The Influence of Solvent on the Inductive Order of Substituents from Infrared Measurements on 4-Substituted Camphors: a New Model of Inductive Effects

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4-Substituted camphors (1)—(24) have been chosen as purely inductive models of substituent effects in order to study the effect of solvent on the inductive order of substituents. The probe was the carbonyl stretching vibration, the frequency of which was measured in (i) the gas phase, (ii) non-polar solvents (heptane and carbon tetrachloride), (iii) a hydrogen-bonding acceptor solvent (pyridine), (iv) a hydrogen-bonding donor solvent (hexafluoropropan-2-ol), and (v) an amphoteric solvent (methanol). Correlation analysis shows the consistency of data for gas-phase and apolar solvents, the deviation of hydrogen-bonding donor substituents (OH, $NHCO_2Et$, NH_2, CO_2H, $CONH_2$) in pyridine, and the deviation of hydrogen-bonding acceptor substituents (all except H, alkyls, C_6H_5, $CH{=}CH_2$, halogens) in hexafluoropropan-2-ol. In methanol the two kinds of deviation are so attenuated that most substituents behave inductively, in the same way as in apolar solvents. This explains the apparent, but fallacious independence of the inductive scale of substituents (defined mainly in alcoholic or aqueous media) on the solvent.

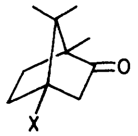
Most of our knowledge of substituent effects has come from a study of chemical reactivity measured in water, mixed aqueous solvents, and alcohols.[1] In recent years the measurement of spectral properties (i.r. and u.v. frequencies and intensities, and n.m.r. shifts) and of ionization potentials, the development of theoretical calculations, and the study of ion–molecule reactions by mass spectroscopy have together made available data for substituted molecules and ions in the gas phase and in ' inert ' solvents and have given a contemporary aspect to the study of the solvent dependence of substituent effects. In respect of linear free energy relationships and more generally correlation analysis, this question of solvent dependence was raised in particular by Jaffé,[2] who noted the systematic variation of σ values of the OH substituent with solvent composition; since that time, however, the problem has only been dealt with in an incomplete manner (see for example pp. 28, 20, 444, 166, and 169 respectively of references 3, 4, 5, 1, and 6).

The field has been characterised by a lack of systematic studies; indeed only two seem noteworthy. In the first, the influence of solvent on the inductive [7a] and resonance [7b] scales of substituents has been assessed from ^{19}F chemical shifts in *meta*- and *para*-substituted fluorobenzenes and particular inductive constants have been determined for different types of solvent. In the second, comparison of protonic acidities and basicities in the substituted aniline–anilinium,[8] pyridine–pyridinium,[8] and phenol–phenoxide [9] systems in the gas phase and in aqueous solution showed that solvent influences on the scale of substituent inductive effects are caused largely by specific substituent solvation; by contrast the scales of substituent π delocalisation may depend on both specific substituent solvation and non-specific dipolar mesomeric moment solvation.

However, these studies refer to molecules in which the inductive and resonance effects are operating simultaneously and a number of assumptions are necessary to factorise these effects. The assumption that the variation of ^{19}F chemical shifts in *meta*-substituted fluorobenzenes originates only from inductive effects has been criticized;[10,11] moreover the F atom probe is a π electron donor which may modify the electronic properties of substituents. In respect of protonic acidities and basicities the substituent effects are taken as the sum of inductive and resonance effects; the ratio of the resonance effects at the *meta*-relative to the *para*-position is, like the ratio of the inductive effects, taken to be approximately constant.[8,9]

The approximations involved together with the associated accumulation of errors led us to consider cautiously the differences found between the inherent gas-phase substituent scale and that derived from aqueous solutions. Furthermore, when several effects are operating, there is no simple way of separating the solvation of the reaction centre and of the substituent (note the difficulties encountered by Happer [12] in discussion of the solvent dependence of substituent constants from ^{13}C chemical shifts in substituted styrenes); it is thus difficult to separate the effects of non-specifically solvated substituents from their specifically solvated counterparts.

We have attempted to simplify this problem by studying solvation effects in bicyclic compounds in which only inductive effects operate (as pioneered by Ritchie [13] with 4-substituted bicyclo[2.2.2]octanecarboxylic acids). To this end we have combined the experimental advantages of modern i.r. spectroscopy with the novelty of 4-substituted camphors as a model for inductive effects; the series studied covers a wide range of substituent character from CO_2^- (1) to NO_2 (24). The probe is the carbonyl stretching vibration, the frequency of which has been measured in the gas phase, and in solution in heptane, carbon tetrachloride, pyridine, hexafluoropropan-2-ol (HFIP), or methanol. The gas phase is the theoretical reference state and both heptane and carbon tetrachloride are expected to solvate all the substituents non-specifically. Pyridine is a hydrogen-bonding acceptor (HBA) solvent able to solvate hydrogen-bonding donor (HBD) substituents specifically; in like vein specific solvation of HBA substituents is effected by the HBD solvent HFIP. Methanol is an amphoteric solvent which specifically solvates both HBA and HBD substituents. Its HBA property is close to that of pyridine according to the β parameters of Kamlet and Taft [14] ($\beta_{MeOH} = 0.62$, $\beta_{pyr} = 0.64$) but its HBD property is much less than that of HFIP ($\alpha_{MeOH} = 0.93$, $\alpha_{HFIP} = 1.95$).[15]



(1) X = $CO_2^-\overset{+}{N}Bu_4$
(2) X = $CO\overset{-}{N}-\overset{+}{N}Me_3$
(3) X = $CO\overset{-}{N}-\overset{+}{S}Me_2$
(4) X = Et
(5) X = Me
(6) X = H
(7) X = $CH{=}CH_2$
(8) X = Ph
(9) X = NMe_2
(10) X = NH_2
(11) X = OH
(12) X = OMe
(13) X = $C{\equiv}CH$
(14) X = $CONH_2$
(15) X = CO_2H
(16) X = $NHCO_2Et$
(17) X = COMe
(18) X = CO_2Me
(19) X = OAc
(20) X = I
(21) X = Cl
(22) X = Br
(23) X = $C{\equiv}N$
(24) X = NO_2

Analysis of substituent solvation is most simply effected by (i) correlations between columns of the data matrix (in which columns refer to solvents and rows to substituents), (ii) detection of deviations, and (iii) considerations of the consistency of both the direction and the relative magnitude of those deviations with the chemistry involved.

Experimental

I.r. spectra in the range 1 650—1 850 cm^{-1} were recorded with a Perkin-Elmer 580B spectrophotometer linked to a PE 3500 data station. The optical system was rigorously purged with dry air. With this apparatus a reproducibility of 0.1 cm^{-1} and a resolution of 1.4 cm^{-1} were realised. When several absorption bands were superimposed they were resolved by the method of Jones [16] who employed a sum of the functions of Gauss and Cauchy.

A CaF_2 cell of variable thickness, 0.01—0.1 cm (according to the transparency of the solvents), and an RiiC-GH-5 cell of 9 cm thickness, heated to 180 °C, were used respectively for solution and gas-phase spectral determinations.

The solvents heptane, carbon tetrachloride, methanol, and HFIP were of spectroscopic grade and were dried over molecular sieves.

The syntheses of 4-substituted camphors have been described.[17]

Results

The i.r. spectra of the carbonyl group stretching vibration of camphor (Figure 1) and its derivatives show that the carbonyl group exists free in the gas phase and experiences a non-specific interaction with the solvents heptane, carbon tetrachloride, and pyridine as shown by the sharp, single bands of Figure 1 (B, C, and D).

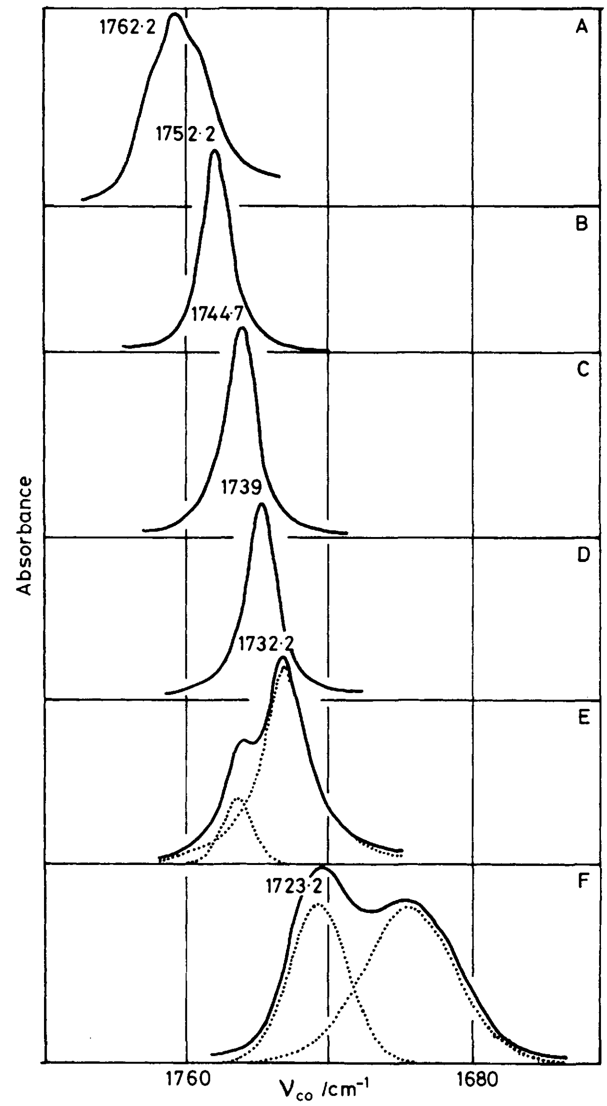
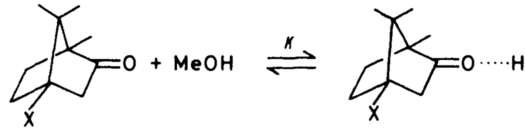


Figure 1. Infrared spectra of camphor in the gas phase (A), and as solutions in heptane (B), carbon tetrachloride (C), pyridine (D), methanol (E), and hexafluoropropan-2-ol (F)



(i)

Two bands are, however, present in methanol (Figure 1E); these are attributed [18] to the presence of both free camphor and a 1 : 1 camphor–methanol complex associated with an equilibrium constant K [equation (i)]. The position of this equilibrium is a function of the basicity of the carbonyl group. Figure 2 demonstrates how the logarithm of the ratio of the areas of the free and associated carbonyl bands, log (A_a/A_f), varies as a function of ν_{CO}; this frequency is itself proportional to the inductive constant of the substituent, that is to say to the variation of carbonyl basicity brought about by the inductive effect of the substituent. Equation (ii) (in which r, s, and n are respectively correlation coefficient, standard deviation, and number of points) shows that frequencies of the free and associated bands correlate well, and serves to indicate that the dissection of the composite peak into its two components has been achieved with precision. We will concentrate solely

$$\nu_{CO}{}^{a} = 1.24\,(\pm 0.02)\nu_{CO}{}^{f} - 4.38\,(\pm 34) \qquad \text{(ii)}$$
$$r = 0.997 \quad s = 0.3\ \text{cm}^{-1} \quad n = 23$$

on the associated band as it is more sensitive to the effects of substituents than the free band.

In HFIP the camphors also show two carbonyl bands (Figure 1F), of which that at higher frequency is assigned to the 1 : 1 complex [18] (with this solvent there is no free camphor because HFIP is a better HBD and is less self-associated than methanol); the band at lower frequency is

Table 1. Carbonyl frequencies (cm^{-1}) of 4-substituted camphors in the gas phase and in solution in heptane, carbon tetrachloride, pyridine, methanol, and hexafluoropropan-2-ol (HFIP)

No.	X	Gas	Heptane	CCl_4	Pyridine	Methanol free	Methanol associated	log(A_a/ A_f) [a]	HFIP associated
1	$CO_2^-\overset{+}{N}Bu_4$	*b*	*c*	1 738.5	1 733.5	1 745.2	1 731.2	0.83	1 731.0
2	$CO\overset{-}{N}-\overset{+}{N}Me_3$	*b*	1 747.2	1 741.0	1 735.8	1 744.8	1 730.5	0.75	1 725.8
3	$CO\overset{-}{N}-\overset{+}{S}Me_2$	*b*	1 749.8	1 743.8	1 739.0	1 746.6	1 733.1	0.51	1 729.6
4	Et	1 761.5	1 751.7	1 745.0	1 738.6	1 745.4	1 731.3	0.90	1 722.8
5	Me	1 762.3	1 751.8	1 744.7	1 739.5	1 745.3	1 731.9	0.76	1 722.6
6	H	1 762.2	1 752.2	1 744.7	1 739.0	1 745.4	1 732.2	0.79	1 723.2
7	$CH{=}CH_2$	1 762.4	1 753.4	1 746.9	1 741.4	1 747.2	1 734.0	0.69	1 725.1
8	Ph	1 761.9	1 753.2	1 746.4	1 741.1	1 746.8	1 733.2	0.70	1 725.6
9	NMe_2	1 761.7	*ca.* 1 752.4	1 745.8	1 739.5	1 747.8	1 734.3	0.55	1 750.7
10	NH_2	1 763.8	1 753.6	1 747.7	1 741.0	1 749.3	1 735.9	0.68	1 736.8
11	OH	1 766.3	1 756.1	1 750.3	1 741.5	1 749.7	1 736.5	0.52	1 736.7
12	OMe	1 764.8	1 754.7	1 748.8	1 744.0	1 749.7	1 736.6	0.59	1 735.9
13	$C{\equiv}CH$	1 764.6	1 756.3	1 750.1	1 744.9	1 750.6	1 738.3	0.46	1 732.3
14	$CONH_2$	*d*	*ca.* 1 755.4	1 750.5	1 743.3	1 750.3	1 737.3	0.53	1 737.0
15	CO_2H	*d*	1 757.4	1 752.1	1 743.8	1 750.9	1 738.3	*d*	1 735.2
16	$NHCO_2Et$	*d*	1 756.5	1 751.0	1 743.0	1 750.2	1 737.1	*d*	1 735.3
17	COMe	*d*	1 755.4	1 749.9	1 744.3	1 750.0	1 737.3	0.41	1 734.9
18	CO_2Me	*d*	1 755.9	1 751.1	1 745.1	1 751.1	1 738.0	*d*	1 735.4
19	OAc	*d*	1 757.4	1 753.1	1 747.9	*d*	*d*	*d*	1 737.3
20	I	1 766.8	1 758.2	1 753.2	1 747.1	1 753.3	1 741.4	0.29	1 735.4
21	Cl	1 768.3	1 759.2	1 753.5	1 749.2	1 754.2	1 743.0	0.18	1 737.0
22	Br	1 767.7	1 759.4	1 754.0	1 748.4	1 753.9	1 742.2	0.31	1 737.1
23	CN	1 768.8	1 762.0	1 756.6	1 751.6	1 756.7	1 745.8	0.06	1 745.0
24	NO_2	1 770.0	1 763.8	1 758.9	1 753.5	1 758.6	1 747.8	0.12	1 746.8

[a] Logarithm of the ratio of the area of the band of the complex to the area of the band of the free molecule. [b] Insufficient vapour pressure. [c] Not soluble. [d] The presence of one or several other carbonyl bands precludes definitive measurement of the C(2)=O carbonyl absorption.

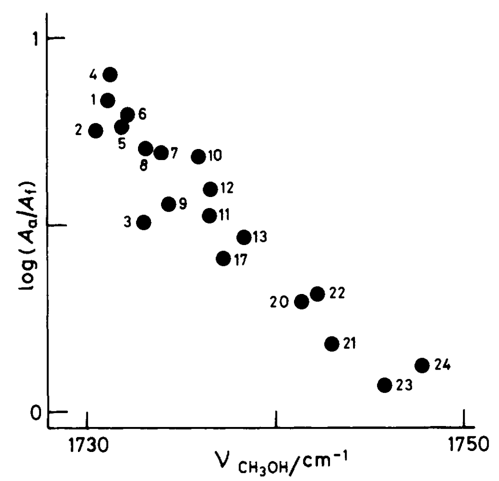


Figure 2. Relationship between log(A_a/A_f) (proportional to the fraction of the free camphor) and ν_{CO} (proportional to the basicity of the camphor); correlation coefficient $r = 0.95$ for 20 points; numerals refer to Table 1

due to complexes of higher order.[18] We will be concerned exclusively with the absorption of the 1 : 1 complex since it is generally more intense and its maximum is measured with greater precision.

In Table 1 the carbonyl frequencies of the substituted camphors (1)—(24), obtained both in the gas phase and in various solvents, are collated.

Discussion

Choice of Reference State.—Linear relationships exist between the frequencies given in the first three columns of Table 1 (gas phase, heptane, carbon tetrachloride). Figure 3 shows that there are no systematic or significant deviations. We have accordingly chosen solutions in carbon tetrachloride as a reference rather than either the gas phase or solutions in heptane, which can respectively exhibit low vapour pressure and low solubility in certain cases, thereby hindering the precision of measurement.

Specific Solvation of HBD Substituents by Pyridine.—Figure 4A shows that inductive effects of 18 substituents can be measured by the same inductive constant (*e.g.* σ_I) for a non-polar solvent (carbon tetrachloride) or an HBD solvent (pyridine). In effect, there exists a linear correlation [equation (iii)] between the carbonyl frequencies in carbon tetrachloride and in pyridine. However, the HBD substituents NH_2, OH, $NHCO_2Et$, $CONH_2$, and CO_2H are depressed with respect to the line expressed by equation (iii); these substituents are therefore less electron-withdrawing in pyridine than in carbon tetrachloride. This behaviour accords with a specific solvation by pyridine of HBD substituents. Consideration of the three valence-bond structures (25)—(27) [19] shows that the electron density on A increases as a result of hydrogen-bond formation, with the consequence that the substituent AH becomes less electron-withdrawing. The deviations (in cm^{-1}) increase in the sequence $C{\equiv}CH < NH_2 < CONH_2 < NHCO_2Et < CO_2H < OH$, which is not the order of hydrogen-bond donor

$$\nu_{CO}(\mathrm{pyr}) = 1.00\,(\pm 0.03)\nu_{CO}(\mathrm{CCl_4}) - 11\,(\pm 44) \qquad \text{(iii)}$$
$$r = 0.995 \quad s = 0.6\ \mathrm{cm^{-1}} \quad n = 18$$

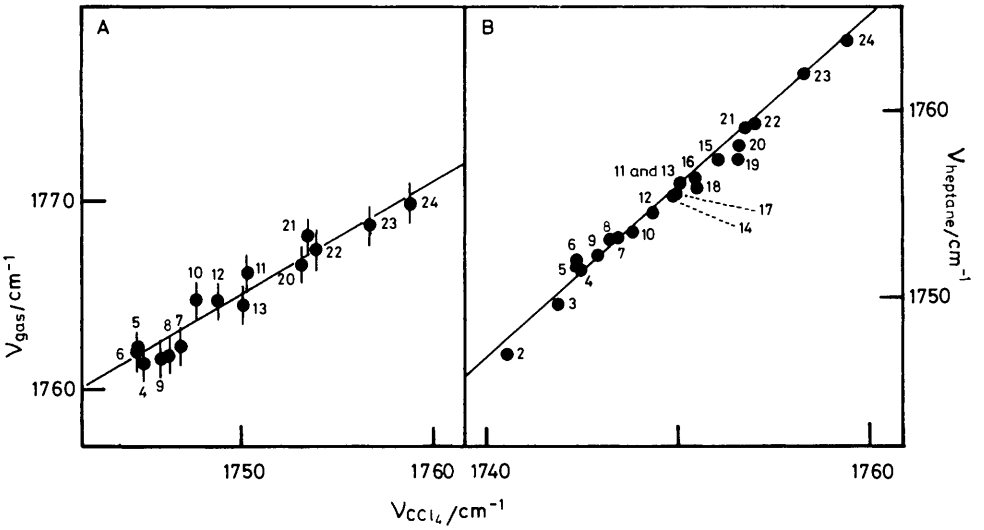


Figure 3. Relationships between ν_{CO}(gas) and ν_{CO}(CCl_4) (A) (r = 0.975 for 15 points) and ν_{CO}(heptane) and ν_{CO}(CCl_4) (B) (r = 0.990 for 23 points) for camphors; numerals refer to Table 1

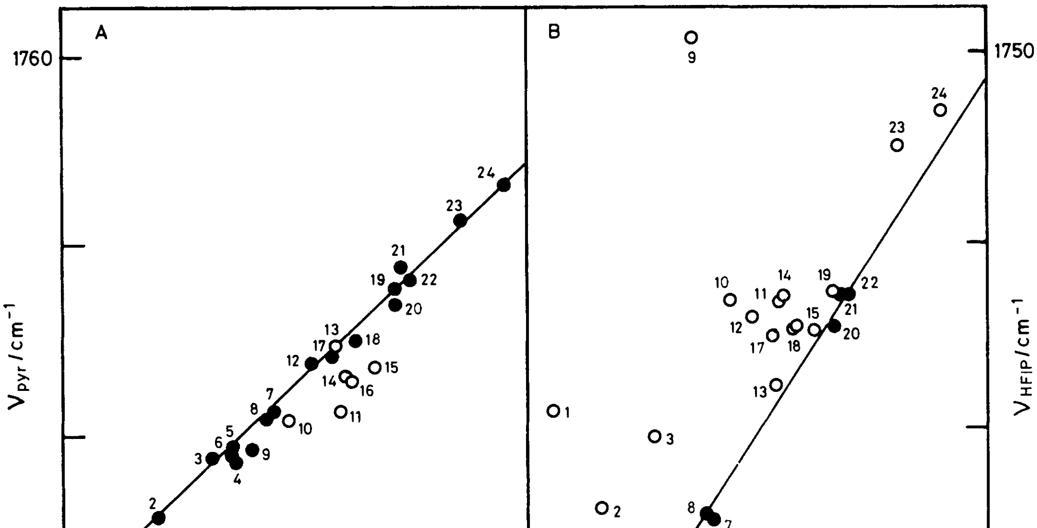


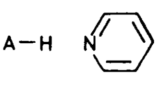
Figure 4. Relationships between ν_{CO}(pyr) and ν_{CO}(CCl_4) (A) (○ HBD substituents; ● other substituents) and ν_{CO}(HFIP) and ν_{CO}(CCl_4) (B) (● substituents used for drawing the reference line; ○ other substituents) for camphors; numerals refer to Table 1

capacity of R–AH[19] (RC≡CH < RNH_2 < $RCONH_2$ < $RNHCO_2Et$ < ROH < RCO_2H). The reason is that the hydrogen bond can develop a partial negative charge either on a substituent atom which is in direct contact with the transmitter group, or on an atom more remote. A combination of two factors, (i) the strength of the hydrogen bond and (ii) the separation between the atom carrying the hydrogen and the carbonyl group, can therefore explain the order of the deviations.

We note that these two factors are such that the specific solvation of the substituent C≡CH is not observed. Table 2 summarises the data relevant to this discussion.

In the case of the substituents $CONH_2$, $NHCO_2Et$, and CO_2H, the change from carbon tetrachloride to pyridine does not correspond to a change from a free to a hetero-associated state but rather from an auto-associated (since the substrate concentration is *ca.* 0.02M) to a hetero-associated state; thus for CO_2H we can observe the values shown in equation (iv).

We feel however that the electron-attracting effect of these cyclic dimeric substituents is close to that of the monomer, since if an initial hydrogen bond renders the substituent less electron-attracting by development of a partial negative charge on oxygen $O^{(1)}$, the second hydrogen bond will



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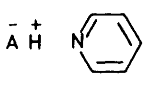

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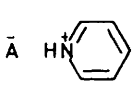

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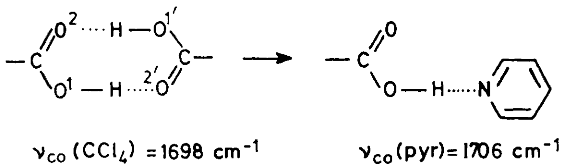
Table 2. Deviations (cm^{-1}) of carbonyl stretching frequencies brought about by HBD substituents in pyridine, and enthalpy of formation (ΔH_f/kcal mol^{-1}) of similar hydrogen bonds

Substituent	Deviation	n[a]	$-\Delta H_f$[b]
C≡CH	~0	2	2.0 (RC≡CH···N)
NH_2	−1.3	1	3.4 ($PhNH_2$···N)
$CONH_2$	−1.8	2	4.6 [MeCON(Me)H···N]
$NHCO_2Et$	−2.6	1	5.1 [$PhN(CO_2Et)H$···N]
CO_2H	−2.9	2	11.0 ($PhCO_2H$···N)
OH	−3.4	1	7.0 (PhOH···N)

[a] Number of bonds between the atom carrying the hydrogen and the transmitter group. [b] Data taken from ref. 19.



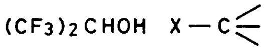
(iv)

induce an inverse effect, *viz.* development of a partial positive charge on oxygen $O^{(2)}$ (see later).

Specific Solvation of HBA Substituents by HFIP.—A comparison of inductive effects in a non-polar (carbon tetrachloride) and in an HBD solvent (HFIP) shows (Figure 4B) deviations of HBA substituents in an enhanced sense with respect to the line of reference defined by equation (iii), which passes through the points for H, Me, Et, Ph, $CH=CH_2$ and halogens. These eight substituents are at best only feebly HBA in character and thus are not specifically solvated by HFIP. The ' enhanced ' deviations of HBA substituents show that they are more electron-attracting in HFIP than in carbon tetrachloride, as indicated by the limiting structure (30) of the available valence-bond structures (28)—(30) which show that a partial positive charge is developed on the basic site of the substituent. As noted above, the order of deviations may be explained by a combination of two factors, the hydrogen bond and the separation. In Table 3 deviations attributed to HBA substituents are shown. The most important deviation is shown by NMe_2, a substituent that we believe to be almost completely protonated in HFIP since it becomes more electron-attracting than NO_2 and approaches the σ_I value of $^+NMe_3$; the σ_I values are σ_I (NO_2) = 0.67, σ_I ($^+NMe_3$) = 1.07, σ_I (NMe_2) = 0.17. The other deviations are consonant with the known basicity sequences (> means more basic than):

$Me_2N > H_2N$ (tertiary amines > primary amines)
MeO > HO (ethers > monomeric alcohols)
$\mathrm{CO\overset{-}{N}\text{–}\overset{+}{N}Me_3} > CONH_2 > COMe > CO_2Me$ (amidates > amides > ketones > esters).

Finally we note that HFIP is considered to be essentially an HBD solvent since the basicity of the lone pairs of the hydroxylic oxygen is practically offset by the two CF_3 groups (β_{HFIP} *ca.* 0 on the Kamlet–Taft scale).[15]



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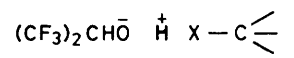

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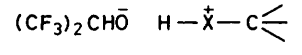

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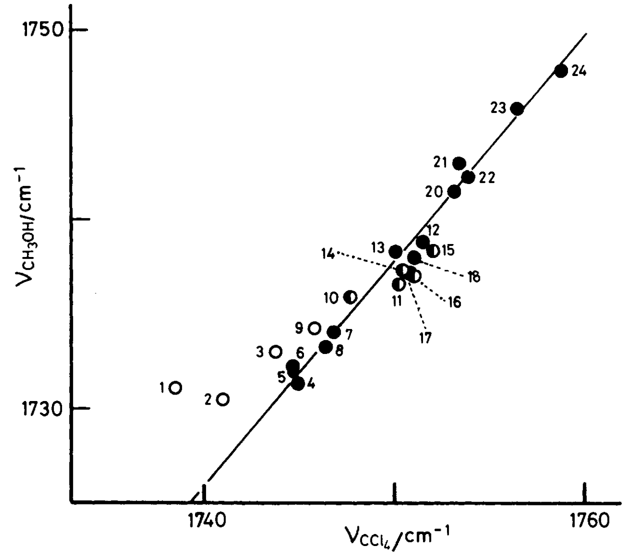

Figure 5. Relationship between ν_{CO}(MeOH) and $\nu_{CO}(CCl_4)$ for camphors (● substituents used for drawing the reference line; ○ strong HBA substituents; ◐ HBD substituents); numerals refer to Table 1

Specific Solvation of HBD Substituents and HBA Substituents by Methanol.—Comparison of inductive effects in a non-polar solvent and in a solvent such as methanol which shows both HBA and HBD characteristics should therefore lead to both types of deviation previously encountered. However, since methanol is a weaker HBD than HFIP, and since, moreover, it exhibits strong self-association which in part inhibits its hetero-association with HBA substituents, it is seen that a number of these substituents are so weakly solvated that they now define a common line, expressed by equation (v), together with the substituents H, Me, Et, Ph, $CH=CH_2$, and halogens. Significant 'enhanced' deviations are only observed (Figure 5) for strongly HBA substituents (Me_2N, H_2N, CO_2^-, $\mathrm{CO\overset{-}{N}\text{–}\overset{+}{N}Me_3}$, $\mathrm{CO\overset{-}{N}\text{–}\overset{+}{S}Me_2}$); these are the same five which also deviate the most in HFIP. The situation of the substituent NH_2 *above* the line expressed by equation (v) is interesting since it demonstrates that solvation of the type β-α ··· NH_2 prevails over that of the type NH_2 ··· β-α (where β and α represent respectively the basic and acidic sites of methanol). These competitive solvations β-α ··· AH and AH ··· β-α for HBD substituents which can also function as HBA thus explain that the depressions brought about by the substituents CO_2H, OH, $NHCO_2Et$, and $CONH_2$ are less in methanol than in pyridine, notwithstanding the similar basicity of these two solvents. In Table 4 the deviations recorded for particular substituents in methanol are collated.

$$\nu_{CO}(\mathrm{MeOH}) = 1.17\ (\pm0.04)\nu_{CO}(\mathrm{CCl_4}) - 307\ (\pm68) \qquad (v)$$
$$r = 0.994 \quad s = 0.6\ \mathrm{cm^{-1}} \quad n = 14$$

Table 3. Deviations (cm^{-1}) of carbonyl stretching frequencies brought about by HBA substituents in HFIP and enthalpy of formation (ΔH_f/kcal mol^{-1}) of similar hydrogen bonds

Substituent	Deviation	*n* [a]	$-\Delta H_f$ [b]
NMe_2	+26.4	1	11.5 $[(CF_3)_2CHOH\cdots NEt_3]$
$CO_2^-\overset{+}{N}Bu_4$	+18.1	2	
NH_2	+9.5	1	
$CO\overset{-}{N}-\overset{+}{N}Me_3$	+9.0	2	
$CO\overset{-}{N}-\overset{+}{S}Me_2$	+8.4	2	
OMe	+6.9	1	7.2 $[(CF_3)_2CHOH\cdots OEt_2]$
OH	+5.4	1	
$CONH_2$	+5.3	2	8.2 $[(CF_3)_2CHOH\cdots O{=}CMe(NMe_2)]$
COMe	+4.2	2	6.7 $[(CF_3)_2CHOH\cdots O{=}CMe_2]$
$C\equiv N$	+3.8	2	5.9 $[(CF_3)_2CHOH\cdots N\equiv CMe]$
$NHCO_2Et$	+2.9	3	
CO_2Me	+2.8	2	5.9 $[(CF_3)_2CHOH\cdots O{=}CMe(OEt)]$
NO_2	+2.0	2	
OAc	+1.6	3	
$C\equiv CH$	+1.3	1—2	
CO_2H	+1.0	2	

[a] Number of bonds between the hydrogen bond ' receptor atom ' and the transmitter group. [b] Data taken from ref. 19.

Table 4. Deviations (cm^{-1}) of carbonyl stretching frequencies brought about by some substituents in methanol

HBA substituent	Deviation	HBA and HBD substituent	Deviation
$CO_2^-\overset{+}{N}Bu_4$	+6.9	NH_2	+0.8
$CO\overset{-}{N}-\overset{+}{N}Me_3$	+3.3	CO_2H	−1.9
$CO\overset{-}{N}-\overset{+}{S}Me_2$	+2.6	$NHCO_2Et$	−1.8
NMe_2	+1.4	OH	−1.6
		$CONH_2$	−1.0

Conclusion.—The 4-substituted camphors constitute a novel model series for the study of inductive effects of substituents and effectively supplement data from other cyclic, bicyclic, tricyclic, spirocyclic, and heterobicyclic systems. On account of a time scale which permits direct observation of species in solution, insofar as band widths are not too great with respect to the difference in frequencies of the bands to be resolved, infrared spectroscopy presents itself as a method of choice for studying the influence of specific solvation on the electrical effects of substituents.

The σ_I scale, recently re-evaluated by Charton,[1] refers to properties measured in water, alcohols, aqueous alcoholic mixtures, or other aqueous solvents which resemble methanol. The relationships obtained in this work between data referring to gas phase, non-polar solvents, pyridine, and methanol show that this ' methanol-type ' scale will accurately measure inductive effects of the majority of substituents in solvents whose properties apparently differ significantly from those of methanol. But we must be aware that the inductive effect of strong HBD (*e.g.* OH) or HBA (*e.g.* NMe_2) substituents depends on their interaction with respectively strong HBA or HBD solvents. We feel that the data reported in this work can serve as an unambiguous source of reference for substituent–solvent interactions.

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