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Aromatic solvent effect on the rotational isomerism in 2-hydroxy-5-methyl-3-nitroacetophenone

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ABSTRACT: The internal rotation of the hydroxyl group in 2-hydroxy-5-methyl-3-nitroacetophenone (**I**) is associated with the transformation of the O—H$\cdots$O$_2$N bond (weakly polar **Ib** conformer) into the O—H$\cdots$O=C bond (strongly polar **Ib** conformer). The standard Gibbs energy, ΔG°, for the **Ia** $\rightleftharpoons$ **Ib** conformational equilibrium was estimated in benzene and its 10 alkyl derivatives using dipole moment measurements and infrared spectroscopy. The parent Onsager–Böttcher model for the continuum–homogeneous dielectric medium completely fails to predict the dependence of ΔG° on the relative permittivity, ε, of the solvent. The size of the solvent molecules seems to be the important factor qualifying the conformer–solvent interaction. The continuum–heterogeneous model of two concentric dielectric continua with local and bulk relative permittivities and the mean spherical approximation (MSA) approach allow consideration of this factor in the series of the aromatic solvents investigated. In addition to these two models, a satisfactory description of the solvents' influence is achieved in terms of the correlation of ΔG° with the dipolarity/polarizabilty parameter π^* of the solvents.

KEYWORDS: intramolecular hydrogen bonds; conformational equilibrium; dipole moments; aromatic solvents; two-dielectric continua; mean spherical approximation

INTRODUCTION

It has been noted in previous studies[1–4] on conformational equilibria that benzene and, to a lesser extent, toluene behave as if their relative permittivities were distinctly higher than the bulk value of ~2.3. A value of $\varepsilon = 7.5$ has been proposed for benzene to explain its influence on various conformational phenomena.[3,4] It is interesting that mesitylene (1,3,5-trimethylbenzene) and *tert*-butylbenzene exert a nearly normal effect, following their bulk ε. A similar influence of benzene and its alkyl derivatives has been observed on the proton transfer equilibria in hydrogen-bonded complexes formed between phenols and triethylamine.[5] Again, benzene is effectively much more polar than mesitylene, which is isodielectric with it. The specificity of aromatic solvents also reveals itself in NMR spectroscopy, where the proton signals of the dipolar solutes in aromatic solvents are shifted upfield in comparison with their position in a magnetically isotropic solvent such as tetrachloromethane.[6–8] The phenomenon of aromatic solvent-induced shift (ASIS) has been investigated in numerous cases. The most accepted approach to explain the ASIS is based on the dipolar site of the solute–solvent cluster model.[6] The aromatic shift is believed to be connected with site factors and a solvent parameter. The former depend on the size of the solvent molecules and their intrinsic properties (e.g. molecular dipolarity and polarizability, electron donor–acceptor ability). For the series of alkylbenzenes, the size effect is directly related to the concentration of benzene rings in the neighbourhood of the solute.[6] Moreover, the aromatic solvents (or cosolvents) lower the activation barrier much strongly than could result from the dielectric models.[9] The high catalytic ability of aromatic compounds has been attributed to interactions involving multipoles and to London's forces.[9]

In a previous study,[10] we investigated the solvent effect on the rotational isomerism in 2-hydroxy-5-methyl-3-nitroacetophenone (Scheme 1). This particular isomerism is connected with the transformation of two intramolecular hydrogen bonds and drastic changes in the dipole moments of both conformers[10] [$\mu(\mathbf{Ia}) = 1.41$ D and $\mu(\mathbf{Ib}) = 6.60$ D]. Generally, the position of the **Ia** $\rightleftharpoons$ **Ib** equilibrium is controlled by the solvent dipolarity. However, also in this case the behaviour of benzene is more similar to that of 1-chlorobutane ($\varepsilon = 7.138$) than to the almost isodielectric with it tetrachloromethane ($\varepsilon = 2.228$).

In order to gain more information on the abnormal influence of aromatic solvents on this equilibrium, we determined the effective dipole moment of **I** in many alkylated benzenes and also cyclohexene and tetrachloroethylene for comparison. Additionally, the infrared

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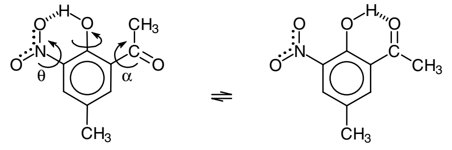

Ia **Ib**

Scheme 1. Conformational equilibrium in 2-hydroxy-5-methyl-3-nitroacetophenone

spectra in the range of the stretching vibration of the C=O group in **I** in the same set of solvents were measured. Both methods allow quantitative determination of the equilibrium constant and the corresponding standard Gibbs energy change, ΔG°. The effect of the solvent on ΔG° will be discussed on the basis of two parameters of the solvent: relative permittivity and molecular size. For descriptive purposes we chose a model of two dielectric solvent layers and a model applying the mean spherical approximation (MSA) approach, which indirectly or directly permit the inclusion of the size effect of the solvent molecules. Finally, to analyse the solvent dependence of ΔG°, we also consider empirical scales of solvent polarity. The Kamlet–Taft dipolarity/polarizability parameter π^* was determined for the solvents investigated and then used in the correlation analysis.

EXPERIMENTAL

The electric dipole moment (μ) was determined by a method described previously.[11] To evaluate the molar dipole polarization of the solute, we used Onsager's local field model[12] and the previously derived expression[11]

$$P = \frac{\left(2\varepsilon_1 + n_1^2\right)\left(\varepsilon_1 - n_1^2\right)M_1}{\varepsilon_1\left(n_1^2 + 2\right)^2 d_1} \times \left(\frac{\alpha\varepsilon_1 - \gamma n_1^2}{\varepsilon_1 - n_1^2} + \frac{2\alpha\varepsilon_1 + \gamma n_1^2}{2\varepsilon_1 + n_1^2} - \frac{2\gamma n_1^2}{n_1^2 + 2} - \alpha - \beta + \frac{M_2}{M_1}\right) \tag{1a}$$

where ε, d and n are relative permittivity, density and refractive index, respectively, and M is the molecular mass. The coefficients α, β and γ are defined as follows:

$$\alpha\varepsilon_1 = \left(\frac{\mathrm{d}\varepsilon_{12}}{\mathrm{d}x_2}\right)_{X_2\to 0}; \beta d_1 = \left(\frac{\mathrm{d}d_{12}}{\mathrm{d}x_2}\right)_{X_2\to 0}; \gamma n_1^2 = \left(\frac{\mathrm{d}n_{12}^2}{\mathrm{d}x_2}\right)_{X_2\to 0} \tag{1b}$$

The subscripts 1, 2 and 12 refer to the solvent, solute and solution, respectively; x_2 is the molar fraction of the solute. The range of x_2 used in the dipolar measurements was between 1×10^{-3} and 5×10^{-3}. The dipole moment of **I** at 25 °C was calculated according to $\mu = 0.21986\sqrt{P}$. The average of the absolute deviations from their mean did not exceed 0.03 D. The effective dipole moment of **I** can be expressed as $\langle\mu^2\rangle = \mu_a^2 x_a + \mu_b^2 x_b$, where x_a and x_b are the molar fractions of both conformers in equilibrium. The values of μ_a and μ_b were computed on the basis of vectorial addition of the dipole moments of the parent components (nitrobenzene, acetophenone, phenol and toluene) assuming the theoretical [DFT/B3LYP6–31G + (d,p)] structures of both conformers.[10] The μ_a and μ_b values were 1.41 and 6.60 D, respectively. Having obtained x_a and x_b, the standard Gibbs energy was estimated from the relation $\Delta G^\circ(\mu) = -\mathrm{RT}\ln(x_\mathrm{b}/x_\mathrm{a})$. The $\Delta G^\circ(\mu)$ values were estimated with an accuracy of $\pm 0.08\,\mathrm{kJ\,mol^{-1}}$. The infrared spectra were recorded on a Nicolet 205FT-IR spectrophotometer with a resolution of $1\,\mathrm{cm^{-1}}$ in KBr cells. The molar concentration (c) of **I** was in the range 0.01–0.05 M. The spectra shown in Fig. 1 were normalised in such a way that the product cl was kept constant. The spectroscopic standard Gibbs energy was estimated from the relation $\Delta G^\circ(\mathrm{IR}) = -\mathrm{RT}\ln(A_\mathrm{b}\varepsilon_\mathrm{a}/A_\mathrm{a}\varepsilon_\mathrm{b})$. The $\varepsilon_\mathrm{a}/\varepsilon_\mathrm{b}$ ratio adopted in all solvents was calculated by the DFT method and was equal to 0.59.[10]

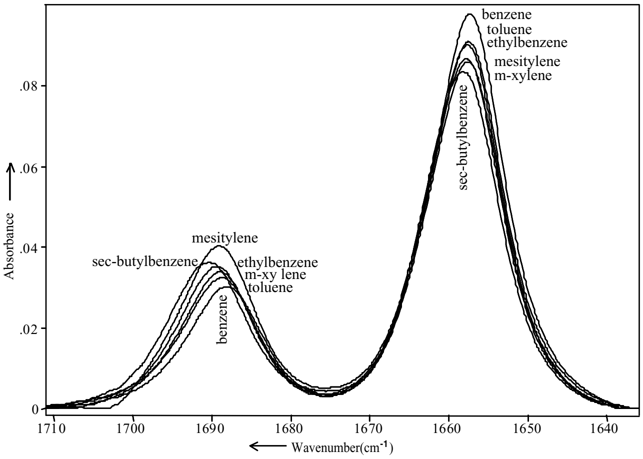

Figure 1. Infrared spectra in the ν(C=O)region of **I** in selected aromatic solvents

The π^* values for the solvents under investigation were defined, following previous procedures,[13–16] as

$$\pi^* = \frac{\nu(\mathrm{s}) - \nu(\mathrm{C_6H_{12}})}{\nu(\mathrm{DMSO}) - \nu(\mathrm{C_6H_{12}})} \tag{2}$$

where ν(s) is the wavenumber of the maximum of the indicator band. Cyclohexane and DMSO were used as references by taking $\pi^*(\mathrm{C_6H_{12}}) = 0$ and $\pi^*(\mathrm{DMSO}) = 1$ by definition. 4-Methoxynitrobenzene and 4-dimethylaminonitrobenzene were used as indicators. Thus the average values of π^* were estimated (see Table 2) and applied in the correlation analysis. The UV–visible spectra were recorded on a Cary 1 spectrophotometer.

2-Hydroxy-5-methyl-3-nitroacetophenone (Aldrich, 99%), 4-methoxynitrobenzene (Aldrich, 97%) and 4-dimethylaminonitrobenzene (Lancaster, 98%) were

Table 1. Dipole moments of 2-hydroxy-5-methyl-3-nitroacetophenone in a different solvents

Solvent	$\alpha\varepsilon_1$	β	γn_1^2	μ (D)
Benzene	43.846	0.7689	0.4757	5.56
Toluene	35.106	0.7416	0.6789	5.36
p-Xylene	28.281	0.5897	0.4826	5.26
m-Xylene	29.533	0.6401	0.5754	5.29
o-Xylene	32.689	0.6650	0.6526	5.39
Ethylbenzene	30.912	0.6463	0.5998	5.38
Mesitylene	24.144	0.5673	0.3835	5.14
Isopropylbenzene	25.570	0.5032	0.4097	5.26
n-Butylbenzene	21.861	0.5470	0.5310	5.14
sec-Butylbenzene	22.919	0.4675	0.4030	5.24
tert-Butylbenzene	22.653	0.3773	0.2486	5.24
Cyclohexene	25.046	0.8016	0.6755	4.58
Tetrachloroethylene	26.948	0.2628	0.4552	4.65

used as received. All solvents were purified by standard methods[17] and were dried by sodium or 4 Å molecular sieves.

RESULTS AND DISCUSSION

The dipole moments and coefficients in Eqn (1a) for **I** in the aromatic solvents and in cyclohexene and tetrachloroethylene are given in Table 1.

Figure 1 shows the IR spectra in the ν(C=O) region for **I** in selected solvents.

Two very well separated bands correspond to the two conformers with the hydrogen-bonded C=O group (**Ib**, the lower wavenumber band) and the free C=O group (**Ia**, the higher wavenumber band). Both the dipolar and infrared data prove the **Ia** $\rightleftharpoons$ **Ib** conformational equilibrium to be evidently dependent on the solvent. The standard Gibbs energies corresponding to this equilibrium are given in Table 2.

Since the ΔG° values obtained by both methods are close, their average value (see Table 2) will be used for further discussion. The exception is tetrachloroethylene, in which the ΔG°(IR) value is markedly higher than that obtained from the dipole moment. The lack of infrared data in cyclohexene is due to its strong absorption in the region 1690–1635 cm^{-1}. In Table 2, the macroscopic and molecular parameters of the solvents are also given. The dependence of ΔG° on the solvent can now be discussed quantitatively. Keeping in mind the significant differences in the dipole moments of the two conformers, it seems that dipolar interactions are those controlling the position of the **Ia** $\rightleftharpoons$ **Ib** equilibrium in the solution. Therefore, in the first attempt to describe the solvent effect on ΔG°, the Onsager–Böttcher parent continuum–homogeneous dielectric model will be explored.

Onsager–Böttcher (OB) model

According to this model, the dipolar contribution to the standard Gibbs energy is given by[12,18–21]

$$\Delta G^\circ(\mathrm{OB}) = -N_\mathrm{A}\frac{\mu_\mathrm{b}^2 - \mu_\mathrm{a}^2}{a^3}\frac{f(\varepsilon)}{1 - 2\frac{\alpha}{a^3}f(\varepsilon)} \qquad (3)$$

where $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ and the α/a^3 ratio is estimated as equal to 0.32.[10] The radius of the spherical solvent cavity a has been assessed previously, using the apparent molar volume of **I** in different solvents, as equal to 3.92 Å.[10] Figure 2 shows the dependence of ΔG° on the reaction field factor $f(\varepsilon)/[1 - 2\alpha f(\varepsilon)/a^3]$.

The lack of correlation indicates that relative permittivity is not the sole parameter determining the magnitude of the solvation effect. On the other hand, the comparison shown in Table 2 of ΔG° in cyclohexene and tetrachloroethylene with (isodielectric to them) benzene, *p*-xylene

Table 2. Selected parameters of the aromatic solvents and the standard Gibbs energy values of the **Ia** $\rightleftharpoons$ **Ib** equilibrium

Solvent	ε_1	r_s (Å)	π^*	$\Delta G^\circ(\mu)$[a]	ΔG°(IR)[a]	ΔG°[a]
Benzene	2.274	3.28	0.56	−2.05	−1.71	−1.88
Toluene	2.376	3.49	0.52	−1.46	−1.22	−1.34
p-Xylene	2.268	3.66	0.39	−1.19	−0.83	−1.01
m-Xylene	2.360	3.66	0.40	−1.27	−0.97	−1.12
o-Xylene	2.556	3.63	0.54	−1.54(5)	−1.17	−1.36
Ethylbenzene	2.406	3.65	0.43	−1.51	−0.97	−1.24
Mesitylene	2.291	3.81	0.37	−0.88	−0.69	−0.78(5)
Isopropylbenzene	2.373	3.82	0.38	−1.19	−0.77	−0.98
n-Butylbenzene	2.351	3.96	0.39	−0.88	−0.65	−0.76(5)
sec-Butylbenzene	2.402	3.96	0.35	−1.14	−0.72(5)	−0.93
tert-Butylbenzene	2.359	3.95	0.36	−1.14	−0.68	−0.91
Cyclohexene	2.204(5)	—	0.14	0.43	—	0.43
Tetrachloroethylene	2.276	—	0.28[c]	0.28	1.14	0.71
Cyclohexane	2.016	—	0	1.96[b]	1.83[b]	1.89(5)

[a] Values are given in kJ mol^{-1}.
[b] Values taken from Ref. 10.
[c] Value from Ref. 14.

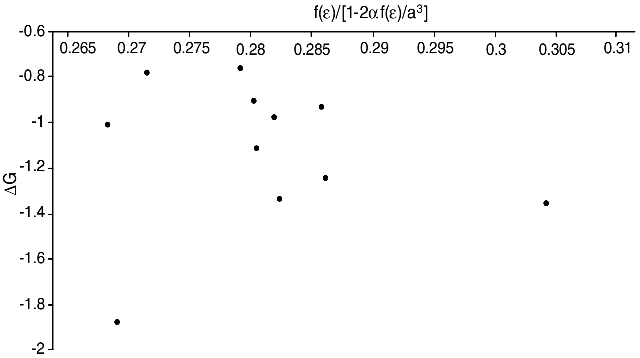

Figure 2. Dependence of the standard Gibbs energy, ΔG°, for the **Ia** $\rightleftharpoons$ **Ib** equilibrium in aromatic solvents on the Onsager–Böttcher reaction field factor

and mesitylene would confirm that aromatic solvents are effectively more polar than non-aromatic ones. Even a superficial glance at Table 2 and Fig. 1 would suggest that the size of the molecule of a solvent is, besides its relative permittivity, an important factor in the conformer–solvent interaction. That is why we address our attention to these modifications of the original Onsager–Böttcher model, which directly or indirectly makes allowance for the size of solvent molecules.

Beveridge–Schnuelle (BS) model of two-dielectric continua

If the solvent molecules interact locally with the dipolar sites of the solute (or with its overall dipole moment), then the nearest region of the solute will be characterised by local relative permittivity. Owing to an at least partial loss of rotational freedom by the solvent molecules, the first sphere of solvation (the cybotactic region) has a lower permittivity than the bulk value. A simple model of the spatial variation in relative permittivity around the spherical cavity with the centrally located solute dipole was given by Beveridge and Schnuelle.[22] The spherical cavity is surrounded by two concentric continua (see Fig. 3), with a local relative permittivity ε_l and a bulk ε. In fact, this model assumes that the dipolar interaction can be partitioned into two contributions, arising from the short-range (local orientational) interaction ($\Delta G_l{}^\circ$) and the long-range interaction with the macroscopic (bulk) dielectric medium ($\Delta G_b{}^\circ$). The BS model, neglecting the molecularity of the medium, is still a continuum one and thus cannot evaluate the magnitude of the local interaction. However, it does allow us to simulate the decrease in ε and, which is important, makes it possible to relate the thickness of the first solvation sphere with the size of the solvent molecules. According to this model, the dipolar Gibbs energy is now given by[22–24]

$$\Delta G^\circ(\mathrm{BS}) = -N_\mathrm{A}(\mu_\mathrm{b}^2 - \mu_\mathrm{a}^2)\frac{f(\varepsilon, \varepsilon_l, a, b)}{1 - 2\frac{\alpha}{a^3}f(\varepsilon, \varepsilon_l, a, b)} \quad (4a)$$

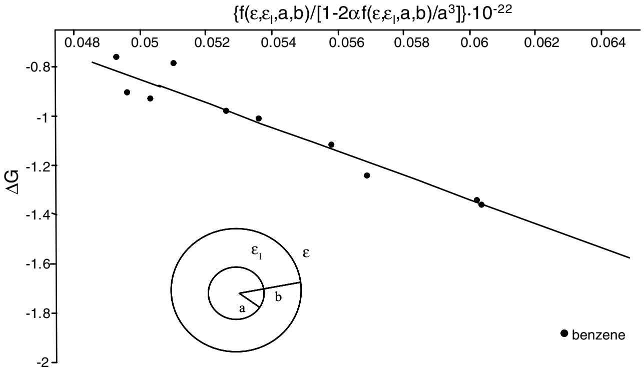

Figure 3. Dependence of the standard Gibbs energy, ΔG°, for the **Ia** $\rightleftharpoons$ **Ib** equilibrium in aromatic solvents on the Beveridge–Schnuelle reaction field factor

Two terms contribute to the reaction field factor $f(\varepsilon, \varepsilon_l, a, b)$:

$$f(\varepsilon,\ \varepsilon_l,\ a,\ b) = f_1(\varepsilon,\ \varepsilon_l,\ a) + f_2(\varepsilon,\ \varepsilon_l,\ a,\ b) \quad (4b)$$

where

$$f_1(\varepsilon,\ \varepsilon_l, a) = \frac{(\varepsilon_\mathrm{a} - 1)}{(2\varepsilon_\mathrm{a} + 1)a^3} \quad (4c)$$

and

$$f_2(\varepsilon, \varepsilon_l, a, b) = \frac{(\varepsilon_\mathrm{b} - 1)}{(2\varepsilon_\mathrm{b} + 1)b^3}\left(1 - \frac{1 - \varepsilon_\mathrm{a}}{2\varepsilon_\mathrm{a} + 1}\right) \quad (4d)$$

The second term mostly depends on the interaction between the dipole and the bulk of the solvent. Its magnitude is determined not only by ε, but also by the thickness $(b - a)$ of the spherical layer.

The permittivities ε_b and ε_a appearing in Eqns (4c) and (4d) are defined as

$$\varepsilon_\mathrm{b} = \frac{\varepsilon}{\varepsilon_l} \quad (4e)$$

and

$$\varepsilon_\mathrm{a} = \varepsilon_l\left[1 + \frac{2(1 - \varepsilon_l)(1 - \varepsilon_\mathrm{b})a^3}{(2\varepsilon_\mathrm{b} + 1)b^3}\right]^{-1} \quad (4f)$$

If $\varepsilon_l = \varepsilon$, then $\varepsilon_\mathrm{a} = \varepsilon$ and the BS model turns into the parent OB model. The model discussed needs parameterisation. The number of solvent molecules in the first solvation sphere cannot be too high, so in our simulations we accepted the thickness $(b–a)$ to be equal to the radius of the solvent molecule (see Table 2). We also assume that $\varepsilon_l = 1$.

Figure 3 shows that, excluding benzene, a good linear dependence of ΔG° on $f(\varepsilon, \varepsilon_l, a, b)$ is obtained. The appropriate equation for all the aromatic solvents is

$$\Delta G^\circ(\mathrm{BS}) = 2.36(\pm 0.43) - 63.49(\pm 7.87)f(\varepsilon, \varepsilon_l, a, b)(n = 11, r = 0.94) \quad (5a)$$

where n is the number of solvents and r is the correlation coefficient. If the data point for benzene is omitted, then one obtains

$$\Delta G^{\circ}(\mathrm{BS}) = 1.63(\pm 0.26) - 49.48(\pm 4.83) f(\varepsilon, \varepsilon_1, a, b)\ (n = 10,\ r = 0.96) \tag{5b}$$

The slope of the line, equal to 49.48 kJ mol^{-1}, is twice as large as the theoretical value of 25.1 kJ mol^{-1}. Moreover, the intercept is distinctly lower than the Gibbs energy of 8.50 kJ mol^{-1} yielded by the DFT/B3LYP6–31G + (d,p) method.[10] These discrepancies should be ascribed to the local interactions, represented by the $\Delta G_1{}^{\circ}$ term. This seems to be approximately constant in the case of the alkylbenzenes, whereas for benzene the $\Delta G_1{}^{\circ}$ energy is about 0.4 kJ mol^{-1} more negative.

Mean spherical approximation model (MSA)

In this model, a hard sphere of the dipolar solute of radius r embedded in a fluid consisting of hard polarizable spheres of radius R is considered.[25–27] The dipolar part of the standard Gibbs energy is now a more complicated function of the relative permittivity, r and R, but is still accessible in its analytical form:[26]

$$\Delta G^{\circ}(\mathrm{MSA}) = -N_A \frac{(\mu_b^2 - \mu_a^2)}{r^3} \cdot \frac{f(x,u)}{1 - 2\frac{\alpha}{a^3} f(x,u)} \tag{6a}$$

where

$$f(x,u) = \frac{\varepsilon - 1}{2ux^3\left(\frac{1-u}{1-2u}\right)^3 + 2\varepsilon[1 + (1-2u)x]^3 + \left(1 + \frac{1-u}{1-2u}x\right)^3} \tag{6b}$$

In Eqn (6b), $x = R/r$ and $u = 3\xi/(1 + 4\xi)$. The parameter ξ appears in the MSA theory for the pure solvent and is related to ε by the following expression:

$$\varepsilon = \frac{(1+4\xi)^2(1+\xi)^4}{(1-2\xi)^6} \tag{6c}$$

The two extreme cases of Eqn (6b) can be considered. First, when R goes to zero, then $f(x, u)$ receives the Onsager $(\varepsilon–1)/(2\varepsilon + 1)$ factor and Eqn (6a) becomes identical with Eqn (3). Second, the limit of $f(x, u)$ is 0.5, as in the two previous models. It is obvious that MSA suffers from a shortcoming similar to the Onsager–Böttcher model in assuming the structure of the solvent near the solute dipole to be identical with that of a pure, hard-sphere fluid. On the other hand, contrary to the continuum approach, this model considers the molecular nature of the solvent. In a simulation of the relation ΔG° vs $f(x, u)$, the solvent radii were calculated from the molar volumes of pure solvents. We also assumed that ξ is related to the macroscopic relative permittivity ε. The r value was applied identical with $a = 3.92$ Å [see Eqns (3) and (4)]. The dependence of ΔG° on $f(x, u)$ is presented in Fig. 4.

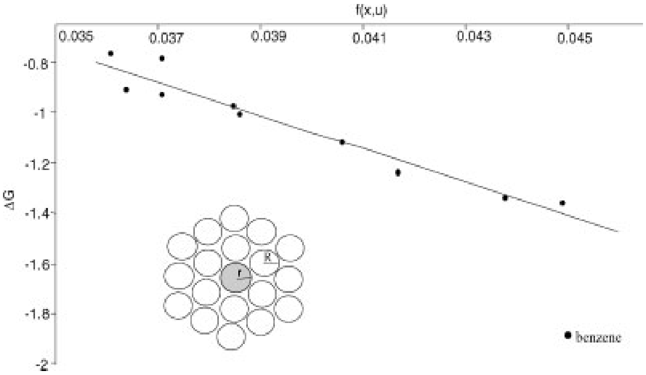

Figure 4. Dependence of the standard Gibbs energy, ΔG°, for the **Ia** $\rightleftharpoons$ **Ib** equilibrium in aromatic solvents on the MSA factor $f(x, u)$

As can be seen, this model also describes fairly well the sequence of the solvent changes in ΔG°. The linear relations are now:

$$\Delta G^{\circ}(\mathrm{MSA}) = 2.34(\pm 0.52) - 86.66(\pm 13.06) f(x,u)\ (n = 11, r = 0.91) \tag{7a}$$

and

$$\Delta G^{\circ}(\mathrm{MSA}) = 1.57(\pm 0.24) - 66.30(\pm 5.96) f(x,u)\ (n = 10, r = 0.97) \tag{7b}$$

The experimental slope is again twice as large as the calculated value of 41.6 kJ mol^{-1} and the point for benzene drops off the line for the alkylbenzenes by ca. 0.5 kJ mol^{-1}. The local isomer–solvent interaction, which seems to be responsible for these discrepancies, depends on several molecular properties, such as dipole and quadrupole moments, molecular polarizability and its anisotropy, electron donor–acceptor ability and size and shape of a molecule and is therefore hard to model. This is why for the description of the solvent effect on the **Ia** $\rightleftharpoons$ **Ib** equilibrium the parameter of dipolarity/polarizability π^* of the solvent was also included.

Correlation with the π^* parameter

The dipolarity/polarizability parameter π^* is believed to describe the electrostatic and dispersive solute–solvent interactions. It also includes all structural effects occurring in the cybotactic region. The values of π^* for many aromatic solvents are known.[13–16] However, to obtain a

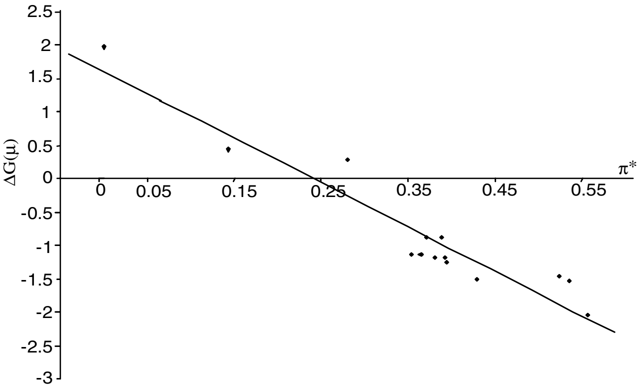

Figure 5. Correlation between ΔG° of the **Ia** $\rightleftharpoons$ **Ib** equilibrium and the π* parameter of the solvent

coherent scale for all the solvents that we tested, we determined it independently using 4-methoxynitrobenzene and 4-dimethylaminonitrobenzene as the solvatochromic probes. The average values of π* are shown in Table 2. In Fig. 5, the correlation of ΔG° with π* is shown, and also data on cyclohexane,[10] cyclohexene and tetrachloroethylene. All the correlated ΔG° values were determined by the dipolar method (see Table 2 and Ref. 10).

The equation of the straight line is now

$$\Delta G^\circ(\pi^*) = 1.59(\pm 0.25) - 6.62(\pm 0.62)\pi^* \quad (n = 14,\ r = 0.95) \tag{8}$$

A good relationship between the standard Gibbs energies and the π* parameters originates mainly from the structural similarity of the probe and the investigated compounds. The parameter π*, estimated for the gaseous phase, equals -1.06 ± 0.10.[28] From Eqn (8), one obtains a ΔG° value for the **Ia** $\rightleftharpoons$ **Ib** equilibrium in the gaseous phase of 8.61 kJ mol^{-1}. Hence the extrapolated Gibbs energy is in excellent, surely not coincidental, agreement with the theoretical value of 8.50 kJ mol^{-1}.[10]

CONCLUSION

Singularity of the effect of benzene and its alkyl derivatives on **Ia** $\rightleftharpoons$ **Ib** conformational equilibrium results from the presence of local orientation ordering of the solvent microstructure, which is mainly due to the dipolar interaction. Such an effect is important in non-polar (or slightly polar) aromatic solvents, whose molecules have a strong anisotropy of polarizability and explains their effective polarity. Owing to the steric effect, the local interaction in benzene is more effective (by ~0.5 kJ mol^{-1}) than in other alkylbenzenes. On the other hand, the local ordering causes the long-range electrostatic interaction (effect of the reaction field) to be weakened. Moreover, the magnitude of the long-range interaction depends on the size of the solvent molecules. The models of two solvation spheres and the MSA predict this dependence in the series of alkylbenzenes very well. Finally, the correlation of ΔG° with the parameter of the solvent dipolarity/polarizability π* allowed us to describe the influence of all the solvents tested, predicting surprisingly well the standard Gibbs energy of the **Ia** $\rightleftharpoons$ **Ib** equilibrium in the gaseous phase.

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