The apparent dipole moments and molar volumes of 1,3-benzothiazole and some derivatives, in nonpolar solvents

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The apparent molecular polarizations at infinite dilution, $P_{2\infty}$, molecular refractions, R_D, dipole moments, μ_2, polarizabilities, α, and partial molar volumes, $V^0_{2,m}$, of 1,3-benzothiazole and some derivatives at position two or three, have been determined from relative permittivity, density and refractive index measurements in *n*-hexane or 1,4-dioxane solutions at 25 °C.

The R_D and $V^0_{2,m}$ values correlate well for all substances studied, independently of the solvent used. The $P_{2\infty}$ values appear to be slightly dependent on the solvent showing the presence of specific interactions as hydrogen bond.

The apparent relative permittivity, ε_2', and the refraction index extrapolated at the IR region, n_{IR}, have been estimated for all solutes. In the case of 1,3-benzothiazole and its 2-methyl derivative, these results have been compared with the relative permittivities measured at 25 °C at low and high frequencies, respectively, by the Cole–Cole dynamic method, showing a good agreement.

The apparent dipole moments and their changes with the corresponding substituent group have been determined by three different methods. From the measurement of dipole moment it has been unambiguously established that the tautomeric equilibrium between 2-mercapto-1,3-benzothiazole and 2-thioxo-3*H*-1,3-benzothiazole is strongly displaced to the latter. Changes in the apparent molar solution volumes and apparent molar polarizations of the solutes in the considered solvents are qualitatively discussed.

Comparison between pK_a values reported in the literature and the corresponding $\sqrt{\mu}$ values for free base benzothiazole derivatives have been carried out as well as the appropriate qualitative discussion.

Introduction

Substituted derivatives of benzothiazole show several interesting biological properties, for instance antimicrobial[1,2] or antimycobacterial,[3] and are also used in the preparation of dyes,[4] and organic synthesis of the thermostable polymers[5] and herbicides acting as photosynthesis inhibitors.[6] The dielectric behaviour of substituted 1,3-benzothiazoles (see Fig. 1) in solution is strongly conditioned by the fact that the axis of dipole moment is not aligned with the axis of maximum polarizability. In fact, the knowledge of the measure of the dielectric polarisation data is useful to understand the very important role that the molecular interactions play in the studied relationships between chemical structure and biological activity.[7] Several spectroscopic studies of acid–base equilibria by Forlani *et al.*[8–10] and Zabala *et al.*[11] have been undertaken in the last few years, and a good correlation between the pK_a values obtained there and the dipole moments determined in this paper has been found.

The present paper is concerned with a set of some derivatives of: **(1)** 1,3-benzothiazole substituted on position two or three (see Fig. 1): **(2)** 2-methyl-1,3-benzothiazole, **(3)** 2-amino-1,3-benzothiozole, **(4)** 2-mercapto-1,3-benzothiazole (or its tautomer **(5)** 2-thioxo-3*H*-1,3-benzothiazole), **(6)** 2-(methylmercapto)-1,3-benzothiazole (or its isomer **(7)** 2-thioxo-3-methyl-1,3-benzothiazole), and **(8)** 2-(4-aminophenyl)-6-methyl-1,3-benzothiazole. The dipole moment, as well as the polarizability, together with the apparent molar volume, the molar refraction for the D_{II} sodium line and the apparent molar polarization have been measured in solutions of nonpolar solvents *n*-hexane (for compounds **1** and **2**) or 1,4-dioxane (compounds **3** to **8**) at 25 °C.

Dipole moments of solutes **1** and **4** to **7** have been determined by Oseper *et al.*[12] Vasil'eva *et al.*[13] and Gur'yanova *et al,*[14] in benzene solution. In some of these cases, the molar refractions were deduced from that corresponding to benzothiazole by applying the additivity rule for atomic refractions.

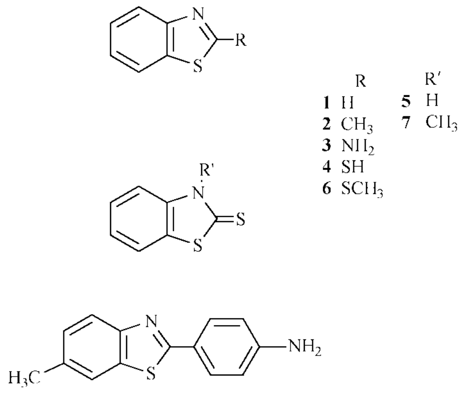

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Fig. 1 Solutes studied: **(1)** 1,3-benzothiazole; **(2)** 2-methyl-1,3-benzothiazole; **(3)** 2-amino-1,3-benzothiazole; **(4)** 2-mercapto-1,3-benzothiazole or its tautomer; **(5)** 2-thioxo-3*H*-1,3-benzothiazole; **(6)** 2-(methylmercapto)-1,3-benzothiazole; **(7)** 2-thioxo-3-methyl-1,3-benzothiazole; and **(8)** 2-(4-aminophenyl)-6-methyl-1,3-benzothiazole.

1,4-Dioxane was selected as a solvent because of the moderate solubility of the **3** to **8** solutes, and the nonpolar solvent behaviour, despite the possibility of specific interactions like hydrogen bonds or charge transfer complexes occurring.

Experimental

n-Hexane from Scharlau and 1,4-dioxane p.a. grade from Merck were used after two fractional distillations. The solvents were dried over sodium wire before use. The measured densities were 0.6551 ± 0.0004 and 1.0285 ± 0.0005 g cm^{-3} for *n*-hexane and 1,4-dioxane respectively; also, the refractive indices were measured as 1.3722 ± 0.0005 and 1.4201 ± 0.0007 and the relative permittivities were 1.8518 ± 0.0006 and 2.2087 ± 0.0006 for *n*-hexane and 1,4-dioxane, respectively. All of these measurements were made at 25.00 ± 0.05 °C. Moreover, the standard errors of the different properties mentioned above were determined by using four replicated measurements of each one and its average values.

Except for solute **3** which was supplied by Sigma, all solutes were supplied by Aldrich Chemie. The compounds **1** and **2**, being liquids, were purified by two fractional distillations over potassium hydroxide under reduced pressure under a nitrogen atmosphere in order to avoid possible oxidations until colourless liquids with constant boiling points of 231 °C and 238 °C, respectively, were observed. In such cases of pure liquids, the values of relative permittivity, ε' and dielectric loss, ε'', were measured in the 200 MHz to 20 GHz frequency range in a HP 8510C Network Analyzer by using a Dielectric Probe Kit and the software HP 85070A. From the symmetric distribution of the relaxation times, an observed Cole–Cole[15] empirical relation has been applied and the parameter values ε_0, 5.90 and 4.52 and ε_∞, 3.58 and 3.62, respectively, have been deduced.

The other solid solutes, **3** to **8**, were purified by a standard fractional sublimation method[16] with a vacuum oil trap, until no further change in their melting points was observed. The last melting points observed in a Büchi 535 apparatus by a standard method are listed in Table 1 together with ones reported by other authors.[17–19] A good agreement has been found.

Relative permittivities were measured by a W.T.W. Model DM 01 dipolometer (frequency 2 MHz) by using a thermostated DFL1 precalibrated cell. Refractive indices were measured for the D_{II} sodium line (5896 Å) on a Pulfrich type refractometer from Bellingham and Stanley. A quick flow of water was conducted through the heating block supporting the prism in order to maintain the temperature constant within ±0.05 °C. The liquid solution was preheated before performing the measurements. The densities were determined using a pycnometer with a graduated neck which was previously calibrated with high purity water.

NMR-proton spectra of a sample of 2-mercapto-1,3-benzothiazole **(4)** or its tautomer **5** using $CDCl_3$ as a solvent, were carried out on a 400 MHz NMR spectrometer under suitable experimental conditions.

Table 1 Melting point values of benzothiazoles (in °C)

Compound	Reference	This work
2-Amino-1,3-benzothiazole	132[a]	128.0 ± 0.1
2-Mercapto-1,3-benzothiazole	180.2–181.7[b]	179.5 ± 0.1
2-(Methylmercapto)-1,3-benzothiazole	—	43.0 ± 0.1
2-Thioxo-3-methyl-1,3-benzothiazole	87.5–89[b]	88.4 ± 0.1
2-(4-Aminophenyl)-6-methyl-1,3-benzothiazole	193–195[c]	193.0 ± 0.1

[a] See ref. 17. [b] See ref. 18. [c] See ref. 19.

IR spectra in CCl_4 (Merck Uvasol grade) were taken with a Bomem MB100 FTIR spectrophotometer for qualitative purposes.

Method

In the following relations, the variables with subscript 1 refer to solvent and those with subscript 2 correspond to solute. The double subindex 12 denotes the magnitudes corresponding to the solution.

The least-squares method of the linear regression with several observations on y at each x has been carried out on a Macintosh computer using the standard SPSS v4.01 to obtain the appropriate standard error parameters. In fact, four observations on the variable y_{12} have been performed at eight weight fractions, ω_2. All calibrations needed were statistically handled with a similar procedure.

In all cases linear relations have been found for both the relative permittivity, ε_{12}, and the specific volumes, v_{12}, as well as the square of the refractive indices n_{12}^2 of the solutions against their weight fractions ω_2. Eqns. (1)–(3) were used.

$$\varepsilon_{12} = \varepsilon_1 + \alpha\omega_2 \tag{1}$$

$$v_{12} = v_1 + \beta\omega_2 \tag{2}$$

$$n_{12}^2 = n_1^2 + \gamma\omega_2 \tag{3}$$

The fitted parameters α, β and γ calculated as limiting values of $(\partial\varepsilon_{12}/\partial\omega_2)_{\omega_2=0}$, $(\partial v_{12}/\partial\omega_2)_{\omega_2=0}$ and $(\partial n_{12}^2/\partial\omega_2)_{\omega_2=0}$, respectively, are listed in Table 2 with their corresponding standard error calculations.

The apparent molar polarization at infinite dilution, $P_{2\infty}$, was calculated from the Halverstadt and Kumler[20] eqn. (4), where M_2 is the molecular weight of solute.

$$P_{2\infty} = M_2[3\alpha v_1/(\varepsilon_1 + 2)^2 + (v_1 + \beta)(\varepsilon_1 - 1)/(\varepsilon_1 + 2)] \tag{4}$$

The apparent molar refraction of the solute, R_D, appears to be constant in the concentration range studied, therefore we have used its mean value derived from the Few and Smith[21] equation as given in eqn. (5), with r_{12_i} being the specific

$$R_D = M_2\left[r_1 + \sum_{i=1}^{j}(r_{12_i} - r_1)\Big/\sum_{i=1}^{j}\omega_{2_i}\right] \tag{5}$$

refraction of the i^{th} solution. The polarizability of solutes, α_{a+e}, can now be derived from R_D by means of relation (6),[22]

$$\alpha_{a+e} = \frac{3R_D}{4\pi N_A} \tag{6}$$

with N_A being the Avogadro constant. The $P_{2\infty}$ and R_D parameters with their corresponding standard errors are listed in Table 2.

The apparent dipole moments of dissolved 1,3-benzothiazoles, μ_2, have been calculated by the application of three different methods. According to the method first used by Lange[23]

Table 2 Polarization data in *n*-hexane (Hx) or 1,4-dioxane (D)

Compound	Solvent	α	β	γ	$(d\varepsilon_{12}/dY_2)_{Y_2=0}$	$P_{2\infty}^{a}$	R_D^{a}	$V_{2,m}^{0}$ [a]
1,3-Benzothiazole	Hx	1.7 ± 0.1[b]	−0.78 ± 0.01	0.48 ± 0.01	3.46 ± 0.06	94 ± 3	41.2 ± 0.5	100 ± 3
2-Methyl-1,3-benzothiazole	Hx	1.04 ± 0.02	−0.77 ± 0.01	0.50 ± 0.02	2.03 ± 0.01	72.8 ± 0.7	47 ± 1	113 ± 2
2-Amino-1,3-benzothiazole	D	3.6 ± 0.6	−0.21 ± 0.06	0.6 ± 0.1	4.1 ± 0.4	111 ± 9	45 ± 2	113 ± 9
2-Mercapto-1,3-benzothiazole	D	20.5 ± 0.6	−0.30 ± 0.01	0.90 ± 0.03	30 ± 3	603 ± 10	55 ± 1	112 ± 1
2-(Methylmercapto)-1,3-benzothiazole	D	2.2 ± 0.3	−0.23 ± 0.01	0.67 ± 0.04	2.9 ± 0.2	105 ± 5	55.7 ± 0.9	134 ± 2
2-Thioxo-3-methyl-1,3-benzothiazole	D	17.76 ± 0.05	−0.08 ± 0.01	0.89 ± 0.03	18.5 ± 0.4	582 ± 2	70 ± 2	161 ± 2
2-(4-Aminophenyl)-6-methyl-1,3-benzothiazole	D	6.0 ± 0.3	−0.11 ± 0.04	0.96 ± 0.06	6.7 ± 0.5	298 ± 7	94 ± 2	207 ± 11

[a] In cm^3 mol^{-1}. [b] Errors are taken as the standard error.

Table 3 Apparent relative permittivity and refraction index at IR region data of benzothiazoles in *n*-hexane (Hx) or 1,4-dioxane (D)

Compound	Solvent	ε'_2	n_{2IR}
1,3-Benzothiazole	Hx	5.29 ± 0.14	1.75 ± 0.04
2-Methyl-1,3-benzothiazole	Hx	3.88 ± 0.02	1.77 ± 0.04
2-Amino-1,3-benzothiazole	D	6.4 ± 0.6	1.73 ± 0.11
2-Mercapto-1,3-benzothiazole	D	31.8 ± 3.4	1.97 ± 0.03
2-(Methylmercapto)-1,3-benzothiazole	D	5.1 ± 0.3	1.76 ± 0.03
2-Thioxo-3-methyl-1,3-benzothiazole	D	21.6 ± 0.4	1.81 ± 0.03
2-(4-Aminophenyl)-6-methyl-1,3-benzothiazole	D	8.9 ± 0.6	1.86 ± 0.07

Errors are taken as the standard error.

Table 4 Dipole moment values[a] and their standard errors of benzothiazoles in *n*-hexane (Hx) or 1,4-dioxane (D)

		μ_2			
Compound	Solvent	eqn. (7)	eqn. (8) or eqn. (9)	eqn. (10)	values in benzene at 25 °C
1,3-Benzothiazole	Hx	1.60 ± 0.09	1.61 ± 0.08	1.5 ± 0.2	1.46[b]
2-Methyl-1,3-benzothiazole	Hx	1.12 ± 0.06	1.11 ± 0.04	1.0 ± 0.2	
2-Amino-1,3-benzothiazole	D	1.8 ± 0.3	1.8 ± 0.3	1.8 ± 0.5	
2-Mercapto-1,3-benzothiazole	D	5.2 ± 0.1	5.3 ± 0.1	4.8 ± 0.3	4.03,[b] 4.67,[c] 4.02[d]
2-(Methylmercapto)-1,3-benzothiazole	D	1.6 ± 0.2	1.6 ± 0.2	1.5 ± 0.2	1.43,[b] 1.33[e]
2-Thioxo-3-methyl-1,3-benzothiazole	D	5.00 ± 0.02	5.10 ± 0.01	4.9 ± 0.3	4.84[b]
2-(4-Aminophenyl)-6-methyl-1,3-benzothiazole	D	3.1 ± 0.1	3.2 ± 0.1	3.0 ± 0.5	

[a] Dipole moments values in Debyes. [b] See ref. 12. [c] See ref. 13. [d] In ref. 13 at 40 °C. [e] See ref. 14.

and applied to binary solutions at constant temperature by Errera[24] and Williams *et al.*,[25] we have used relation (7), where

$$\mu_2 = 0.0128 \times 10^{-18} \sqrt{(P_{2\infty} - R_D)T} \qquad (7)$$

$P_{2\infty}$ and R_D are calculated as mentioned before at absolute temperature T and the apparent dipole moment is expressed in units of Debye.

In the second approach eqn. (8) is derived from the

$$\langle\mu_2^2\rangle = (27kT/4\pi N_A)[M_2/\rho_1(\varepsilon_1 + 2)^2](\alpha - \gamma) \qquad (8)$$

Guggenheim–Smith[26–28] method which can only be applied for the solvents where $\varepsilon_1 \approx n_1^2$, as occurs in *n*-hexane. However, a modified expression of eqn. (8) for a 1,4-dioxane solution has been applied[26–28] as in eqn. (9), with k being the Boltzmann

$$\langle\mu_2^2\rangle = (27kT/4\pi N_A)[M_2/\rho_1(\varepsilon_1 + 2)(n_1^2 + 2)](\alpha - \gamma) \qquad (9)$$

constant, N_A the Avogadro constant, ρ_1 the density, ε_1 the relative permittivity, and n_1 the refractive index of pure solvent. The parameters α and γ have previously been defined.

Finally, for the third method a more complex expression is obtained from the Onsager–Kirkwood liquid theory,[29–31] eqn. (10), where $V_{2,m}$ is the apparent molar volume of solute

$$\langle\mu_2^2\rangle = [27kTV_{2,m}/4\pi N_A(2\varepsilon_1 + 1)^2][(2\varepsilon_1 + n_{1IR}^2)/(n_{2IR}^2 + 2)]^2 \{[(2\varepsilon_1^2 + 1)/3\varepsilon_1^2](d\varepsilon_{12}/dY_2)_0 - (2\varepsilon_1 + 1)^2(n_{2IR}^2 - \varepsilon_1)/3\varepsilon_1(2\varepsilon_1 + n_{2IR}^2)\} \qquad (10)$$

(in cm^3 mol^{-1}) and n_{iIR} is the refractive index of solvent ($i = 1$) or solute ($i = 2$) at IR frequency that has been derived from the value of the magnitude measured at the sodium D_{II} line frequency, according to the Cauchy relationship (11).[32]

$$[(n^2 - 1)/(n^2 + 2)]_{IR} = (1/1.007)[(n^2 - 1)/(n^2 + 2)]_{D_{II}} \qquad (11)$$

The partial molar volume $V^0_{2,m}$ of the solute at infinite dilution can be derived from the plots of the molar volumes of solution $V_{12,m}$ against their molar fractions f_2 which in all cases showed no deviation from linearity. Eqn. (12) was then employed.[33] The corresponding values of $V^0_{2,m}$ are listed in the last column of Table 2.

$$V_{12,m} = V^0_{1,m} + (V^0_{2,m} - V^0_{1,m})f_2 \qquad (12)$$

The slope $(d\varepsilon_{12}/dY_2)_{Y_2=0}$ listed in Table 2 is calculated as a limiting value at infinite dilution from the relationship between the relative permittivity of the solution and the volume fraction Y_2 of the solute in the concentration range C_2 (mol L^{-1}) studied. Eqn. (13) was used,[31] with the apparent molar volume

$$\varepsilon_{12} = \varepsilon_1 + [(d\varepsilon_{12}/dY_2)_{Y_2=0}V_{2,m}]C_2 \qquad (13)$$

$V_{2,m}$ used in eqns. (9) and (12) being the value of the partial molar volume of solute $V^0_{2,m}$ obtained by eqn. (11).

From the parameters ε_1 and $(d\varepsilon_{12}/dY_2)_{Y_2=0}$ the apparent relative permittivity of solutes ε_2' was estimated[31] from eqn. (14).

$$\varepsilon_2' = \varepsilon_1 + (d\varepsilon_{12}/dY_2)_{Y_2=0} \qquad (14)$$

The apparent relative permittivity of solutes as well as the corresponding ones for the extrapolated refractive indices, n_{2IR}, at IR frequency and their respective estimated standard errors are listed in Table 3.

The results obtained from the three methods for the dipole moments and their corresponding standard errors are listed in Table 4. Some values obtained by other authors in different conditions are also shown for comparative purposes.

Results and discussion

The parameters α, β, γ and $(d\varepsilon_{12}/dY_2)_{Y_2=0}$ derived from the appropriate equations, along with $P_{2\infty}$, R_D and $V^0_{2,m}$ obtained from them, as well as their corresponding standard error estimations measured in *n*-hexane or 1,4-dioxane are listed in Table 2.

In Fig. 2(a) the parameters R_D and $V^0_{2,m}$ are shown for all solutes and a good correlation has been found. The apparent molar volumes of solutes **2**, **3** and **4** (or its tautomer **5**) are the same within the error range and they appear not to be affected by the solvent interaction effect, in spite of the different nature

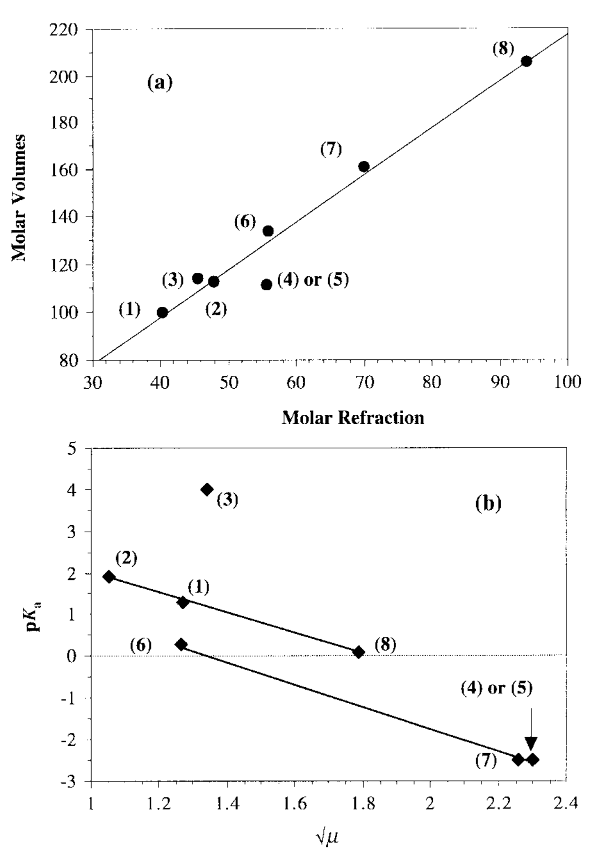

Fig. 2 (a) Correlation between molar volumes, $V^0_{2,m}$, in cm^3 mol^{-1} and molar refraction, R_D in cm^3 mol^{-1} of solutes at 25 °C. (b) Relation between the pK_a values determined by other authors and the $\sqrt{\mu}$ determined in this paper for the thiazole derivatives studied.

of the substituent groups. The -CH$_3$, -NH$_2$ and -SH (or =S) groups added to position two of the thiazole ring do not cause a significant change in the volume size of the solute. However, the molar refraction of solute **4** or its tautomer **5** is higher than those corresponding to the solute **2** and **3**. This indicates that the major contribution to R_D is from the species with high polarizability, as is the case for the tautomer **5**, since the presence of the C=S bond leads to deviation from linearity (the C=S bond is more polarizable than the single bonds: C–SH (**4**), C–CH$_3$ (**2**) and C–NH$_2$ (**3**) as can be seen.

If we compare the rise of the $V^0_{2,m}$ values on going from solute **1** to solute **2**, and solute **4** (or **5** to solute **6**), and so on, the value can be seen to increase in the case of solute **6** with respect to **4** although, in both cases, only one -H group has been substituted by the -CH$_3$ group. This can be explained by the different positions which have been taken into account in order to compare the same magnitude, provided that in the former case it was the position two at the heterocyclic ring being in the latter at the chain of the sulfur atom.

Furthermore, to compare the $V^0_{2,m}$ and R_D values going from solute **6** to its isomer **7** the rise is higher than expected given that no new extra atoms or groups have been added. This can be explained if we assume that two simultaneous effects must be taken into account in the behaviour of these isomers. The first is due to geometric considerations, since the volume increase when a -CH$_3$ group is added to the N3 position is higher than that corresponding to addition to position two of the thiazole ring. The second effect is the normal increase of the molar polarizability caused by the C=S bond which was previously discussed for the tautomer **5** being in this case magnified by the presence of the inductive (+I) group-CH$_3$ at the N3 position, and furthermore, the absence of any tautomeric equilibrium contribution to the C=S bond in the isomer **7**.

Finally, in the case of 2-(4-aminophenyl)-6-methyl-1,3-benzothiazole, the above mentioned properties, R_D and $V^0_{2,m}$, appear to be well correlated and fitted from standard physical-organic mesomeric effect[34] considerations.

The apparent relative permittivity, ε', and the refraction index extrapolated at IR region n_{2IR} for all solutes studied, have been estimated at 25 °C using eqns. (14) and (11) respectively and are listed in Table 3. In the case of the liquid solutes **1** and **2**, both relative permittivity and dielectric loss have been measured by the Cole–Cole dynamic method,[35,36] and the values determined at low and high frequency compared with the corresponding ones listed in Table 3, ($\varepsilon' = \varepsilon'_0$ and $(n_{2IR})^2 = \varepsilon''$). In all cases no more than 15% deviation has been observed.

From the ε' values listed in Table 3 two kinds of solutes can be distinguished. The former, which has $\varepsilon' < 10$, and can be typified by the presence of a C=N bond in the thiazole ring, and the latter, with $\varepsilon' > 20$, which is characterized by the presence of the thioxo group, C=S, at position two of the heterocyclic thiazole ring. Therefore, the high ε' value of the solute involves the presence of some substituent group and/or a bond order that confers a high value for the apparent molar polarization, $P_{2\infty}$, of the solute, as can be seen in Table 2.

The apparent dipole moment values derived from all solutes in *n*-hexane or 1,4-dioxane are listed in Table 4, together with the corresponding ones found by other authors. A good agreement has been found with the three methods employed, although our values are slightly higher than those obtained by other authors. This is probably due to the fact that those authors used the additivity rule for the atomic refractions, and benzene as a solvent. Some authors[37–41] suggest that a difference between μ_2 in 1,4-dioxane and μ_2 in benzene larger than 0.10 D can be attributed to the presence of strong interaction forces such as hydrogen bonding effects. However, from the values listed in Table 4, we cannot unambiguously conclude the presence of hydrogen bonding interactions between solute and solvent because the values given by other authors are too different to be compared.

On the other hand, from the measurements of the apparent dipole moment we can explain that the tautomeric equilibrium between (**4**) 2-mercapto-1,3-benzothiazole and its tautomer (**5**) 2-thioxo-3*H*-1,3-benzothiazole is strongly displaced to the latter in 1,4-dioxane solution. Thus the μ_2 value of the former should be similar to that for 2-(methylmercapto)-1,3-benzothiazole if their electronic structures were similar, but as we can see from Table 4, the value is in fact very similar to that for the solute (**7**) 2-thioxo-3-methyl-1,3-benzothiazole, therefore confirming that the equilibrium is displaced towards the electronic structure type 2-thioxo. Two additional experiments have been carried out in order to corroborate this argument. In the first place, the IR spectra for the **4** to **7** species were taken in CCl$_4$ and one broad band at 3400 cm^{-1} was detected except for the **6** and **7** species so indicating the presence of the N–H bond type 2-thioxo. The *ab initio* calculations and the Möller–Plesset second order perturbational level corrections have been carried out for two species in equilibrium,[42] and from the results we can assert that the most stable and probable species in solution is the 2-thioxo-3*H*-1,3-benzothiazole by about 6 kJ mol^{-1}.

The correlation between the pK_a values reported by Forlani *et al.*[8–10] and Zabala *et al.*,[11] for the equilibrium $BH^+ \rightleftharpoons B + H^+$ and $\sqrt{\mu}$ for free base benzothiazole derivatives in which the protonation site is the N3 position are shown in Fig. 2(b) for qualitative and comparative purposes.

Except for the case of 2-amino-1,3-benzothiazole, we can distinguish two parallel relations between pK_a and $\sqrt{\mu}$ values which indicates that the electronic structure is involved in the acid–base mechanism for protonated 1,3-benzothiazole derivatives in the ground state. Two groups can be distinguished: one made of derivatives **1** to **2** and the solute **8**, without the sulfur atom at the position two; and the second group formed by the derivatives **4** or **5** together with the solute **6** and its isomer **7**.

The apparent disagreement observed in the case of 2-amino-1,3-benzothiazole must be attributed to the interaction mesomeric effect of the -NH_2 substituent group in the conjugated position with the reaction centre (as for 2-substituted thiazoles with respect to the N3 position). When the substituents are in a conjugated position it is commonly accepted[8] that the interaction by mesomeric effects is considered to be more important than the inductive effects. The deviation observed in Fig. 2(b) is that for the -NH_2 substituent, which is usually considered to have strong mesomeric properties, and consequently the 2-amino-1,3-benzothiazole basicity must be higher than that expected from the basicity of the other 1,3-benzothiazole derivatives, in good accordance with Forlani *et al.*[8–10] and Albert *et al.*[43,44]

Concerning the second group derivatives **4** to **7**, another good relationship between the pK_a values and $\sqrt{\mu}$ can be observed as it involves the change in the electronic effects caused by the different nature of the -R substituent in the two position. The structures of type C=S are more acidic than those of type -SCH_3 and so on. Furthermore, the close proximity in Fig. 2(b) of the correlation pK_a–$\sqrt{\mu}$ for the isomer **7** and the tautomer **5** is an additional reinforcement for unambiguously establishing that the tautomeric equilibrium between 2-mercapto-1,3-benzothiazole and 2-thioxo-3*H*-1,3-benzothiazole is strongly displaced to the latter in dioxane solution.

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