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Spectroscopic studies on *N,N*-dimethylamides—II* Substituent effect on infrared carbonyl stretching vibrations and hydroxyl frequency shifts of *para*- and *meta*-substituted *N,N*-dimethylbenzamides and cinnamamides†

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Abstract—Carbonyl stretching frequencies $\nu_{C=O}$ and hydroxyl frequency shifts $\Delta\nu_{OH}$ of phenol as a proton donor, of series of *para*- and *meta*-substituted *N,N*-dimethylbenzamides and -cinnamamides were measured in CCl_4.

Results are correlated with the substituent constants of SWAIN and LUPTON [2] and with the carbonyl π-bond orders and the oxygen π-electron densities obtained in an H.M.O. ($\Omega = 1.4$) calculation. Infrared frequencies are correlated with the amide rotational barriers.

INTRODUCTION

IN CONNECTION with our investigations concerning the substituent effects on the amide rotational barriers in *N,N*-dimethylcarboxamides, we studied the carbonyl stretching frequencies of some *para*- and *meta*-substituted *N,N*-dimethylbenzamides and -cinnamamides of dilute solutions in carbon tetrachloride. The absorption due to the carbonyl stretching vibration is shifted when the electronic distribution is changed. These shifts have been correlated with the substituent constants e.g. in substituted acetophenones [3], benzophenones [4], benzoylchlorides [5] and recently in chalcones [6], substituted in both aromatic rings.

Additional information on the charge distribution in the amide group may be obtained from a study of the OH-stretching frequency shifts, $\Delta\nu_{OH}$, of a standard proton donor such as phenol. Such systems of a proton donor and a proton acceptor have been studied extensively (for a recent review, see Ref. [7]). GRAMSTAD and

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* Part I, Ref. [1].

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[1] P. K. KORVER, K. SPAARGAREN, P. J. VAN DER HAAK and TH. J. DE BOER, *Org. Magn. Res.* **2**, 295 (1970).

[2] C. G. SWAIN and E. C. LUPTON, JR., *J. Am. Chem. Soc.* **90**, 4328 (1968).

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[6] N. L. SILVER and D. W. BOYKIN, JR., *J. Org. Chem.* **35**, 759 (1970).

[7] A. S. N. MURTHY and C. N. R. RAO, *Appl. Spectry Rev.* **2**, 69 (1968).

Fuglevik [8] studied the intermolecular hydrogen bond association of *N*,*N*-disubstituted amides with phenol and pentachlorophenol as proton donors. They found linear relationships between the frequency shift $\Delta\nu_{OH}$ and ΔH, ΔG, ΔS, the thermodynamic parameters for the association and $\nu_{1/2}$ and $\varepsilon_{max} \times \nu_{1/2}$. They observed a linear correlation between $\nu_{C=O}$ and $\Delta\nu_{OH}$, which is a measure for the ability of the amide to form a hydrogen bond.

As both the i.r. frequencies and the amide rotational barriers are modified on substitution we correlated $\nu_{C=O}$ with $\Delta G^{\ddagger}_{298.2}$. The rotational barriers will be discussed in a subsequent paper.

Linear free energy relationships

The empirical relationships between structure and reactivity involve the logarithms of rate- or equilibrium-constants and are, as such, linear free energy ($\Delta G^{\ddagger}$) relationships. Since the formulation of the earliest relationship, the Brönsted catalysis law (1924), Hammett [9] has developed the familiar equation (1), especially for aromatic systems:

$$\log (k/k_0) = \rho\sigma. \tag{1}$$

With this relation one can describe quantitatively the influence exerted by *para*- and *meta*-substituents on the rate of aromatic side chain reactions. However, the substituent "constants" σ, which should be ideally independent of the nature of the reaction, (characterized by ρ) have turned out not to be unique. To solve this problem many suggestions have been made (for recent reviews see Shorter [10] and Swain and Lupton [2]).

In our opinion, the most elegant method is the one recently introduced by Swain and Lupton [2], who showed that any set of substituent constants (σ_m, σ_p, σ' *etc.*) is a linear combination of any two others. They introduced two new sets, F and R, the so called field- and resonance-constants. The linear combination $fF + rR$ replaces the classical σ value. The field- and resonance-capabilities of a substituent in any circumstances are mixed as required for the actual process. This removes the problem of the duality of substituent constants [11] and forms an extension of Wepster's "sliding scale" [12].

F and R are proposed [2] as more accurately defined and physically significant independent variables for correlating or predicting substituent effects on all kinds of rates, equilibria and physical properties.

As the resonance ability of a substituent is different in *meta*- and *para*-positions, the Swain and Lupton method should be applied to *meta*- and *para*-substituted series separately. Any substituent-effect can thus be quantitatively expressed by a field- and resonance-component, $\rho f'F$ and $\rho r'R$ respectively, with the reaction constant ρ, the weighting factors f' and r' characteristic for the type of reaction and F and R characteristic for the substituent. In correlations of observed properties, ρ cannot be independently determined and $\rho f'$ and $\rho r'$ are replaced by f and r respectively.

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[8] T. Gramstad and W. J. Fuglevik, *Acta Chem. Scand.* **16**, 1369 (1962).

[9] L. P. Hammett, *Chem. Rev.* **17**, 125 (1935).

[10] J. Shorter, *Chem. Brit.* **5**, 269 (1969).

[11] L. P. Hammett, *Physical Organic Chemistry*. McGraw-Hill, New York (1940).

[12] H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. Trav. Chim.* **78**, 815 (1959).

It is preferable to use a three parameter equation (like equation (2)) to avoid forcing the correlation to go through the origin, since measurement on the unsubstituted compound with $F = 0$, $R = 0$, are no more accurate than those on substituted ones. From

$$\Delta G^{\ddagger} = fF + rR + \Delta G_0^{\ddagger} \tag{2}$$

one calculates f, r and $\Delta G_0^{\ddagger}$.

Swain and Lupton [2] further define the sensitivity to resonance effects as the "per cent resonance":

$$\%R = 22.8\,|r|/(0.365\,|f| + 0.228\,|r|). \tag{3}$$

The scaling factors (0.365 and 0.228) have been introduced "to correct for the fact that f values on the average will be smaller than r values," because the average variation of F is greater than that of R.

Error limits of $\%R$ are easily obtained [2], assuming that the errors of f and r are not correlated. Standard deviations of f and r and $\Delta G_0^{\ddagger}$ are obtained in the least squares calculation.

As we now have available a set of substituent constants (F and R) which might be "orthogonal and complete," i.e. independent and with the possibility to account for any substituent effect, it is interesting to apply them on some physical properties [1] of N,N-dimethylamides.

It should be kept in mind, however, in all discussions on the $\%R$ found, that the separation of field- and resonance-effects is rather artificial and that the actual calculation of the $\%R$ with the introduced scaling factors is somewhat arbitrary.

RESULTS AND DISCUSSION

Carbonyl stretching frequencies $\nu_{C=O}$, hydroxyl frequency shifts $\Delta\nu_{OH}$, together with the amide rotational barrier $\Delta G^{\ddagger}_{298.2}$, obtained from a total line shape analysis at 0.25 M in $CDCl_3$ are presented in Table 1. π-Bond orders of the C—N and C=O amide bonds and the π electron density of the carbonyl oxygen are obtained with an H.M.O. ($\Omega = 1.4$) calculation.

Field- and resonance-effects

Recently Silver and Boykin [6] tried to correlate the carbonyl stretching vibrations of acetophenones, benzophenones and chalcones with the substituent constants F and R of Swain and Lupton [2]. The poor results of this first reported treatment of the i.r. data are partly due to the fact that the data of the *para*- and *meta*-substituted compounds were lumped together. Considering only *para*-substituted compounds, we recalculated their data, using a multi-correlation-least-squares program* and tabulated the results together with our experimental work, in Table 2.

Let us first consider the substituent effect as calculated from the p_{Ka} values, for six *para*-substituted benzoic acids and six cinnamic acids.

p-benzoic acids: $p_{Ka} = -(0.56 \pm 0.01)F - (1.03 \pm 0.02)R + (4.19 \pm 0.01)$
S.D. = 0.01 c.c. = 1.000.

p-cinnamic acids: $p_{Ka} = -(0.28 \pm 0.07)F - (0.46 \pm 0.14)R + (4.46 \pm 0.05)$
S.D. = 0.06 c.c. = 0.953.

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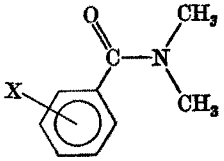
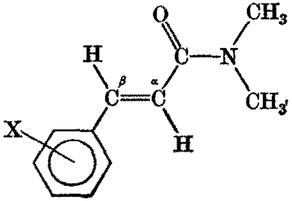
* We are indebted to Dr. C. W. F. Kort for valuable discussions and use of his program Lak-8, written in ALGOL 60 for the Electrologica-X8 computer.

Table 1. Amide rotational barriers ($\Delta G^{\ddagger}_{298.2}$), carbonyl stretching frequencies ($\nu_{C=O}$) and hydroxyl frequency shifts ($\Delta\nu_{OH}$) of *N*,*N*-dimethylbenzamides and -cinnamamides. Bond orders (p) and π-densities (q) from H.M.O. ($\Omega = 1.4$) calculation.





X	p_{C-N}	$\Delta G^{\ddagger}_{298.2}$ kcal/mole	$p_{C=O}$	$\nu_{C=O}$ cm^{-1}	q_O	$\Delta\nu_{OH}$ cm^{-1}	p_{C-N}	$\Delta G^{\ddagger}_{298.2}$ kcal/mole	$p_{C=O}$	$\nu_{C=O}$ cm^{-1}	q_O	$\Delta\nu_{OH}$ cm^{-1}
p-NO_2	0.4200	16.35	0.8153	1651.9	1.3586	254	0.4109	16.94	0.7987	1660.9	1.3670	297
p-CN	0.4199	16.21	0.8143	1652.5	1.3570	265	0.4111	16.74	0.7986	1660.4*	1.3659	310*
p-Br	0.4176	15.58	0.8130	1646.1	1.3679	287	0.4094	16.53	0.7971	1658.8	1.3722	325
p-Cl	0.4174	—	0.8128	1647.3	1.3684	289	0.4094	16.51	0.7970	1658.5	1.3724	326
p-F	0.4165	15.24	0.8116	1646.8	1.3709	294	0.4089	16.42	0.7964	1659.6	1.3737	330
H	0.4181	15.67	0.8138	1645.9	1.3665	294	0.4097	16.39	0.7975	1658.1	1.3714	325
p-CH_3	0.4152	—	0.8100	1644.1	1.3751	307	0.4081	16.29	0.7955	1657.0	1.3759	335
p-OCH_3	0.4150	14.50	0.8094	1642.5	1.3746	309	0.4081	16.06	0.7953	1656.2	1.3757	336
m-NO_2	0.4190	—	0.8149	1652.1	1.3639	265	0.4102	—	0.7981	1661.8*	1.3701	305*
m-CN	0.4191	—	0.8151	1651.5	1.3636	268	0.4102	—	0.7982	1661.9*	1.3700	320*
m-Br	0.4180	—	0.8136	1648.5	1.3669	281	0.4096	—	0.7974	1659.8	1.3716	320
m-Cl	0.4180	—	0.8136	1648.5	1.3670	279	0.4096	—	0.7974	1660.1	1.3717	315
m-F	0.4177	—	0.8133	1648.2	1.3678	280	0.4095	—	0.7972	1659.9	1.3721	320
H	0.4181	15.67	0.8138	1645.9	1.3665	294	0.4097	16.39	0.7975	1658.1	1.3714	325
m-CH_3	0.4172	—	0.8126	1645.3	1.3696	300	0.4092	—	0.7968	1657.7	1.3730	330
m-OCH_3	0.4175	—	0.8130	1646.5	1.3687	300	0.4093	—	0.7970	1658.1	1.3726	327

* Saturated solution.

Table 2. Correlation of carbonyl stretching frequencies ($\nu_{C=O}$) and of hydroxyl frequency shifts ($\Delta\nu_{OH}$) with substituent constants F and R.

$$Y = fF + rR + Y_0$$

Subst.	Compounds	Y cm^{-1}	f	r	Y_0 cm^{-1}	%R	S.D.	Corr. coef.	Ref.
para	acetophenones	$\nu_{C=O}$	7.2 ± 1.4	15.8 ± 2.7	1690.2 ± 1.0	58 ± 6	1.4	0.962	[3]
para	chalcones	$\nu_{C=O}$	4.5 ± 0.7	8.1 ± 1.2	1665.7 ± 0.5	53 ± 5	0.7	0.974	[6]
para	benzamides	$\nu_{C=O}$	4.5 ± 0.9	10.2 ± 1.5	1645.9 ± 0.7	59 ± 4	0.9	0.965	this work
meta	benzamides	$\nu_{C=O}$	4.9 ± 0.4	4.0 ± 0.7	1646.1 ± 0.3	34 ± 4	0.4	0.987	this work
para	cinnamamides	$\nu_{C=O}$	2.5 ± 0.7	3.6 ± 1.2	1657.8 ± 0.5	48 ± 11	0.7	0.892	this work
meta	cinnamamides	$\nu_{C=O}$	3.2 ± 0.3	2.7 ± 0.6	1658.2 ± 0.2	34 ± 5	0.3	0.978	this work
para	benzamides	$\Delta\nu_{OH}$	−28 ± 3	−53 ± 5	296 ± 2	54 ± 3	2.9	0.988	this work
meta	benzamides	$\Delta\nu_{OH}$	−26 ± 3	−24 ± 5	295 ± 2	37 ± 6	3.1	0.974	this work
para	cinnamamides	$\Delta\nu_{OH}$	−17 ± 4	−39 ± 8	327 ± 3	59 ± 8	4.4	0.943	this work
meta	cinnamamides	$\Delta\nu_{OH}$	−15 ± 4	−9 ± 7	327 ± 3	27 ± 17	4.3	0.836	this work

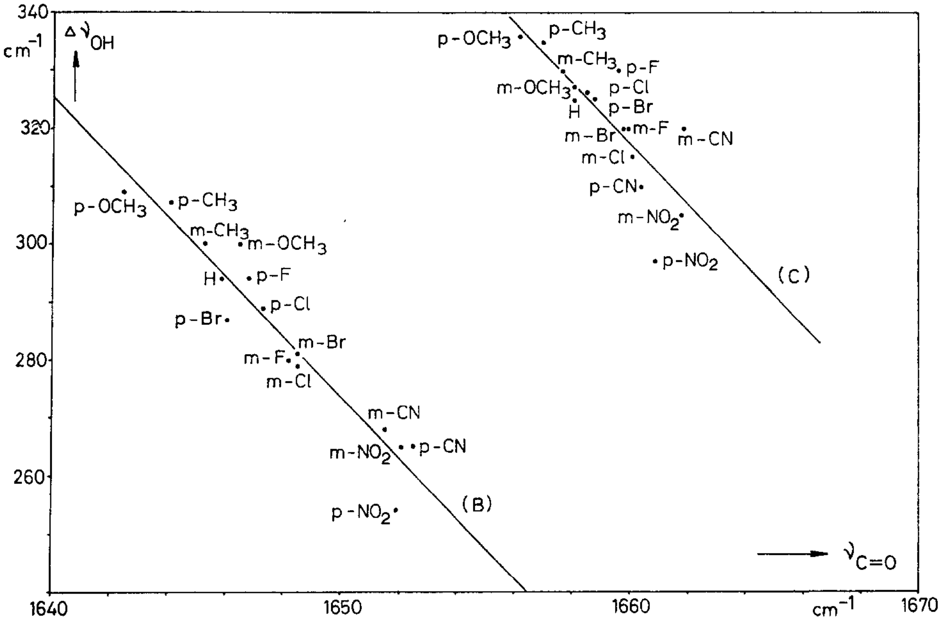


Fig. 1. Infrared hydroxyl frequency shift of phenol ($\Delta\nu_{OH}$) *vs.* carbonyl stretching frequency ($\nu_{C=O}$) of *N*,*N*-dimethylbenzamides (B) and -cinnamamides (C).

For the benzoic acids we calculate $\%R = 53 \pm 1$, exactly the same value as was reported by Swain [2] for the $\%R$ in σ_p. The cinnamic acids show a smaller substituent effect. As both f and r are halved, the per cent resonance is the same ($\%R = 51 \pm 10$) as for the benzoic acids. The correlation, however, is much poorer!

Although most of the correlation coefficients for the i.r. data in Table 2 are satisfactory, the error limits of the $\%R$ are such that the per cent resonance in all *para*-substituted series does not differ significantly from 53 per cent, which means that a comparable correlation would have been obtained with the ordinary σ_p values. However, in *meta*-substituted compounds the observed ($\%R = 34$) per cent resonance is significantly larger than that of Hammett's σ_m ($\%R = 22$, Ref. [2]). This means that the *meta*-substituents in these amides seem to exercise a somewhat larger resonance effect on $\nu_{C=O}$ and $\Delta\nu_{OH}$, than they do in the dissociation reaction of benzoic acids.

Figure 1 shows a satisfactory correlation of $\Delta\nu_{OH}$ and $\nu_{C=O}$ of the substituted *N*,*N*-dimethylbenzamides, whereas the data of the cinnamamides show more scattering.

$$\text{Benzamides:} \quad \Delta\nu_{OH} = -(5.200 \pm 0.4)\nu_{C=O} + (8854 \pm 656)$$

$$\text{S.D.} = 4.6 \qquad \text{c.c.} = 0.959.$$

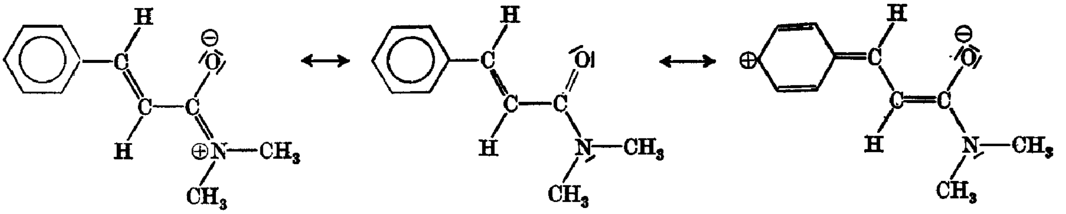
$$\text{Cinnamamides:} \quad \Delta\nu_{OH} = -(5.202 \pm 1.0)\nu_{C=O} + (8953 \pm 1680)$$

$$\text{S.D.} = 6.4 \qquad \text{c.c.} = 0.793.$$

From the correlation of the benzamides we expect the carbonyl stretching vibration of the cinnamamides to be around 1640 cm⁻¹, which is 20 cm⁻¹ below the observed value. As we have shown before [13] this difference is due to the *s-cis* conformation of the *N*,*N*-dimethylcinnamamides.

Hückel molecular orbital ($\Omega = 1.4$) *treatment*

In the substituted *N*,*N*-dimethylbenzamides and -cinnamamides there is a cross-conjugation of carbonyl and nitrogen, (the amide resonance), and of carbonyl with the rest of the molecule:



The amide resonance will reduce the substituent effect on the carbonyl stretching vibration, as **Korver** [14] concluded from a comparison of the series of substituted benzamides with the benzoic acids and acetophenones. In addition, in the series of *N*,*N*-dimethylbenzamides, the non-planar arrangement of the amide plane and the benzene ring will reduce the substituent effect on $\nu_{C=O}$ and $\Delta\nu_{OH}$. It is difficult to predict from a discussion of the mesomeric structures whether the π-bond orders $p_{C=O}$ and p_{C-N} will be similarly affected by the substituent. An H.M.O. ($\Omega = 1.4$) calculation shows that p_{C-N} and $p_{C=O}$ are linearly correlated:

$$\text{Benzamides:}\quad p_{C-N} = (0.8202 \pm 0.06)p_{C=O} - (0.2492 \pm 0.05)$$
$$\text{S.D.} = 0.0004 \qquad \text{c.c.} = 0.962.$$
$$\text{Cinnamamides:}\quad p_{C-N} = (0.8431 \pm 0.04)p_{C=O} - (0.2626 \pm 0.03)$$
$$\text{S.D.} = 0.0001 \qquad \text{c.c.} = 0.985.$$

But then we may expect a correlation for the rotational barrier $\Delta G^{\ddagger}$, which will be related to p_{C-N} and the carbonyl stretching vibration $\nu_{C=O}$. Indeed (Fig. 2) both series show fair correlations:

$$\textit{para}\text{-subst. benzamides:}\quad \Delta G^{\ddagger} = (0.1619 \pm 0.03)\nu_{C=O} - (251.1 \pm 55)$$
$$\text{S.D.} = 0.29 \qquad \text{c.c.} = 0.904.$$
$$\textit{para}\text{-subst. cinnamamides:}\quad \Delta G^{\ddagger} = (0.1563 \pm 0.02)\nu_{C=O} - (242.7 \pm 41)$$
$$\text{S.D.} = 0.10 \qquad \text{c.c.} = 0.922.$$

It is noteworthy that $\nu_{C=O}$ of *para*- and *meta*-substituted *N*,*N*-dimethylbenzamides and -cinnamamides show a very poor correlation with $p_{C=O}$ (Fig. 3): c.c. $\simeq$ 0.85 for all four series.

From Fig. 4 we learn that the π-density on the carbonyl oxygen, as obtained from an H.M.O. ($\Omega = 1.4$) calculation, roughly correlates with $\Delta\nu_{OH}$ of the whole series of *para*- and *meta*-substituted benz- and cinnamamides. The *meta* series show very poor correlations (c.c. 0.842 and 0.662 for benz- and cinnamamides respectively),

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[13] C. Kruk and K. Spaargaren, *Spectrochim. Acta* **27A,** 77 (1971).

[14] P. K. Korver, Thesis, Amsterdam (1966).

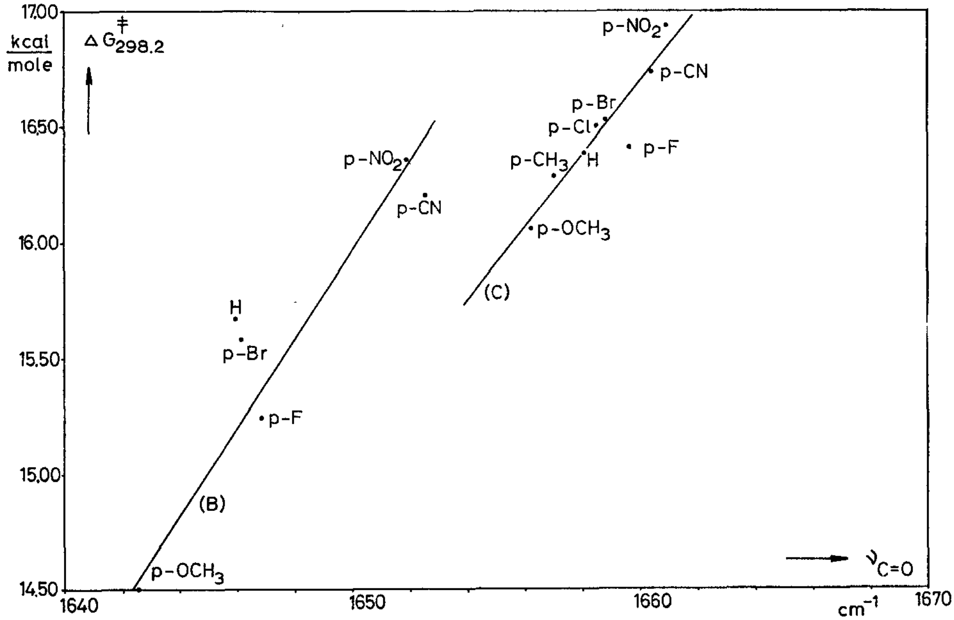

Fig. 2. Amide rotational barrier ($\Delta G^{\ddagger}$) *vs.* i.r. carbonyl stretching frequency ($\nu_{C=O}$) of *para*-substituted *N*,*N*-dimethylbenzamides (B) and -cinnamamides (C).

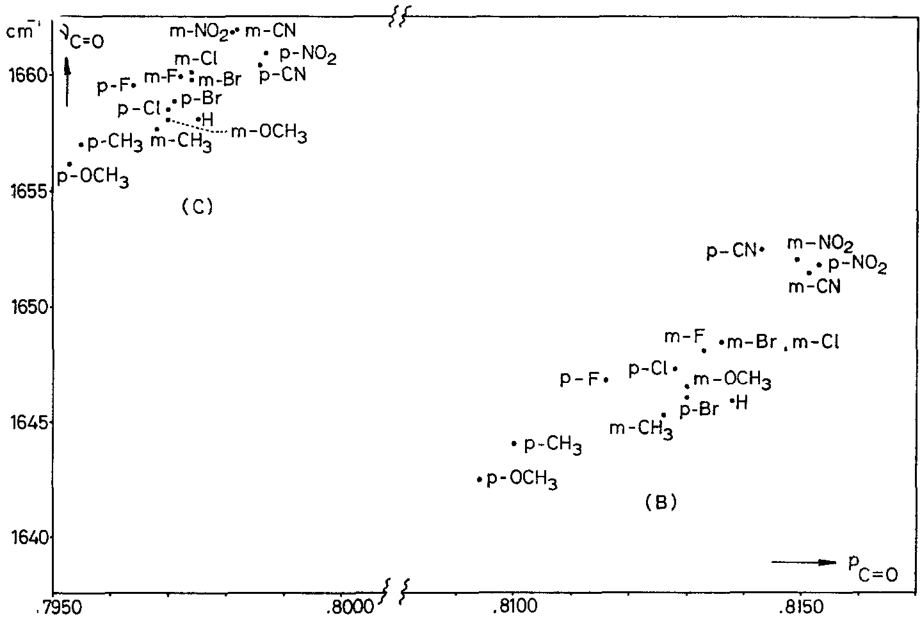

Fig. 3. Infrared carbonyl stretching frequency ($\nu_{C=O}$) *vs.* π-bond order ($p_{C=O}$) from H.M.O. ($\Omega = 1.4$) calculation of *N*,*N*-dimethylbenzamides (B) and -cinnamamides (C).

which is not surprising, since the substituent effect is so small. The calculated standard deviations are of the same order as the experimental uncertainties (± 5 cm^{-1}).

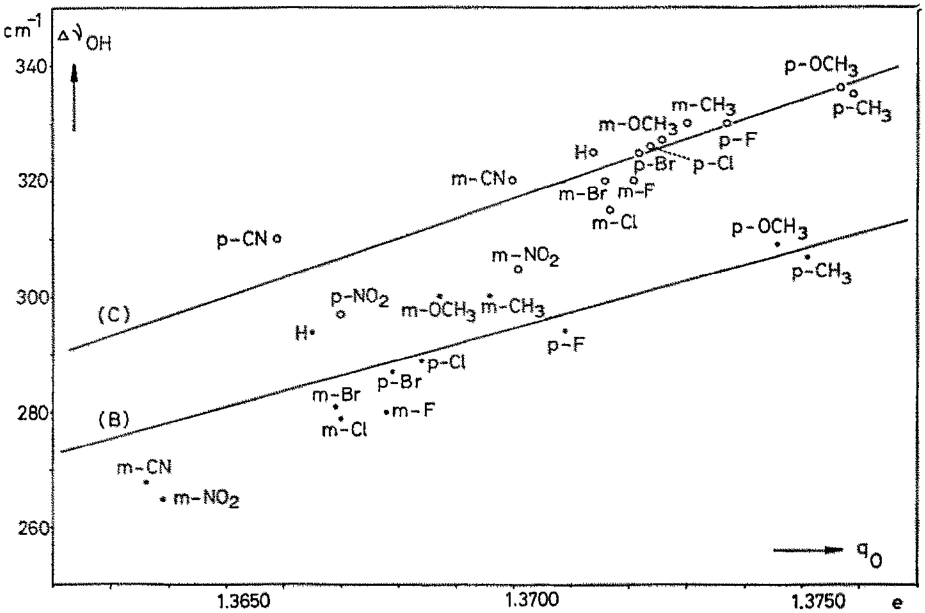

Fig. 4. Infrared hydroxyl frequency shift of phenol ($\Delta\nu_{OH}$) *vs.* π-electron density on carbonyl oxygen (q_0) from H.M.O. ($\Omega = 1.4$) calculation of *N*,*N*-dimethylbenzamides (B) and -cinnamamides (C). Regression lines are based on *para*-substituted compounds only.

The *para*-substituted compounds show fair correlations:

para-subst. benzamides: $\Delta\nu_{OH} = (2739 \pm 350)q_0 - (3458 \pm 480)$
S.D. = 6.1 c.c. = 0.947.

para-subst. cinnamamides: $\Delta\nu_{OH} = (3362 \pm 530)q_0 - (4288 \pm 730)$
S.D. = 5.2 c.c. = 0.921.

EXPERIMENTAL

Synthesis

N,N-*dimethylbenzamides.* The *para*- and *meta*-substituted *N*,*N*-dimethylbenzamides were synthesized from the corresponding acid chlorides and dimethylamine in ethereal solution. Details and physical constants were reported by KORVER [14].

α,β-*Unsaturated* N,N-*dimethylcarboxamides.* Whenever available, commercial cinnamic acids were used as the starting material; otherwise, they were synthesized from the corresponding aldehydes by a Knoevenagel condensation, with malonic acid in pyridine/piperidine, analogous to the method of DUTT [15].

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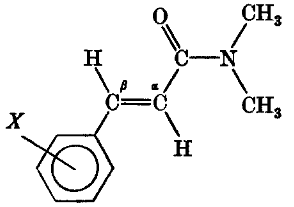
[15] S. DUTT, *Chem. Zentr.* **2**, 1853 (1925).

Table 3. Melting points (uncorrected) after crystallisation from various solvents of *N,N*-dimethylcinnamamides



X	Melting point Exp. °C	Lit. °C	Recrystallized from	Ref.
p-NO_2	175–176		chloroform/ether	
p-CN	188		light petroleum (40–60)	
p-Br	126–127		carbon tetrachloride	
p-Cl	127–128	125.2–125.6	light petroleum (40–60)	[17]
p-F	100		light petroleum (40–60)	
H	100	101–102	benzene	[18]
p-CH_3	108–109		light petroleum (40–60)	
p-OCH_3	107–108	100.0–100.8	ether	[17]
m-NO_2	149		carbon tetrachloride	
m-CN	170–171		carbon tetrachloride	
m-Br	101		carbon tetrachloride	
m-Cl	88–89		light petroleum (40–60)	
m-F	76–77		pentane	
m-CH_3	72		pentane	
m-OCH_3	88		light petroleum (40–60)	
H(αCH_3)			(prep. G.L.C. silicon S.E. 30)	
H(αC_6H_5)	91	84–85	light petroleum (40–60)	[19]

Trans-α-methyl-cinnamic acid was prepared according to KUSKOV [16] from benzaldehyde and propionic anhydride with boron trioxide. The *cis*- and *trans*-acids were esterified with diazomethane and separated by G.L.C. (column: 3 m silicone SE 30, temperature 190°C).

The *trans*-α-methyl-cinnamate was saponified with alcoholic potassium hydroxide and recrystallized. Thionyl chloride was added to the cinnamic acid and, after three hours of refluxing, the excess of thionyl chloride was evaporated at reduced pressure. To suppress formation of byproducts, a calculated amount of dimethylamine (in ether) was added slowly to the cooled ethereal solution of the crude cinnamic acid chloride. After two hr of refluxing, the mixture was poured into water/chloroform. Compounds were purified by recrystallisation (see Table 3).

N,N-dimethyl-(*trans*)-2-butenamide and -(*trans*)-2-methyl-2-butenamide were prepared in a similar way.

Infrared spectra

Infrared spectra were taken on a Perkin–Elmer model 125 grating spectrometer. The instrument was flushed with nitrogen. All measurements were carried out at

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[17] A. D. DELANEY, D. J. CURRIE and H. L. HOLMES, *Can. J. Chem.* **47**, 3273 (1969).

[18] D. PAPA, E. SCHWENK, F. VILLANI and E. KLINGSBERG, *J. Am. Chem. Soc.* **72**, 3885 (1950).

[19] R. FUKS, R. BUYLE and H. G. VIEHE, *Angew. Chem.* **78**, 594 (1966).

Table 4. Coulomb- and resonance integrals of hetero substituents for H.M.O. ($\Omega = 1.4$) calculation

Substituent	u	v	h_u	k_{uv}
OCH_3	O	C	1.75	0.8
F	F	C	2.5	0.7
Cl	Cl	C	2.0	0.4
Br	Br	C	1.5	0.3
NH_2	N	C	1.5	0.8
$N(CH_3)_2$	N	C	1.0	0.8
CN	C	C	0.0	0.9
	N	C	1.5	1.25
NO_2	N	C	2.0 (1.8)	0.8 (0.9)
	O	N	1.0 (1.5)	0.7 (1.7)
C=C	C	C	0.0	1.1
C—C	C	C	0.0	0.9
CH_3	inductive model $h_{C\alpha}$:	−0.5		

34°C, in 10 mm cells. The absorptions of the carbonyl stretching vibrations ($\nu_{C=O}$) were measured in dilute solution (10 mg/10 ml) of CCl_4, dried over P_2O_5. Peak positions were determined by averaging the results of three measurements and are believed to be accurate to ± 0.4 cm^{-1}. The calibration of the instrument was checked against indigenous water vapour in the air.

The hydroxyl stretching frequency shifts ($\Delta\nu_{OH}$) were measured in dilute solutions (10 mg/10 ml) of CCl_4, dried over P_2O_5, to which 2 mg of phenol were added as the proton donor. Peak positions were determined by recording each spectrum three times and are believed to be accurate to ± 5 cm^{-1}.

H.M.O. ($\Omega = 1.4$) *calculations*

In all calculations we used the parameters of Table 4 which were taken from Refs. [20, 21] except those for CN. Much better results were obtained with the NO_2-parameters from Ref. [22], given in parentheses in Table 4. In addition the correction $h_{C\alpha NO_2} = 0.25$ was used in these cases. Reported results were calculated with the NO_2-parameters taken from Ref. [22].

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