Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 5. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

Transalkylation and Transphenylation of Quaternary Pyridinium Salts: Conversion of Primary Amines Into bis-Homologous Acids

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Abstract

Alkyl, aryl and substituted aryl amines are converted into pentacyclic pyridinium trifluoromethanesulphonates **3** in good yield. The latter, when reacted with cyano-ethylacetate or diethylmalonate give the substituted esters **4** and **5**, which are hydrolysed to substituted acetic acids. Thus the conversion of primary amines into bis-homologous acids is realised.

We have demonstrated the utility of pyridinium salts to prepare aryl thiocyanates [1] and N-piperidine derivatives [2]. But, whilst we have easily succeeded in the transarylation and transbenzylation of N-aryl and N-benzyl-2,4,6-triphenylpyridinium and N-aryl and N-benzyl-2,4-diphenyl-5,6-dihydronaphtho [1,2-b] pyridinium tetrafluoroborates, we failed in the transalkylation of the said N-alkyl pyridinium derivatives, due to their unsufficient steric hinderance [3]. However we succeeded in the conversion of N-allyl-2,4-diphenyl-5,6-dihydronaphtho-[1,2-b]pyridinium tetrafluoroborate, probably due to its conjugated system.

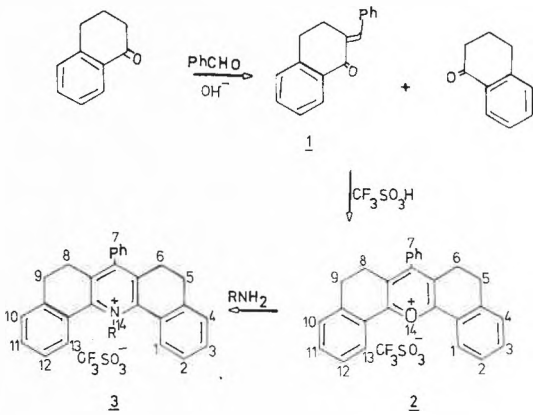
We wish to show now, that not only aryl but also alkyl derivatives of cyanoacetic and malonic esters may be prepared from primary amines via pentacyclic pyridinium salts in a new two-step process.

The invention consists in a pyridinium system[2,4], the N-substituted-7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h]-acridinium trifluoromethanesulfonates **3** prepared from 7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] xanthylium trifluoromethanesulfonate **2** and the appropriate amine. The xanthylium salt **2** itself was prepared by condensation of 2-benzylidene-1-tetralone (**1**) with 1-tetralone in the presence of trifluoromethanesulfonic acid. **2** was isolated in 51 % yield and was characterised by its analytical data. Scheme 1.

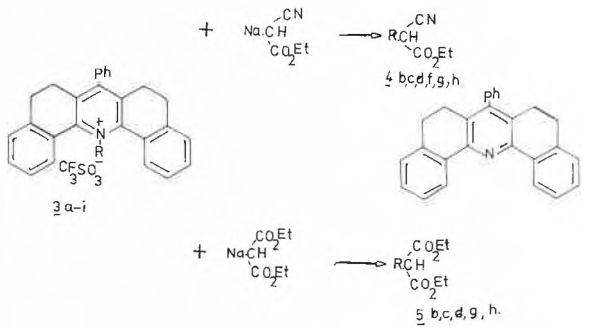
When aromatic amines are used, high reaction temperatures are required to obtain the pyridinium salt **3**, probably for steric reasons. The compounds **3a-i** were characterised by their elemental analysis and spectral data.

Just as alkylating agents 14-R-7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] acridinium trifluoromethanesulfonates were used for the preparation of alkyl-, aryl- and substituted aryl-derivatives of cyanoacetic (**4**) and malonic (**5**) esters, according to the nature of R in the starting RNH_2 (scheme 2).

Scheme 1:



Scheme 2:



This transalkylation and transarylation into sodium ethylcyanoacetate and sodium diethylmalonate proceeds very smoothly, espically in 1,4-dioxane at reflux temperature. **4** and **5** are easily hydrolized to the R-acetic acids, meaning—and this is probably the most interesting

Table 1: Physical and analytical data of N-substituted-7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] acridinium trifluoromethanesulfonates (**3a–3i**).

Compd.	R	Yield (%)	M.P.* °C	Formula	Found (%) C	H	N	S	Required (%) C	H	N	S
3a	Methyl	91	261	$C_{29}H_{24}F_3NO_3S$	67.0	4.7	2.8	6.0	66.5	4.6	2.7	6.1
3b	Amyl	69	175	$C_{33}H_{32}F_3NO_3S$	68.0	5.6	2.5	5.7	68.3	5.5	2.4	5.5
3c	n-Octyl	62	148	$C_{36}H_{38}F_3NO_3S$	69.6	6.2	2.1	5.1	69.5	6.2	2.3	5.2
3d	Phenyl	96	308	$C_{34}H_{26}F_3NO_3S$	70.8	4.5	2.6	5.5	69.7	4.5	2.4	5.5
3e	m-Methylphenyl	73	306	$C_{35}H_{28}F_3NO_3S$	69.9	4.8	2.5	5.4	70.1	4.7	2.3	5.3
3f	p-Methylphenyl	84	322	$C_{35}H_{28}F_3NO_3S$	69.6	4.7	2.4	5.3	70.1	4.7	2.3	5.3
3g	p-Methoxyphenyl	90	310	$C_{35}H_{28}F_3NO_4S$	68.4	4.7	2.5	5.1	68.3	4.6	2.3	5.2
3h	p-Chlorophenyl	86	336	$C_{34}H_{25}ClF_3NO_3S$**	66.0	4.2	2.4	5.2	65.9	4.1	2.3	5.2
3i	m-Chloro-p-methylphenyl	75	340	$C_{35}H_{27}ClF_3NO_3S$***	66.7	4.5	2.4	5.3	66.3	4.3	2.2	5.1

* White needles, crystallised from isopropyl alcohol. ** Found: Cl 5.6; Calc.: Cl 5.7 %. *** Found: Cl 5.6; Calc.: Cl 5.6 %.

Table 2: PMR-spectra (60 Hz)* of N-substituted-7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] acridinium trifluoromethanesulfonates (**3a–3i**).

Compd.*	Aromatic protons	$-CH_2CH_2-$	Alkyl groups
3a	8.3–8.0 (2H, m); 7.8–7.1 (11H, m)	2.8 (8H, m)	4.55 (3H, s)
3b	8.3–7.9 (2H, m); 7.9–7.1 (11H, m)	3.0 (8H, m)	5.5 (2H, t); 1.6–0.5 (9H, m)
3c	8.4–8.0 (2H, m); 7.9–7.1 (11H, m)	2.9 (8H, m)	5.5 (2H, t); 1.6–0.5 (15H, m)
3d	7.8–6.8 (16H, m); 6.8–6.5 (2H, d)	2.9 (8H, br)	–
3e	7.8–6.9 (15H, m); 6.9–6.6 (2H, d)	2.9 (8H, br)	2.3 (3H, s)
3f	7.7–6.7 (15H, m); 6.7–6.4 (2H, d)	2.9 (8H, br)	2.4 (3H, s)
3g	7.9–6.9 (15H, m); 6.9–6.6 (2H, d)	2.9 (8H, br)	4.0 (3H, s)
3h	7.8–6.8 (15H, m); 6.8–6.5 (2H, d)	2.9 (8H, br)	–
3i	7.8–6.8 (14H, m); 6.8–6.5 (2H, d)	2.8, (8H, br)	2.46 (3H, s)

* δ = ppm
** $CF_3CO_2H/CDCl_3$ mixture used as solvent.

feature of this investigation—that a method has been found to transform any primary amine into its bis-homologous acid.

Table 1 gives yields, melting points and analytical data of the pyridinium salts **3a–3i**. The highly symmetrical molecules account for the high melting points, especially when R is an aromatic residue (**3d–i**).

The IR-spectra of the acridinium salts **3** show the typical trifluoromethanesulfonate bands at 1270 cm^{-1} and 1030 ± 5 cm^{-1}. The band at 1270 ± 5 cm^{-1} is the most intense band of the parent pyrylium trifluoromethanesulfonates (**2**).

The second intense and sharp band at 1030 ± 5 cm^{-1} in the above compounds arises from the anion. In the IR-spectra of the N-amyl and N-octyl derivatives strong bands appear at 2945 s, 2920 s, 2842 s (cm^{-1}). Not all of them are present in the spectra of the pyrylium salts (**2**); they could be the C–H streching bands of the N-alkyl chain. Other differences in these pentasubstituted pyridinium systems are the two bands in the region of 1570–1615 cm^{-1}, instead of the usual three bands observed in this region.

Preparation of cyanoacetic **4** *or malonic* **5** *esters*

N-Substituted-7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] acridinium trifluoromethanesulfonate, when refluxed with sodium salts of cyanoacetic or malonic esters in 1,4-dioxane gave the corresponding esters in yields between 70 and 90 % (Tables 3 and 4). The esters were identified by comparing their IR-spectra and thin layer chromatography with those of authentic samples. The reaction appears to be general and thus represents a feasible synthetic route for the conversion of primary amines into **4** or **5** and by saponification into the free R-acetic acids.

Experimental part

The IR-spectra were measured with a Perkin-Elmer Spectrophotometer 237, using bromoform mull and the PMR-spectra with a Perkin-Elmer R 12 instrument (60 Hz), (Me_4Si as internal standard) using a $CF_3CO_2H/CDCl_3$ mixture as solvent. Melting points were determined with a Gallenkamp melting point apparatus.

1. *7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] xanthylium trifluoromethanesulfonate* (**2**).

2-Benzylidene-1-tetralone (15.5 g, 0.065 mol) and 1-tetralone (8.8 g, 0.06 mol) were condensed in the presence of trifluoromethanesulfonic acid (9.0 g, 0.06 mol) at 85 °C for 4 hs. After cooling, the reaction product was stirred with diethylether and filtered (18.8 g, 51 %); primas, M.P. 304 °C. Recrystallisation was not necessary. $C_{28}H_{21}F_3O_4S$. Found: C 65.8; H 4.0; S 6.1 %, required: C 65.9; H 4.1; S 6.3 %. IR-signals at 1618 s, 1605 ms, 1570 ms, 1510 m, 1478 s, 1440 m, 1420 s, 1320 m, 1270 s, 1210 ms, 1038 s, 896 m, 796 m, 775 s, 758 s. PMR-spectra: a- Aromatic protons: 8.70–8.09 (2H,m); 8.0–7.1 (11H,m). b- $-CH_2CH_2-$ 3.03 (8H,m).

2. *N-Alkyl-7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] acridinium trifluoromethanesulfonates* (**3a–c**):
7-Phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] xanthylium trifluoromethanesulfonate (2.5 g, 0.0048 mol) was stirred with the special primary amine (0.005 mol) in methanol (10 ml) at room temperature for 2 hs. Diethylether was added (20 ml) and the solid obtained was filtered and recrystallised from isopropyl alcohol giving white needles of **3a–c**, (Table 1).

3. *N-Aryl-7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] acridinium trifluoromethanesulfonates* (**3d–e**).
A mixture of pyrylium trifluoromethanesulfonate **2** (1.8 g, 0.0035 mol) and the aryl amine (0.004 mol) was refluxed in dimethylformamide (10 ml) for 3 hs. The solution was cooled; ether (50 ml) was added with continuous stirring. The solid precipitate was filtered and washed with ether (30 ml) giving the acridinium trifluoromethanesulfonates **3d–e**. Recrystallisation from isopropyl alcohol gave white needles (Table 1).

4. *R-Substituted ethyl-α-*cyanoacetates (**4b,c,d,f,g** and **h**).
The appropriate N-substituted acridinium trifluoromethanesulfonate **3** (10 mmol), sodium ethylcyanoacetate (15 mmol) and 1,4-dioxane (50 ml) were refluxed for 7 hs, then the volume of the reaction mixture was reduced to ⅓ and added to water (200 ml), the 7-phenyl-5,6,8,9-tetrahydro-dibenzo [c,h] acridine formed during the reaction precipitated and was filtered. The ester layer was extracted with ether (200 ml) followed by fractional distillation of the extract (Table 3).

Table 3: Physical data of ethyl-α-R-cyanoacetates.
$R-CH(CN)-COOC_2H_5$

	R	B.P. °C/mm	Yield (%)	$n_D/t°$	$d_4/t°$	References
4b	Amyl	101/3	79	1.4270/25	–	[5]
4c	n-Octyl	162/15	84	1.4381/23	–	[6]
4d	Phenyl	126/2	78	1.5017/24	1.090/20	[7]
4f	p-Methyl-phenyl	121/1	87	1.5047/20	–	[7]
4g	p-Methoxy-phenyl	153/2	80	1.5175/23	1.148/24	[8]
4h	p-Chloro-phenyl	148/1	75	1.5181/25	–	[9]

5. *R-Substituted diethylmalonates* (**5b,c,d,g** and **h**).
The preceeding method was used with sodium diethylmalonate instead of sodium ethylcyanoacetate to give the ethyl-α-R-malonates of Table 4.

Table 4: Physical data of ethyl-α-R-malonate.
$R-CH(COOC_2H_5)-COOC_2H_5$ (**5**)

	R	B.P. °C/mm	Yield (%)	$n_D/t°$	$d_4/t°$	References
5b	Amyl	123/6	82	1.4253/22	–	[10]
5c	n-Octyl	153/7	91	1.4315/25	–	[11,12]
5d	Phenyl	166/18	78	1.4913/20	1.0950/20	[13]
5g	p-Methoxy-phenyl	153/2.5	80	1.4995/23	1.115/24	[8]
5h	p-Chloro-phenyl	123/0.2	70	1.4999/25	–	[9]

6. *R-Substituted acetic acids from* **4** or **5** (**6b,c,d,f,g** and **h**).
To obtain **6b** and **6c** (Table 5), the cyanoacetic (**4**) or malonic esters (**5**) were hydrolysed and decarboxylated simultaneously to the free acids by refluxing for 2 h with dilute hydrochloric acid (15%). The reaction mixture was extracted with diethylether and gave oils, which were fractionally distilled to give heptanoic or decanoic acids **6b** and **6c**. The isolation of **6d,f,g** and **h** differs from the method above.
The hydrochloric acid mixture obtained was chilled in ice for 4 h and the phenylacetic acids **6d,f,g** and **h** were filtered off (Table 5).

Table 5: Physical data of R-substituted acetic acids (**6**).
RCH_2-COOH

	R	M.P. °C	B.P. °C/mm	Yield (%)	Product	References
6b	Amyl	–	223/760	79	Heptanoic acid n_D^{20} 1.4221; D_4^{20} 0.918	[14]
6c	n-Octyl	31.5	170/25	82	Decanoic acid n_D^{40} 1.4286; D_4^{40} 0.8858	[14]
6d	Phenyl	76	–	79	Phenylacetic acid	[15]
6f	p-Methyl-phenyl	92	–	90	p-Methyl-phenylacetic acid	[16]
6g	p-Hydroxy-phenyl	149	–	71	p-Hydroxy-phenylacetic acid	[17]
6h	p-Chloro-phenyl	104	–	75	p-Chloro-phenyl acetic acid	[17]

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Solvatochromic Shifts and Polarity of Solvent Mixtures *

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Abstract

The local polarity of solvent mixtures near a polar solute molecule can be very different from the mixture's bulk polarity. A general mechanism which determines the local polarity is the "dielectric enrichment" which is described by the thermodynamic equilibrium in a solvent shell enriched in polar solvent. This equilibrium and the resulting local polarity can be described quantitatively by the balance between the electrostatic stabilization energy and the entropy of unmixing of a solvent shell enriched in polar solvent.

The "polarity" of a medium plays an important role in many areas of chemistry. It affects reaction rate constants, thermodynamic equilibria, optical and nuclear spectra, etc. In photophysics the polarity of a medium determines the relative energies of the electronic states of solute molecules, as shown by the solvatochromic and thermochromic shifts of absorption and fluorescence spectra. These shifts are broadly related to the functions

$$\varphi(D) = \frac{D-1}{D+2} \quad \text{or} \quad f(D) = \frac{2(D-1)}{2D+1}$$

of the static dielectric constant D of the solvent; these functions provide therefore useful quantitative measurements of the solvent polarity.

In the case of mixtures of two solvents the polarities are in general not additive [1]. As an example fig. 1 shows the solvatochromic shifts of the first absorption bands of 4-nitrobiphenyl and 4-nitroaniline in mixtures of ether and dimethylformamide.

It is a common observation that small concentrations of a polar solvent B in a less polar solvent A have a much greater effect on the solvatochromic shifts than would be expected from the simple additivity of their polarities weighted by their mole fractions x_A, x_B (which would result in a nearly linear shift as shown by the dotted lines in figure 1).

The deviations from additivity have been usually explained in terms of specific associations between the solute and one of the component solvents of the mixtures, or by associations between the solvents. Such explanations may be important in certain specific cases, but we wish to suggest that there is also a completely general mechanism for all these non-additive polarity effects; this

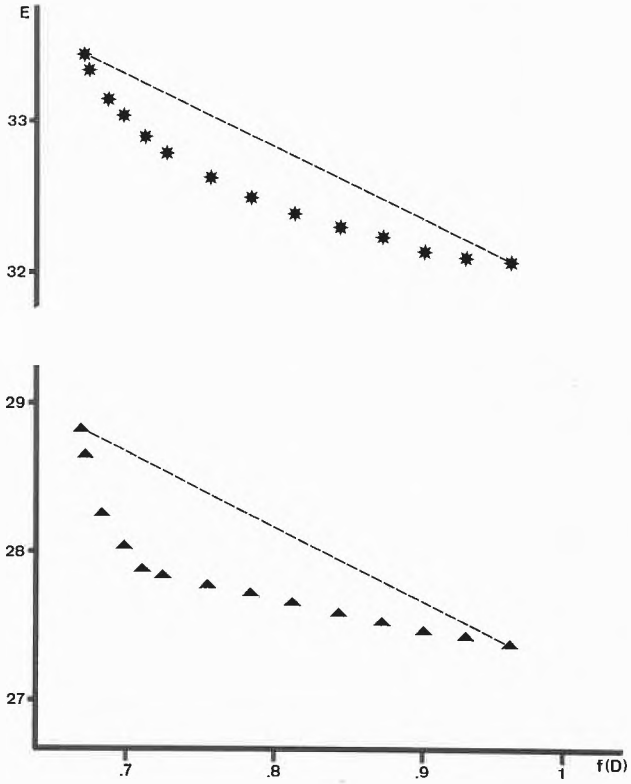

Fig. 1: Solvatochromic shifts of the first absorption band of 4-nitrobiphenyl (*) and 4-nitroaniline (▲) in mixtures of di-ethyl ether/dimethyl-formamide at 20 °C.
Abcissa, $f(D) = 2(D-1)/(2D+1)$ of bulk solvent mixture; Ordinate, E transition energy in kilokaiser ($10^3\,cm^{-1}$).

mechanism is the "dielectric enrichment" in polar solvents of the solvent shell of polar solute molecules in mixtures of solvents of different polarity. This dielectric enrichment results from the thermodynamic equilibrium at each point of the solvent shell, of coordinates r, θ, near a solute molecule of dipole moment $\vec{\mu}$ (fig. 2).

Let x_A, x_B be the mole fractions of the less polar solvent A and the more polar solvent B in the bulk of the mixture (at a great distance from any solute molecule) and y_A, y_B the mole fractions at a point r, θ of the solvent shell. The condition for thermodynamic equilibrium is

$$\frac{\partial\, d\, E_{r,\vartheta}}{\partial y_B} - T\,\frac{\partial\, d\Delta S_{r,\vartheta}}{\partial y_B} = 0 \qquad (1)$$

The energy term in $dE_{r,\vartheta}$ is the increase in electrostatic solute-solvent stabilization energy when the solvent

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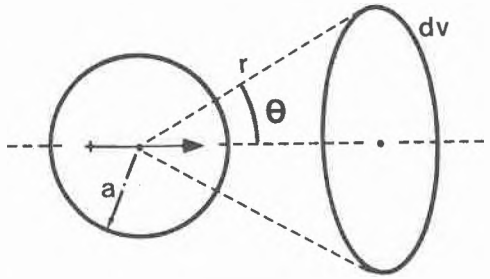

Fig. 2: Coordinates of a dipole/solvent shell system.

mixture at r, θ is enriched in polar solvent from the bulk mole fraction x_B to the local mole fraction y_B. The entropy term in $d\Delta S_{r,\vartheta}$ is the entropy of unmixing of the solvent from the bulk composition x_A, x_B to the local composition y_A, y_B.

If the solute molecule is a rigid, non-polarizable dipole of permanent dipole moment $\vec{\mu}$, the equilibrium condition is [2]

$$\frac{y_A}{y_B} = \frac{x_A}{x_B} e^{-z \cos^2 \vartheta \, r^{-6}} \tag{2}$$

where

$$z = \frac{9 \mu^2 \Delta f_{AB} M}{8 \pi R T \delta} \quad \text{if} \quad \Delta f_{AB} = f(D_B) - f(D_A)$$

if M is the mean molecular weight of solvent A and B, δ their mean density, $f(D_A)$ and $f(D_B)$ their dielectric constant functions (polarity functions) as defined above; R being the gas constant and T the absolute temperature. This simple "continuous dielectric" model shows that for small values of r the ratio y_A/y_B of non-polar to polar solvent becomes very small, even when the bulk ratio x_A/x_B is large. Therefore, when the parameter Z is large (in other words, μ and Δf are both large), the solvent shell in the immediate vicinity of a solute dipole consists almost entirely of polar solvent even in the absence of specific associations (such as hydrogen-bonding).

The r^{-6} dependence of the y_A/y_B ratio shows that the transition from the zone of enrichment (where $y_B \simeq 1$) to the zone of undisturbed solvent ($y_B \simeq x_B$) is abrupt. Because of the $\cos^2 \theta$ dependence on the angle from the solute dipole direction, each solute molecule is surrounded by two symmetric lobes of dielectric enrichment (fig. 3).

The dielectric enrichment model therefore gives a simple picture of a solute dipole in a mixture of two solvents. For each bulk solvent composition there are two zones of polar solvent near the dipole; these zones increase in size as the bulk polar solvent mole fraction x_B increases (fig. 4).

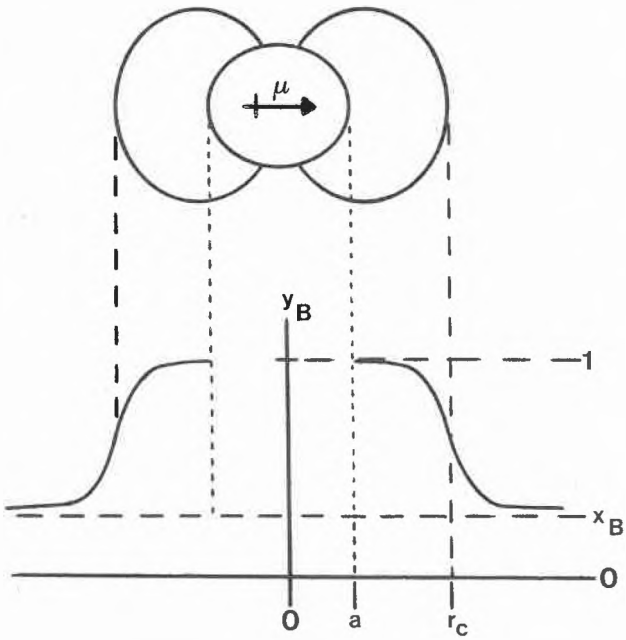

Fig. 3: Calculated distribution of polar solvent (y_B) near a solute dipole.
The angular distribution shows the "critical distance" r_c within which the solvent shell consists of pure polar solvent.
The radial distribution shows the polar solvent mole fraction as a function of the distance; a is the molecular radius
Parameters for computation: $\mu = 6$ Debye
$f(D)_B - f(D)_A = 0.5$
$a = 3.5$ A

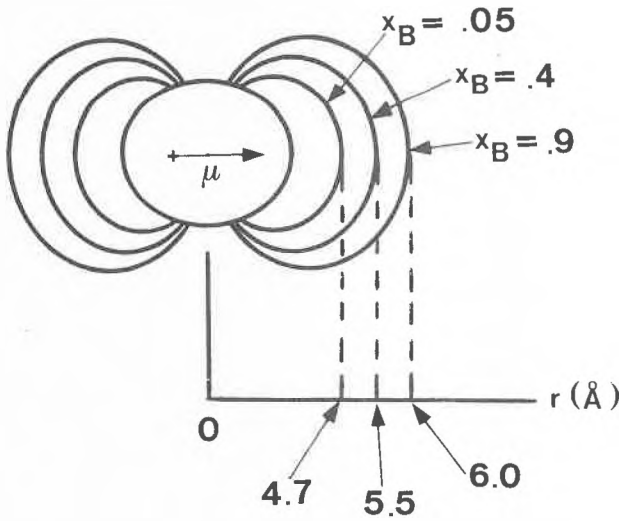

Fig. 4: Variation of the critical distance r_c with the bulk composition of a solvent mixture
Parameters for computation: $\mu = 6$ Debye
$f(D)_B - f(D)_A = 0.5$

The differential stabilization energy of the solute-solvent system for each point r, θ of the solvent shell, of volume $dv_{r,\vartheta}$ is

$$dE = \frac{9 \mu^2 \cos^2 \vartheta}{4 \pi r^6} f(D)_{r,\vartheta} \, dv_{r,\vartheta} \tag{3}$$

where

$$f(D)_{r,\vartheta} = y_A f(D_A) + y_B f(D_B)$$

the total solute-solvent stabilization energy is obtained by the integration of $dE_{r,\vartheta}$ over all space (r from the molecular radius a to ∞, θ from 0 to π). This double

integral can be evaluated in practice by the double summation

$$E = -\mu^2 \sum_{r=a}^{n} \sum_{\vartheta=0}^{\pi} [f(D_A) + \Delta f_{AB}\, y_B(r,\vartheta)] \left[\frac{1}{r^3} - \frac{1}{(r+dr)^3}\right] [\cos^3\vartheta - \cos^3(\vartheta + d\vartheta)] \quad (4)$$

for which simple computer programs have been worked out for any desired degree of approximation.

The deviation from linearity of solvatochromic shifts in solvent mixtures (as shown in figure 1) must be explained by this increased stabilization energy. In fig. 5 comparisons are made between experimental and calculated shifts (from equation 4).

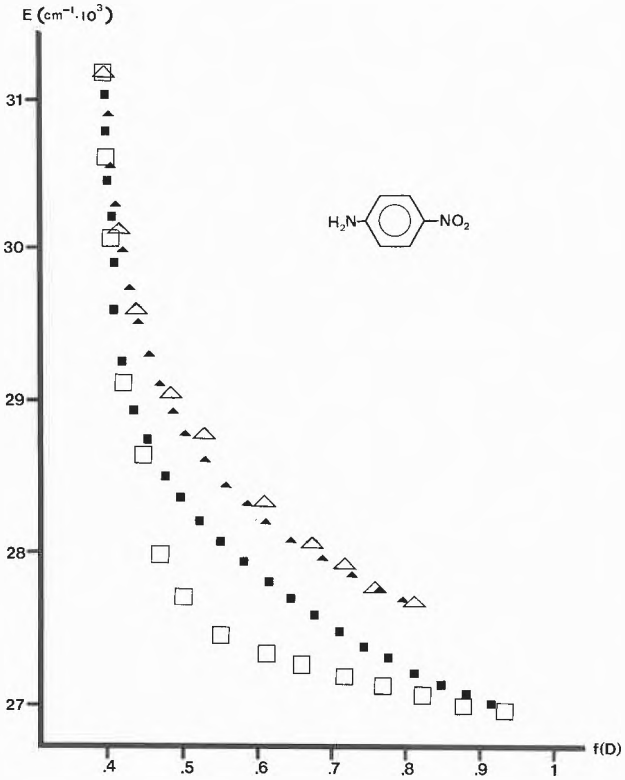

Fig. 5: Comparison of experimental and calculated (equation 4) solvatochromic shifts of 4-nitro-aniline in mixtures of
a) cyclohexane/tetrahydrofuran; △ exp., ▲ calc.
b) cyclohexane/l-butanol; □ exp., ■ calc.

It can be seen that the dielectric enrichment model reproduces quite well the general shape of the experimental curves E versus $f(D)_{lin}$. For a polar solute molecule like 4-nitroaniline, quantitatively correct results are obtained for solvent mixtures free of specific associations (ether/DMF, cyclohexane/THF for instance). The model underestimates the non-linearity in paraffin/alcohol mixtures, but even then some 90 % of the excess stabilization energy is explained by the effect of dielectric enrichment. The most important implications of this model concern the solvatochromic and thermochromic shifts of molecular absorption and emission spectra. In particular, the very large shifts of fluorescence bands in solvent mixtures of low bulk polarity have often been ascribed to various types of exciplexes. According to the present model, it appears that such interpretations may need to be reconsidered to take into account the general mechanism of dielectric enrichment which is quite distinct from complex formation [3]. The description of a "complex" requires both a fixed geometry and a fixed stochiometry of the interacting molecules, in contrast with the unspecific association due to dielectric enrichment.

Conclusions

Although the polarity of a pure solvent can be described reasonably accurately by its dielectric constant functions $\varphi(D)$ or $f(D)$, the very concept of polarity needs to be redefined for solvent mixtures. The "polarity" can no longer be seen as an intrinsic property of the mixture, independent of the presence of any solute. A distinction must be made between the solute-independent bulk polarity and the solute-determined local polarity which results from the general effect described as dielectric enrichment, to which other effects such as specific associations (e.g. H-bonding) may be superimposed. Polarity-dependent molecular properties of the solute will then be determined by this local polarity.

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