NITRO GROUPS AS PROTON ACCEPTORS IN HYDROGEN BONDING[1]

W. F. Baitinger,[2] P. von R. Schleyer,[3] T. S. S. R. Murty and L. Robinson[4]

Frick Chemical Laboratory, Princeton University,
Princeton, New Jersey

Abstract—Nitro compounds can participate in both intermolecular and intramolecular hydrogen bonding, as revealed by IR spectroscopic evidence. This conclusion contradicts recent literature reports, which are shown to be in error. Spectral shifts of OH proton donors bonding to nitro compounds are small, indicating the weakly basic character of the NO_2 function. The magnitude of intermolecular spectral shifts to nitro compounds depend markedly on proton acceptor concentration; the desirability of making such measurements by extrapolation to infinite dilution is emphasized. The data reveal appreciable ground state resonance interaction between NO_2 groups and aromatic rings in nitrobenzene and its derivatives.

The pronounced difference in physical behaviour distinguishing *o*-nitrophenol, which forms a strong intramolecular hydrogen bond between the hydroxyl and nitro groups, from *m*- and *p*-nitrophenol, for which intramolecular association is impossible, is so well known as to be perhaps the most frequently encountered textbook example of "chelation". The effect of "chelation" on physical properties, e.g., melting point, boiling point, steam volatility and intermolecular association, is covered in fundamental chemistry courses. As early as thirty years ago,[5] such intramolecular association was postulated as a result of observation of the melting points and ultraviolet and visible spectra of nitroresorcinols. In the 1930's, pioneer infrared spectroscopic evidence for chelation[6-9] was based on the invariable absence of the characteristic infrared OH peak at the usual position in phenols with an *ortho* nitro group. The displacement of the OH peak to "abnormal" positions was interpreted as indicative of strong intramolecular association. The acceptor properties of the nitro group were compared to the carbonyl group, e.g., in salicylaldehyde, another system for which physical properties also confirm chelation.[7,9]

[1] Paper XIII of a series on hydrogen bonding; paper XII, W. F. Baitinger and P. von R. Schleyer, *J. Org. Chem.*, **29**, 989 (1964).

[2] American Cyanamid Junior Research Fellow, 1960–1962; National Institutes of Health Fellow, 1962–1963; Ph.D., Princeton University, 1964.

[3] Alfred P. Sloan Research Fellow.

[4] A. B. Thesis, Princeton University, 1960.

[5] W. Baker, *J. Chem. Soc.*, 1684 (1934).

[6] O. R. Wulf and V. Liddel, *J. Amer. Chem. Soc.*, **57**, 1464 (1935).

[7] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and V. Liddel, *Nature, Lond.* **135**, 147 (1935).

[8] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and V. Liddel, *J. Amer. Chem. Soc.*, **58**, 548 (1936).

[9] J. Errera and P. Mollet, *C.R. Acad. Sci., Paris* **200**, 814 (1935); *J. Phys. Radium* **6**, 281 (1935) [*Chem. Abstr.* **30**, 5125 (1936)].

Numerous investigations[10-20] of the spectra of o-nitrophenol and its analogs have appeared subsequently in the literature. Quite early Gordy[10] cited the identity of IR spectra of o-nitrophenol in benzene and nitrobenzene as conclusive evidence of a strong intramolecular hydrogen bond. This intramolecular hydrogen bond has been studied with relation to NMR chemical shifts,[14] UV spectra,[11,13] polarographic reduction,[12] physical state,[15,16] and inductive, steric, and conformational effects.[17,19,20] There appears to be no doubt that a strong intramolecular hydrogen bond is present in o-nitrophenol.

The intramolecular bond formed in o-nitrophenol represents a "special" case. Its unusual strength is a result of the resonance contribution, I. Resonance simultaneously increases both the proton donor ability of the OH group and the proton

I
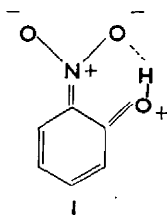
acceptor ability of the NO_2 function, resulting in very large hydrogen bonded OH spectral shifts of 300–500 cm^{-1} in the 3 μ region for this type of system.[17,21] In contrast, when the NO_2 and OH groups are in different molecules, as in $C_6H_5NO_2$ and C_6H_5OH, very much smaller OH $\cdots O_2N$ spectral shifts ($\Delta v = 70$–100 cm^{-1}) are observed.[22] Such intermolecular hydrogen bonding, although definitely established to be present, must be very much weaker than in the special o-nitrophenol intramolecular cases.[23]

[10] W. Gordy, J. Chem. Phys. 7, 167 (1939).

[11] W. Luttke and R. Mecke, Z. Phys. Chem. 196, 56 (1951).

[12] L. W. Reeves, E. A. Allen and K. O. Stromme, Canad. J. Chem. 38, 1249 (1960).

[13] P. A. D. de Maine, A. G. Goble and A. G. Maddock, Spectrochim. Acta 15, 1054 (1959).

[14] I. Gränacher, Helv. Phys. Acta 34, 272 (1961).

[15] V. v. Keussler and G. Rossmy, Z. Electrochem. 60, 136 (1956).

[16] M. St. C. Flett, Spectrochim. Acta 10, 21 (1957).

[17] A. W. Baker and A. T. Shulgin, J. Amer. Chem. Soc. 80, 5358 (1958).

[18] H. Hoyer, Chem. Ber. 89, 146 (1956).

[19] R. A. Nyquist, Spectrochim. Acta 19, 1655 (1963).

[20] H. Musso, Chem. Ber. 95, 1711, 1722 (1962).

[21] Numerous studies of o-nitroanilines also confirm the presence of an intramolecular hydrogen bond between the amino and nitro groups: O. R. Wulf and V. Liddel, J. Amer. Chem. Soc. 57, 1464 (1935); H. O. Chaplin and L. Hunter, J. Chem. Soc. 375 (1938); A. M. Buswell, J. R. Downing and W. H. Rodebush, J. Amer. Chem. Soc. 61, 3252 (1939); D. E. Hathway and M. St. C. Flett, Trans. Faraday Soc. 45(321), 1 (1949); L. K. Dyall and A. N. Hambly, Aust. J. Chem. 2, 513 (1958); L. K. Dyall and A. N. Hambly, Chem. & Ind. 268 (1958); T. Urbanski and V. Dabrowska, ibid. 1206 (1958); A. G. Moritz, Spectrochim. Acta, 15, 242 (1959); A. G. Moritz, ibid. 16, 1176 (1960); J. H. Richards and S. Walker, Trans. Faraday Soc. 57, 418 (1961); A. Moritz, Spectrochim. Acta 18, 671 (1962); H. Musso, Chem. Ber. 95, 1711 (1962).

[22] Data from this paper.

[23] W. Gordy, J. Amer. Chem. Soc. 60, 605 (1938); also W. Gordy and A. H. Nielsen, J. Chem. Phys. 6, 12 (1938).

Investigations of intermolecular hydrogen bonding have involved various nitro compounds and such proton donors as HCl,[24-27] C_6H_5OH,[28,29] CH_3OH and CH_3OD,[27,30] H_2O,[27,31,32] pyrrole,[27,33] and other donors of varying acidity.[33] In most of these studies, nitro compounds were included among a large number of miscellaneous bases and little specific attention was directed to the nitro results. Nitro groups uniformly formed definite, but rather weak hydrogen bonds, judging from the magnitudes of the spectral shifts either in the fundamental, or first or second overtone regions. This conclusion has been further supported by more refined recent studies on CH_3NO_2[31,32,34] and $C_6H_5NO_2$;[35-37] deviations from Kirkwood–Bauer–Magat plots were interpreted as indicating intermolecular hydrogen bonding as bulk medium effects were insufficient to account for the shifts observed.

On the basis of this evidence, one would expect that the nitro group could function perfectly well as a proton acceptor in intramolecular hydrogen bonding in aliphatic systems. Flett[16] included β-nitroethanol in a survey of intramolecular hydrogen bonding; only a broad band centering at 3588 cm⁻¹ in CCl_4 solution was reported, a value significantly displaced from the normal primary alcohol frequency of about 3636 cm⁻¹. Kuhn et al.[38] reported data for the same compound in CCl_4 which were significantly different—"free" band at 3623 cm⁻¹ and bonded band at 3608 cm⁻¹—but concluded that the "gauche" form in β-nitroethanol was more stable, due to the formation of a weak, intramolecular hydrogen bond. Robinson[4] reached the same conclusion after an IR investigation of a number of β-nitroalcohols. Spectroscopic shifts of both ultraviolet and infrared peaks for the NO_2 group have been interpreted as evidence for intramolecular bonds in nitroalcohols with two β-hydroxyl groups.[39]

With the background presented, it appeared conclusive that the NO_2 group can act as a proton acceptor in hydrogen bonding systems, although the interaction is weak in all instances with the exception of the "special" case of o-nitrophenol and its analogs. It was particularly surprising to us that intramolecular hydrogen bonding in β-nitroalcohols has been refuted recently.[40,41] The evidence cited in support of

[24] D. Williams, *Phys. Rev.* **50**, 219 (1936).

[25] W. Gordy and D. C. Martin, *J. Chem. Phys.* **7**, 99 (1939).

[26] W. Gordy, *Ibid.* **9**, 215 (1941).

[27] L. J. Bellamy, H. E. Hallam and R. L. Williams, *Trans. Faraday Soc.* **54**, 1120 (1955).

[28] R. Mecke, *Z. Electrochem.* **52**, 269 (1948).

[29] R. Mecke, *Discuss. Faraday Soc.* **9**, 161 (1950).

[30] W. Gordy, *J. Chem. Phys.* **7**, 93 (1939).

[31] P. Saumagne and M. L. Josien, *Bull. Soc. Chem. France* 813 (1958).

[32] E. Greimacher, W. Luttke and R. Mecke, *Z. Electrochem.* **59**, 23 (1955).

[33a] L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.* **55**, 220 (1959); [b] P. V. Huong, *Rev. Inst. Franc. Pétrole* **18**(9) 1 (1963).

[34] M. L. Josien, *Pure & Appl. Chem.* **4**, 33 (1962).

[35] M. L. Josien and N. Fuson, *J. Chem. Phys.* **22**, 1169 (1954).

[36] M. L. Josien and G. Sourisseau in *Symposium on Hydrogen Bonding, Ljubljana*, 1957 (Edited by D. Hadzi). Symposium Publications Division, Pergamon Press (1959).

[37] M. L. Josien and N. Fuson, *J. Chem. Phys.* **22**, 1264 (1954).

[38] M. Kuhn, W. Luttke and R. Mecke, *Z. Analyt. Chem.* **57**, 680 (1963).

[39] T. Urbanski, *Bull. Acad. Polon. Sci., Cl* III, **1**, 239 (1953); *Ibid.* **4**, 87, 381 (1956); Z. Eckstein, T. Urbanski and W. Sobotka, *Ibid.* **5**, 679 (1957); T. Urbanski, *Tetrahedron* **6**, 1 (1959); T. Urbanski and D. Ciercierska, *Roczniki Chem.* **29**, 11 (1955); T. Urbanski, *Ibid.* **31**, 37 (1957).

[40] H. E. Ungnade and L. W. Kissinger, *Tetrahedron* **19**, Suppl. 1, 121 (1963).

[41] H. E. Ungnade, E. D. Loughran and L. W. Kissinger, *J. Phys. Chem.* **66**, 2643 (1962).

this contention was based on IR spectral studies using an instrument equipped with a low resolution NaCl prism, previously shown to be inadequate for such investigations.[42] It is impossible to achieve the resolution necessary to interpret hydrogen bonding spectra using NaCl IR spectrometers, when the spectral shifts are of as small a magnitude as would be expected here.

We have sought here to clarify this problem by a comparison of intermolecular and intramolecular hydrogen bonding involving nitro groups and by studying the influence of structure upon spectral behaviour. In addition, the possible relationship between IR spectral shifts and other parameters, such as hydrogen bonding enthalpies[43] and functional group basicities[44] has prompted our interest in the problems associated with the determination of meaningful spectral shifts. Pitfalls are illustrated here.

RESULTS AND DISCUSSION

Intermolecular hydrogen bonding

In order to establish conclusively that the nitro group can act as a proton acceptor and to serve as a calibration for intramolecular results, intermolecular hydrogen bonding of methanol and phenol to a variety of nitro compounds was studied in CCl_4 solution by IR spectroscopy. A dilute solution of a proton donor in an inert solvent displays a single absorption band (e.g., O—H stretch). If a substance incapable of forming a hydrogen bond is added, there is little alteration in the spectrum, either in band position, shape or intensity. Addition of a proton donor, on the other hand, gives rise to a new, broad and intense band at a lower frequency but the "free" peak position and appearance is changed little, except for a progressive decrease in intensity as the concentration of proton acceptor increases. This latter behavior, specifically characteristic of hydrogen bonding,[45] is observed for the nitro compounds studied here. Results from the two donors (Table 1) are in close agreement. Phenol, the stronger acid, gives spectral shifts ($\Delta\nu$) two to three times as large as methanol. There is no doubt from these results that the nitro group is acting as a proton acceptor, a conclusion in agreement with the literature.[23–37]

Ideally, spectral shifts should be measured in the gas phase in the absence of any perturbing environment. In practice, vapour phase measurements are difficult, especially for large, involatile molecules, and most spectral studies are done in solution. Many of the early investigations of intermolecular hydrogen bonding used a solution of proton donor in a given base, the latter serving both as a proton acceptor and as solvent. It has been emphasized recently[46]—and we will stress here—that this practice is highly undesirable. A constant environment is necessary for meaningful comparison of data for different compounds.

A second procedure, now in general use for spectral shift measurements, employs

[42] P. von R. Schleyer, C. Wintner, D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. 14, 1 (1959).
[43] M. D. Joesten and R. S. Drago, *J. Amer. Chem. Soc.* **84**, 3817 (1962); M. L. Josien, *J. Chim. Phys.* in press (1963) (*International Symposium on Solvation Phenomena, Alberta, Canada*, August, 1963, *Abstracts*, p. 19); A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.* **85**, 1233, 1715 (1963) and refs. therein cited.
[44] For a review, see: E. M. Arnett in *Progress in Physical Organic Chemistry* (Edited by S. G. Cohen, A. Streitwieser, Jr. and R. W. Taft) Vol. I, Interscience Publishers, 1963, p. 223ff.
[45] G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*. W. H. Freeman and Co., San Francisco, Calif. (1960).
[46] A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.* **85**, 371, 866 (1963).

TABLE 1. INTERMOLECULAR HYDROGEN BONDING OF METHANOL AND PHENOL TO NITRO COMPOUNDS

Compound	M.p. or b.p. (mm)[a]	Methanol			Phenol		
		ν free[b]	ν bonded	$\Delta\nu$	ν free[c]	ν bonded	$\Delta\nu$
Nitromethane	100·5° (760)	3637	3611	26	3605	3522	83
Nitroethane	114° (760)	3637	3610	27	3606	3522	84
1-Nitropropane	131° (760)	3638	3610	28	3608	3522	86
2-Nitropropane	119·5° (760)	3638	3609	29	3608	3518	90
2-Methyl-2-nitropropane	126° (760)	3640	3610	30	3608	3518	90
1-Chloro-1-nitropropane	162·5° (760)	3638	none	—	3608	3562	46
1,1-Dichloro-1-nitropropane	144·5° (760)	3638	none	—	3608	d	—
Nitrobenzene	207° (760)	3636	3609	27	3606	3521	85
o-Nitroanisole	271° (760)	3638	3598	40	3608	3524	84
m-Nitroanisole	35·5°	3634	3606	28	3606	3516	90
p-Nitroanisole	59°	3640	3598	42	3608	3507	101
o-Nitrotoluene	215° (760)	3640	3610	30	3607	3524	83
m-Nitrotoluene	221° (760)	3640	3613	27	3608	3525	83
p-Nitrotoluene	51°	3640	3606	34	3609	3519	90
Nitromesitylene	43°	3641	3616	25	3609	3532	77

[a] M.ps are corrected; b.ps are uncorrected. All physical constants check literature values satisfactorily.

[b] Solvent CCl_4; CH_3OH conc., 1 μl/ml; nitro compound conc., 100 μl/ml.

[c] Solvent CCl_4; ϕOH conc., 1 mg/ml; nitro compound conc., 100 μl/ml.

[d] At low concns of nitro compound, only a broad shoulder appears on the low frequency side of the free peak. See Table 2 for $\Delta\nu^\infty$ for this compound.

a solution of proton donor and acceptor in an "inert" solvent, often CCl_4. It is not generally appreciated that this procedure, if uncritically used, can also be unsatisfactory. Often, but not always, spectral shifts are highly sensitive to the concentration of proton acceptor employed, this being the component ordinarily used in excess.[46] Discrepancies in the literature between reported spectral shift values may be due chiefly to a lack of uniformity of conditions, rather than to experimental errors. In order to predict when this spectral shift–concentration dependence is to be expected we have suggested that a comparison be made between the G values[46] of solvent and acceptor. These G values are empirical solvent shift parameters applicable to hydrogen bonding situations.[46] When the G values of solvent and acceptor are nearly the same, then little concentration dependence of spectral shifts are observed, but when the G values are different, a marked concentration dependence is to be expected. The G values of CCl_4 (69) and of CH_3NO_2 (99) are very different, and variations of spectral shifts with concentration are extreme: $\Delta\nu_{phenol} = 103$ cm^{-1} in pure CH_3NO_2, 88 cm^{-1} in 20 mole% CH_3NO_2 in CCl_4, and 68 cm^{-1} in 1 mole% CH_3NO_2 in CCl_4 (Table 2 and Fig. 1). Other nitro compounds, expected also to have high G values, behave similarly (Table 2 and Figs. 1 and 2); spectral shifts vary greatly with concentration.

Hydrogen bonding spectral shifts have considerable potential not only as indicators of the strength of hydrogen bonds (see below) but also measures of ground state electron availability and basicity, and as clues to the electronic and steric influences of substituent groups.[45] For meaningful comparison of spectral shift values, it is desirable that standard conditions be chosen. We propose that hydrogen bonding

TABLE 2. CONCENTRATION DEPENDENCE OF Δν (TO PHENOL)[a]

Compound	∞ Dil.[b]	Mole % nitro compound									
		1	3	5	8	10	20	40	60	80	100
Nitromethane	64	68	75	(77)[c]	—	82	(84)[d]	(90)[e]	(92)[f]	(98)[g]	103
Nitroethane	66	69	74	78	82	84	88	96	100	104	—
2-Nitropropane	68	71	78	82	85	—	90	97	101	—	—
2-Methyl-2-nitropropane	73	76	80	82	86	89	94	—	—	—	—
1-Chloro-1-nitropropane	35–45	—	—	—	sh	sh	46	52	—	—	58
1,1-Dichloro-1-nitropropane	20–30	—	—	—	—	—	sh	35	38	—	42
Nitrobenzene	67	70	74	77	80	82	90	93	98	100	102
o-Nitroanisole	76	78	82	84	86	89	92	98	102	—	104
m-Nitroanisole	76·5	78	80	82	(86)[h]	—	—	—	—	—	—
p-Nitroanisole	86	90	96	100	(102)[i]	—	—	—	—	—	—
o-Nitrotoluene	74	76	80	81	83	86	92	94	—	—	100
m-Nitrotoluene	71	73	77	79	82	85	88	94	—	—	100
p-Nitrotoluene	77–78	—	83	88	(91)[j]	—	—	—	—	—	—
Nitromesitylene	(67)[k]	—	73	75	77	79	(81)[l]	—	—	—	—

[a] The concentration of phenol was varied over the range ca. 1–10 mg/ml to permit observation of the bonded peak. Δν's calculated using a constant value of 3610 cm^{-1} on the free peak of phenol.

[b] Values obtained by extrapolation of curves (Figs. 1 and 2) to infinite dilution. Depending on what curvature is assumed, various values of $\Delta \nu^{\infty}$ can be obtained (see text), so that such values are only approximations.

[c] Value determined at 6 mole % nitromethane.

[d] Value determined at 15 mole % nitromethane.

[e] Value determined at 25 mole % nitromethane.

[f] Value determined at 50 mole % nitromethane.

[g] Value determined at 75 mole % nitromethane.

[h] Value determined at 8·5% nitroanisole which represents solubility limit.

[i] 6·6% p-nitroanisole; solubility limit.

[j] 7·3% o-nitrotoluene; solubility limit.

[k] Steric hindrance of the 2,6-methyl groups appears to limit access to the nitro group at low concentrations and the bonded peak cannot be detected; the extrapolated value here is less reliable.

[l] 13% nitromesitylene; solubility limit.

spectral shifts be determined in CCl$_4$ solution at a variety of proton donor and proton acceptor concentrations. "Standard" spectral shifts due to an intermolecular association should be determined by extrapolating proton acceptor (and, as much as possible, proton donor) concentrations to infinite dilution. If this procedure is not possible, then as low a concentration as feasible of donor and acceptor should be employed.

The desirability of this choice of standard conditions is shown by the following illustration. Table 1 lists the spectral shifts obtained for phenol and methanol with various nitro compounds at the same concentration, in this case, approximately 10% v/v in CCl$_4$. This is the typical way data of this type have been reported in the literature. Table 2 presents the same spectral shifts as a function of acceptor concentration; these data are plotted in Figs. 1 and 2. Only phenol could be used effectively for this study, since the small spectral shifts observed with methanol prevented use of a wide range of concentrations. It is seen from Figs. 1 and 2 that there is considerable
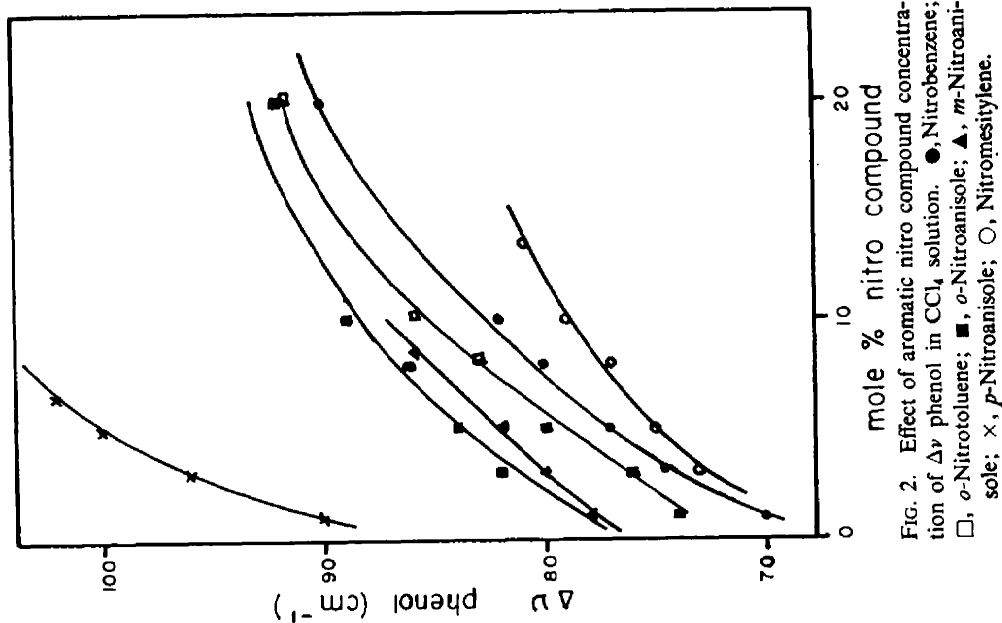
FIG. 2. Effect of aromatic nitro compound concentration of $\Delta\nu$ phenol in CCl$_4$ solution. ●, Nitrobenzene; □, o-Nitrotoluene; ■, o-Nitroanisole; ▲, m-Nitroanisole; ×, p-Nitroanisole; ○, Nitromesitylene.
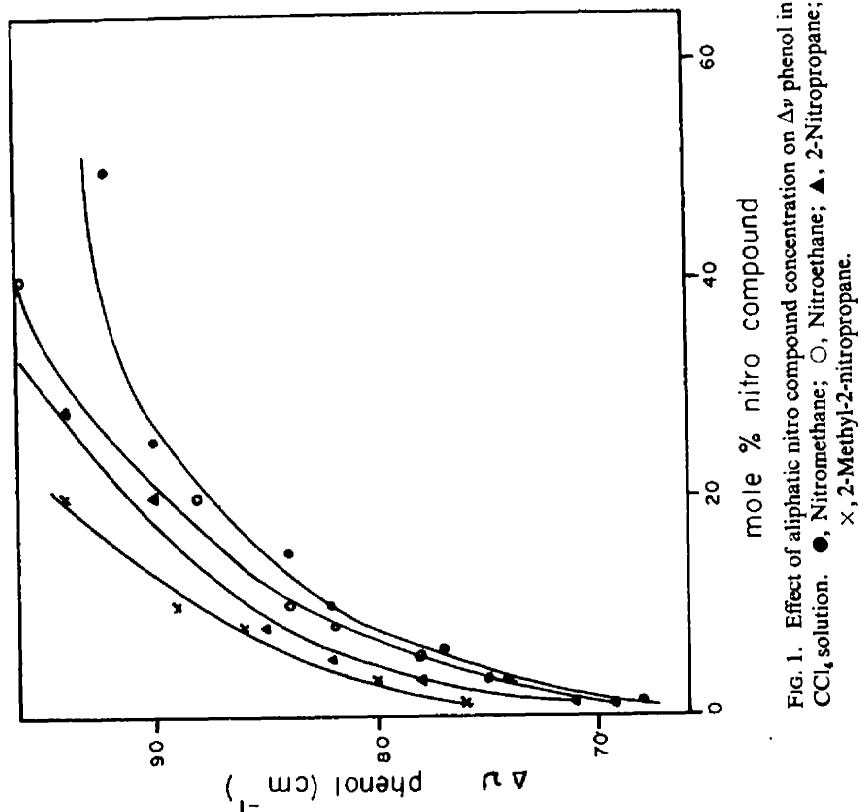

FIG. 1. Effect of aliphatic nitro compound concentration on $\Delta\nu$ phenol in CCl$_4$ solution. ●, Nitromethane; ○, Nitroethane; ▲, 2-Nitropropane; ×, 2-Methyl-2-nitropropane.

concentration dependence of $\Delta\nu$, and the maximum effect is found at low mole percentages of acceptor. This curvature unfortunately makes estimation of spectral shift at infinite dilution less precise, but at worst such errors should amount to only 2–3 cm^{-1}. Table 3 lists spectral shifts at infinite dilution; comparison with the data of Table 1 shows that, in every case, the magnitude of $\Delta\nu$ is considerably less at infinite dilution, but the diminution varies in magnitude from compound to compound and sometimes the absolute order is altered. This is emphasized in Figs. 1 and 2 where the slopes of the curves vary considerably from compound to compound. In an earlier study with nitriles as acceptors,[46] cases were found where similar curves

TABLE 3. RELATIONSHIP OF σ^* AND $\Delta\nu$ FOR RNO$_2$ AND RCN COMPOUNDS

R	σ^*	$\Delta\nu^\infty$RNO$_2$ to phenol[a]	$\Delta\nu^\infty$RC≡N[b]	
			to methanol	to phenol
t-Butyl	−0·30	73	85	169
i-Propyl	−0·19	68	84	166
Ethyl	−0·01	66	81	165
Methyl	−0·00	64	78	159
Phenyl	+0·60	67[c]	73	153
RCHCl	~+1·1	35–45	51	117
RCCl$_2$	~+1·9	20–30	—	84

[a] Data from Table 2.
[b] Data from A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.* **85**, 866 (1963)
[c] $\Delta\nu = 49$ predicted on the basis of σ^*; see text.

crossed, so that the apparent basicity order would be a function of the concentration at which the spectral measurements were made! Clearly, arbitrary choice of a single concentration for spectral shift measurements (as in Table 1) is an improper procedure, even though in most, but not all, instances the order of hydrogen bond basicities would be the same as at infinite dilution.

The variation of concentration dependence of spectral shift from compound to compound is not hard to understand in a qualitative way. A nitroalkane has a "potent" functional group attached to an "inert" hydrocarbon framework which can vary in size and shape from compound to compound. In a large molecule the nitro group forms a small part of the whole, "G" should be less, and a smaller concentration–$\Delta\nu$ dependence would be expected.

We have demonstrated earlier, for a large number of nitriles that a very good linear relationship exists between intermolecular spectral shifts and σ^*, the Taft–Hammett inductive parameter for the substituent groups.[47] The same holds true here, for the limited number of aliphatic nitro compounds studied (Tables 1–3). The basicity of the nitroalkanes depends on substitution type: 1°, 2°, 3°. Introduction of an α-chloro group—and to a greater extent two such groups—has a pronounced base weakening effect.

The aromic nitro compounds are particularly informative, since the dual nature of the benzene ring—electron release by resonance and electron withdrawal by induction—is clearly evident. From $\sigma^* = +0·600$ for phenyl and the data for the aliphatic compounds (Table 3), $\Delta\nu^\infty_{\text{phenol}} \cong 50$ cm^{-1} can be estimated in contrast to the

[47] R. W. Taft, Jr., in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) Chapter 13. J. Wiley and Sons, Inc., New York, N.Y. (1956).

observed value of 67 cm⁻¹. The latter value, actually greater than that observed for nitromethane and nitroethane, must be due to appreciable ground state resonance interaction between the nitro group and the ring (II). Alkyl groups attached to the benzene ring enhance the nitro group basicity, judging from the nitrotoluene data of
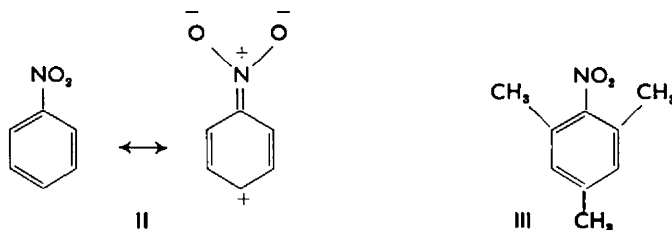
Tables 2 and 3. Despite this fact $\Delta\nu^\infty$ for nitromesitylene (III) is just about the same as for nitrobenzene, indicating steric inhibition of resonance in the former compound.[48] The marked difference between $\Delta\nu$ for p-nitroanisole and the *meta* isomer in which direct resonance interaction between nitro and methoxyl is impossible, and the *ortho* isomer in which such resonance must be at least partially inhibited furnishes another example of the same effect. Although we have not rigorously established the point, hydrogen bonding in these nitroanisoles is almost certainly to the nitro group and not to the methoxyl oxygen. $\Delta\nu_{\text{phenol}} = 158$ cm⁻¹ for bonding to oxygen in anisole, but this value should be drastically reduced by the attachment of a strongly electron withdrawing nitro group to the aromatic ring.[46]

Badger and Bauer[49] suggested very early that a relationship exists between the magnitude of the spectral shift and hydrogen bonding enthalpy. Recent investigations have shown that this generalization, while failing for intimate comparisons between hydrogen bonds of different types, nevertheless has a qualitative significance: large spectral shifts mean strong hydrogen bonds and small spectral shifts connote weak associations.[43,45] Nitro groups give rise to small spectral shifts due to intermolecular hydrogen bonding. We conclude, in agreement with the literature, that nitro groups can form definite, but weak hydrogen bonds with proton donors. The very weak basicity of the nitro group has been established by other methods; nitro compounds are unprotonated even in 100% H_2SO_4.[44] Despite the formal negative charge distributed between the two oxygen atoms, the nitro group, composed only of electronegative atoms, is an electron demanding rather than an electron rich function.

Intramolecular hydrogen bonding

If nitro groups can act as proton acceptors in intermolecular hydrogen bonding, then, provided a suitable geometrical situation is present, intramolecular association involving nitro groups would also be expected, with spectral shifts of comparable magnitude. Examination of Stuart–Briegleb models reveals that the arrangement of atoms in a β-nitroethanol should be quite conducive to intramolecular hydrogen bonding. There is virtually no rotational barrier around a C—NO₂ bond[49a] and, in the skew conformation of β-nitroethanol, there should be excellent overlap between

[48] B. M. Wepster, *Progress in Stereochemistry* (Edited by W. Klyne and P. B. D. de la Mare) Vol. II; Chap. 4. Butterworths, London (1958).
[49] R. M. Badger and S. H. Bauer, *J. Chem. Phys.* **5**, 839 (1937); R. M. Badger, *Ibid.* **8**, 288 (1940).
[49a] E. Tannenbaum, R. D. Johnson, R. J. Myers and W. D. Gwinn, *J. Chem. Phys.* **22**, 949 (1954).

at least one of the filled oxygen *p*-orbitals and the hydroxyl hydrogen atom. The intramolecular hydrogen bonding ring which would be thus formed is six-membered, often found to be particularly favoured when both enthalpy and entropy factors are taken into consideration.

Data for the nitroalcohols studied are summarized in Table 4, but the actual IR

TABLE 4. INTERMOLECULAR AND INTRAMOLECULAR HYDROGEN BONDING IN NITRO ALCOHOLS

Compound	M.p. or b.p. (mm)	Lit. ref.	νOH	$\nu_{OH}{}^l$ Bonded to Bu$_3$O*
2-Nitroethanol	100·5° (10)	a	3604[g]	3412
2-Nitrobutanol	54–5°	b	3620[h]	3415
2-Methyl-2-nitropropanol	85–7°	c	3604[g]	3415
3-Nitropropanol	60–3° (0·8)	d	3639[i]	3438
2-Methyl-2-nitropropane-1,3-diol	146·8–7·8°	e	3631 sh 3605[j] ~3560 sh[k]	3415
2-Ethyl-2-nitropropane-1,3-diol	56–7°	f	3632 sh 3605[j] ~3550 sh[k]	3411

* Average for primary alcohols without electronegative substituents 3490 ± 4 cm^{-1}.

[a] J. C. Earl, F. C. Ellsworth, E. C. S. Jones and J. Kenner, *J. Chem. Soc.* 2697 (1928).

[b] J. Pauwels, *Chem. Zbl.* 1898 I, 193.

[c] H. B. Hass and D. E. Hudgin, *J. Amer. Chem. Soc.* 76, 2692 (1954).

[d] L. Henry, *Chem. Zbl.* 1897 II, 337.

[e] G. Cesaro, *Ibid.* 1897 II, 179.

[f] B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.* 32, 34 (1940).

[g] Peak unsymmetrical on high frequency side; shoulder at ~3632 cm^{-1}.

[h] Shoulder at ~3630 cm^{-1}; peak unsymmetrical on low frequency side.

[i] Very weak shoulder at ~3570 cm^{-1}.

[j] OH intramolecularly bonded to NO$_2$.

[k] OH intramolecularly bonded to OH. Ref. 5c.

[l] J. Greer, Princeton University.

spectra (Fig. 3) are more instructive, since they emphasize the differences from the normal behavior of unassociated alcohols. The "free" hydroxyl stretching peak of a variety of primary alcohols appears as a sharp (half band width $\simeq$ 25–30 cm^{-1}) but somewhat asymmetrical band between 3630 and 3643 cm^{-1}; this asymmetry is attributed to conformational inhomogeneity.[50] A β-nitro substituent, in the absence of hydrogen bonding, should have little influence on the position or appearance of the OH spectrum, judging from the behavior of other functional groups when they are constrained in a conformation which precludes intramolecular association. In actual fact, only the spectrum of 3-nitropropanol (Fig. 3) has a "normal" appearance, and even there "extra" shoulders on the low frequency side of the adsorption band suggest that intramolecular hydrogen bonding may be occurring to a minor extent. The β-nitroalcohols (Fig. 3) all gave broad (half band width $\simeq$40–50 cm^{-1}), and quite unsymmetrical spectra in the 3503–3620 cm^{-1} range. The shape and position of these bands undoubtedly indicate an intramolecular hydrogen bond between the hydroxyl and the nitro group.[16,38] In all spectra, a shoulder at about 3630 cm^{-1} appears, which we attribute to the "free" hydroxyl, present in a small percentage relative to

[50] P. von R. Schleyer, *J. Amer. Chem. Soc.* 83, 1368 (1961); Ref. 17 therein cited.

the bonded species. The unusually complicated "bonded" peak may be due to a number of hydrogen bonded conformations involving one or both oxygen atoms of the nitro group. No reliable spectral shift can be measured from these curves without further analysis, but it is clear that $\Delta\nu$'s of the order of 10–28 cm^{-1} are reasonable. This range agrees moderately well with the intermolecular results of methanol bonding to the nitroalkanes ($\Delta\nu = 26$–30 cm^{-1}, Table 1). There are many well established examples of intramolecular hydrogen bonding, e.g., ethylene glycol and its monoethers,

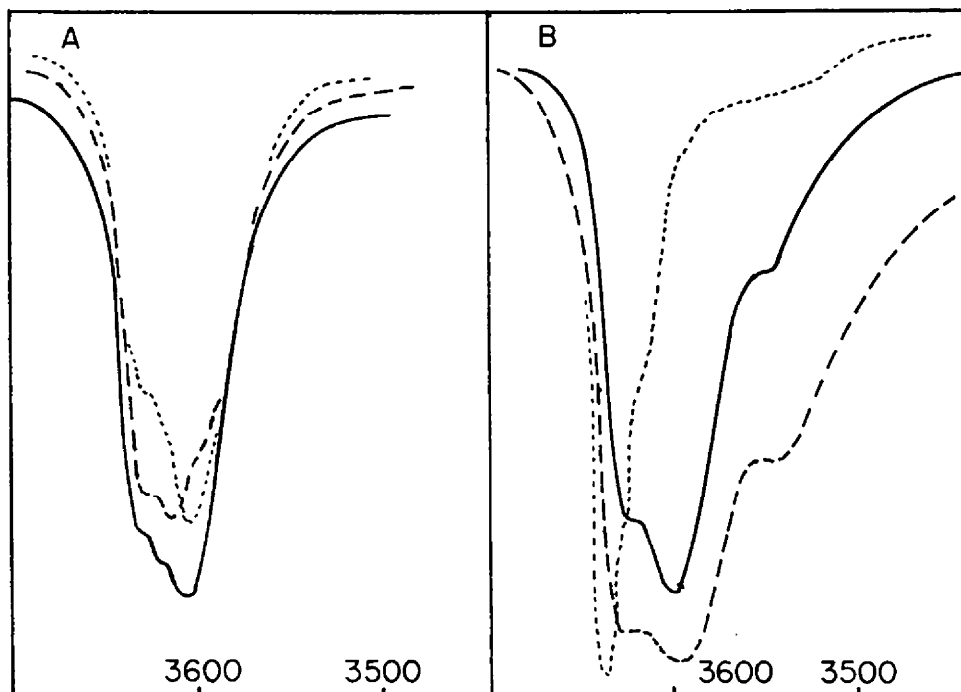FIG. 3. Spectrum A: ————2-Nitroethanol; – – – – 2-Nitrobutanol;
. . . . . . 2-Methyl-2-nitropropanol.
Spectrum B: . . . . . . 3-Nitropropanol; ———— 2-Methyl-2-nitropropane-1,3-diol;
– – – – – 2-ethyl-2-nitropropane-1,3-diol. Conditions: ca. 0·005M solns in CCl_4.

and ethylene chlorohydrin, where $\Delta\nu$'s are no larger than those observed here.[43,51] We believe that the evidence is incontrovertible that intramolecular hydrogen bonding is present in β-nitroalcohols.

This conclusion stands in direct contradiction to that reported recently[40,41] which we believe to be based in part on erroneous interpretations of inadequate data. In fact, certain of the observations for which no adequate explanation was given[40,41] are completely consistent with the idea that intramolecular hydrogen bonding is occurring.

The major points in contention, as far as the IR spectral observations are concerned, are these:

1. Various β-nitroalcohols were said to show only "monomeric" OH stretching bands in the 2·75–2·79 μ region in CCl_4, $CHCl_3$ and CH_2Cl_2.[40] The IR instrument employed was equipped with a NaCl prism, incapable of resolving better than

[51] M. Tichy, *Chem. Listy* **54**, 506 (1960) gives an excellent review.

30 cm^{-1} in this region and of giving the fine detail shown in Fig. 3 necessary for interpretation of the results. A band at 2·75 μ may be "free", but a shift of only 0·02 or 0·03 μ can indicate hydrogen bonding. This emphasizes the necessity of using high resolution equipment before any conclusions can be drawn in studies of this type. Small ν_{NO_2} frequency shifts in β-nitroalcohols relative to comparable but non-bonded nitro compounds[40] possibly are also evidence for intramolecular hydrogen bonding, but we have not verified this here.

2. The spectrum of 0·1 M methanol in CCl$_4$, showing monomeric (2·74 μ), dimeric (2·85 μ) and polymeric (2·98 μ) bands, was altered by replacing the solvent by CH$_3$NO$_2$. The dimer and polymer bands disappeared, but the "monomer" band increased in intensity and shifted to 2·77 μ.[40] This was interpreted as showing "that the nitro groups in nitromethane are capable of breaking up hydrogen bonds but the nature of this interaction is unknown."[40] In actual fact, a new hydrogen bond to nitromethane was being formed (Table 1), but the instrument used[40] was incapable of resolving the true "monomer" and the CH$_3$OH . . . O$_2$NCH$_3$ bonded peaks.

3. It was claimed that nitro groups present either externally (as nitromethane with 1,3-propanediol)[40] or internally (as in 2-methyl-2-nitropropane-1,3-diol)[40] somehow inhibited intramolecular OH . . . OH hydrogen bonding, and a similar effect was noted for intermolecular OH . . . OH association of nitro alcohols.[41] This "inhibition" of OH . . . OH hydrogen bonding is merely due to competitive OH . . . O$_2$N association in these instances. The high resolution spectra of two 2-alkyl-2-nitropropane-1,3-diols (Fig. 3b and Table 4) show this clearly since they display a free OH band as a shoulder near 3632 cm^{-1}, an OH . . . O$_2$N bonded peak near 3604 cm^{-1} and an OH . . . OH interaction as a shoulder near 3550 cm^{-1}. This behavior is typical in such circumstances. The nitro group is a weaker proton acceptor site than the second OH group, but hydrogen bonding to nitro is favored because of its proximity. Entropy factors thus can play the chief role in determining the site of hydrogen bonding when two possibilities exist as is the case for the nitrodiols.

The magnitude of the OH . . . OH spectral shift, ca. 82 cm^{-1}, is comparable to that of other propane-1,3-diols studied earlier.[50] This result shows the balancing effect of the electron withdrawing nitro group on the OH . . . OH bonding—at once rendering the OH groups less basic, but enhancing their acidity. The enhanced proton donor ability of these nitroalcohols can be demonstrated by intermolecular hydrogen bonding studies with dibutyl ether (Table 4). For these compounds an OH . . . OR$_2$ bonded peak near 3415 cm^{-1} was observed, a frequency significantly different from that usually found for such association with ordinary primary alcohols, ca. 3490 cm^{-1}.[51] In short, we find nothing unexpected in the behavior of these nitro containing molecules which is similar to that of other weak hydrogen bond formers.

EXPERIMENTAL

Source of compounds. 2-Nitroethanol was prepared according to the procedure of Gorski and Makarow.[52] 3-Nitropropanol was prepared by reaction of 3-bromo-1-propanol (Eastman Kodak) with AgNO$_2$ in ether for 24 hrs at room temp to give the desired nitroalcohol, b.p. 60–3° (0·8 mm).[53] IR and NMR spectra confirmed the structure of the nitroalcohol obtained. The remaining compounds were commercially available and were recrystallized or redistilled before use. Physical constants are presented in Tables 1 and 4.

[52] I. M. Gorski and S. P. Makarow, *Ber. Dtsch. Chem. Ges.* 67, 996 (1934).
[53] W. Noland and P. Hartman, *J. Amer. Chem. Soc.* 76, 3227 (1954).

Infrared spectroscopic techniques. The IR spectroscopic measurements were carried out on a Perkin–Elmer Model 421 Grating Spectrometer. Reagent grade CCl_4, dried over P_2O_5 and decanted immediately before use, was the solvent. Cells varying in thickness from 0·1 mm to 20 mm were used, increasing the path length as the concentration of the acceptor was decreased in the intermolecular hydrogen bonding studies; 10 mm cells were used for the intramolecular studies. For the intermolecular spectral determinations, the concentration of the proton donor was kept at a minimum for satisfactory results (ca. 1–3 μl or mg/ml of sol); the proton acceptor was added at the desired concentration. Vertical scale expansion was used to enhance the resolution of the weaker bonding examples. For the intramolecular work, solutions of nitroalcohol or nitrodiol at 0·005M or less were employed to avoid interference from intermolecular associations. The calibration of the instrument was checked frequently against indigenous water vapor in the air; all values of ν are thus corrected. Individual runs were duplicated and the reproducibility was shown to be good. Sharp peaks could be reproducibly determined with accuracy of ± 1 cm^{-1}; broader peaks to ± 2 cm^{-1}; and shoulders to ± 4 cm^{-1}.