

Polarity and Basicity of Solvents. Part 1. A Thermosolvatochromic Comparison Method

Pierre Nicolet and Christian Laurence*

Laboratoire de Spectrochimie Moléculaire, Ex-Faculté des Sciences, 2, Rue de la Houssinière, 44072 Nantes, France

A thermosolvatochromic comparison method for measuring polarity and basicity parameters of solvents, which takes advantage of variations in solvent properties with temperature (0–105 °C), is proposed. The effects of the vibrational structure of the absorption bands on (i) the reference (homomorphism) line of non-hydrogen-bond donor and non-hydrogen-bond acceptor solvents and the temperature line of hydrogen-bond acceptor solvents, and thus on (ii) the precision and sensitivity of the method, are analysed for a range of indicators. 4-Nitroanisole and 4-nitrophenol are recommended as reference polarity and basicity indicators, respectively. The reference (homomorphism) line is to be taken from data for gas-state, perfluorinated hydrocarbons, alkanes, CCl₄ and/or C₂Cl₄, 1,2-dichloroethane, and mono- and poly-halogenated benzenes.

Kamlet, Abboud, and Taft (KAT) recently proposed a solvatochromic comparison method^{1–5} for measuring the polarity, acidity, and basicity of solvents.† The polarity π^* , acidity α , and basicity β scales defined by this method have been found valuable in the deduction of an impressive number of linear solvation energy relationships in reactivity and spectroscopy.^{5,6}

However, the subsequent extension of these scales brought to light certain difficulties. Brady and Carr⁷ were unable to determine the π^* values of perfluorinated solvents when using indicators with absorption bands showing vibrational structure. Essfar and his co-workers⁸ were only able to obtain the π^* value of the gas state with limited precision. Some β values determined by the solvatochromic comparison method go against chemical intuition. For example we find that the HCO₂Et β value is lower than that of HCO₂Me,⁹ that the β values of monohalogenobenzenes are greater than that of benzene,¹⁰ and that the 3-picoline β value is greater than that of 4-picoline.⁹ Especially dramatic are the variations in β values for a given solvent published in successive articles by the same authors.^{11–13} More generally, Kolling¹⁴ has observed that the solvent parameters taken from the solvatochromic comparison method have relatively large uncertainties.

Aside from its accuracy, the solvatochromic comparison method is also seen to lack sensitivity. Neither the basicity of benzene and toluene nor the acidity of dichloromethane is accounted for, which leads to the unhappy choice of these solvents as non-hydrogen-bond acceptors (non-HBA) and non-hydrogen-bond donors (non-HBD) when defining the reference line of the solvatochromic comparison method (see later). Likewise, this method leads to a null β value for butyl chloride,⁹ whereas the enthalpy of hydrogen-bond formation of 4-fluorophenol with this base is -8.08 kJ mol⁻¹.¹⁵

In this work we show that, in the main, these difficulties arise from an imperfect application of the solvatochromic comparison principle imagined by KAT, and that this principle may be retained as a fundamental tool for unravelling and quantifying the multiple solvent effects on condition that (i) the effect of temperature on the solvatochromism is taken into account, that (ii) the variations in the shape of the indicator absorption bands, which arise from their vibrational structure, are the same,

† In this article, acidity and basicity respectively have the restricted meanings of hydrogen-bond-donor acidity and hydrogen-bond-acceptor basicity, whereas polarity designates the non-specific solvent interactions caused by dipolarity, multipolarity, and polarizability.

Table 1. Polarity and basicity indicators

| Indicators | No. | $\lambda_{\max.}/\text{nm}^a$ |
|--|------|-------------------------------|
| 4-Nitrophenol | (1) | 283.6 |
| 4-Nitroanisole | (2) | 291.8 |
| 4-Nitroaniline | (3) | 318.8 |
| <i>N</i> -Methyl-4-nitroaniline | (4) | 339.0 |
| <i>N,N</i> -Dimethyl-4-nitroaniline | (5) | 352.0 |
| <i>N,N</i> -Diethyl-4-nitroaniline | (6) | 359.5 |
| <i>N,N</i> -Diethyl-3,4-dinitroaniline | (7) | 364.2 |
| <i>N</i> -Methyl-4-nitrosoaniline | (8) | 375.2 |
| <i>N,N</i> -Diethyl-4-nitrosoaniline | (9) | 398.6 |
| 4-Aminoacetophenone | (10) | 283.7 |
| 4-Dimethylaminoacetophenone | (11) | 313.5 |
| 4-Diethylaminobenzaldehyde | (12) | 329.0 |
| Methyl 4-dimethylaminobenzoate | (13) | 298.4 |
| 4-Dimethylaminobenzonitrile | (14) | 280.2 |

^a Wavelength of the overall band maximum for the π - π^* transition of longest wavelength in heptane at 25 °C

through the range of solvents, for the two homomorphs, that (iii) the reference (homomorphism) line is fixed by the largest possible range of solvents, from the gas to the most polar non-HBA and non-HBD solvents, and that (iv) the limits imposed by the non-transparency of solvents are removed by the use of very thin cells.

In essence the modifications we propose exploit the effect of temperature on the solvatochromism of the indicators, and for this reason we have called the method of defining solvent polarity and basicity parameters presented here a thermosolvatochromic comparison method.

Experimental

Products.—The indicators studied are listed in Table 1. They were purified by repeated recrystallisation from EtOH. The solvents were analysed by gas-phase chromatography on columns of Carbowax and SE 30, purified on a vacuum line, and dried by chromatography on columns of either ground 4 Å molecular sieve and/or basic alumina, activated *in vacuo* at 400 °C. After drying, no water was detected by i.r. in the $\nu(\text{OH})$ region for a 1 mm cell. The solutions were prepared in a dry box and filtered on Millipore (0.25 μ) before use.

Spectra. The spectra of the solvent and of the solution were taken in the range 500–250 nm with a Perkin-Elmer apparatus,

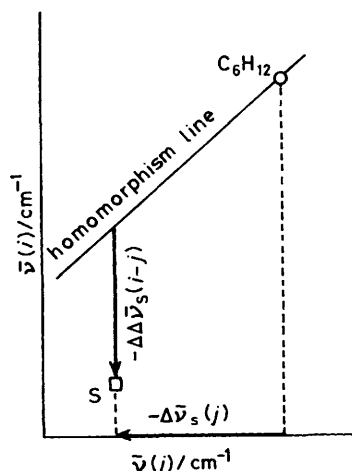


Figure 1. The solvatochromic comparison principle

with a 2 nm slit for liquids and a 0.25 nm slit for gases. A PE 3500 data station with PECDS software was used for storing the spectra, subtracting that of the solvent from that of the solution, and locating the overall band maximum. The apparatus was periodically calibrated with a PE holmium oxide glass filter. The values of peaks between 279 and 420 nm were reproducible to within ± 0.2 nm and agreed within 0–0.3 nm with the accepted values.¹⁶

Cells.—The cells were thermoregulated to within ± 0.1 °C in the 0–105 °C range, with a Coleman 570–0701 digital controller and a Coleman 550–0555 thermoelectric single-cell holder. They were equipped with bulb tubes filled with silicone oil in order to regulate the internal pressure of the solutions at high temperature. A 10 cm cell which could be heated to 250 °C was built in the laboratory for the spectra of indicators in the gas state. A 10 cm cell was needed for the perfluorinated solvents in which the indicators are only slightly soluble. A 1 cm cell was sufficient for the alkanes. For the other transparent solvents a 0.1 cm cell was generally used. For the less transparent solvents we recommend a sealed 30 μm cell; this enables the field of use of the solvent to be greatly enlarged. The use of such thin cells allows the study of indicators which absorb at shorter wavelengths, for example the very important 4-nitrophenol–4-nitroanisole couple, with solvent sampling unbiased by transparency problems.

Results and Discussion

The wavenumbers of the maxima of the long-wavelength bands of the indicators (1)–(14) are given in Table 2 for indicators in the gas state; in Table 3 for indicators (1)–(7) in solution; and in Table 4 for indicators (8)–(14) in solution. Only the results for non-HBA and non-HBD (nos. 1–32), HBD (nos. 33–35), and those HBA solvents mentioned in the text are given. The full results for HBA solvents will be given in Part 2.

The Solvatochromic Comparison Principle.—The polarity of a solvent S is measured by the bathochromic shift relative to cyclohexane, $-\Delta\tilde{\nu}_s$, of the $\pi-\pi^*$ transition of greatest wavelength of non-HBD indicators (e.g. 4-nitroanisole). The basicity of the same solvent is measured by the supplementary bathochromic shift $-\Delta\Delta\tilde{\nu}_s$ manifested by the HBD indicator ‘homomorph’ of the first (e.g. 4-nitrophenol is the ‘homomorph’ of 4-nitroanisole). Plotting (Figure 1) the wavenumber of an HBD indicator *i* as a function of its non-HBD homomorph *j*,

for the non-HBD and non-HBA solvents, gives a reference line of the equation $\tilde{\nu}(i) = a_{ij} \tilde{\nu}(j) + b_{ij}$; the HBA solvents fall below this line. The polarity π^* and basicity β scales are the means of the normalised values $-\Delta\tilde{\nu}_s(j)$ and $\Delta\Delta\tilde{\nu}_s(i-j)^*$ [equations (1) and (2)] for several indicators *j* and several homomorph couples *i/j*, respectively.

$$-\Delta\tilde{\nu}_s(j) = \tilde{\nu}_s(j) - \tilde{\nu}_{\text{Ch}}(j) \quad (1)$$

$$-\Delta\Delta\tilde{\nu}_s(i-j) = [a_{ij} \tilde{\nu}_s(j) + b_{ij}] - \tilde{\nu}_s(i) \quad (2)$$

Ch refers to cyclohexane

Thermosolvatochromism of Indicators (1)–(14).—The application of the foregoing principle suffers from ignoring the influence of the temperature on the band maxima of the indicators in solution. In the gas state, the spectra of the indicators (1)–(14), measured for the largest range of temperatures possible in view of the need for a good signal-to-noise ratio and of the stability of the compounds, do not show an intrinsic thermochromism (the gradients $d\tilde{\nu}/dT$ are close to zero). In solution, gradients which vary between +2 and +17 $\text{cm}^{-1} \text{deg}^{-1}$, according to the indicator and solvent used, are observed (Table 2). These hypsochromic shifts can be attributed, at least for non-HBD indicators (for HBD indicators in HBA solvents, see later), to the variations in the macroscopic properties of the solvent (density, refractive index, dielectric constant) with temperature.¹⁷ We have therefore called this influence of temperature on the solvatochromism ‘thermosolvatochromism’.

It is evident that this thermosolvatochromism requires temperature control of the solvents so as to obtain abscissae and ordinates of the homomorphism plot at identical temperatures. Without this precaution, diurnal, seasonal, and/or local thermal variations (e.g. of the apparatus), which may be as much as 15 °C, markedly lower the reproducibility of the measurements.†

On the other hand, thermosolvatochromism allows the following.

(a) Multiplication of the number of points taken for the reference (homomorphism) line, therefore enabling this line to be fixed with greater precision (standard deviations of the regression coefficient and of the intercept are smaller); this is fundamental as the deviations $-\Delta\Delta\tilde{\nu}$ of HBA solvents are calculated in relation to this line. For example, the equation of the reference line of the pair (1)/(2) with 22 solvents at 25 °C and in the gas state gives (for 23 points) equation (3), whereas in the

$$\tilde{\nu}(1) = 1.0378 (\pm 0.0115) \tilde{\nu}(2) - 0.37 (\pm 0.39) \quad (3)$$

gas state and with the same solvents at temperatures of 0, 25, 50, 75, and 105 °C (within the limits allowed by the melting and boiling points), this equation‡ becomes (for 74 points) equation (4). Even more important, the multiplication of points enables

$$\tilde{\nu}(1) = 1.0434 (\pm 0.0075) \tilde{\nu}(2) - 0.57 (\pm 0.29) \quad (4)$$

the visualisation of certain anomalies in the reference line. Thus in the case of aromatic solvents, a ‘hump’ becomes apparent on the reference line of the pair (3)/(6) (Figure 2), which makes this

* And other non-solvatochromic quantities.

† If the only cause is the reproducibility of the apparatus, the error is of the order of 20 cm^{-1} . A 10 °C temperature variation for an indicator and solvent of 10 $\text{cm}^{-1} \text{deg}^{-1}$ will cause a supplementary error of 100 cm^{-1} .

‡ On the homomorphism plot the errors are equivalent on the $\tilde{\nu}(i)$ and $\tilde{\nu}(j)$ axes: the equations are obtained by the least-squares method in the direction orthogonal to the reference line.

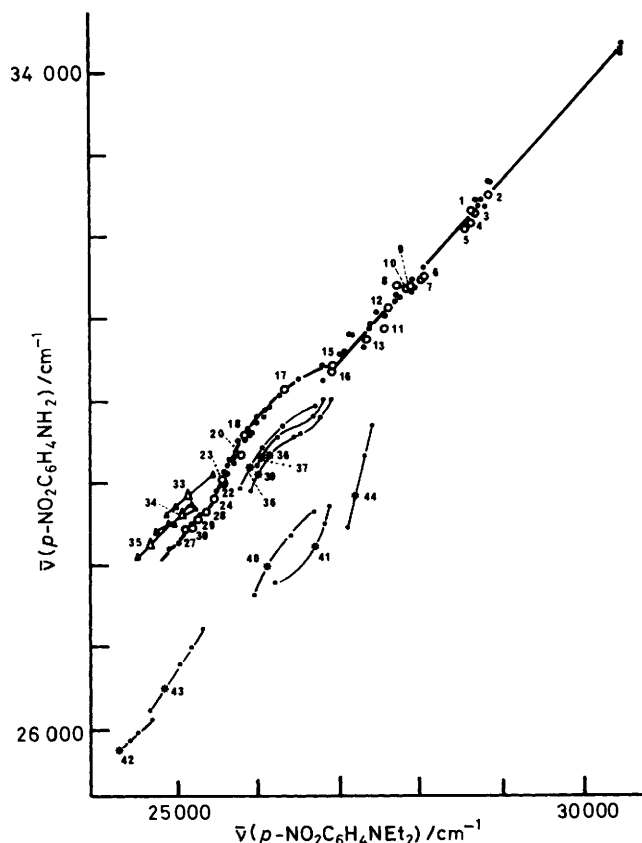


Figure 2. Thermosolvatochromic comparison of 4-nitroaniline and *N,N*-diethyl-4-nitroaniline. The reference line is curved from C_2Cl_4 (no. 16) to C_6H_5Cl (no. 24). The numbering of the solvents relates to Table 2. HBD solvents lie above this line and HBA solvents below. The temperature curves of certain HBA solvents [toluene (36), *p*-xylene (37), mesitylene (38), prehnitene (39), 2,5-dimethyltetrahydrofuran (40), and *N,N*-dimethylpiperazine (41)] are abnormal

non-HBD, non HBA solvents: ○ (25 °C), ● (other temp.)
 HBD solvents: △ (25 °C), ▲ (other temp.)
 HBA solvents: * (25 °C), * (other temp.)

pair suspect for defining the polarity scales, as well as for the basicity scales.

(b) Solid solvent parameters to be obtained at ambient temperature. For example, in the case of *p*-dichlorobenzene (m.p. 53 °C),[†] 1,2,3-trichlorobenzene (m.p. 52 °C), and 1,2,3,4-tetrachlorobenzene (m.p. 46 °C), polarity has been characterized from 60 to 105 °C with the indicators (3)–(6). The polarity and basicity of tetramethylene sulphone (m.p. 27 °C) were also characterized from 30 to 50 °C with the indicators (1)–(3), (5), and (6).

(c) Solvent parameters to be obtained at temperatures other than ambient. Hitherto solvent parameters were determined either at 25 °C (for Z and E_T^{19}), or at an undefined ambient temperature[‡] (the case of π^* , α , and β). However, they are sometimes used for the correlation of kinetic data obtained at higher temperatures. This implies a linear relationship between the parameter at ambient temperature and the parameter at a higher temperature. This hypothesis is proved for polarity

[†] *p*-Dichlorobenzene is one of the 354 usual solvents selected in ref. 18.

[‡] This practice should be avoided. It is a matter of the reputation of 'empirical' parameters as compared with physical constants (refractive index, dielectric constant), generally given in tables at 20 and/or 25 °C.¹⁸

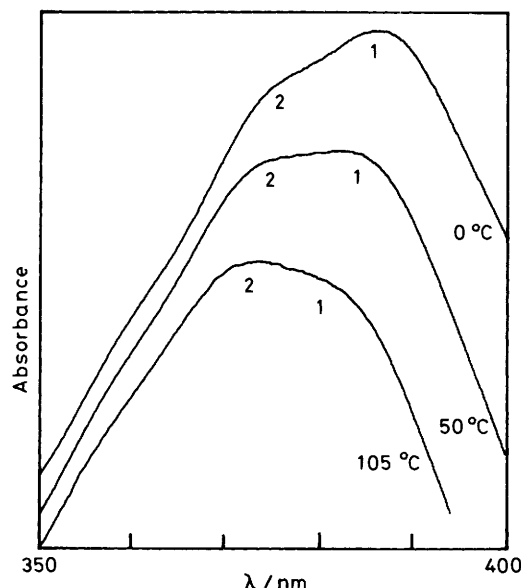


Figure 3. Top of the *N,N*-diethyl-4-nitroaniline band in prehnitene solution at 0, 50, and 105 °C. The overall band maximum is determined at 0 and 50 °C by the vibronic transition 1 and at 105 °C by the vibronic transition 2

parameters such as π^* .[§] Theoretically it could be less true for the parameters α and β , which depend on the equilibrium of the formation of hydrogen bonds between the solute and the solvent, and, for solvents which are at the same time HBA and HBD, on their auto-association equilibrium.⁵ In particular, $-\Delta\Delta\bar{\nu}$ has been claimed¹ to depend on the formation constant of hydrogen-bond complexes of 4-fluorophenol with HBA solvents. In this case a linear relationship between $-\Delta\Delta\bar{\nu}(T_1)$ and $-\Delta\Delta\bar{\nu}(T_2)$ [*i.e.* $\beta(T_1)$ and $\beta(T_2)$] is impossible, as the equilibrium of the formation of 4-fluorophenol complexes with the HBA molecules does not obey the compensation law.²¹

In practice it is hard to predict how much the variation of $\bar{\nu}$ with temperature for HBD indicators in HBA solvents depends on the variation with temperature of the equilibrium constant for the formation of hydrogen bonds between the indicator and the solvent. It should be noted that the correlation coefficient of $\Delta\Delta\bar{\nu}_0(1)-(2)$ *vs.* $\Delta\Delta\bar{\nu}_{75}(1)-(2)$ is 0.993 for 13 HBA solvents whereas that of $\Delta\Delta\bar{\nu}_0(3)-(5)$ *vs.* $\Delta\Delta\bar{\nu}_{75}(3)-(5)$ is 0.929 for 21 HBA solvents. Correlations between kinetic data at high temperatures and solvent parameters at ambient temperature should therefore be undertaken with caution.

(d) The observation of changes with temperature in the relative intensities of the vibronic component bands, which cause and/or accompany the shift of the overall band maximum (Figure 3). It becomes evident that an absorption band, even of Gausso-Lorentzian form, results from the superposition of many vibronic transitions and that the band does not move without changing shape, even if it is not apparent whether the change in shape causes and/or accompanies the shift.

[§] It should be noted however that correlation coefficient of $\pi^*(T_1)$ *vs.* $\pi^*(T_2)$ decreases when the difference $T_1 - T_2$ increases [0.999 for $\Delta\bar{\nu}_0(2)$ *vs.* $\Delta\bar{\nu}_{25}(2)$ and 0.991 for $\Delta\bar{\nu}_0(2)$ *vs.* $\Delta\bar{\nu}_{105}(2)$ for 18 solvents]. In fact the thermal gradients are not the same for all the solvents (Table 2). This may explain why the logarithm of the rate constant for the solvolysis of *t*-butyl chloride at 120 °C for 8 solvents and the gas state²⁰ is more closely related to $\Delta\bar{\nu}_{105}(2)$ ($r = 0.960$ for 9 points) than $\Delta\bar{\nu}_{25}(2)$ ($r = 0.945$).

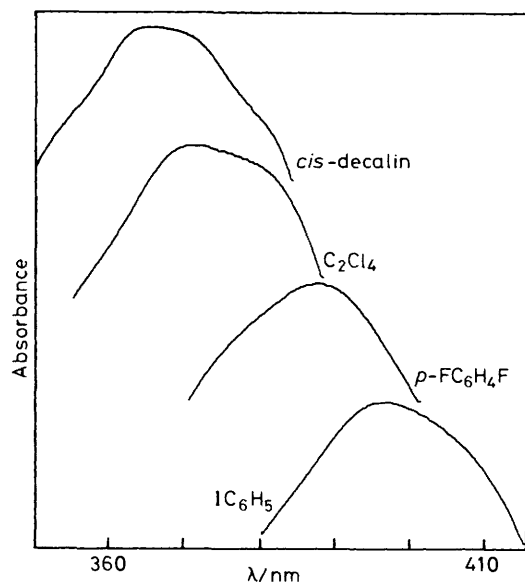


Figure 4. The change in band shape of *N,N*-diethyl-4-nitroaniline on passing from C_2Cl_4 to *p*-fluorobenzene and the return to the initial shape with iodobenzene

Vibrational Anomalies in the Thermosolvatochromic Comparison Method.—The same 'intensity swings' observed with changing temperature are also observed when the solvent changes (Figure 4). In consequence, it becomes hard to discern, for two homomorphs, whether or not the overall band maxima are determined by vibronic transitions concordant at each axis of the homomorphism plot. For example, the band shape of the indicator (6) changes on passing from weakly polar solvents (perfluoroalkanes, alkanes, C_2Cl_4) to weakly polar polyhalogenated aromatic solvents (e.g. *p*-difluorobenzene) and returns to its initial shape in more polar solvents (Figure 4). Since the indicator (3) retains an almost Gausso-Lorentzian form, a 'hump' appears on the reference line of the pair (3)/(6) (Figure 2) for the hydrocarbons C_6F_6 , *p*- FC_6H_4F , *p*- ClC_6H_4Cl , and 1,2,3,4-tetrachlorobenzene. The same phenomenon occurs for HBA solvents with a polarity between those of C_6F_6 and *p*- FC_6H_4F , that is for toluene, *p*-xylene, mesitylene, prehnitene, 2,5-dimethyltetrahydrofuran, and *N,N*-dimethylpiperazine, and explains the abnormal* temperature curves of these HBA solvents (Figure 2). The deviations below the reference line of perfluorinated solvents and the gas state for (3)/(7) and of the gas state for (10)/(11) are also probably due to vibrational anomalies. In general not only the precision but also the physical significance of the results obtained by the solvatochromic comparison principle are affected by these vibrational anomalies.

A study of the influence, on the vibrational structure, of the nature of the electron-donor group D, of the electron-acceptor group A, and of the solvent for the 14 indicators DC_6H_4A used in this work shows that the importance of the vibrational structure (a) decreases with increasing temperature and (Figure 5) solvent polarity; (b) increases in the order $OH \sim OMe \sim NH_2 < NHMe < NEt_2$ (Figure 6); and (c) increases in the order $CN < COMe < NO_2 < CO_2Me < COH < NO$ (Figure 7). The sequence in the nitrogen substituents in Figure 6 is probably explained by an increasing insulation of the

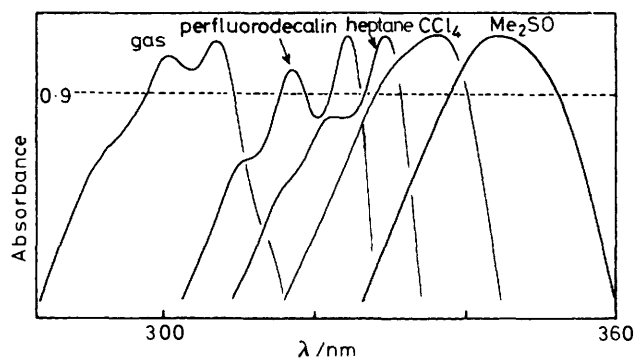


Figure 5. Influence of solvent polarity on the fine structure of 4-diethylaminobenzaldehyde band at 25 °C (85 °C in the gas state)

chromophore from the solvent on passing from the amino to the *N,N*-diethylamino group.

There is no indicator which retains its vibrational structure for the complete solvent range. For example, (9) and (12), which have the most favourable A and D groups for a fine structure, lose this at CCl_4 in Figure 5. Furthermore comparison of the indicator (9), which has a smoothed band, with the indicator (6), which shows a fine structure, leads to anomalies shown in Figure 2. One is thus restricted to indicators with bands which remain Gausso-Lorentzian from the gas state right through to the most polar solvents. This is the case for 4-nitrophenol and 4-nitroanisole, which moreover are very good homomorphs as their structures only differ by one CH_2 group. If an NH hydrogen-bond donor, in complement to the OH donor (1), needs to be studied, the pair (3)/(5) should be retained in preference to the pairs (4)/(5) (despite its good homomorphism, being the donor of only one hydrogen bond it leads to $\Delta\Delta\bar{\nu}$ values which are too low) and (3)/(6) [(3) and (6) differ by four CH_2 groups; the homomorphism is thus of low quality and in consequence gives rise to band shapes which are too dissimilar].

The KAT approach to the vibrational problems was apparently simplified, by choosing (i) 'to determine the overall band maximum by taking the midpoint between the two positions on the spectrum where O.D. (optical density) = 0.9 O.D._{max}'³ and (ii) to take the average of the results given by a large number of indicators. The unusual† and arbitrary character of the first choice, which cannot give coherent results for the indicators (9) and (12) (see Figures 5 and 7) and which results only in a smoothing at the top of the band should be noted; one might just as well use indicators such as (1) and (2) the bands of which are already smoothed. As for the second choice, it will be shown in a later paper that it is better to study one good model with precision than to take the average of results obtained from many poor models.

Choice of Solvents for Fixing the Reference Line.—It is essential to fix the reference line as well as possible, as (i) any error in its equation will lead to non-random errors in $\Delta\Delta\bar{\nu}$; thus too large an intercept at the origin and too small a slope will give values which are too small for the less polar bases (e.g. NEt_3) and too big for the more polar bases (e.g. hexamethylphosphoric triamide); and (ii) the basicity of weakly HBA solvents and the acidity of weakly HBD solvents may then be shown. This objective may be attained if the solvents chosen (i) are non-HB and (ii) possess the largest polarity range.

The second criterion is fulfilled by using, at one extreme of the range, the gas state and perfluorinated compounds. At the other

* Normal curves are straight segments parallel to the reference line or of greater slope (see Part 2).

† The overall band maximum is usually used and has been claimed^{2,2,3} to be a reasonable approach when the 0-0 transition is not resolved.

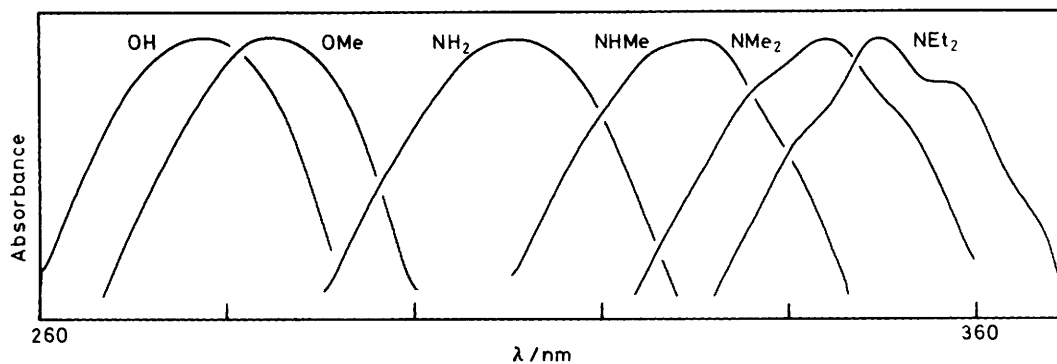


Figure 6. Influence of the nature of the electron-donor group D on the vibrational structure of the $p\text{-DC}_6\text{H}_4\text{NO}_2$ bands in perfluorodecalin at 25 °C

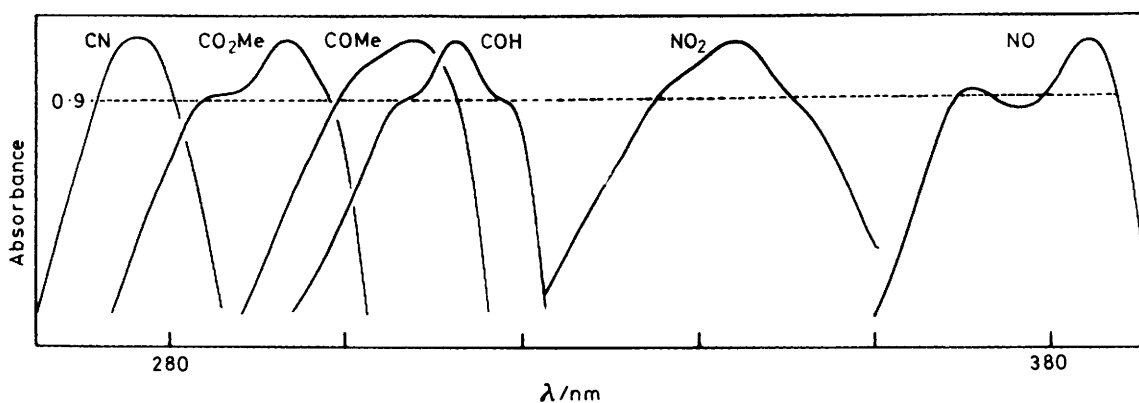


Figure 7. Influence of the nature of the electron-acceptor group A on the fine structure of $p\text{-AC}_6\text{H}_4\text{NMe}_2$ bands in perfluorodecalin at 25 °C

Table 2. Temperature influence on the overall band maxima of indicators (1)–(14)

| No. | Gas phase: $10^{-3} \bar{\nu}^a/\text{cm}^{-1}$ | Solution: $(d\bar{\nu}/dT)/\text{cm}^{-1} \text{ deg}^{-1}$ | | | | | |
|------|--|---|-------------------|------------------|-------------------|-------------------|-------------------|
| | | PFD ^b | Hept ^c | DCE ^d | Bu ₂ O | HMPT ^e | Et ₃ N |
| (1) | 37.98 (90), 37.88 (120), 38.08 (150), 38.11 (225) | 5 | 7 | 8 | 7 | 5 | 7 |
| (2) | 37.08 (90), 37.11 (150), 37.17 (225) | 5 | 5 | 7 | 6 | 6 | 6 |
| (3) | 34.27 (120), 34.37 (140), 34.30 (175) | 5 | 6 | 8 | 14 | 4 | 17 |
| (4) | 32.61 (120), 32.62 (140), 32.63 (175) | 5 | 6 | 8 | 10 | 4 | 13 |
| (5) | 31.34 (120), 31.37 (140), 31.31 (175), 31.35 (225) | 3 | 4 | 5 | 6 | 4 | 8 |
| (6) | 30.53 (190) | 2 | 4 | 7 | 4 | 6 | 4 |
| (7) | 30.81 (185) | | 5 | 10 | 6 | 5 | 7 |
| (8) | 28.69 (110), 28.70 (130), 28.79 (185) | 5 | 4 | 5 | 6 | 3 | 8 |
| (9) | 27.12 (110), 27.12 (130), 27.12 (185), 27.12 (205) | 3 | 3 | 5 | 5 | 4 | 5 |
| (10) | 37.24 (85), 37.27 (110), 37.29 (130), 37.29 (185) | | | | | | |
| (11) | 34.06 (110), 34.06 (185) | | | | | | |
| (12) | 32.61 (85), 32.60 (110), 32.61 (130) | 2 | 2 | 4 | 3 | 3 | 3 |
| (13) | 36.11 (85), 36.09 (130), 36.01 (185) | | | | | | |
| (14) | 36.98 (85), 36.98 (110), 36.97 (130), 36.93 (185) | | | | | | |

^a Wavenumber; temperature (°C) between brackets; our values are to be preferred to those of ref. 8 which used cells ten times thinner and lower temperatures. ^b Perfluorodecalin. ^c Heptane. ^d 1,2-Dichloroethane. ^e Hexamethylphosphoric triamide.

extreme it is hard to go very far without violating the first criterion. We plan the use of iodobenzene, polyhalogenated benzenes, and/or CH_2I_2 . From the gas state to CH_2I_2 the transition of indicator (5) undergoes a bathochromic shift of 6700 cm^{-1} whereas in the hexane–1,2-dichloroethane range used by KAT^{1,5} the shift is only 3000 cm^{-1} .

The first criterion cannot be absolutely satisfied. An infrared spectroscopy study (a method of choice for detecting hydrogen bonds) shows that pentafluoropyridine, benzene, toluene, and, to a lesser extent, the monohalogenated benzenes form complexes with 4-nitrophenol which may be detected in CCl_4 at 20 °C, but that this is not so for polyhalogenated benzenes. But

Table 3. Wavenumbers ($\times 10^{-3}$, in cm^{-1}) of the overall band maxima of indicators (1)–(7) in various solvents at different temperatures

| No. | Non-HBD and non-HBA solvents | $T/^\circ\text{C}$ | Indicators | | | | | | | | |
|-----|------------------------------|--------------------|--------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | | (1) | (2) | (3) | (4) | (5) | (6) | (7) | | |
| 1 | Perfluoromethylcyclohexane | 0 | | 35.11 | | | | 29.17 | 28.68 | | |
| | | 25 | 36.24 | 35.26 | 32.32 | 30.40 | 29.25 | 28.74 | | | |
| | | 50 | | | 32.48 | 30.53 | 29.33 | 28.82 | | | |
| | | 75 | 37.00 | 35.50 | 32.73 | 30.64 | 29.43 | 28.87 | | | |
| 2 | Perfluorohexane | 25 | 36.26 | 35.26 | 32.52 | 30.53 | 29.36 | 28.84 | | | |
| | | 3 | FC-75 ^b | 25 | 36.06 | 35.11 | 32.29 | 30.35 | 29.19 | 28.69 | |
| | | | | 50 | 36.23 | 35.24 | 32.49 | 30.50 | 29.30 | 28.75 | |
| 4 | Perfluorodecalin | 75 | 36.39 | 35.30 | 32.69 | 30.58 | 29.42 | 28.83 | | | |
| | | 0 | | | 32.01 | 30.16 | 29.04 | 28.57 | 28.70 | | |
| | | 25 | 36.09 | 35.07 | 32.16 | 30.26 | 29.09 | 28.62 | 28.74 | | |
| | | 50 | 36.18 | 35.17 | 32.29 | 30.39 | 29.16 | 28.67 | 28.79 | | |
| 5 | Perfluoro-1-methyldecalin | 75 | 36.27 | 35.27 | 32.37 | 30.52 | 29.24 | 28.72 | 28.83 | | |
| | | 105 | 36.43 | 35.50 | 32.49 | 30.60 | 29.32 | 28.75 | | | |
| | | 25 | | | 32.10 | 30.24 | 29.04 | 28.56 | | | |
| | | 50 | | | 32.22 | 30.33 | 29.11 | 28.60 | | | |
| 6 | 2-Methylbutane | 75 | 36.45 | 35.26 | 32.39 | 30.45 | 29.19 | 28.67 | | | |
| | | 0 | 35.27 | 34.36 | 31.37 | 29.56 | 28.48 | 27.94 | | | |
| | | 25 | 35.49 | 34.49 | 31.52 | 29.72 | 28.59 | 28.06 | | | |
| 7 | Pentane | 0 | 35.20 | 34.31 | 31.32 | 29.54 | 28.44 | 27.93 | 27.42 | | |
| | | 25 | 35.40 | 34.47 | 31.47 | 29.70 | 28.54 | 28.03 | 27.55 | | |
| 8 | Tetramethylsilane | 0 | 35.17 | 34.26 | 31.21 | 29.43 | 28.31 | 27.55 | 27.37 | | |
| | | 25 | 35.35 | 34.41 | 31.41 | 29.62 | 28.46 | 27.72 | 27.48 | | |
| 9 | Hexane | 0 | 35.17 | 34.26 | 31.24 | 29.46 | 28.35 | 27.77 | 27.36 | | |
| | | 25 | 35.35 | 34.38 | 31.39 | 29.59 | 28.45 | 27.89 | 27.46 | | |
| | | 50 | 35.49 | 34.53 | 31.54 | 29.75 | 28.54 | 28.01 | | | |
| 10 | Heptane | 0 | 35.07 | 34.12 | 31.21 | 29.36 | 28.30 | 27.72 | 27.35 | | |
| | | 25 | 35.26 | 34.27 | 31.37 | 29.50 | 28.41 | 27.82 | 27.46 | | |
| | | 50 | 35.42 | 34.38 | 31.52 | 29.66 | 28.51 | 27.93 | 27.61 | | |
| | | 11 | Dodecane | 0 | 34.87 | 34.07 | 30.95 | 29.19 | 28.07 | 27.49 | 27.22 |
| 25 | 35.03 | | | 34.15 | 31.10 | 29.27 | 28.18 | 27.56 | 27.28 | | |
| 50 | 35.17 | | | 34.25 | 31.27 | 29.39 | 28.25 | 27.62 | 27.35 | | |
| 12 | Cyclohexane | 75 | 35.29 | 34.33 | 31.35 | 29.52 | 28.32 | 27.70 | 27.42 | | |
| | | 105 | 35.37 | 34.44 | 31.50 | 29.62 | 28.38 | 27.80 | 27.51 | | |
| | | 25 | 35.06 | 34.12 | 31.13 | 29.31 | 28.18 | 27.62 | 27.28 | | |
| | | 50 | 35.22 | 34.25 | 31.26 | 29.43 | 28.28 | 27.70 | 27.36 | | |
| 13 | <i>cis</i> -Decalin | 75 | 35.38 | 34.37 | 31.42 | 29.59 | 28.37 | 27.78 | 27.50 | | |
| | | 0 | 34.51 | 33.81 | 30.62 | 28.94 | 27.77 | 27.32 | 27.00 | | |
| | | 25 | 34.72 | 33.91 | 30.74 | 29.01 | 27.86 | 27.34 | 27.06 | | |
| | | 50 | 34.88 | 33.98 | 30.88 | 29.09 | 27.93 | 27.38 | 27.11 | | |
| 14 | <i>trans</i> -Decalin | 75 | 35.03 | 34.08 | 30.97 | 29.18 | 28.00 | 27.40 | 27.17 | | |
| | | 105 | 35.12 | 34.14 | 31.08 | 29.29 | 28.06 | 27.46 | | | |
| | | 0 | | | 30.68 | | | | 27.04 | | |
| | | 25 | | | 30.83 | | | | 27.11 | | |
| 15 | Tetrachloromethane | 50 | | | 30.96 | | | | 27.18 | | |
| | | 75 | | | 31.09 | | | | 27.24 | | |
| | | 105 | | | 31.24 | | | | 27.31 | | |
| | | 0 | 34.28 | 33.44 | 30.23 | 28.47 | 27.18 | 26.78 | 26.56 | | |
| 16 | Tetrachloroethylene | 25 | 34.54 | 33.62 | 30.42 | 28.65 | 27.32 | 26.92 | 26.75 | | |
| | | 50 | 34.75 | 33.81 | 30.66 | 28.82 | 27.46 | 27.06 | 26.90 | | |
| | | 0 | 34.22 | 33.37 | 30.18 | 28.45 | 27.21 | 26.85 | 26.49 | | |
| | | 25 | 34.39 | 33.52 | 30.35 | 28.60 | 27.31 | 26.92 | 26.64 | | |
| 17 | Hexafluorobenzene | 50 | 34.57 | 33.64 | 30.48 | 28.71 | 27.40 | 27.02 | 26.78 | | |
| | | 75 | | 33.78 | 30.62 | 28.85 | 27.50 | 27.07 | 26.92 | | |
| | | 105 | | | 30.81 | 28.98 | 27.62 | 27.17 | 27.03 | | |
| | | 0 | 33.90 | 33.31 | 29.91 | 28.11 | 26.95 | 26.13 | 25.99 | | |
| 18 | Trichloroethylene | 25 | 34.23 | 33.47 | 30.13 | 28.32 | 27.06 | 26.32 | 26.18 | | |
| | | 50 | | 33.61 | 30.32 | 28.50 | 27.20 | 26.53 | 26.39 | | |
| | | 75 | | 33.77 | 30.48 | 28.66 | 27.28 | 26.85 | | | |
| | | 0 | 33.68 | 32.78 | 29.32 | 27.39 | 26.07 | 25.68 | 25.73 | | |
| 19 | Carbon disulphide | 25 | 33.94 | 32.96 | 29.58 | 27.60 | 26.35 | 25.84 | 25.87 | | |
| | | 50 | 34.11 | 33.16 | 29.82 | 27.84 | 26.71 | 25.99 | 26.03 | | |
| | | 75 | 34.31 | 33.34 | 30.02 | 28.14 | 26.89 | 26.22 | 26.21 | | |
| | | 0 | | | | | 25.97 | 25.60 | 25.65 | | |
| 20 | 1,4-Difluorobenzene | 25 | | | | 26.25 | 25.72 | 25.79 | | | |
| | | 0 | | 32.78 | 29.11 | 27.32 | 26.01 | 25.65 | 25.58 | | |
| | | 25 | 33.69 | 32.95 | 29.34 | 27.48 | 26.19 | 25.79 | 25.71 | | |
| | | 50 | | 33.11 | 29.60 | 27.68 | 26.54 | 25.93 | 25.85 | | |
| 75 | | 33.26 | 29.80 | 27.86 | 26.77 | 26.07 | 26.02 | | | | |

Table 3 (continued)

| No. | Non-HBD and non-HBA solvents | T/°C | Indicators | | | | | | |
|--------------|------------------------------|------|------------|-------|-------|-------|-------|-------|-------|
| | | | (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| 21 | 1,4-Dichlorobenzene | 75 | | | 29.62 | 27.77 | 26.49 | 25.84 | 25.91 |
| | | 105 | | | 29.86 | 28.02 | 26.75 | 26.09 | 26.08 |
| 22 | Fluorobenzene | 0 | | | 28.79 | 27.04 | 25.75 | 25.44 | 25.28 |
| | | 25 | | | 28.97 | 27.20 | 25.91 | 25.57 | 25.45 |
| | | 50 | | | 29.20 | 27.34 | 26.09 | 25.70 | 25.59 |
| | | 75 | | | 29.46 | 27.51 | 26.38 | 25.82 | |
| 23 | 1,3-Dichlorobenzene | 0 | 33.27 | 32.39 | 28.84 | 27.07 | 25.72 | 25.44 | 25.32 |
| | | 25 | 33.46 | 32.55 | 29.02 | 27.21 | 25.85 | 25.54 | 25.44 |
| | | 50 | 33.58 | 32.70 | 29.20 | 27.33 | 25.95 | 25.61 | |
| | | 75 | 33.66 | 32.83 | 29.38 | 27.44 | 26.12 | 25.73 | |
| | | 105 | | 33.01 | 29.62 | 27.61 | 26.42 | 25.87 | |
| 24 | Chlorobenzene | 0 | 33.16 | 32.31 | 28.65 | 26.89 | 25.60 | 25.31 | 25.14 |
| | | 25 | 33.32 | 32.49 | 28.82 | 27.06 | 25.75 | 25.46 | 25.32 |
| | | 50 | 33.50 | 32.67 | 29.04 | 27.23 | 25.91 | 25.58 | 25.47 |
| | | 75 | 33.70 | 32.85 | 29.29 | 27.38 | 26.10 | 25.73 | 25.62 |
| 25 | 1,2,3,4-Tetrachlorobenzene | 105 | 33.87 | 33.11 | 29.58 | 27.59 | 26.42 | 25.91 | |
| | | 50 | | | 28.80 | 27.07 | 25.72 | 25.42 | |
| | | 75 | | | 28.99 | 27.25 | 25.90 | 25.56 | |
| | | 105 | | | 29.29 | 27.38 | 26.08 | 25.69 | |
| 26 | 1,2,3-Trichlorobenzene | 75 | | | 28.90 | 27.13 | 25.77 | 25.48 | |
| | | 105 | | | 29.11 | 27.31 | 25.95 | 25.62 | |
| 27 | 1,2-Dichloroethane | 0 | 32.99 | 32.23 | 28.24 | 26.43 | 25.36 | 24.89 | 24.66 |
| | | 25 | 33.21 | 32.37 | 28.46 | 26.70 | 25.48 | 25.10 | 24.88 |
| | | 50 | 33.37 | 32.54 | 28.64 | 26.88 | 25.60 | 25.26 | 25.08 |
| | | 75 | 33.59 | 32.72 | 28.82 | 27.03 | 25.74 | 25.40 | |
| 28 | Bromobenzene | 0 | 33.00 | 32.13 | 28.53 | 26.81 | 25.52 | 25.24 | 24.97 |
| | | 25 | 33.19 | 32.28 | 28.65 | 26.95 | 25.64 | 25.36 | 25.17 |
| | | 50 | 33.33 | 32.47 | 28.84 | 27.10 | 25.77 | 25.47 | 25.33 |
| | | 75 | 33.46 | 32.62 | 28.95 | 27.21 | 25.89 | 25.57 | 25.47 |
| | | 105 | 33.72 | 32.84 | 29.20 | 27.32 | 26.08 | 25.69 | |
| 29 | 1,2-Dichlorobenzene | 0 | 32.95 | 32.10 | 28.42 | 26.61 | 25.43 | 25.12 | 24.85 |
| | | 25 | 33.15 | 32.27 | 28.57 | 26.88 | 25.52 | 25.25 | 25.03 |
| | | 50 | 33.32 | 32.42 | 28.72 | 26.96 | 25.66 | 25.35 | 25.20 |
| | | 75 | 33.40 | 32.57 | 28.87 | 27.07 | 25.77 | 25.43 | |
| 30 | Iodobenzene | 105 | 33.47 | 32.71 | 29.02 | 27.20 | 25.89 | 25.54 | |
| | | 0 | | | 28.28 | 26.41 | 25.32 | 25.02 | 24.76 |
| | | 25 | | 32.10 | 28.46 | 26.70 | 25.45 | 25.19 | 24.96 |
| | | 50 | | | | 26.87 | 25.59 | 25.32 | 25.14 |
| | | 75 | | | | 27.00 | 25.71 | 25.42 | 25.27 |
| 31 | Di-iodomethane | 105 | | | | 27.17 | 25.87 | 25.56 | 25.41 |
| | | 25 | | | | 25.81 | 24.62 | 24.22 | 24.28 |
| 32 | 1,2-Dibromobenzene | 0 | | | 28.06 | | | | 24.60 |
| | | 25 | | | 28.32 | | | | 24.78 |
| HBD solvents | | | | | | | | | |
| 33 | Chloroform | 0 | 33.23 | 32.27 | 28.62 | 26.59 | 25.40 | 24.85 | |
| | | 25 | 33.48 | 32.47 | 28.85 | 26.93 | 25.61 | 25.16 | 25.28 |
| | | 50 | 33.69 | 32.67 | 29.07 | 27.16 | 25.81 | 25.39 | |
| 34 | Dichloromethane | 0 | 33.12 | 32.22 | 28.42 | 26.43 | 25.34 | 24.74 | 24.72 |
| | | 25 | 33.32 | 32.36 | 28.63 | 26.76 | 25.48 | 25.08 | 24.91 |
| 35 | Bromoform | 25 | 32.72 | 31.93 | 28.27 | 26.31 | 25.22 | 24.69 | 24.89 |
| | | 50 | | | 28.51 | 26.67 | 25.39 | 24.98 | 25.09 |
| | | 75 | | | 28.74 | | 25.53 | 25.18 | 25.26 |
| HBA solvents | | | | | | | | | |
| a | Pentafluoropyridine | 0 | 33.34 | 32.89 | 29.08 | 27.31 | 26.13 | 25.62 | |
| | | 25 | 33.62 | 33.06 | 29.31 | 27.49 | 26.33 | 25.77 | |
| | | 50 | 33.90 | 33.18 | 29.59 | 27.68 | 26.58 | 25.89 | |
| | | 75 | | 33.32 | 29.80 | 27.89 | 26.77 | 26.08 | |
| a | Toluene | 0 | 33.38 | 32.74 | 28.93 | 27.29 | 26.06 | 25.75 | 25.61 |
| | | 25 | 33.59 | 32.94 | 29.19 | 27.45 | 26.46 | 25.88 | 25.76 |
| | | 50 | 33.77 | 33.09 | 29.44 | 27.63 | 26.75 | 26.04 | 25.90 |
| | | 75 | 33.94 | 33.21 | 29.69 | 27.87 | 26.85 | 26.30 | 26.10 |
| | | 105 | 34.16 | 33.43 | 29.92 | 28.17 | 27.01 | 26.70 | 26.25 |
| a | Benzene | 25 | 33.47 | 32.81 | 29.09 | 27.33 | 26.10 | 25.76 | 25.62 |
| | | 50 | 33.68 | 32.98 | 29.33 | 27.51 | 26.49 | 25.91 | 25.77 |
| | | 75 | 33.91 | 33.19 | 29.59 | 27.70 | 26.71 | 26.08 | 25.93 |
| a | Tetramethylene sulphone | 30 | 32.12 | 31.96 | 26.85 | | 24.77 | 24.44 | |
| | | 50 | 32.19 | 32.02 | 26.95 | | 24.86 | 24.50 | |

^a Numbering will be given in Part 2. ^b Trade name of perfluorocarbons produced by the 3M company; main constituent perfluorobutyltetrahydrofuran.

Table 4. Wavenumbers ($\times 10^{-3}$, in cm^{-1}) of the overall band maxima of indicators (8)—(14) in various non-HBA and non-HBD solvents at different temperatures

| No. | Solvent | $T/^\circ\text{C}$ | Indicators | | | | | | |
|-----|---------------------|--------------------|---------------------------|---------------------------|-------|-------|---------------------------|-------|-------|
| | | | (8) | (9) | (10) | (11) | (12) | (13) | (14) |
| 4 | Perfluorodecalin | 0 | 27.10, ^a 27.86 | 25.56, ^a 26.61 | | | 30.83, ^a 31.56 | | |
| | | 25 | 27.22, ^a 27.87 | 25.62, ^a 26.64 | 36.00 | 32.51 | 30.86, ^a 31.59 | 34.11 | 36.18 |
| | | 50 | 27.37, 27.87 ^a | 25.68, ^a 26.66 | | | 30.91, ^a 31.60 | | |
| | | 75 | 27.69 ^b | 25.75, ^a 26.67 | | | 30.98, 31.64 ^a | | |
| | | 105 | 27.82 ^b | 25.83, ^a 26.67 | | | 31.07, 31.66 ^a | | |
| 10 | Heptane | 0 | 26.54 | 25.01, ^a 25.96 | | | 30.34, ^a 31.00 | | |
| | | 25 | 26.65 | 25.09, ^a 25.99 | 35.25 | 31.90 | 30.40, ^a 31.04 | 33.51 | 35.69 |
| | | 50 | 26.81 ^b | 25.17 | | | 30.46 | | |
| | | 75 | 26.95 ^b | 25.25 | | | 30.52 | | |
| 12 | Cyclohexane | 25 | 26.53 | 24.95, ^a 25.88 | 34.99 | 31.82 | 30.29 | 33.40 | 35.59 |
| | | 50 | 26.63 | 25.03 | | | 30.36 | | |
| | | 75 | 26.74 ^b | 25.11 | | | 30.40 | | |
| 13 | <i>cis</i> -Decalin | 0 | 26.16 | 24.69, ^a 25.64 | | | 30.06 | | |
| | | 25 | 26.30 | 24.75, ^a 25.66 | 34.58 | 31.51 | 30.12 | 33.20 | 35.42 |
| | | 50 | 26.46 ^b | 24.82, ^a 25.66 | | | 30.18 | | |
| | | 75 | 26.60 ^b | 24.89 | | | 30.25 | | |
| | | 105 | 26.70 ^b | 24.97 | | | 30.30 | | |
| 14 | Tetrachloromethane | 0 | 26.04 | 24.52 | | | 29.63 | | |
| | | 25 | 26.17 | 24.65 | 34.14 | 31.07 | 29.76 | 32.65 | 34.55 |
| | | 50 | 26.29 | 24.77 | | | 29.93 | | |
| | | 75 | 26.41 | 24.89 | | | 30.14 | | |
| 16 | Trichloroethylene | 0 | 25.46 | 24.05 | | | 29.43 | | |
| | | 25 | 25.62 | 24.20 | 33.81 | 30.84 | 29.53 | 32.51 | 34.57 |
| | | 50 | 25.76 | 24.33 | | | 29.63 | | |
| | | 75 | 25.91 | 24.46 | | | 29.74 | | |
| 27 | 1,2-Dichloroethane | 0 | 24.88 | 23.53 | | | 29.24 | | |
| | | 25 | 25.01 | 23.65 | 33.54 | 30.59 | 29.34 | 32.37 | 34.20 |
| | | 50 | 25.13 | 23.78 | | | 29.44 | | |
| | | 75 | 25.27 | 23.90 | | | 29.52 | | |

^a Maximum of the most intense vibronic transition. ^b Very flat top.

ultraviolet spectroscopy only shows the difference in hydrogen-bond strengths of the excited and ground states of the indicators, and the others are perhaps not as strong HBDs as 4-nitrophenol.* It is therefore not evident that all these weakly HBA solvents will deviate from the reference line in a significant manner. In the same way the HBD strengths of CHCl_3 , CHBr_3 , CH_2I_2 , CH_2Cl_2 , $\text{HCCl}=\text{CCl}_2$, and tri- and tetra-halogenobenzenes have already been shown,²⁵ and thermodynamic data for hydrogen-bond formation between CHCl_3 , CHBr_3 , and CH_2Cl_2 and a certain number of bases have been determined.²⁴ However, according to the solvatochromic comparison principle, the weakly HBD solvents should only deviate above the reference line if there exists a detectable difference in the basicities of the groups A of the two homomorphs, which is hard to predict [in principle the basicity of the group A = NO_2 increases in the order, (3) < (4) < (5) < (6), of the electron-donating strength of D].

For these reasons, rather than to reject systematically all the weakly HBD and HBA solvents, which would have curtailed our sampling at the lower end of the reference line, we preferred to test statistically the residuals of these questionable solvents with respect to the standard deviation of the estimate of a reference line calculated from reliable or only slightly suspect solvents (gas state, perfluoroalkanes, Me_4Si , alkanes, CCl_4 , C_2Cl_4 , polyhalogenated benzenes, and 1,2-dichloroethane) and to reject only those with residuals at 25°C † significant at the 0.05 level for at least one of the pairs (1)/(2), (3)/(5), (3)/(6), and (4)/(5). The results are as follows:

(a) Pentafluoropyridine, toluene, and benzene, which are

weak HBAs, and CHCl_3 , CHBr_3 and CH_2Cl_2 , which are weak HBDs, should be eliminated.

(b) On the one hand $\text{C}_6\text{H}_6\text{F}$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$, and $\text{C}_6\text{H}_5\text{I}$, and on the other 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, CH_2I_2 ‡ and $\text{HClC}=\text{CCl}_2$ § may be retained as the very weak HBA character of the first group and very weak HBD character of the second cannot be detected by the solvatochromic comparison principle.

The application of these criteria to the data in Tables 2—4 gives the equations (5)—(11) for the reference line.

$$\bar{\nu}(1) = 1.0434 \bar{\nu}(2) - 0.57 \quad r = 0.9980 \quad n = 74 \quad (5)$$

$$\bar{\nu}(3) = 0.9841 \bar{\nu}(5) + 3.49 \quad r = 0.9969 \quad n = 99 \quad (6)$$

$$\bar{\nu}(4) = 0.9778 \bar{\nu}(5) + 1.84 \quad r = 0.9985 \quad n = 105 \quad (7)$$

$$\bar{\nu}(3) = 1.0845 \bar{\nu}(6) + 1.19 \quad r = 0.9978 \quad n = 65^\parallel \quad (8)$$

$$\bar{\nu}(3) = 1.1275 \bar{\nu}(7) + 0.35 \quad r = 0.9957 \quad n = 70^\parallel \quad (9)$$

$$\bar{\nu}(8) = 1.0815 \bar{\nu}(9) + 0.53 \quad r = 0.9988 \quad n = 25 \quad (10)$$

$$\bar{\nu}(10) = 1.2857 \bar{\nu}(11) + 5.84 \quad r = 0.9970 \quad n = 7^{**} \quad (11)$$

‡ This solvent however has only been tested for the pair (4)/(5), which is the least sensitive to HBD solvent effects.

§ This solvent however has not been tested for the pair (3)/(6) (it lies in the 'hump'), which is the most sensitive to HBD solvent effects.

¶ The solvents which lie in the 'hump' are not included.

|| The gas state and perfluorinated solvents are not included (see earlier).

** The gas state is not included (see earlier).

* In the ground state, anilines are much weaker HBDs than phenols.²⁴

† When the temperature increases these residuals must decrease regularly.

From these equations $\Delta\Delta\bar{\nu}$ may be calculated for HBA solvents at different temperatures. For example, for tetramethylene sulphone, $-\Delta\Delta\bar{\nu}_{30}$ (1)—(2) = 657 cm^{-1} ; $-\Delta\Delta\bar{\nu}_{30}$ (3)—(5) = 1 016 cm^{-1} ; $-\Delta\Delta\bar{\nu}_{50}$ (1)—(2) = 650 cm^{-1} ; $-\Delta\Delta\bar{\nu}_{50}$ (3)—(5) = 1 005 cm^{-1} .

Conclusion

The thermosolvatochromic study of 14 indicators in many solvents and in the temperature range 0—105 °C has enabled us to define the optimum conditions for measuring solvent parameters from the solvatochromic comparison principle. We shall show in a later paper that the results obtained by this thermosolvatochromic method differ from those in the literature and give a less unitary view of the solvent polarity and basicity parameters than that advocated by KAT with their parameters π^* and β .

Acknowledgements

We thank Dr. Kamlet for a sample of the indicator (6) and Dr. Krygowski for a sample of the indicator (7). Mrs. Luçon, Miss Helbert, and Mr. Lopez are thanked for their aid.

References

- 1 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377.
- 2 R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2886.
- 3 R. R. Minesinger, M. E. Jones, R. W. Taft, and M. J. Kamlet, *J. Org. Chem.*, 1977, **42**, 1929.
- 4 M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 6027.
- 5 M. J. Kamlet, J. L. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1981, **13**, 485.
- 6 A series of 28 articles (up to this date) entitled 'Linear Solvation Energy Relationships' treats this subject. Part 28: R. W. Taft, J. L. Abboud, and M. J. Kamlet, *J. Org. Chem.*, 1984, **49**, 2001.
- 7 J. E. Brady and P. W. Carr, *Anal. Chem.*, 1982, **54**, 1751.
- 8 M. Essfar, G. Guihéneuf, and J. L. Abboud, *J. Am. Chem. Soc.*, 1982, **104**, 6786.
- 9 M. J. Kamlet, J. L. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
- 10 G. Collier, I. A. Pickering, and J. Shorter, 2nd EuChem Conference on Correlation Analysis in Organic Chemistry, Hull, 1982.
- 11 T. M. Krygowski, E. Milczarek, and P. K. Wrona, *J. Chem. Soc., Perkin Trans 2*, 1980, 1563.
- 12 T. M. Krygowski, J. P. Radomski, A. Rzeszowiak, P. K. Wrona, and C. Reichardt, *Tetrahedron*, 1981, **37**, 119.
- 13 T. M. Krygowski, C. Reichardt, P. K. Wrona, C. Wyszomirska, and V. Zielkowska, *J. Chem. Res. (S)*, 1983, 116.
- 14 O. W. Kolling, *Anal. Chem.*, 1981, **53**, 54.
- 15 E. M. Arnett, L. J. E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1970, **92**, 2365.
- 16 J. M. Vandenberg, *J. Opt. Soc. Am.*, 1961, **51**, 802.
- 17 P. Suppan and C. Tsiamis, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1553.
- 18 J. A. Riddick and W. B. Bunger, 'Organic Solvents,' 3rd ed., in 'Techniques of Chemistry,' ed. A. Weissberger, Wiley-Interscience, New York, 1970, vol. II.
- 19 C. Reichardt, 'Solvent Effects in Organic Chemistry,' Verlag Chemie, Weinheim, 1979.
- 20 I. A. Koppel and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, 1969, **6**, 504.
- 21 E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, 1974, **96**, 3875.
- 22 H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962.
- 23 P. Suppan, *J. Chem. Soc. A*, 1968, 3125.
- 24 M. D. Joesten and L. J. Schaad, 'Hydrogen Bonding,' Dekker, New York, 1974.
- 25 A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1963, **85**, 1715.

Received 15th July 1985; Paper 5/1195