Substituent Effects in Infrared Spectroscopy. Part 6.[1] *meta-* and *para-*Substituted *N*-Ammoniobenzamidates

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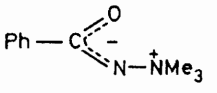
The i.r. spectra from 1 300 to 1 650 cm^{-1} of a number of *meta*- and *para*-substituted *N*-ammoniobenzamidates have been studied. The strong bands near 1 560 and 1 355 cm^{-1} in water are assigned to asymmetrical and symmetrical stretching vibrations of the CO$\bar{N}$ group. The coupling of ν_a(CO$\bar{N}$) and ν_8 ring modes is shown up by the solvent variation method. It causes the failure of the Hammett equation for ν_a(CO$\bar{N}$). The similarity of the mechanics of vibration of the benzamidate and benzoate groups is emphasized.

THE i.r. spectra of amidates $RCO\text{-}\bar{N}\text{-}\overset{+}{N}R'_3$ show a very strong absorption (called in this work amidate I band) in the 1 555—1 600 cm^{-1} region which is assigned [2-4] to a carbonyl stretching vibration lowered by a major contribution to the actual structure of the resonance form $RC\bar{O}\text{-}N\text{-}\overset{+}{N}R'_3$. A second strong absorption near 1 350 cm^{-1} (called the amidate II band) was tentatively attributed to the $\nu(C\text{-}\bar{N})$ mode by analogy with amides.[4]

In benzamidates $XC_6H_4CO\bar{N}\overset{+}{N}Me_3$, the ν_{8a} and ν_{8b} ring modes of mono- or di-substituted benzenes appear at 1 620—1 580 cm^{-1}.[3,4] Their proximity with the amidate I band presumably gives rise to a strong coupling.[4] Therefore the amidate (I) band has not been clearly distinguished in previous studies.[3,4]

From a spectroscopic viewpoint, *N*-trimethylammoniobenzamidate (1) is probably closer to the tetramethylammonium benzoate ion pair (2) or even nitrobenzene (3) than to *NN*-dimethylbenzamide (4).



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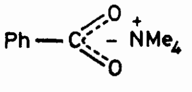

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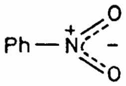

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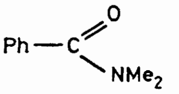

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This similarity and the lack of a detailed study of their i.r. spectra led us to study the amidate I and II bands of a series of *meta*- and *para*-substituted *N*-trimethylammoniobenzamidates (*p*-OMe, -Me, -F, -Br, -CF$_3$, -CN, -NO$_2$, and *m*-Me, -OMe, -F, -CF$_3$, -CN, -NO$_2$). In particular we have (i) described the amidate I and II bands as pseudo-asymmetrical and symmetrical stretching vibrations of the CO$\bar{N}$ group rather than ν(C=O) or $\nu(C\text{-}\bar{N})$, (ii) investigated the coupling of ring modes with the amidate I band by the solvent variation method, and (iii) studied the effects of substituents on the amidate I and II bands.

RESULTS AND DISCUSSION

General Aspect of the I.r. Spectra of meta- *and* para-*Substituted* N-*Trimethylammoniobenzamidates from* 1 300 *to* 1 650 *cm*$^{-1}$ (*in* D$_2$O *and* CH$_2$Cl$_2$).—The same pattern of bands, the wavenumbers of which are summarized in Table 1, occurs for all compounds (see Figure 1). Thus

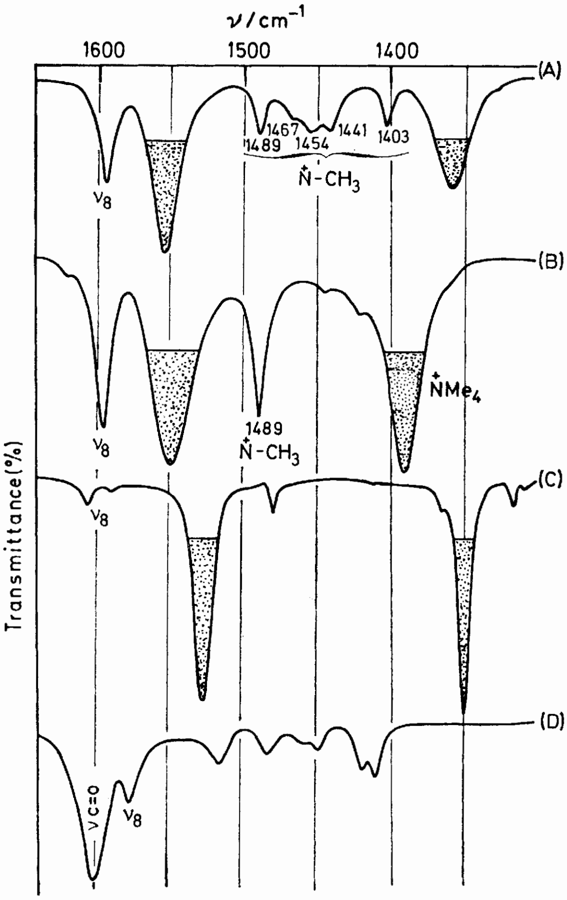

FIGURE 1 I.r. spectra of (A) *N*-trimethylammoniobenzamidate, (B) tetramethylammonium benzoate (in D$_2$O), (C) nitrobenzene (in CHCl$_3$), and (D) *NN*-dimethylbenzamide (in D$_2$O)

(i) the amidate II band is found between 1 353 and 1 357 cm^{-1} in D$_2$O (1 332—1 338 cm^{-1} in CH$_2$Cl$_2$) except for the *m*-CF$_3$ substituted compound where an increase to 1 362 cm^{-1} (1 346 cm^{-1} in CH$_2$Cl$_2$) may be caused by

TABLE 1

I.r. wavenumbers (cm^{-1}) of substituted *N*-trimethylammoniobenzamidates in CH_2Cl_2 and D_2O solutions [a]

Substituent	CH_2Cl_2								D_2O				
	ν_8				Amidate I		$\overset{+}{N}(CH_3)_3$ [b]	Amidate II	ν_8		Amidate I	$\overset{+}{N}(CH_3)_3$ [b]	Amidate II
H			1 599	(470)	1 562	(520)	1 486.5	1 338		1 594	1 553.5	1 489	1 357
para													
OMe	1 606	(590)	1 598	(590)	1 559.5	(380)	1 487	1 338	1 608.5	1 593.5	1 549.5	1 489	1 355
Me		sh	1 594	(390)	1 555	(370)	1 487	1 338	1 611.5	1 588.5	1 548	1 488.5	1354.5
F	1 611	(490)	1 601	(390)	1 569	(490)	1 487	1 337	*c*	1 605	1 558.5	1 489	1 355
Br	1 599	(620)	1 587	(sh)	1 556	(360)	1 486	1 333	1 589		1 549	1 488	1 355
CF_3	1 616.5	(sh)	1 605	(400)	1 565	(580)	1 487	*d*	1 619	1 597	1 559	1 489	1 356
CN			1 598.5	(590)	1 555	(320)	1 486	1 355		1 591	1 552.5	1 489	1 353.5
NO_2	1 615.5	(220	sh		1 582	(1 000) [e]	1 486.5	1 330 [i]	1 613	sh	1 573	1 489	*f*
meta													
Me	1 609	(160)	1 596	(250)	1 566	(470)	1 486.5	1 332	1 607	1 593	1 556.5	1 489	1 355
OMe	1 606	(sh)	1 598	(270)	1 569	(760)	1 486	1 333	sh	1 598	1 558.5	1 488	1 355
F	1 613	(200)	1 604	(220)	1 570	(760)	1 486	1 333	1 615	1 599	1 562	1 489	1 355.5
CF_3	1 616	(350)	1 602	(260)	1 574	(420)	1 486	1 346	1 617	1 601	1 565	1 489	1 362
CN	1 609	(400)	1 596	(sh)	1 568	(390)	1 486	1 333	1 607	1 591	1 564	1 489	1 355
NO_2	1 613	(sh)	1 603.5	(640)	1 567	(340) [g]	1 486	1 335 [h]	1 617	1 598	1 561.5	1 489	*f*

[a] In parentheses approximate molecular extinction coefficient (l mol^{-1} cm^{-1}). sh = shoulder. [b] Band of highest wavenumber and intensity in the CH_3 deformation region. [c] Overlapped band. [d] Overlapped by the $\nu(CF_3)$ band at 1 322 cm^{-1}. [e] $\nu_a(NO_2)$ 1 523 cm^{-1}. [f] Overlapping of $\nu_s(NO_2)$ and $\nu_s(CO\bar{N})$. [g] $\nu_a(NO_2)$ 1 527 cm^{-1}. [h] $\nu_s(NO_2)$ 1 352 cm^{-1}. [i] $\nu_s(NO_2)$ 1 346 cm^{-1}.

interaction with the CF_3 valence vibration at 1 322 cm^{-1} (1 315 cm^{-1} in CH_2Cl_2). (ii) A series of five bands insensitive to substitution, at 1 403, 1 441, 1 454, 1 467 and 1 489 cm^{-1}, is attributed to deformation modes of the methyl groups linked to a quaternary nitrogen. The isoelectronic $C(CH_3)_3$ group gives rise to the asymmetric CH_3 deformation vibration near 1 465 cm^{-1} and to two symmetric CH_3 deformations near 1 395 and 1 368 cm^{-1}.[5] The greater number of bands may be attributed to non-equivalence of the methyl groups * and the shift to higher wavenumbers to the sensitivity of the methyl deformation frequencies to the electronegativity of the attached atom.[5] We note that the tetramethylammonium cation also absorbs strongly at 1 489 cm^{-1} (see Figure 1). (iii) The ν_{19a} ring mode is intense enough to be observed only for the strong mesomeric substituents OMe, Me, F, and Br in the *para*-position (1 507, 1 507, 1 503, and 1 480 cm^{-1}, respectively, in CH_2Cl_2). The ν_{19b} ring mode is probably hidden by the $\overset{+}{N}(CH_3)_3$ absorptions and is therefore difficult to assess. (iv) The amidate I band is found between 1 548 and 1 573 cm^{-1} in D_2O. This peak is not always the highest in the spectrum and confusion may arise from neighbouring absorptions and sometimes from more intense ν_8 ring modes. Any doubt is removed by the solvent variation method (see below). (v) The ν_{8a} and ν_{8b} ring modes occur between 1 620 and 1 580 cm^{-1}. Their intensity depends both on the conjugation of the substituent with the ring and with the function [7] and on the intensity sharing with the neighbouring amidate I band (see below).

Description of the Amidate I and II Bands as Pseudo $\nu_a(CO\bar{N})$ *and* $\nu_s(CO\bar{N})$.—Figure 1 compares the i.r. spectra from 1 300 to 1 650 cm^{-1} in aqueous solution of *N*-trimethylammoniobenzamidate with that of tetramethylammonium benzoate,† nitrobenzene, and *NN*-dimethylbenzamide. Two strong bands in the 1 550 and 1 350 cm^{-1} regions appear for the three first compounds. In nitrobenzene and benzoate anion their assignment as asymmetrical and symmetrical stretching vibration, $\nu_a(CO\bar{O})$ or (NO_2) and $\nu_s(CO\bar{O})$ or (NO_2) is well known. The similarity in the frequencies of the isoelectronic carboxylate and nitro-groups has already been noticed [9] and explained by their common C_{2v} symmetry and very nearly identical force constants, masses, and geometries. In the same way, the amidate group looks much like the carboxylate group; the geometry of the *N*-trimethylammoniobenzamidate molecule [6] permits one to give to the $C_6H_4CO\bar{N}$ fragment a local pseudo-C_{2v} symmetry; the masses are very similar and both carboxylate and amidate groups bear a delocalized negative charge. Therefore the appearance of two strong bands in the *N*-trimethylammoniobenzamidate i.r. spectrum near to the carboxylate absorptions can be explained by a strong coupling between the CO and $C\bar{N}$

TABLE 2

The wavenumbers (cm^{-1}) and intensities (10^{-4} l mol^{-1} cm^{-2}) of (pseudo) ν_a and ν_s bands in amidate, carboxylate, and nitro-groups

Compound	Solvent	ν_a	A_a	ν_s	A_s
$C_6H_5CO\bar{N}\overset{+}{N}Me_3$	D_2O	1 553.5	1.31	1 357	0.77
$C_6H_5CO\bar{O}\overset{+}{N}Me_4$	D_2O	1 549	2.24	1 390	1.77
$C_6H_5NO_2$	$CHCl_3$ [a]	1 527.5	1.11	1 349.5	0.71

[a] Nitrobenzene is not soluble in D_2O. The influence of solvents on the frequencies and intensities of the nitro group vibrations is presumably weak (C. N. R. Rao, ' Spectroscopy of the Nitro Group,' in ' The Chemistry of the Nitro and Nitroso Groups,' ed. S. Patai, Wiley, New York, 1969, part 1, p. 79).

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* In the solid state, the quaternary nitrogen substituents and the methyl hydrogen atoms are fully staggered and the molecular conformation results in two methyl groups being closer to the carbonyl than the third.[6]

† In dilute aqueous solution tetramethylammonium benzoate exists as ions. Rigorously, the spectrum of the ion pair should have been compared. But it is known [8] that the frequencies of the carboxylate group are nearly the same in the ion and in the ion pair with the big cations $\overset{+}{N}R_4$. In the rest of this paper, we shall use the carboxylate frequencies of sodium benzoates for comparison with the amidate frequencies of *N*-ammoniobenzamidates.

valence vibrations leading to pseudo-asymmetrical and symmetrical stretching vibrations. Table 2 summarizes the frequencies and integrated intensities of the corresponding bands of *N*-trimethylammoniobenzamidate, benzoate anion, and nitrobenzene.

The Coupling of Ring Modes with Pseudo $\nu_a(\mathrm{CO\bar{N}})$.—Interaction and intensity borrowing between aromatic ring stretching, ν_8, and the carboxylate ion antisymmetric stretching mode has been suggested [10] in benzoate salts from comparison of the intensities of ν_8 in the salt and in the corresponding benzoic acid. An analogous mixing was also found to occur between ν_8 and $\nu_a(\mathrm{NO_2})$ in nitrobenzene from deuteriation studies.[11] The pseudo-asymmetrical $\mathrm{CO\bar{N}}$ stretching vibration in *N*-ammoniobenzamidate occurs in $\mathrm{D_2O}$ at 1 553.5 cm^{-1} and may be classified as a pseudo b vibration if we admit a pseudo-C_{2v} symmetry of the $\mathrm{C_6H_5CO\bar{N}}$ fragment. Interaction with ν_{8b} * at 1 595 cm^{-1} is then conceivable because these modes are of the same (pseudo) symmetry and are reasonably close to each other. It gives rise to a repulsion of the two bands and sharing of intensities; indeed the ν_{8b} intensity is abnormally high (*ca.* 4 000 l mol^{-1} cm^{-2}). Katritzky and Topsom have shown [7] that the ν_8 intensity was mainly dependent on the substituent resonance effect. This high value of intensity would lead to σ°_R $(\mathrm{CO\overset{-}{N}\overset{+}{N}Me_3})$ *ca.* 0.47, a value incompatible with the resonance substituent constant of other COX groups.[7]

The solvent-variation method [12] furnishes proof of coupling. Indeed the study of the two model compounds $\mathrm{C_6H_5COMe}$ for ν_8 and $\mathrm{MeCO\overset{-}{N}\overset{+}{N}Me_3}$ for pseudo $\nu_a(\mathrm{CO\bar{N}})$ has shown that the solvent effect on ν_8 is small and/or random whereas the pseudo $\nu_a(\mathrm{CO\bar{N}})$ frequency decreases and its intensity increases with the polarity and/or the acidity of the solvent (Table 3). If the solvent effect moves aside ν_8 and pseudo $\nu_a(\mathrm{CO\bar{N}})$, it decouples partially these two modes and we should observe the sum of partial decoupling and solvent effects on the frequencies and intensities as schematized in Table 4. These expectations are confirmed for all the substituted *N*-ammoniobenzamidates and illustrated for *N*-ammoniobenzamidate in Figure 2. When the solvent becomes more polar (i) the ν_{8a} frequency and intensity are regularly lowered by partial decoupling from 1 601.5 in tetrachloroethylene to 1 591.5 cm^{-1} in hexafluoropropan-2-ol and from 4 800 in dichloromethane to 2 800 l mol^{-1} cm^{-2} in hexafluoropropan-2-ol; (ii) the pseudo ν_a $(\mathrm{CO\bar{N}})$ intensity increases both by partial decoupling and solvent effects (6 900 in $\mathrm{CH_2Cl_2}$ and 13 100 l mol^{-1} cm^{-2} in $\mathrm{D_2O}$); and (iii) the pseudo $\nu_a(\mathrm{CO\bar{N}})$ frequency varies less regularly than the model compound due to opposite effects of solvent and partial decoupling. From the reference solvent $\mathrm{C_2Cl_4}$ it moves by 1.7 cm^{-1} in $\mathrm{CH_2Cl_2}$, 10.2 cm^{-1} in $\mathrm{D_2O}$, and 7.5 cm^{-1} in $\mathrm{(CF_3)_2CHOH}$ instead of 3.5, 14.9, and 16 cm^{-1}. Finally the solvent-variation method shows that pseudo $\nu_a(\mathrm{CO\bar{N}})$ is always the low frequency band in the band pattern between 1 550 and 1 620 cm^{-1}, even if not the most intense in polar solvents.

TABLE 3

Solvent effect on ν_8 and pseudo ν_a $(\mathrm{CO\bar{N}})$ for the two model compounds acetophenone and *N*-trimethylammonioacetamidate

	ν_8 $(\mathrm{C_6H_5COMe})$			ν_a $(\mathrm{CO\bar{N}})$ $\mathrm{MeC\overset{-}{N}\overset{+}{N}O\overset{+}{N}\ NMe_3}$		
Solvent	Wavenumber (cm^{-1})		Intensity (10^{-4} l mol^{-1} cm^{-2})	Wavenumber	Solvent variation (cm^{-1})	Intensity (10^{-4} l mol^{-1} cm^{-2})
$\mathrm{C_2Cl_4}$	1 599.3	1 582.9	0.09	1 586.9	0	not soluble
$\mathrm{CH_2Cl_2}$	1 599.3	1 582.7	0.09	1 583.4	3.5	1.47
$\mathrm{D_2O}$	Not soluble			1 572	14.9	2.03
$\mathrm{(CF_3)_2CHOH}$	1 601.1	1 584.3	0.18	1 570.9	16.0	1.69

TABLE 4

Solvent and decoupling effects on ν_8 and amidate I bands

	ν_8		Amidate I	
	Solvent effect	Decoupling effect	Solvent effect [a]	Decoupling effect
Frequency	No	↘	↘	↗
Intensity	No	↘	↗	↗

[a] Increasing of polarity and/or acidity.

The Effect of Ring Substitution on Pseudo $\nu(\mathrm{CO\bar{N}})$.—The frequency of vibration of functional groups attached to an aromatic ring depends on ring substitution and sometimes follows the Hammett relation $\nu = \nu_0 + \rho\sigma_{m,p}$.[13] Whenever such a correlation is obeyed for vibrations it is probable that factors other than the electrical effects of substituents on the force constants of the function are either constant, linearly dependent on σ, or absent. Such is the case for the $\mathrm{SO_2^-}$ stretching vibrations in sodium sulphinates [14] and for the carbonyl stretching vibration in *NN*-dimethylbenzamides [15] (Table 5).

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* Interaction with ν_{8a} also occurs for *N*-ammoniobenzamidates substituted by *para*-substituents of symmetry less than C_{2v}, and by *meta*-substituents. Strictly speaking interaction with ν_{8b} alone occurs only in nitrobenzene and benzoate anion (true C_{2v} symmetry).

TABLE 5

Correlation of group frequencies with substituent constant σ

Vibrator	Series	Solvent	ν_0 [a]/cm^{-1}	ρ [b]/cm^{-1}	r [c]	n [d]	Ref.
Series obeying the Hammett equation							
ν (CO)	$\mathrm{ArCONMe_2}$	$\mathrm{CCl_4}$	1 645.9	8.9	0.976	15	15
ν_{as} ($\mathrm{SO_2}$)	$\mathrm{ArS\overset{-}{O_2}\overset{+}{N}a}$	$\mathrm{H_2O}$	1 011.9	18.6	0.986	14	14
ν_s ($\mathrm{SO_2}$)	$\mathrm{ArS\overset{-}{O_2}\overset{+}{N}a}$	$\mathrm{H_2O}$	963.2	7.9	0.963	14	14
Series not obeying the Hammett equation							
ν_{as} ($\mathrm{NO_2}$)	$\mathrm{ArNO_2}$	$\mathrm{CHCl_3}$	1 530.5	16	0.83		16
ν_s ($\mathrm{NO_2}$)	$\mathrm{ArNO_2}$	$\mathrm{CHCl_3}$	1 344	~0 [e]			16
ν_{as} ($\mathrm{C\overset{-}{O_2}}$)	$\mathrm{ArC\overset{-}{O_2}\overset{+}{N}a}$	$\mathrm{D_2O}$	1 548	20.2	0.80	24	9
ν_s ($\mathrm{C\overset{-}{O_2}}$)	$\mathrm{ArC\overset{-}{O_2}\overset{+}{N}a}$	$\mathrm{D_2O}$	1 391	1.0	<0.01	24	9
pseudo ν_a ($\mathrm{CO\overset{-}{N}}$)	$\mathrm{ArCO\overset{-}{N}\overset{+}{N}Me_3}$	$\mathrm{D_2O}$	1 553.5	13.8	0.68	14	This work
pseudo ν_s ($\mathrm{CO\overset{-}{N}}$)	$\mathrm{ArCO\overset{-}{N}\overset{+}{N}Me_3}$	$\mathrm{D_2O}$	1 357	1.0	0.15	12	This work

[a] Experimental wavenumber for the unsubstituted compound. [b] Sensitivity to substituent effects. [c] Correlation coefficient. [d] Number of substituents. [e] Practical independence on positive σ values.

Contrariwise the $\mathrm{NO_2}$ and $\mathrm{CO_2^-}$ stretching vibrations in nitrobenzenes and sodium benzoates do not follow the Hammett equation with precision [9,16] (Table 5).

The correlation of amidate stretching vibrations in benzamidates with Hammett σ values is very similar to that of nitro and carboxylate groups. Table 5 shows that in all three series (i) the correlation coefficient is low for ν_{as} and ν_s and (ii) there is a tendency for ν_{as} to increase with increasing σ or with increasing electron-withdrawing character ($\rho > 0$) and for ν_s to be insensitive to ring substitution (ρ *ca.* 0).

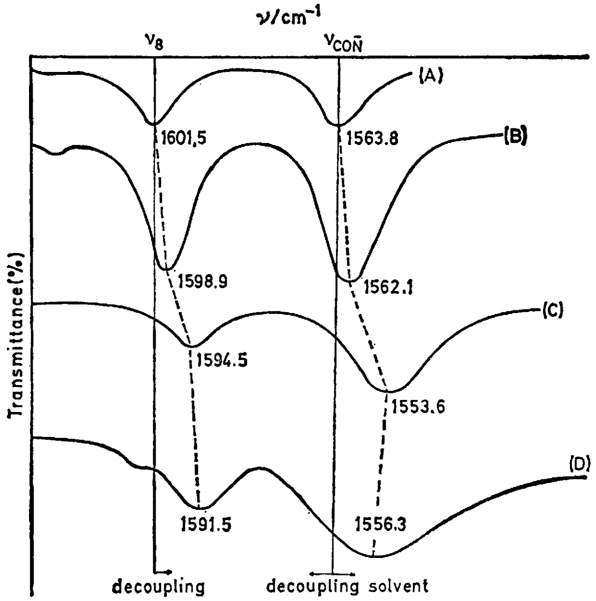

FIGURE 2 I.r. spectra (not on the same scale of intensity) of *N*-trimethylammoniobenzamidate in (A) tetrachloroethylene, (B) dichloromethane, (C) deuterium oxide, and (D) hexafluoropropan-2-ol. The $\nu_8 : \nu$ $\mathrm{CO\overset{-}{N}}$ intensity ratios are respectively, 1.2, 1.4, 3.2, and 4.1

Like nitrobenzenes and benzoic acid salts, *N*-ammoniobenzamidates constitute a new series where the coupling of ring vibrations ν_8 with pseudo ν_{as} causes the failure of the Hammett equation in i.r. spectroscopy.

Dunn and McDonald [9] observed that substituent effects on the asymmetric vibration frequencies are similar for the aromatic carboxylate and nitro groups. Equation (1) shows a good correlation between the pseudo-asymmetric benzamidate and benzoate frequencies. Moreover we found a close correlation

$$\nu_{as}(\mathrm{CO_2^-}) = 1.34\ \nu_{as}(\mathrm{CON}) - 532 \qquad (1)$$

(correlation coefficient r 0.97 for 14 points)

$$\nu_{8a,b}(\mathrm{XC_6H_4CO_2^-}) = 0.89\ \nu_{8a,b}(\mathrm{XC_6H_4CO\overset{-}{N}}) + 174 \qquad (2)$$

(r 0.98 for 21 points)

between $\nu_{8a,b}$ ring vibrations in *N*-ammoniobenzamidates and sodium benzoates [equation (2)]. This again emphasises the similarity of the $\mathrm{XC_6H_4CO_2^-}$ anion and of the $\mathrm{XC_6H_4CO\overset{-}{N}}$ fragment from the point of view of mechanics of vibrations and thus supports the assignment of the amidate I band in *N*-ammoniobenzamidates as pseudo ν_{as} $\mathrm{CO\overset{-}{N}}$ perturbed by mechanical coupling with ring vibrations.

EXPERIMENTAL

Materials.—The preparation of the *N*-trimethylammoniobenzamidates has already been described.[17] Tetramethylammonium benzoate is prepared by the stoicheiometric neutralization of benzoic acid with tetramethylammonium hydroxide in methanol, followed by evaporation of the solvent.

Aqueous solutions of the benzamidates used in this study are completely stable during the recording of the spectra. Indeed $\mathrm{Me_3\overset{+}{N}\overset{-}{N}COPh}$ as a prototype was recovered unchanged after eight days dissolution in water.

I.r. Spectra.—These were obtained with a Beckman IR-12 spectrophotometer in cells with $\mathrm{CaF_2}$ windows and path lengths varying with the solvent from 0.025 mm [$\mathrm{D_2O}$, $\mathrm{(CF_3)_2CHOH}$] to 1 mm ($\mathrm{C_2Cl_4}$). I.r. spectra of sodium *m*-fluoro-, *m*-trifluoromethyl-, and *m*-cyanobenzoates were recorded to complete the results of Dunn and McDonald [9] by making 0.25M solutions of the acids in a 0.3M freshly prepared solution of sodium hydroxide in deuterium oxide. This last solution was kept in the reference beam. ν_{8a},

ν_{8b}, $\nu_a(\mathrm{CO\overset{-}{O}})$, and $\nu_s(\mathrm{CO\overset{-}{O}})$ frequencies are 1 613sh, 1 601, 1 561, 1 386 (*m*-F); 1 617, 1 602, 1 568, 1 388 (*m*-CF_3); 1 609, 1 592, 1 564, 1 386 (*m*-CN) cm^{-1}.

Integrated Intensities.—The integrated absorptions A were calculated from the concentration C (mol l^{-1}), the path length l (cm), and the absorbances $\log_{10}(I_0/I)$ at wavenumbers $\bar{\nu}$ according to $A = (Cl)^{-1} \log_{10}(I_0/I)d\bar{\nu}$. Areas were integrated by Simpson's method over a range of wavenumbers varying from 70 to 140 cm^{-1}. The dissymmetry of most bands prevented a mathematical decomposition of overlapping bands. The decomposition was made by a graphical method and the attained precision was not high.

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REFERENCES

[1] Part 5, C. Laurence and M. Berthelot, *J. Chem. Soc., Perkin Trans. 2*, 1979, 98.

[2] W. J. McKillip, E. A. Sedor, B. M. Culbertson, and S. Wawzonek, *Chem. Rev.*, 1973, **73**, 255.

[3] M. Liler and D. G. Morris, *J. Chem. Soc., Perkin Trans. 2*, 1977, 909.

[4] J. F. Gal and D. G. Morris, *J. Chem. Soc., Perkin Trans. 2*, 1978, 431.

[5] N. B. Colthup, L. H. Daly, and S. E. Wiberley, 'Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1975, 2nd edn.

[6] A. F. Cameron, N. J. Hair, D. G. Morris, and D. M. Hawley, *Chem. Commun.*, 1971, 725.

[7] A. R. Katritzky and R. D. Topsom, *Chem. Rev.*, 1977, **77**, 639.

[8] A. Regis and J. Corset, *J. Chim. Phys.*, 1979, **76**, 107.

[9] G. E. Dunn and R. S. McDonald, *Can. J. Chem.*, 1969, **47**, 4577.

[10] A. S. Wexler, *Spectrochim. Acta, Part A*, 1967, **23**, 1319.

[11] R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J. Chem. Soc., Perkin Trans. 2*, 1974, 247.

[12] J. F. Bertran, L. Ballester, L. Dobrihalova, N. Sanchez, and R. Arrieta, *Spectrochim. Acta, Part A*, 1968, **24**, 1785.

[13] R. T. C. Brownlee, J. Di Stefano, and R. P. Topsom, *Spectrochim. Acta, Part A*, 1975, **31**, 1685.

[14] B. J. Lindberg, *Acta Chem. Scand.*, 1967, **21**, 2215.

[15] K. Spaargarem, C. Kruk, T. A. Molenaar-Langeveld, P. K. Korver, P. J. Van der Haak, and T. J. de Boer, *Spectrochim. Acta, Part A*, 1972, **28**, 965.

[16] O. Exner, S. Kovac, and E. Solcaniova, *Collect. Czech. Chem. Commun.*, 1972, **37**, 2156.

[17] A. M. Murray, Ph.D. Thesis, University of Glasgow, 1975.