit. m.p. 94·5° (B. H. Chase and D. H. Hey, *J. Chem. Soc.*, 1952, 553). [c] Lit. m.p. 123·5—124° (B. H. Chase and D. H. Hey, *J. Chem. Soc.*, 1952, 553).

TABLE 11

Amides of 6 , 5-, 4-, and 3-nitro-2-benzoylbenzoic acids

Amide	M.p. (*T*/°C)	Yield (%)	$\nu_{max.}$ (Nujol)/cm^{-1}	Analysis Found (%) C	H	N	Required (%) C	H	N
(XVIIa)	204	90	3450—3250, 1710, 1685, 1545, 1350	62·70	3·7	10·0	62·2	3·7	10·4
(XVIIb)	219	85	3350, 1685, 1540, 1350	63·4	4·25	9·85	63·0	4·2	9·85
(XVIIc)	194	91	3350—3200, 1705, 1685, 1540, 1350	62·5	3·85	10·45	62·2	3·7	10·4
(XVIId)	199—200	94	3310, 1682, 1540, 1350	62·8	4·0	9·65	63·0	4·2	9·85
(XVIIe)	190	88	3380—3200, 1705, 1682, 1540, 1350	62·15	3·45	9·65	62·2	3·7	10·4
(XVIIf)	195	90	3310, 1680, 1545, 1360	63·0	4·2	10·2	63·0	4·2	9·85
(XVIIg)	201—202	92·5	3400—3250, 1710, 1682, 1540, 1355	62·2	3·65	10·1	62·2	3·7	10·4
(XVIIh)	219—220	88	3290, 1682, 1542, 1350	63·4	4·4	10·2	63·0	4·2	9·85

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