658. *Infrared Spectra of Substituted Salicylaldehydes.*

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Infrared data are reported for a group of substituted salicylaldehydes and some related compounds with particular reference to nitro-derivatives. The character of the hydroxyl, carbonyl, and nitro-absorptions of 3-nitrosalicylaldehyde (in chloroform or carbon tetrachloride) indicates that the phenolic group is hydrogen-bonded chiefly to the nitro-group, whereas in 2-hydroxy-3-nitroacetophenone and methyl 3-nitrosalicylate the chelated *o*-hydroxy-carbonyl species predominate. The effects of acetonitrile and pyridine on the hydrogen-bond equilibria are discussed.

After the early spectroscopic investigations of hydrogen bonding in salicylaldehyde [1] many studies have been made of the infrared absorption of this compound, which exhibits a diffuse hydroxyl band [2] near 3150 cm.$^{-1}$ and a sharp carbonyl band at 1669 cm.$^{-1}$ (in carbon tetrachloride).[3] As with other *ortho*-hydroxycarbonyl compounds, the stability of the hydrogen bond renders the absorption somewhat insensitive to the physical state of the compound: thus the salicylaldehyde carbonyl band is reported as virtually the same in chloroform, acetonitrile, and butan-1-ol solutions.[4] However, for pyridine or

[1] Errera and Mollet, *J. Phys. Radium*, 1935, **6**, 281.
[2] Errera and Sack, *Trans. Faraday Soc.*, 1938, **34**, 728; Martin, *Nature*, 1950, **166**, 474.
[3] Hunsberger, *J. Amer. Chem. Soc.*, 1950, **72**, 5626.
[4] Yamada, *Bull. Chem. Soc. Japan*, 1959, **32**, 1051.

trimethylamine solutions a band is observed near 1680 cm.$^{-1}$ and is regarded [5] as a " free " carbonyl band, the phenolic group being hydrogen-bonded to the basic solvent. In this paper we report studies on a number of substituted salicylaldehydes and related compounds in several solvents with reference to the effects of alkyl and nitro-substituents. Particular attention has been given to 3-nitrosalicylaldehyde and its analogues, in which alternative hydrogen bonds may be formed. The possibility of competitive intramolecular hydrogen bonding in aromatic systems was adumbrated by Hoyer,[6] and Baker and Kaeding [7] recently provided a spectroscopic demonstration of coexisting alternative hydrogen-bonded forms of 2,6-unsymmetrically disubstituted phenols. Since the completion of our experiments, Hoyer and Hensel [8] have presented evidence for this type of rotational isomerism in 3,5-dinitrosalicylaldehyde.

Experimental

Materials.—Most of the substituted salicylaldehydes were kindly supplied by Professor M. Crawford and Mr. J. W. Rasburn.[9] 3-Nitro-, 5-nitro-, and 3,5-dinitro-salicylaldehyde,[10] 5-nitro-β-resorcylaldehyde,[11] 2-hydroxy-3-nitro-,[12] 2-hydroxy-5-nitro-,[12] 2-hydroxy-4-methyl-,[13] and 2-hydroxy-4,6-dimethylacetophenone [14] were prepared essentially by the methods cited. Methyl esters were prepared with diazomethane. All samples were finally purified by sublimation or short-path distillation at 0·1 mm. Purity of liquid samples was checked by gas–liquid chromatography: a minor impurity was detected in the sample of *o*-fluorobenzaldehyde. Pyridine for spectroscopic measurements was redistilled twice from potassium hydroxide immediately before use: other solvents were purified as described previously.[15]

Measurements.—Most of the results shown in Table 1 were determined with a Unicam S.P.100 spectrophotometer operated under dry-air conditions as described elsewhere: [15] the remainder of the work was carried out with a Mark II version of this instrument used under a vacuum. Water vapour was used for calibration in the 1300—1750 and 3500—3650 cm.$^{-1}$ regions, and methane in the 2700—2900 cm.$^{-1}$ region.[16] The computed theoretical spectral slit widths (for the Mark II instrument) were 6, 4, 4, and 5 cm.$^{-1}$, at 3500, 1650, 1350, and 650 cm.$^{-1}$, respectively. Apparent extinction coefficients (ε_a) are expressed as l. mole^{-1} cm.$^{-1}$. Spectra recorded from 650 to 3650 cm.$^{-1}$ of substituted salicylaldehydes as Nujol mulls or liquid films will appear in the D.M.S. Index (Butterworths) as spectral cards Nos. 7583—7599.

Results and Discussion

1600—3650 cm.$^{-1}$ *Region.*—Data for the hydroxyl, aldehyde C–H, and carbonyl absorptions of a group of substituted salicylaldehydes and some related compounds are recorded in Table 1. The carbonyl bands are close to the region of " aromatic " absorption and the possibility of vibrational resonance with combination bands has been invoked [5] to account for the strong band near 1650 cm.$^{-1}$ in salicylaldehyde (cf. Fig. 1). However, the most intense bands in the 1600—1700 cm.$^{-1}$ region are regarded as carbonyl group vibrations since they occur at the expected frequencies and undergo normal solvent shifts. The designation of the 1634 cm.$^{-1}$ band of β-resorcylaldehyde (No. 7) as a carbonyl vibration [17] seems in error. Alkyl substituents increase the band width but the integrated

[5] Chiorboli and Mirone, *Ann. Chim. (Italy)*, 1958, **48**, 363.
[6] Hoyer, *Z. Elektrochem.*, 1956, **60**, 381; 1957, **61**, 313; *Chem. Ber.*, 1956, **89**, 146.
[7] Baker and Kaeding, *J. Amer. Chem. Soc.*, 1959, **81**, 5904.
[8] Hoyer and Hensel, *Z. Elektrochem.*, 1960, **64**, 958.
[9] Crawford and Rasburn, *J.*, 1956, 2155.
[10] von Miller, *Ber.*, 1887, **20**, 1927; Lovett and Roberts, *J.*, 1928, 1975.
[11] Gattermann, *Annalen*, 1907, **357**, 313.
[12] Lindemann and Romanoff, *J. prakt. Chem.*, 1929, **122**, 214.
[13] Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56.
[14] Smith and Opie, *J. Org. Chem.*, 1941, **6**, 427.
[15] Brooks, Eglinton, and Morman, *J.*, 1961, (*a*) 106; (*b*) 661.
[16] Downie, Magoon, Purcell, and Crawford, *J. Opt. Soc. Amer.*, 1953, **43**, 941.
[17] Pinchas, *Analyt. Chem.*, 1957, **29**, 334.

intensities are not strikingly altered; the value for salicylaldehyde agrees with that given by Yamada[4] ($A = 2{\cdot}6 \times 10^4$ l. mole^{-1} cm.$^{-2}$ in carbon tetrachloride or chloroform; cf. also Krueger and Thompson[18]). The marked lowering of the carbonyl frequency in 6-methyl-3-t-butylsalicylaldehyde (No. 5) and in 2-hydroxy-4,6-dimethylacetophenone (No. 22) parallels the effects attributed to steric compression in the salicylic acid series.[15b]

The 5-nitroaldehydes (Nos. 8, 9, and 11) show carbonyl bands similar to those of their parent compounds (Nos. 1, 3, and 5), but the spectra of the 3-nitro-derivatives are strikingly different (Fig. 1); in every example the principal band in the carbonyl region occurs near 1700 cm.$^{-1}$ with minor variations depending on the substituent at the 5-position. A second, smaller band is noted near 1670 cm.$^{-1}$. The relative optical density

TABLE 1. *Hydroxyl, aldehyde* C–H *and carbonyl absorptions of substituted salicylaldehydes and related compounds.*

Compound		Carbon tetrachloride						Chloroform		
No.	Substituents	ν_{OH} [b]	ν_{CH}		ν_{CO}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε_a	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε_a
Salicylaldehydes [j]										
1	None	(3150)	2840	2749	1669	7	1030	1666	9	840
2	5-Bu^t	(3180)	2831	2740	1663	14	830	1656	18	675
3	3-Pr^i	(3130)	2840	2747	1661 ‡	(25)	460	1653	(33)	465
4	3,5-Bu$_2^t$	(3100)	2839	2742	1654	14	625	1648	19	655
5	3-Bu^t, 6-Me	(3000)	weak	weak	1641	17	550	1635 [c]	24	490
6	3-OMe [d]	(3150)	2841 [e]	2745	1661	13	665	1659	17	580
					1678sh	*	<170	1676	15 †	180
					1695	*	<55			
7	4-OH [f]	(3060)	2835	2747	1660	10	975	1657	15	745
8	5-NO$_2$	(3095)	2861	2734	1674	8	1045	1670	13	895
9	3-Pr^i, 5-NO$_2$	(3100)	2851	2737	1668	14	645	1665	16	565
10	3-Ph, 5-NO$_2$	3065	2852	2738	1666	11	665	1663	15	625
11	3-Bu^t, 5-NO$_2$, 6-Me	(2950)	2876	—	1646	15	580	1643	18	550
12	3-NO$_2$	3170	2876	2770	1701	8	620	1694	13	455
					1676	14	110	1673	17	185
13	3,5-(NO$_2$)$_2$	(3140)	2881	2773	1707	7	615	1702	10	440
					1680	11	205	1677	13 †	250
								1653	16 †	250
14	3-NO$_2$, 5-Bu^t	3195	2874	2766	1700	6	810	1694	12	495
					1674	13	110	1670	*	215
15	3-NO$_2$, 5-Cl	3200	2878	2766	1702	7	685	1697	11	510
					1678	10	110	1675	12	175
16	3-NO$_2$, 5-OMe	3220	2878 [g]	2766	1700	11	525	1694	14	480
					1679	*	55	1676	*	110
17	3-NO$_2$, 5-Ph	3185	2875	2765	1700	8	665	1694	14	455
					1675	12	125	1671	15	220
18	4-OH, 5-NO$_2$	3160	2845	(2730)	1674	(10)	785	1674	11	650
				(2760)	1665	(10)	1035	1663	*	1090
2-Hydroxyacetophenones [k]										
19	None	(3025)	—	—	1646	12	655	1642	17	620
20	3-Me	(3000)	—	—	1641	12	540	1638	16 †	445
								(1630sh)	*	*
21	4-Me	(2960)	—	—	1640	(22)	515	1637	21 †	590
					(1627sh)	*	<290	(1624sh)	*	*
22	4,6-Me$_2$	(2950)	—	—	1629	*	(450)	1628	17 †	540
								(1610sh)	*	*
23	5-NO$_2$	(3000)	—	—	1657	18	555	1653	21	520
24	3-NO$_2$	(3100)	—	—	1693	12	250	1684	23 †	115
					1658	13	310	1656	17	390
Methyl salicylates										
25	5-NO$_2$	(3140)	—	—	1690	13	680	1687	18	570
26	3-NO$_2$	(3100)	—	—	1690	13	575	1688	16	525
					1722	*	<60			
					1746	*	60			
27	3,5-(NO$_2$)$_2$	(3000)	—	—	1695	12	675	1695	14	680
					1727	*	*			
					1751	*	50			

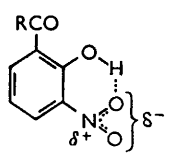
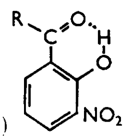
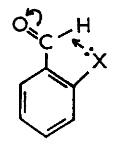
[18] Krueger and Thompson, *Proc. Roy. Soc.*, 1959, *A*, **250**, 22.

TABLE 1. (*Continued.*)

No.	Compound Substituents	Carbon tetrachloride ν_{OH} [b]	ν_{CH}	ν_{CH}	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε_a	Chloroform ν_{CO}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε_a
Benzaldehydes [m]										
28	*o*-OMe	—	2862	2759	1695	7	735	1688	14	510
					1666 [n]	*	60	1665 [n]	13 †	170
29	*o*-F	—	2860	2762	1703	7	685	1698	13	*
					(1684sh)	*	<70	1683	8 †	*
30	*o*-NO_2	—	2869	2766	1706	10	520	1702	14	450
			2890							
31	*m*-OMe	—	2834	2726	1709	10	640	1702	15	505
					1686 [n]	11 †	105	1684 [n]	12	225
32	*m*-Cl	—	2827	2724	1709	9	730	1703	12	910
33	*m*-NO_2	—	2833	2730	1713	11	530	1708	12	615
			2809		1727 [n]	9	175	1727 [n]	10 †	105
34	2,3-$(OMe)_2$	—	2858	2745	1696	9	620	1690	18	410
35	3,4-$(OMe)_2$	—	2839	2754	1701	11 †	410	1698	14 †	290
			2812	2721	1687	10 †	460	1682	16	565

Values in parentheses are approximate. — No band present. * Not measured. † Estimated by band reflection. ‡ Unsymmetrical band. [b] The approximate band centre is cited. [c] Fused to aromatic band at 1616 cm.$^{-1}$. [d] The carbonyl nature of the bands cited is discussed in the text. [e] Superimposed aldehyde and methoxyl bands. [f] Free OH band at 3593 cm.$^{-1}$. [g] A band at 2839 cm.$^{-1}$ is ascribed to methoxyl (ref. *h*). [h] Henbest, Meakins, Nicholls, and Wagland, *J.*, 1957, 1462. [i] A strong band at 3095 cm.$^{-1}$ is ascribed to $2\nu_{NO_2}$ (asym.). [j] 0·0017M in CCl_4, *ca.* 0·02—0·06M in $CHCl_3$. [k] 0·0015M in CCl_4, *ca.* 0·02—0·06M in $CHCl_3$. [l] 0·00135M in CCl_4, *ca.* 0·045M in $CHCl_3$ [m] 0·0017M in CCl_4, *ca.* 0·05—0·08M in $CHCl_3$. [n] Not regarded as carbonyl bands (see text).

is unaltered by dilution from 0·06M to 0·0017M in carbon tetrachloride but is affected by the solvent (see below). The major band frequency is indicative of an aromatic aldehyde group not involved in a hydrogen bond, and the minor band is at a typical salicylaldehyde frequency. These absorptions are ascribed to the species (Ia; R = H) and (Ib; R = H)

(Ia)  (Ib)  (II) 

respectively (cf. ref. 8): this assignment is further discussed below. The first overtones of the principal carbonyl bands in 3- and 5-nitrosalicylaldehydes are unusually prominent (Fig. 1) and their positions support the assignments made. The effects of nitro-substituents on the carbonyl absorptions of 2-hydroxyacetophenone and methyl salicylate (Fig. 1) are in harmony with these views. The 5-nitro-derivatives both show single bands. In the spectrum of 2-hydroxy-3-nitroacetophenone two bands are observed, at the frequencies expected for (Ia; R = Me) and (Ib; R = Me), with the latter predominating. Methyl 3-nitrosalicylate exhibits only low absorption in the region expected for form (Ia; R = OMe): the bands at 1722 and 1746 cm.$^{-1}$ probably correspond to two conformations of the methoxycarbonyl group in (Ia; R = OMe).[15a] The principal band, ascribed to (Ib; R = OMe), closely resembles that of the 5-nitro-isomer. Entirely analogous behaviour is shown by methyl 3,5-dinitrosalicylate.

3-Methoxysalicylaldehyde (No. 6) shows complex absorption in the carbonyl region. The more intense bands near 1660 and 1676 cm.$^{-1}$ are presumed to arise from the chelated carbonyl group, while the band near 1695 cm.$^{-1}$ might be interpreted as due to a species analogous to (Ia). The present data do not allow firm assignments to be made.

Comment is necessary on two features of the data for substituted benzaldehydes (Table 1, Nos. 28—35). The carbonyl frequency (benzaldehyde, 1709 cm.$^{-1}$ in CCl_4) is lowered by *ortho*-substitution even by the strongly electron-attracting nitro-group. This is assumed to result from enhanced polarisation of the carbonyl group in the favoured conformation (II) since the frequency shifts are similar to those ascribed to the corresponding species in *ortho*-substituted methyl benzoates.[15a] The occurrence of two bands

FIG. 1.

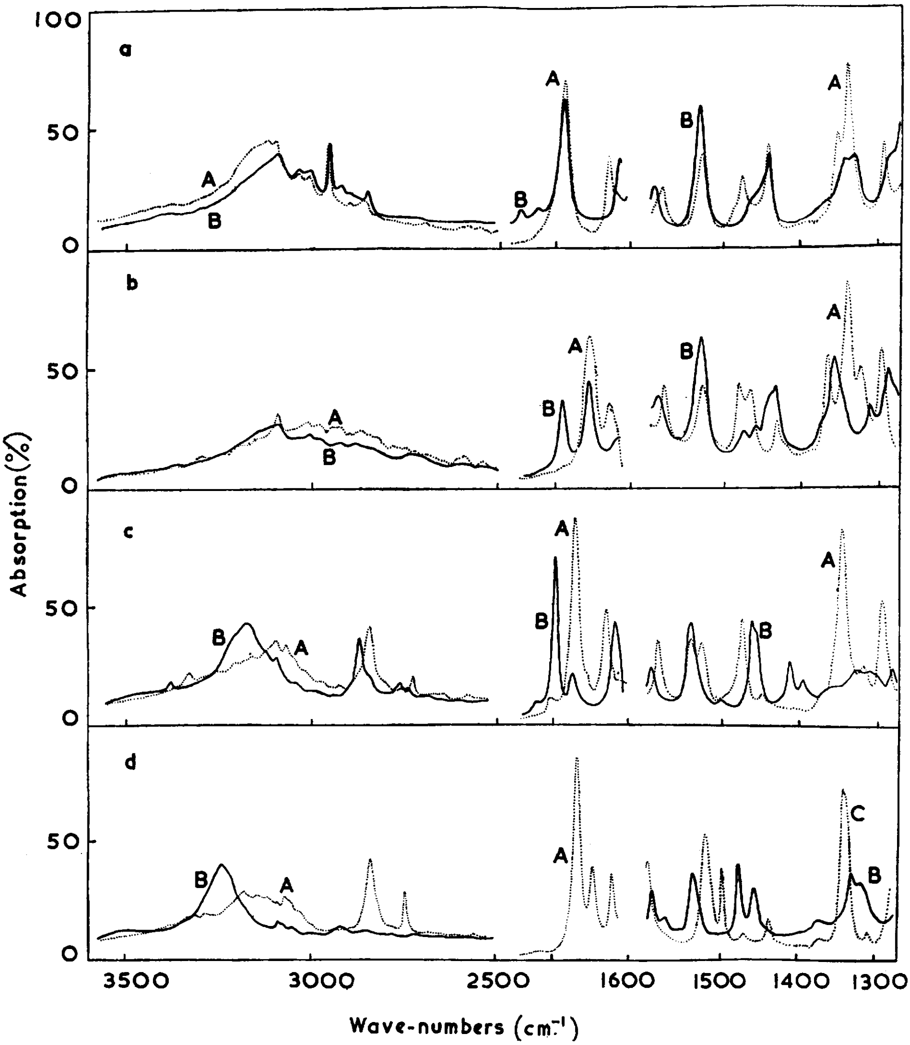


FIG. 1a. A, *Methyl 5-nitrosalicylate*; B, *methyl 3-nitrosalicylate*.
FIG. 1b. A, *2-Hydroxy-5-nitroacetophenone*; B, *2-hydroxy-3-nitroacetophenone*.
FIG. 1c. A, *5-Nitrosalicylaldehyde*; B, *3-nitrosalicylaldehyde*.
FIG. 1d. A, *Salicylaldehyde*; B, o-*nitrophenol*; C, p-*nitrophenol*.

Concentrations as noted in Tables 1 *and* 2: CCl_4 *solutions*, 20 mm. *cells* (3650—2500 cm.$^{-1}$), 5 mm. *cells* (1750—1600 cm.$^{-1}$). $CHCl_3$ *solutions*, 0·11 mm. *cells* (1600—1250 cm.$^{-1}$).

in the carbonyl region of the spectra of *o*- and *m*-methoxybenzaldehyde, *m*-nitrobenzaldehyde, and 3,4-dimethoxybenzaldehyde is also notable. In the first three cases the relatively unperturbed carbonyl band is identifiable by its intensity and position, and by typical solvent shifts: the minor band frequency is solvent-insensitive, but the band intensity falls with increasing separation between this absorption and the carbonyl band. It thus appears probable that these subsidiary bands are combination modes strengthened by resonance with the carbonyl vibrations. The absorption of 3,4-dimethoxybenzaldehyde is regarded as a more extreme example of this effect in which the carbonyl vibration mode contributes to both the observed bands.

In the hydroxyl region, 3-nitrosalicylaldehyde and its derivatives show a single broad band near 3200 cm.$^{-1}$, similar to that of *o*-nitrophenol and distinct from the weaker, diffuse bands near 3150 cm.$^{-1}$ typical of salicylaldehyde (cf. Fig. 1).

The 3-nitrosalicylaldehyde structure is further distinguished by the band attributed to aldehyde C–H stretching which occurs near 2765 cm.$^{-1}$, as compared with the " normal " value near 2740 cm.$^{-1}$. The second band generally associated with benzaldehydes, regarded by Pinchas [17] as a combination band of the C_{OHO}–H in-plane bending vibration near 1380 cm.$^{-1}$ with a ring vibration near 1470 cm.$^{-1}$, occurs near 2875 cm.$^{-1}$ in 3-nitrosalicylaldehyde and its nuclear-substituted derivatives: in the remaining compounds it appears to be near 2840 cm.$^{-1}$ but the assignment is uncertain in aldehydes having alkyl

TABLE 2. *Nitro-group absorptions of nitrosalicylaldehydes and related compounds (ca.* 0·02—0·06M *in* $CHCl_3$).

Compound No.	Substituents	$\nu_{(asym.)}$	$\Delta\nu_{\frac{1}{2}}$ ^{a}	ε ^{a}	$\nu_{(sym.)}$	$\Delta\nu_{\frac{1}{2}}$ ^{a}	ε ^{a}
Salicylaldehydes							
8	5-NO_2	1541	13	245	1347	9	1120
		1526	13	230			
9	3-Pr^i, 5-NO_2	1532	21	385	1352	12	675
					1320	14	695
10	3-Ph, 5-NO_2	1539	20	310	1346	11	730
11	3-Bu^t, 5-NO_2, 6-Me	1523	23	335	1342	*	430
12	3-NO_2	1537	16	280	1350	*	100
					1331	*	100
13	3,5-$(NO_2)_2$	(1554)	*	325	1349	12	1045
14	3-NO_2, 5-Bu^t	1538	18	415	1369	*	(200)
					1325	*	(200)
15	3-NO_2, 5-Cl	1538	19	350	1352	*	<130
					1312	*	185
16	3-NO_2, 5-OMe	1541	14	720	1321	18	390
17	3-NO_2, 5-Ph	1542	15	470	1332	*	<200
					1312	*	<200
18	4-OH, 5-NO_2	1538	18	500	1347 ‡	*	285
2-Hydroxyacetophenones							
23	5-NO_2	1531	18	235	1345	10	985
24	3-NO_2	1532	17	465	1362	21	360
Methyl salicylates							
25	5-NO_2	1530	16	365	1344	10	1130
					1357	12 †	485
26	3-NO_2	1533	12	700	1347	*	<360
					1334	*	<360
Miscellaneous compounds							
36	*o*-Nitrophenol	1540	14	300	1334	12 †	330
					1321	*	265
37	*m*-Nitrophenol	1532	11	1090	1357	9	705
38	*p*-Nitrophenol	1522	12	595	1346	13	1080
39	*o*-Nitroanisole	1527	14	695	1356	19	300
30	*o*-Nitrobenzaldehyde	1532	12	685	1349	10	440
33	*m*-Nitrobenzaldehyde	1539	9	615	1345	7	700

For symbols see Table 1.

C–H bands near 2875 cm.$^{-1}$. Elevation of both " aldehyde " C–H frequencies has been noted [17,19] in 2,3- and 2,6-disubstituted benzaldehydes and attributed to steric effects,[19] though in all the examples, except 2,6-dimethylbenzaldehyde,[19] the effect could be associated with strong dipole interactions, as proposed by Schneider and Bernstein [20] to

[19] West and Whatley, *Chem. and Ind.*, 1959, **333**.
[20] Schneider and Bernstein, *Trans. Faraday Soc.*, 1956, **52**, 13.

account for the raised C–H frequency in solid aldehydes as compared with solutions. Evidently the normal values for 3-alkylsalicylaldehydes (Nos. 3, 4) reflect the stabilisation of the aldehyde C–H environment by the hydrogen bond.

1250—1600 cm.$^{-1}$ *Region.*—The effects of hydrogen bonding on nitro-group vibrations are not well established. One difficulty lies in the complex nature of these vibrations: another is that the regions of absorption concerned are populated by many other strong bands, particularly in aromatic compounds. Even in the nitro-alcohols Urbański's[21] report that the symmetric stretching vibration occurs at 1310 cm.$^{-1}$ in the hydrogen-bonded compounds is confused by the absorption at this frequency due to the alcohol group itself. For *o*-nitrophenol (and *o*-nitroanisole) the reported[22,23] asymmetric stretching frequency (*ca.* 1530 cm.$^{-1}$) is little different from that of nitrobenzene, whereas for *o*-nitroaniline, in which there appears to be no hydrogen bond,[24] an appreciably lower value (1511 cm.$^{-1}$ in $CHBr_3$) has been recorded.[22] In view of the lack of quantitative data for *o*-nitrophenols, the substituted 3-nitrosalicylaldehydes and other relevant compounds have now been examined. The absorption due to nitro-groups was investigated with 0·11 mm. cells to allow adequate transmission over the range 1250—1750 cm.$^{-1}$. Full results were obtained for chloroform solutions (Table 2): where solubility permitted, spectra were determined also for carbon tetrachloride solutions, and no major differences were noted. In the 5-nitro-aldehydes the asymmetric and symmetric nitro-vibrations give rise to sharp, intense bands near 1540 and 1340 cm.$^{-1}$ respectively: only in the 3-isopropyl derivative (No. 9) is there some ambiguity in the latter assignment, as two equally intense bands occur at 1352 and 1320 cm.$^{-1}$. The 3-nitro-aldehydes also exhibit a band near 1540 cm.$^{-1}$ but in the region of the symmetric vibration they are profoundly different: no notably intense band is present, and apart from a general increase in " background " absorption the spectra in the 1300—1400 cm.$^{-1}$ region resemble those of the aldehydes lacking nitro-substituents. The virtual submergence of the symmetric vibration cannot be ascribed purely to hydrogen-bond formation since in spectra of 5-nitro-β-resorcylaldehyde (No. 18) and of *o*-nitrophenol (No. 36) bands attributable to this mode are quite prominent. The effects evidently result from the buttressing inherent in 1,2,3-trisubstitution: thus, from results reported by Dearden and Forbes,[23] the symmetric bands shown by *o*-nitrophenols bearing alkyl substituents in the 3- and/or 6-positions are weaker than those of *o*-nitrophenol and 4,5-dimethyl-2-nitrophenol. (Frequency shifts of the type noted by van Veen, Verkade, and Wepster[25] for 2,3-disubstituted nitrobenzenes are not discernible in our work.) It is concluded that the results are consonant with strong hydrogen bonding between the nitro- and the phenol group in 3-nitrosalicylaldehyde and its congeners. In 2-hydroxy-3-nitroacetophenone and methyl 3-nitrosalicylate, symmetric nitro-bands are observed which are comparable in frequency, intensity, and breadth with those of *ortho*-substituted nitro-compounds lacking hydrogen bonds, *e.g.*, *o*-nitrobenzaldehyde (No. 30) and *o*-nitroanisole (No. 39).

Solvent Studies.—In order to confirm that the results so far described could be correctly construed in terms of equilibria between the hydrogen-bonded species (Ia) and (Ib), the effects of (i) a more polar solvent (acetonitrile) and (ii) a basic solvent (pyridine) were explored. Results for acetonitrile solutions are presented in Table 3. The two carbonyl bands observed in the 3-nitro-derivatives undergo solvent shifts comparable, respectively, with those of typical chelated and unchelated carbonyl groups. The effect on the relative intensity of the bands is significant (cf. Fig. 2). For 3-nitrosalicylaldehyde the ratios of the intensities (ε_a) of the high- and low-frequency bands in CCl_4, $CHCl_3$, and MeCN are respectively 5·6, 2·4, and 1·4: for 2-hydroxy-3-nitroacetophenone, 0·8, 0·3, and *ca.* 0·15.

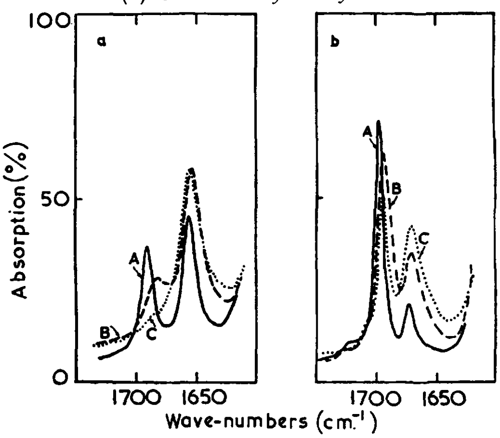
[21] Urbański, *Roczniki Chem.*, 1957, **31**, 53.
[22] Franck, Hörmann, and Scheibe, *Chem. Ber.*, 1957, **90**, 330.
[23] Dearden and Forbes, *Canad. J. Chem.*, 1960, **38**, 1852.
[24] Urbański and Dabrowska, *Chem. and Ind.*, 1958, 1206; Dyall and Hambly, *ibid.*, p. 262.
[25] van Veen, Verkade, and Wepster, *Rec. Trav. chim.*, 1957, **76**, 801.

TABLE 3. *Carbonyl absorptions* (CH_3·CN *solutions, ca.* 0·015M).

	Compound	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε [a]
1	Salicylaldehyde	1666	9	780
		1646 [n]	13	315
33	*m*-Nitrobenzaldehyde	1707	8	765
		1727	*	85
8	5-Nitrosalicylaldehyde	1669	14	715
		1691	*	<65
		1706	*	<65
12	3-Nitrosalicylaldehyde	1696	9	390
		1672	22	295
19	*o*-Hydroxyacetophenone	1645	16	570
23	2-Hydroxy-5-nitroacetophenone	1654	20	555
24	2-Hydroxy-3-nitroacetophenone	1657	20	445
		(1685)	*	<70
28	*o*-Methoxybenzaldehyde	1690	10	690
		1666 [n]	*	125
30	*o*-Nitrobenzaldehyde	1703	13	465
31	*m*-Methoxybenzaldehyde	1704	10	660
		1685 [n]	12 †	175
6	3-Methoxysalicylaldehyde	1658 ‡	20	495
		1675	*	180
		1689	11 †	135

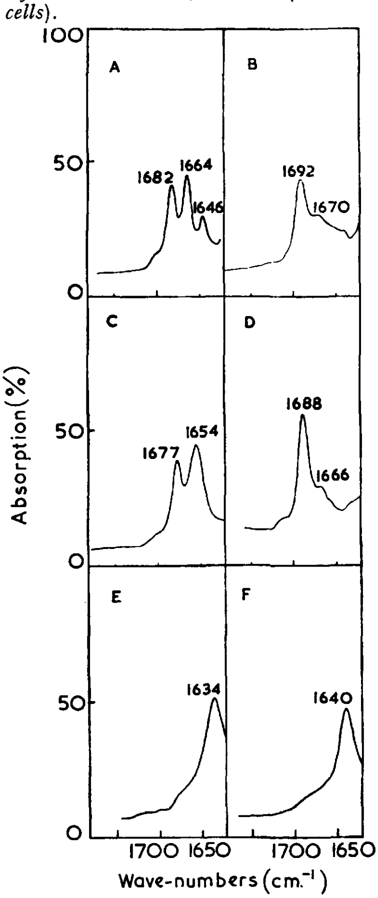
For symbols see Table 1. [n] Not regarded as a carbonyl band.

FIG. 2. (a) 2-*Hydroxy*-3-*nitroacetophenone* (b) 3-*Nitrosalicylaldehyde*.



A, 0·0015M *in* CCl_4 (5 mm. *cells*); B, 0·075M *in* $CHCl_3$ (0·11 mm. *cells*); C, 0·015M *in* Me·CN (0·5 mm. *cells*).

FIG. 3. A, *Salicylaldehyde*; B, 3-*nitrosalicylaldehyde*; C, 5-*t*-*butylsalicylaldehyde*; D, 5-*nitrosalicylaldehyde*; E, 6-*methyl*-3-*t*-*butylsalicylaldehyde*; F, 6-*methyl*-5-*nitro*-3-*t*-*butylsalicylaldehyde*. *Pyridine solutions*, 0·05M (0·11 mm. *cells*).



These results support the view that the observed bands correspond to species (Ia) and (Ib), *i.e.*, the form with the unchelated nitro-group is relatively stabilised by increasing the solvent polarity. From the data of Eda and Ito [26] it may be computed that the dipole

[26] Eda and Ito, *Bull. Chem. Soc. Japan*, 1956, **29**, 524; 1957, **30**, 164.

moment of (Ib) should exceed that of (Ia). Similar intensity effects have been discussed [15a] for other examples of conformational isomerism.

The effects of pyridine on the absorption of *ortho*-hydroxycarbonyl compounds may be expected to be derived chiefly from its bonding to the phenolic hydrogen atom. Carbonyl and nitro-absorption data are recorded in Table 4. The nitro-absorptions are closely similar to those for chloroform and carbon tetrachloride solutions and require no further comment. The carbonyl region, however, shows several features of interest (cf. Fig. 3). Pyridine evidently competes with the carbonyl group in forming a hydrogen bond with the phenolic group and, in the case of salicylaldehyde (cf. ref. 5), gives rise to a new, unchelated aldehydic carbonyl band at 1682 cm.$^{-1}$: the markedly lower frequency than is found for benzaldehyde in pyridine (1707 cm.$^{-1}$) is attributed to electron-donation from pyridine to the phenol group. As similar disruption of the intramolecular bond occurs in 5-t-butylsalicylaldehyde, and is almost complete in the 5-nitro-derivative (No. 8): this is regarded as ensuing from the mesomeric effect of the nitro-group on the phenol acidity, since in relatively non-basic solvents (CCl_4, $CHCl_3$: Table 1) the chelation

TABLE 4. *Carbonyl and nitro-absorptions (pyridine solutions).*[p]

No.	Substituents	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε_a	ν_{NO_2}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε_a	ν_{NO_2}	$\Delta\nu_{\frac{1}{2}}$ [a]	ε_a
Salicylaldehydes										
1	None	1682	13 †	345	—	—	—	—	—	—
		1664	*	400						
		1646 [q]	*	195						
2	5-Bu^t	1677	13 †	325	—	—	—	—	—	—
		1654	20 †	395						
5	3-Bu^t, 6-Me	1634	30 ‡	480	—	—	—	—	—	—
8	5-NO_2	1688	14	560	1527	*	135	1343	11	1035
		(1666)	*	<165						
11	3-Bu^t, 5-NO_2, 6-Me	1640	24	320	1521	20	340	1337	*	380
12	3-NO_2	1692	14	375	1532	24	325	1351	*	240
		(1670)	*	(200)						
2-Hydroxyacetophenones										
19	None	1642	17	515	—	—	—	—	—	—
23	5-NO_2	1650	23	345	1528	17	255	1344	12	825
		1677	*	150						
24	3-NO_2	1654	21	350	1530	17	525	1361	23	345
		1683	*	<110						
Methyl salicylates										
40	None	1678	17	465	—	—	—	—	—	—
25	5-NO_2	1684	20	470	1528	19	365	1343	11	995
		1735	*	120				1356	14 †	390
26	3-NO_2	1685	16	415	1532	16	610	1347	*	280
								1335	*	280

[p] Approx. 0·05M in 0·11 mm. cells. [q] Not regarded as a carbonyl band. For symbols see Table 1.

in 5-nitrosalicylaldehyde appears to be as complete as that in salicylaldehyde. Inhibition of pyridine–phenolhydrogen bonding by steric effects is illustrated by 6-methyl-3-t-butylsalicylaldehyde (No. 5) and its 5-nitro-derivative (No. 11), which exhibit single chelated carbonyl bands, similar in frequency and intensity to those observed in chloroform solution.

Comparison of salicylaldehyde, 2-hydroxyacetophenone, and methyl salicylate shows that only the *ortho*-hydroxy-aldehyde chelation is disturbed by pyridine. This is in accord with the stability order of the intramolecular hydrogen bonds in these three types of compound as implied by the relative extent of competitive bonding by 3-nitro-groups described above [and by the frequency displacements corresponding to the introduction of *o*-OH into the parent compounds Ph·CO·R: R = H, −40; R = Me, −47; R = OMe, −46 cm.$^{-1}$ (CCl_4)]. However, introduction of a 5-nitro-substituent enhances the phenol acidity sufficiently to permit a partial breaking of the intramolecular bonds in both the ketone (No. 23) and the ester (No. 25).

The results described above emphasise the need for care in interpreting the solution spectra of polyfunctional compounds in which different arrangements of hydrogen bonds are possible. In some cases the occurrence of a predominant chelated system may be recognised and the conformations of contiguous groups thereby determined. In general, the spectra must be considered in terms of all the possible conformations of the molecule, with due attention to the influences of intramolecular steric and electronic interactions and of the solvent. These effects may be profound in polarisable systems, as illustrated by the aromatic derivatives discussed in this paper.

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