156. *The Infrared Spectra of Some Nitro-amides.*

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Hydrogen bonding to nitro-groups can perturb the normal amide bands in the infrared spectra of solid nitro-anilides and -naphthalides. Solutions of *m*- and *p*-nitroanilides show normal spectra; intramolecular hydrogen bonding occurs in the *ortho*-isomers except when steric factors preclude chelation. No analogous effect is shown by amides carrying the nitro-group in the acyl portion.

The chemical and biolological importance of systems containing amide groups has resulted in a voluminous literature concerning their infrared spectra.[1-3] However, few reports have appeared of the spectra of amides carrying substituents, other than carboxyl groups,[1,4] which can interfere with their normal structure. The preparation, for other purposes, of a number of nitro-anilides and -naphthalides and related compounds made possible the examination of their infrared spectra and revealed some unexpected features.

Experimental

Materials.—2- and 4-Nitro-1-naphthylamine were prepared by nitrating 1-acetonaphthalide in acetic acid.[5]

N-Acetyl-2,4-dinitro-1-naphthylamine was prepared by Hodgson and Smith's method.[6]

N-o-*Nitrophenyl*-2,3-*methylenedioxybenzamide.*—A solution of 2,3-methylenedioxybenzoyl chloride (92 mg.) and *o*-nitroaniline (90 mg.) in dry benzene (2 ml.) was shaken with anhydrous potassium carbonate at room temperature for 3 days. Working up in the usual manner gave the *amide,* which crystallised from aqueous ethanol in yellow needles (120 mg., 84%), m. p. 179—180° (Found: C, 58·2; H, 3·4; N, 9·8. $C_{14}H_{10}N_2O_5$ requires C, 58·7; H, 3·5; N, 9·8%).

N-(2,3-*Methylenedioxybenzoyl*)-2-*nitro*-1-*naphthylamine.*—Anhydrous potassium carbonate, 2-nitro-1-naphthylamine (600 mg.), 2,3-methylenedioxybenzoyl chloride (640 mg.), and dry benzene (50 ml.) were heated under reflux for 5 hr. The mixture was filtered whilst hot, and the evaporated filtrate was put on to an alumina column. Elution with benzene gave the

[1] Randall, Fowler, Fuson, and Dangl, "Infrared Determination of Organic Structures," Van Nostrand, New York, 1949.

[2] Bellamy, "Infra-red Spectra of Complex Molecules," Chapter 12, Methuen, London, 1958; Jones and Sandorfy, "Chemical Applications of Spectroscopy," pp. 509 *et seq.*, Interscience Publ., Inc., New York, 1956.

[3] Richards and Thompson, *J.*, 1947, 1248.

[4] Fuson, Josien, and Powell, *J. Amer. Chem. Soc.*, 1952, **74**, 1; Micheel and Schleppinghoff, *Chem. Ber.*, 1955, **88**, 763.

[5] Hodgson and Walker, *J.*, 1933, 1205.

[6] Hodgson and Smith, *J.*, 1935, 1854.

amide, which crystallised from benzene in bright yellow needles (140 mg.), m. p. 214—215° (Found: C, 64·2; H, 3·7; N, 8·2. $C_{18}H_{12}N_2O_5$ requires C, 64·3; H, 3·6; N, 8·3%). Unchanged 2-nitro-1-naphthylamine (432 mg.) was recovered in a second fraction. The yield of amide, based on recovered amine, was 83%.

N-Acetyl-*N*-methyl-2,4-dinitro-1-naphthylamine and *N*-methyl-*N*-*o*-nitrophenylbenzamide were prepared by shaking the sodium salts of the secondary amides with dimethyl sulphate in toluene overnight in the cold.

Other anilides and naphthalides were prepared by conventional methods, *viz.*, formyl derivatives with formic acid, acetyl derivatives with acetyl chloride in pyridine, and benzoyl and substituted benzoyl derivatives with the benzoyl chloride and amine (2 mol.) in tetrahydrofuran.

Fluorine-containing amides were kindly presented by Professor J. C. Tatlow.

Spectroscopic Measurements.—Spectra were determined on a Perkin-Elmer model 21 spectrophotometer (sodium chloride optics) with mulls in Nujol and solutions (*ca.* 10^{-3}M) in chloroform. Formanilide became non-crystalline during grinding and its spectrum as a solid was measured for a solid film on rock salt.

Results and Discussion

The frequency of the carbonyl stretching band in simple amides lies at values lower than those found for simple esters and ketones. This is satisfactorily rationalised in terms of two effects which reduce the force constant of the carbonyl bond: (*a*) delocalisation of the lone-pair electrons from the nitrogen atom into the π-electron system of the amide outweighs the inductive effect of nitrogen; (*b*) hydrogen bonding in primary and secondary amides. So in the spectra of simple, secondary amides the carbonyl stretching frequency may be found in the range 1630—1680 cm.$^{-1}$ for solid samples and in the range 1670—1700 cm.$^{-1}$ for dilute solutions.[2]

The introduction of nitro-groups into the amine residue is expected to raise the carbonyl stretching frequency by decreasing the delocalisation of the lone-pair electrons and increasing the inductive action of the nitrogen atom. This is clearly shown by the results for chloroform solutions of the nitro-amides listed in the Table. The spectra obtained from solid samples show similarly increased carbonyl frequencies but these results are complicated by the effects of association. It is apparent that the carbonyl frequencies of these solid samples show a considerably wider spread over series of analogous compounds than do those of the corresponding solutions. On closer examination, two groups of bands are revealed: (i) close to the frequency of the carbonyl band in the solution spectrum; (ii) *ca.* 30 cm.$^{-1}$ lower than the frequency in solution; either one or both of these bands may be present. The lower-frequency bands appear at values close to those expected by analogy with other solid, secondary amides and show the expected effects of hydrogen bonding. Conversely, the higher-frequency bands are to be ascribed to structures in which the carbonyl groups are not hydrogen-bonded. An analogous doubling of the carbonyl frequency in concentrated solutions was reported by Richards and Thompson [3] and similarly ascribed to the presence of both bonded and non-bonded carbonyl groups.

The N–H stretching frequencies for the solid samples do not show any analogous splitting: in all the secondary amides examined the N–H absorption band lies in the range 3300 ± 80 cm.$^{-1}$ consistent with a hydrogen-bonded amino-group. Consequently, if the assignment of the two carbonyl bands is correct it is necessary to postulate the presence of a grouping able to compete with the carbonyl group for the hydrogen bond. The nitro-group in these compounds is potentially capable of this.

The interaction of nitro- and amino-groups in nitro-anilines and -naphthylamines and the possibility of chelation in the *ortho*-substituted compounds have been investigated in detail.[7,8] For the solid state the N–H stretching bands appear at those frequencies expected

[7] Flett, *Trans. Faraday Soc.*, 1948, **44**, 767; Hathaway and Flett, *ibid.*, 1949, **45**, 818; Brysom and Werner, *Austral. J. Chem.*, 1960, **13**, 456; Farmer and Thomson, *Spectrochim. Acta*, 1960, **16**, 559; Moritz, *ibid.*, p. 1176; 1962, **18**, 671.

[8] Dyall and Hambly, *Austral. J. Chem.*, 1958, **11**, 513; Dyall, *Spectrochim. Acta*, 1961, **17**, 291.

Carbonyl and amino stretching frequencies ($cm.^{-1}$) in the spectra of nitro-amides and related compounds.

Compound	Carbonyl bands: Solid: Bonded	Carbonyl bands: Solid: Free	Carbonyl bands: Soln.	Amino-bands: Solid	Amino-bands: Solution: Bonded	Amino-bands: Solution: Free
Substituted formamides						
Ar in H·CO·NHAr						
Ph	1664		1692	3230		3420
o-NO_2·C_6H_4	1687	1717	1712	3290	3350	
p-NO_2·C_6H_4	1670	1690	1703	3260		3440
1-$C_{10}H_7$	1658		1692	3220		3410
2,1-NO_2·$C_{10}H_6$	1673		1707	3340		3400
Substituted acetamides						
Ar in Ac·NHAr						
Ph	1658		1689	3260		3450
o-NO_2·C_6H_4	1670	1700	1707	3365	3370	
m-NO_2·C_6H_4	1674		1702	3260		3440
p-NO_2·C_6H_4	1680		1707	3350		3430
m-CF_3·C_6H_4	1673		1695	3280		3440
2,4-NO_2·$C_6H_3(CF_3)$		1713	1714	3380	3370	
4,2-NO_2·$C_6H_3(CF_3)$	1681		1722	3290		3450
6,2,4-NO_2·$C_6H_2Me_2$	1660		1693	3290		3430
1-$C_{10}H_7$	1658		1689	3280		3440
2,1-NO_2·$C_{10}H_6$	1668	1703	1702	3290		3420
4,1-NO_2·$C_{10}H_6$	1666	1725	1715	3220		3460
2,4,1-$(NO_2)_2C_{10}H_5$,	1680		1714	3260	3390	
,, *N*-Me deriv.		1675	1676	—	—	—
1,2-NO_2·$C_{10}H_6$	1666		1705	3160		3420
2-Nitro-*N*-trifluoroacetyl-3-trifluoromethylaniline	1722		1750	3250	3390	
2-Nitro-*N*-trifluoroacetyl-4-trifluoromethylaniline	1736		1755	3290	3390	
Substituted benzamides						
Ar in Ph·CO·NHAr						
Ph	1656		1674	3330		3440
o-NO_2·C_6H_4		1687	1687	3365	3350	
,, *N*-Me deriv.		1646	1653	—	—	—
p-NO_2·C_6H_4	1658		1692	3260		3440
1-$C_{10}H_7$	1652		1677	3260		3440
2,1-NO_2·$C_{10}H_6$	1660	1690	1699		3360	
4,1-NO_2·$C_{10}H_6$	1655		1688	3260		3440
o-MeO·C_6H_4	1643		1672	3240		3430
p-MeO·C_6H_4	1648		1672	3330		3440
R in R·C_6H_4·CO·NHPh						
o-NO_2	1659		1685	3260		3430
p-NO_2	1650		1681	3320		3430
o-MeO	1653		1663	3310	3370	
p-MeO	1656		1668	3340		3440
R in R·C_6H_4·CO·NH·$C_{10}H_7$-1						
o-NO_2	1659		1686	3240		3420
p-NO_2	1645		1683	3220		3430
o-MeO		1663	1664	3350	3370	
p-MeO	1647		1669	3250		3440
Ar in 2,3-CH_2O_2·C_6H_3·CO·NHAr						
Ph		1686	1687	3300	3370	
2,1-NO_2·$C_{10}H_6$		1693	1685	3350	3370	

for hydrogen-bonded amino-groups; in dilute solution *m*- and *p*-nitroanilines show spectra characteristic of non-bonded amino-groups, while the spectra of the *ortho*-compounds have been variously interpreted as showing weak or no hydrogen bonding. When the amino-group of *o*-nitroaniline is replaced by an acetamido-group the N–H stretching frequency

in solution indicates clearly that intramolecular hydrogen bonding occurs.[8] Our own results confirm this and show that in general *o*-nitro-anilides and -naphthalides are intramolecularly bonded [ν(N–H) 3370 ± 20 cm.$^{-1}$ in chloroform] and may be distinguished from the non-bonded *p*-nitro- and unsubstituted compounds [ν(N–H) 3440 ± 20 cm.$^{-1}$ in chloroform]. The occurrence of free carbonyl groups in solid *o*-nitro-anilides and -naphthalides can be satisfactorily ascribed to the persistence of this intramolecular hydrogen bond into the solid state. However, it is apparent that intermolecular bonding between amido-groups can compete with the intramolecular bond for the hydrogen atom in some of the solid *o*-nitro-amides. Further, there is direct competition between nitro- and carbonyl intermolecular hydrogen bonding in some of the solid *p*-nitro-amides.

The available data are insufficient to rationalise these results completely. Clearly factors other than the ability of nitro- and carbonyl groups to participate in hydrogen bonding are of significance. Amongst these, the packing requirements of the crystal (which in several cases permit two environments for the carbonyl group) and steric effects within the amide molecule are of obvious importance. Steric effects become the determining factor in *o*-nitroanilides which carry an additional *ortho*-substituent. By molecular-weight determinations [9] it was shown that such compounds, unlike other *o*-nitroanilides, were associated in the solid state. The suggestion that such compounds are prevented from intramolecular hydrogen bonding by steric crowding is supported by examination of molecular models. The infrared spectra of 2-methyl-6-nitro- [10] and 2,4-dimethyl-6-nitro-acetanilide confirm this: for the solid state typically bonded N–H and C=O frequencies are shown; in solution both the amino- and the carbonyl group are non-bonded. That the steric requirements of the nitro-group are less than those of the amido-group is shown by 2-nitro-*N*-trifluoroacetyl-3-trifluoromethylaniline which contains a typically bonded amino-group in solution. Chaplin and Hunter [9] suggested that similar effects are demonstrated by the nitronaphthalides. Molecular-weight determinations indicated that while 2-nitro-*N*-acetyl-1-naphthylamine is associated, the isomeric *N*-acetyl-1-nitro-2-naphthylamine is intramolecularly hydrogen bonded. However, the spectra of *N*-acetyl-2-nitro-1-, *N*-formyl-2-nitro-1-, and *N*-acetyl-1-nitro-2-naphthylamine indicate that none of them is chelated in solution (models suggest that the steric requirements of a 1-nitro-group in naphthalene are more stringent than those of 2,6-disubstituted nitrobenzenes). Conversely *N*-acetyl-2,4-dinitro-1- and *N*-benzoyl-2-nitro-1-naphthylamine are intramolecularly hydrogen bonded in solution: in the former the increased strength of the hydrogen bond in the dinitro-compound appears to outweigh the steric compression required to maintain it; in the latter the presence of the bulky aryl substituent appears to force the amido-group into the bonding conformation although the $C_{(8)}$–H bond must suffer displacement by the carbonyl group. The chelate structure of *N*-(2,3-methylenedioxybenzoyl)-2-nitro-1-naphthylamine may be due to a similar effect, but alternatively the hydrogen bond may be due to the methylenedioxy-grouping (see below). No useful variations in either the nitro-group frequencies or the aromatic C–H deformation frequencies of these strained molecules could be detected.

To determine whether a nitro-substituent in the acyl group could compete with the carbonyl group for the hydrogen bond the spectra of *o*- and *p*-nitrobenzoyl-aniline and -1-naphthylamine were examined. The spectra give no indication of hydrogen bonding to the nitro-group. The absence of such a bond can be ascribed to the less acidic nature of the amino-group in these compounds; the failure of the *o*-nitro-derivatives to chelate is additionally due to the unfavourable seven-membered ring that would be formed.

The effect of ring size on the stability of a chelate structure is further demonstrated by a series of methoxy-amides which was examined for comparison. The derivatives of neither *o*- nor *p*-anisidine show hydrogen bonding to the ether group but *N*-*o*-methoxybenzoyl-aniline and -1-naphthylamine are both chelated in solution. However, while the

[9] Chaplin and Hunter, *J.*, 1938, 375.
[10] Buswell, Downing, and Rodebush, *J. Amer. Chem. Soc.*, 1939, **61**, 3254.

chelate structure of the naphthalide persists in the solid giving a relatively high carbonyl frequency, it does not do so in the anilide. This may be contrasted with the behaviour of the analogous methylenedioxybenzoyl derivative of *o*-nitroaniline in which the solid is also chelated, but whether this is due to bonding to the nitro-group or to the increased stability of the hydrogen bond to the ether group is not established.

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