Solvent Effect on the Electronic Polarizability of Benzonitrile

Y. J. Alvarado, P. H. Labarca, N. Cubillán, E. Osorio, and A. Karam [a]

Laboratorio de Electrónica Molecular, Departamento de Química, Fac. Exp. de Ciencias, La Universidad del Zulia, Ap. 526, Grano de Oro, Módulo No. 2, Maracaibo, Venezuela
[a] Laboratorio de Polímeros, Centro de Química, IVIC, Caracas, Venezuela

Reprint requests to Dr. Y. J. A.; E-mail: yalvarado@hotmail.com

Z. Naturforsch. **58a,** 68 – 74 (2003); received September 16, 2002

In this study, the static and dynamic electronic polarizability of benzonitrile is reported. This property was determined using refraction index measurements of neat benzonitrile and CCl_4, THF, C_6H_{12} and CH_3CN diluted solutions. The real refractive index of pure benzonitrile was obtained by refractometry, FTIR transmission spectroscopy and Kramers-Krönig transform. These results indicate that the vibrational contribution to the visible refraction is very small, and the electronic polarizabilities calculated with these values agree with reported values. In binary mixtures, the polarizability of benzonitrile was obtained with the refractometric method proposed by Singer and Garito at five frequencies to obtain the dispersion curve. The local field effects were tested within the Onsager and Lorentz local field approach. The static properties in each solvent was obtained by extrapolation of the Cauchy-type dispersion curve to zero frequency, which gave a monotonic increased as a function of the squared frequency. The polarizabilities obtained in this work agree well with theoretical and experimental data, reported by other authors. The static and dynamic electronic polarizability of benzonitrile was found to be little affected by the dielectric nature of the solvent, and the electric deformability is similar to that of the benzene molecule. The effect of the replacement of the C—H group by N in 4-cyano-pyridine and benzonitrile molecules is discussed.

Key words: Benzonitrile; Polarizability; Solvent Effect.

1. Introduction

The importance of cyano-substituted aromatic compounds in molecular electronic devices and new kinds of mesogenic materials has renewed the interest in their chemical and electronic properties [1, 2]. For example, the benzonitrile (BZCN) moiety is a relevant polar group in molecules present in calamitic and linear and nonlinear optical materials [1, 3 – 5]. Several molecular properties, such dipole moment, polarizability (dynamic and static), polarizability anisotropies, and nonlinear optical properties are currently explored in benzonitrile, cyano-biphenyl, and azulene derivatives by both experimental and theoretical methods [3, 4, 6, 7]. However, intermolecular forces and solvent effects can have a large influences on these properties, and their evaluation is important to allow an adequate comparison of the optical susceptibilities of molecules and their crystals [8 – 13]. In this context we have recently reported the determination and theoretical calculation of solvent effects on the static and dynamic dipole polarizability of highly polarizable heteroaromatic compounds [14, 15].

The dynamic and static polarizability of pure benzonitrile, obtained by refractometric measurements, is reported in the literature. Unfortunately, these values in different solvents are scarce for this reason, the role of intermolecular interactions and the frequency dependence of the polarizability of benzonitrile in solution are unknown [6, 16 – 20]. Based in this, and continuing with our interest in this field, we report in this work a detailed evaluation of the solvent effect in dynamic and static electronic polarizability of benzonitrile.

2. Theory

2.1. Electric Dipole Polarizability

The molecular dipole polarizability α is the linear response of a molecular electronic distribution to the action of an external electric field $\Im$ that induces changes in the permanent molecular dipole moment μ_e according to equation (1) [14, 15, 21].

$$\mu_e(\Im) = \mu_e(\Im = 0) + \alpha \cdot \Im + (1/2!)\beta \cdot \Im^2 + (1/3!)\gamma \cdot \Im^3 + \cdots . \quad (1)$$

Here, $\mu_e(\Im = 0)$ is the permanent dipole moment in the absence of an electric field, α is a second rank tensor that represent the dipole polarizability, and the higher order terms are the first and second hyperpolarizabilities, respectively.

In polarizability studies, the components $\alpha_{ii}(i = x,y,z)$ of the diagonalized α tensor and the associated average polarizability

$$\alpha_{\text{ave}} = \langle\alpha\rangle = \frac{1}{3}(\alpha_{ii} + \alpha_{jj} + \alpha_{kk}) \tag{2}$$

and anisotropy

$$\begin{aligned}\Delta\alpha = \{&\tfrac{1}{2}[(\alpha_{ii} - \alpha_{jj})^2 + (\alpha_{ii} - \alpha_{kk})^2 \\ &+ (\alpha_{jj} - \alpha_{kk})^2]\}^{\frac{1}{2}}\end{aligned} \tag{3}$$

are of great experimental interest.

The average dipole polarizability can be determined experimentally by means of the refractive index η of a gas according to the equation

$$\eta = 1 + \frac{2\pi\langle\alpha\rangle\sigma}{k_B T}, \tag{4}$$

where σ is the pressure. Equation (4) holds if the molecules do not interact with each other. In the condensed phase, each molecule is polarized by the external field and the field produced by surrounding molecules. The total local field F is expressed in terms of the dielectric polarization P as

$$F = E + 4\pi LP, \tag{5}$$

where L is the dimensionless Lorentz factor, which depends on the structure of the phase and equals $1/3$ for cubic and isotropic phases, giving the Lorentz local field

$$F = E + \frac{4\pi}{3}P. \tag{6}$$

The Lorenz-Lorentz equation can be derived from (6):

$$\frac{\eta^2 - 1}{\eta^2 + 2} = \frac{4\pi N\langle\alpha\rangle}{3V}, \tag{7}$$

where N is the number of molecules in the volume V. Equation (7) allows to determine polarizabilities α by measurements of the refraction index η in the off-resonance regime, and the density $\rho = N/V$ in pure compounds [14, 15]. In the resonance region the refractive index is a complex quantity defined as [22, 23]

$$\hat{\eta}(\tilde{\nu}) = \eta(\tilde{\nu}) + i\kappa(\tilde{\nu}), \tag{8}$$

where η and κ are the real and imaginary components of the refractive index, respectively. In liquids, the κ spectrum is obtained from transmission or attenuated total reflection spectra. The η spectrum is obtained from the κ spectrum through the Kramers-Krönig transform as [22, 23]

$$\eta(\tilde{\nu}_i) = \eta(0) + \frac{2}{\pi}P\int_0^\infty \frac{\tilde{\nu}\kappa(\tilde{\nu})}{\tilde{\nu}^2 - \tilde{\nu}_i^2}\,\mathrm{d}\,\tilde{\nu}, \tag{9}$$

where the second term can be split in an infrared and a UV-Visible contribution. For colorless compounds (not absorbing in the visible region) this equation is simplified to

$$\eta(\tilde{\nu}_i) = \eta(0) + A_1\tilde{\nu}_i^2 + A_2\tilde{\nu}_i^4 + \frac{2}{\pi}P\int_{IR}\frac{\tilde{\nu}\kappa(\tilde{\nu})}{\tilde{\nu}^2 - \tilde{\nu}_i^2}\,\mathrm{d}\,\tilde{\nu}, \tag{10}$$

where $\eta(0)$ and the coefficients A_1 and A_2 are obtained by a linear least squares fit of the refractive index at visible frequencies. The evaluation of the integral in the infrared region represents the contribution of infrared-active vibrational modes to the visible refractive index.

For a binary mixture, such as solvent and solute, the refractometric equation of Singer and Garito can be derived from (7), [6, 24].

$$\begin{aligned}\frac{4\pi}{3}N_A\alpha_2^e(\nu) = &\frac{3M_2}{\rho_1(\eta_1^2(\nu)+2)^2}\left(\frac{\partial\eta^2(\nu)}{\partial w}\right)_0 \\ &+ M_2\left[\frac{1}{\rho_1} + \left(\frac{\partial V}{\partial w}\right)_0\right]\frac{\eta_1^2(\nu)-1}{\eta_1^2(\nu)+2}.\end{aligned} \tag{11}$$

Another refractometric expression can be obtained by employing the Onsager [25] local field factors within the Garito and Singer approximation. This equation at the infinite dilution limit becomes [24]

$$\begin{aligned}\frac{N_A}{M_2}\alpha_2^e(\nu)\frac{\eta_1^2(\nu)(\eta_2^2(\nu)+2)}{2\eta_1^2(\nu)+\eta_2^2(\nu)} = &\frac{1}{4\pi\rho_1}\left(\frac{\partial\eta^2(\nu)}{\partial w}\right)_0 \\ &+ \frac{\eta_1^2(\nu)-1}{4\pi}\left(\frac{\partial V}{\partial w}\right)_0 + \frac{\eta_1^2(\nu)-1}{4\pi\rho_1} \\ &- \frac{\eta_1^2(\nu)-1}{4\pi\rho_1}\left[\frac{1}{3\eta_1^2(\nu)}\right]\left(\frac{\partial\eta^2(\nu)}{\partial w}\right)_0,\end{aligned} \tag{12}$$

where w is the solute weight fraction and $\eta_{(\nu)}$, $\eta_1(\nu)$ and $\eta_2(\nu)$ are the solution, solvent and solute real refraction indices at the optical frequency (ν), respectively; ρ_1 is the solution density, M_2 the solute molecular weight, V the specific volume of the solution, N_A

Avogadro's number, and $\alpha_2^e(\nu)$ the electronic contribution from the mean dynamic polarizability of a solute molecule.

In (11) and (12) it is assumed that the solute and solvent are not interacting and that the molecular polarizations are additive. The electronic dynamic polarizability, obtained from (11) and (12), is treated as a frequency-dependent quantity and calculated at different wavelengths. The long-wavelength limit is obtained by an extrapolation to zero frequency of the dynamic mean polarizability $\alpha_2^e(\nu)$. This relationship is referred to as the Cauchy-type dispersion curve, and it gives the behavior of the dispersion of the polarizability in field frequency terms. This curve allows to extrapolate the electronic part only, and the limit value corresponds to the static dipole polarizability. Contributions from infrared-active vibrational modes (vibrational polarizability) are not considered here [26, 27].

3. Methodology

Benzonitrile (99%) was purchased from Merck and used without further purification, although it was kept over molecular sieves to ensure dryness. The solvents were rigorously dried, fractionally distilled by standard methods and stored over molecular sieves.

3.1. Neat Benzonitrile

The infrared spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer with a high sensitivity pyroelectric detector (DLATGS) at nominal resolution of 2 cm^{-1}. A triangular apodization function was used in all cases. The absorbance spectra of benzonitrile were measured in KBr cells with fixed path lengths between 15 and 25 μm, as determined by fringe patterns of empty cells by HYPER-IR software from SHIMADZU corporation. The decadic linear absorption coefficient, $K(\nu)$, of pure benzonitrile was obtained using the Beer-Lambert law. The imaginary refractive indexes, $\kappa(\nu)$, were calculated by the relation $2.303K(\nu) = 4\pi\nu\kappa(\nu)$. The real refractive index spectrum, $\eta(\nu)$, was calculated from the $\kappa(\nu)$ spectrum by the Kramers-Krönig transform between 4000 and 400 cm^{-1}, with a program implemented by Bertie et al. [28, 29]. In order to calculate adequate values of the real refractive index we used this program to correct the imaginary refractive index with an iterative procedure involving Fresnel's equations. Kramers-Krönig relations require a static value of the refractive index. We employed a refractive index of 1.507930, obtained in this work from extrapolation to zero-frequency of the experimental refractometric dynamic refractive index [22].

The dynamical refractive index of benzonitrile in the visible regime obtained by this method does not take in account the infrared contribution. In other words, these values represent the contribution of electronic absorption only. These results were used in the determination of the electronic polarizability of pure benzonitrile and binary solutions.

3.2. Benzonitrile in Solution

The average electronic polarizability dispersion curves of benzonitrile were experimentally determined using refractometric techniques. The refractive index, η, of both, solvent and solutions, were measured with Bellingham and Stanley high resolution ABBE refractometers 60/LR and 60/LR with CCD camera at 20 °C ($\pm$0.1 °C). Spectral lamps of sodium, mercury and cadmium in the wavelength range of 435.8 – 643.8 nm were employed. The density ρ was determined by measuring the period of oscillation of a vibrating sample cell with a sample volume of 1 ml on a DMA-5000 Anton-Paar densitymeter. For each solvent, the values of refractive index at optical frequency (ν) and density, obtained in this work were found to agree with the values previously reported in [14, 15, 21]. A series of solutions of benzonitrile in various solvents was prepared. Their UV-visible absorbance spectra were obtained on a Shimadzu spectrophotometer (model UV-1201). A 1 cm quartz cuvette was used as the sample cell. The weight-fraction concentration *w* ranged from $6.50 \cdot 10^{-3}$ to $8.01 \cdot 10^{-2}$ in all cases. Excellent linear relationships were found for the specific volumes and the square of the refractive indexes of the solutions against their weight-fractions *w* at each frequency of the applied electric field. The reproducibility for the various slopes of the concentration dependence for these data is very high and the uncertainties in dynamic mean electronic polarizabilities obtained in this work are between 1.5% – 2.3%.

4. Results and Discussion

In order to explore the absorption of benzonitrile in the various solvents and avoid measurements in the anomalous dispersion region, UV-VIS spectra between 200 nm and 450 nm were measured, previous to refractometric measurements. The lowest absorption wavelength of this molecule is 290 nm. With this result,

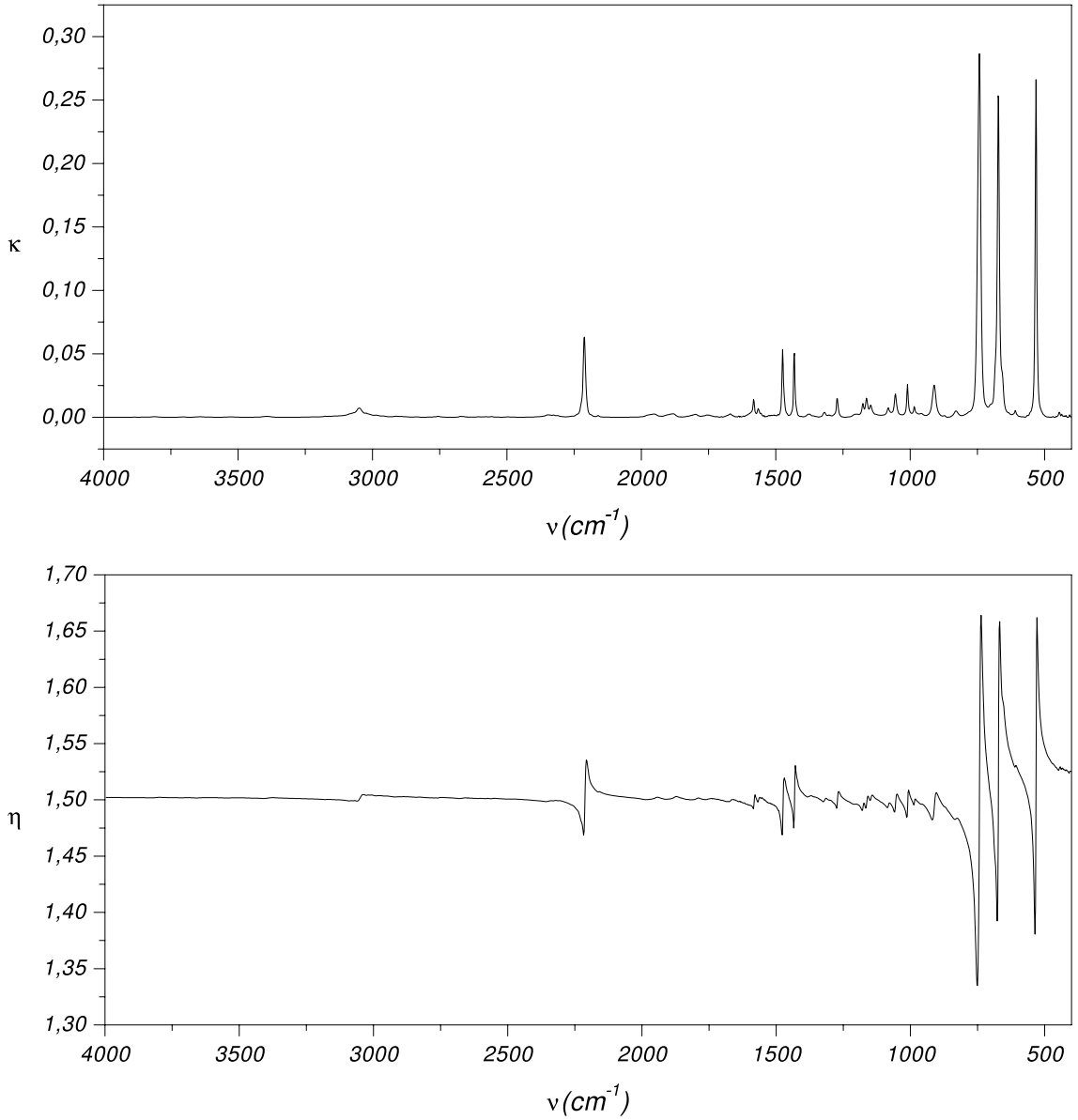

Fig. 1. a) Imaginary refractive index, $\kappa(\nu)$, spectrum of pure benzonitrile (top) and b) Real refractive index, $\eta(\nu)$, spectrum.

the dispersion of dipole polarizability of benzonitrile in off-resonance region was studied.

The dynamic and static real refractive indices of pure benzonitrile, obtained by refractometry, and the respective real refractive indices, corrected for the vibrational contribution, are shown in Table 1. These values were obtained from the *k* spectrum (see Fig. 1a) and the Kramers-Krönig transform evaluated between 4000 and 400 cm^{-1}. The corresponding η spectrum is presented in the Figure 1b. It is noteworthy that the infrared contribution to the visible refractive index is small and is lower that determined for other derivatives of benzene [22].

In fact, the average electronic polarizability values obtained from these results and (7) at both, the

Table 1. Real refractive indices and polarizabilities in the visible region and their corrected values for the contribution of infrared absorption of neat benzonitrile.

$\nu(\mathrm{cm}^{-1})$	η [a]	η_{corr} [b]	$\alpha_2^e(\nu)\cdot 10^{23}$ esu
2.294631	1.553190	1.555396	1.299
1.966182	1.537764	1.537794	1.267
1.831166	1.532265	1.532299	1.255
1.696065	1.527567	1.527607	1.246
			1.245[c]
			1.253[d]
1.553277	1.523240	1.523288	1.237
0	1.502950	1.503060	1.197
			1.196[e]
			1.308[f]

[a] $T = 20$ °C, Refractometric method. [b] $T = 20$ °C, Spectroscopic method [28, 29]. [c] [17]. [d] [16]. [e] [20]. [f] MNDO method, [30].

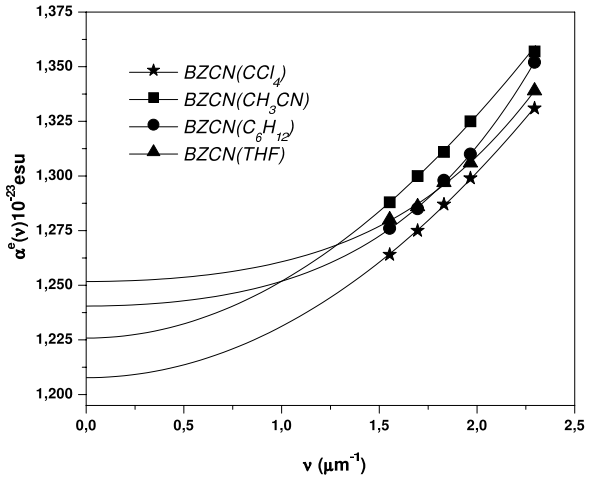

Fig. 2. Experimental dispersion curves of benzonitrile solved in CCl_4, THF, C_6H_{12} and CH_3CN obtained using the Lorentz local field.

sodium D line (1.696065 $\mu\mathrm{m}^{-1}$) and zero frequency agree with previous experimental values reported for pure benzonitrile [16, 17, 20]. However, our static polarizability is overestimated by about 10% if compared with the reported theoretical semi-empirical values [30].

Frequency dependent experimental results of relevant terms in (11) and (12) of Carbon Tetrachloride (CCl_4), Cyclohexane (C_6H_{12}), Tetrahydrofuran (THF) and Acetonitrile (ACN) solutions are reported in Tables 2, 3, 4, and 5, respectively. Corresponding Cauchy-Type dispersion curves of the dipole polarizability of benzonitrile dissolved in the solvents are shown in Figure 2.

Table 2. Results of least squares fits to the concentration dependence of the refraction index, density of solutions and electronic polarizability of benzonitrile in CCl_4.

$\nu(\mathrm{cm}^{-1})$	$(\partial\eta^2/\partial w)_0$ [a]	$\eta_1(\nu)$ [a]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu[b]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu[c]
2.294631	0.365	1.472384	1.331	1.332
1.966182	0.328	1.464933	1.299	1.301
1.831166	0.314	1.462519	1.287	1.288
1.696065	0.310	1.460000	1.275	1.276
			1.230[d]	
			1.197[e]	
1.553277	0.302	1.457779	1.264	1.265
0.00			1.207	1.208

[a] $T = 20 \pm 0.1$ °C, $(\partial\nu/\partial w)_0 = 0.3590$, $\rho_1(\mathrm{g/cm}^3) = 1.593995$. [b] (11), using Lorentz local field. [c] (12), using Onsager local field. [d] Deduced from molar Kerr constant in CCl_4 and Molar Refraction (neat liquid), [20]. [e] Deduced from molar Kerr constant in CCl_4, light scattering (neat liquid) and Molar Refraction (neat liquid), [16].

Table 3. Results of least squares fits to the concentration dependence of the refraction index, density of solutions and electronic polarizability of benzonitrile in cyclohexane.

$\nu(\mathrm{cm}^{-1})$	$(\partial\eta^2/\partial w)_0$ [a]	$\eta_1(\nu)$ [a]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu[b]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu[c]
2.294631	0.275	1.436762	1.352	1.346
1.966182	0.243	1.430139	1.310	1.304
1.831166	0.235	1.427955	1.297	1.292
1.696065	0.226	1.426041	1.285	1.279
1.553277	0.220	1.424079	1.276	1.271
0.00			1.240	1.240

[a] $T = 20 \pm 0.1$ °C, $(\partial\nu/\partial w)_0 = -0.2662$, $\rho_1(\mathrm{g/cm}^3) = 0.778565$. [b] (11), using Lorentz local field. [c] (12), using Onsager local field.

Table 4. Results of least squares fits to the concentration dependence of the refraction index, density of solutions and electronic polarizability of benzonitrile in THF.

$\nu(\mathrm{cm}^{-1})$	$(\partial\eta^2/\partial w)_0$ [a]	$\eta_1(\nu)$ [a]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu[b]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu[c]
2.294631	0.408	1.416648	1.339	1.336
1.966182	0.380	1.411548	1.306	1.304
1.831166	0.373	1.409541	1.297	1.295
1.696065	0.364	1.407681	1.286	1.285
1.553277	0.360	1.406159	1.280	1.279
0.00			1.252	1.243

[a] $T = 20 \pm 0.1$ °C, $(\partial\nu/\partial w)_0 = -0.16212$, $\rho_1(\mathrm{g/cm}^3) = 0.889569$. [b] (11), using Lorentz local field. [c] (12), using Onsager local field.

The dynamic dipole polarizability, obtained with (11) and the Lorentz local field, shows a monotonic increase with the frequency ν, giving a normal dispersion behavior for the electronic polarizability of ben-

Table 5. Results of least squares fits to the concentration dependence of the refraction index, density of solutions and electronic polarizability of benzonitrile in CH_3CN.

$\nu(\mathrm{cm}^{-1})$	$(\partial\eta^2/\partial w)_0$ [a]	$\eta_1(\nu)$ [a]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu [b]	$\alpha_2^e(\nu)$ $\cdot 10^{23}$ esu [c]
2.294631	0.453	1.351053	1.357	1.341
1.966182	0.430	1.346648	1.325	1.311
1.831166	0.419	1.345126	1.311	1.297
1.696065	0.412	1.343688	1.300	1.287
1.553277	0.403	1.342087	1.288	1.275
0.00			1.230	1.220
			1.164 [d]	

[a] $T = 20 \pm 0.1$ °C, $\partial\nu/\partial w = -0.2915$, $\rho_1(\mathrm{g/cm}^3) = 0.781983$. [b] (11), using Lorentz local field. [c] (12), using Onsager local field. [d] 4-cyano-pyridine in acetonitrile solution [36].

zonitrile in all solvents (see Figure 2). From this relationship, the zero-frequency extrapolation gives the values of $1.207 \cdot 10^{-23}$, $1.240 \cdot 10^{-23}$, $1.252 \cdot 10^{-23}$ and $1.230 \cdot 10^{-23}$ esu for the static electronic polarizability of benzonitrile in CCl_4, C_6H_{12}, THF and ACN solutions, respectively (see Tables 2 – 5). A comparison of these results with the static and dynamic values obtained from the Onsager local field approximation (12) shows that they are very close in all cases. This clearly indicates that the induced dipole moments in the benzonitrile molecule are insensitive to local field factors. It is important to notice that the static values of benzonitrile in CCl_4 and ACN are comparable to experimental value obtained for pure benzonitrile (see Table 1). However, the static dipole polarizability in THF is higher than that in pure benzonitrile and other solvents. Furthermore, dynamic value of benzonitrile in CCl_4 at the sodium D line is slightly higher than the values reported in the literature, deduced from molar Kerr constant measurements in CCl_4, light scattering and molar refraction in pure benzonitrile [16, 20].

Figure 2 shows that the electronic polarizabilities of benzonitrile in both the static and optical regime are very close in these aprotic solvents, and that no relationship with the polarity of the solvent exists. Furthermore, the total electric deformabilities, seen as the variation of polarizability at 435,8 nm ($1.966182\ \mu\mathrm{m}^{-1}$) with respect to the static value of benzonitrile, are, 7.1% in THF, 9.1% in C_6H_{12}, and 10.3% in CCl_4 and ACN. With the exception of value for THF solution, these results indicate that the electric properties of benzonitrile are only slightly affected by the dielectric nature of medium. In fact, these values are similar to those for pure benzene and cyclohexane solution [31, 32]. This suggests that the resonance interaction between the π-electrons of the phenyl and cyano group is very small. In contrast, optical anisotropy studies suggest a somewhat larger electronic interaction [4,16]. However Suppan et al., in a study about for solvent influence on the electronic absorption spectra of benzonitrile have suggested that the lowest vacant π^* orbitals of CN have a quite high energy, and in consequence the charge-transfer character of electronic states of benzonitrile can be negligible in comparison with other derivatives of benzene [33]. In addition, Neusser and Siglow reported that there is no detectable charge-transfer state in the cyano group of benzonitrile from the measurements of the Stark shift caused by an electric field up to 700 V/cm [34]. However, theoretically Ishida et al.reported a strong charge polarization in the electronic state of excited benzonitrile by the solvent effect [35].

A preliminary comparative study was carried out between benzonitrile and 4-Cyano-Pyridine (see Table 5) in order to analyze the effect of substitution of the CH group by a nitrogen atom on the electronic polarizability [36]. The static average dipole polarizability of 4-Cyano-Pyridine in acetonitrile solution amounts to $1.164 \cdot 10^{-23}$esu [36], which is by 6% lower than our experimental static value for benzonitrile. This polarizability diminution agrees excellent by with the theoretical results available for cyclic and bicyclic azines [37 – 39]. However, the variation of the polarizability at 435.8 nm with respect to the static value for 4CN-Pyridine is 13.4%, whereas for benzonitrile the corresponding variation is 10.3% [36]. This suggests a bigger contribution of the delocalized π electrons in this molecule than in benzonitrile. Further studies in this context are being performed in our laboratory.

5. Conclusions

According to the refractive index and polarizability values obtained, the infrared contribution to the visible dispersion refraction is very small in neat benzonitrile. The electronic dipole polarizability of benzonitrile is similar in all solvents used in this work, and these values are not significantly influenced by the local field. In general, our values agree well with those reported in the literature. The linear polarization of benzonitrile is only slightly affected by the dielectric nature of the solvent, and its electric deformability is close to that of benzene. The polarizability benzonitrile was found to be higher than that of 4-Cyano-Pyridine, whereas the

electric deformability of the latter compound is higher than of benzonitrile in acetonitrile solvent. Our preliminary analysis of the solvent effect and of the substitution of the CH group by a nitrogen atom on the electronic polarizability of benzonitrile can be qualitatively understood in terms of little electronic conjugation between the aromatic ring and the CN group.

The results obtained in this work will serve as reference for the theoretical treatment of solvent effects on benzonitrile, which is a model molecule for several applications.

Acknowledgements

The authors thank to Fondo Nacional de Ciencia, Tecnología e Innovación (FONACIT, project: Apoyo a grupos No. G-97000593), División de Investigación (DIV-FEC-LUZ, project: FDI) and Consejo de Desarrollo Científico y Humanístico (CONDES-LUZ).

[1] S. Howard, I. Fallis, and D. Willock, Mol. Phys. **97**, 913 (1999).
[2] G. Czechowski, J. Ziolo, S. Rzoska, and M. Paluch, Z. Naturforsch. **57a**, 244 (2002).
[3] P. Navard and P. Flory, J. Chem. Soc., Faraday Trans. 1, **82**, 3367 (1986).
[4] P. Flory and P. Navard, J. Chem. Soc., Faraday Trans. 1, **82**, 3381 (1986).
[5] P. Kumar, V. Pisipati, A. Rajeswari, and S. Sreehari, Z. Naturforsch. **57a**, 184 (2002).
[6] L. Cheng, W. Tam, S. Stevenson, G. Meredith, G. Rikken, and S. Marder, J. Phys. Chem. **95**, 10631 (1991).
[7] M. Barzoukas, A. Fort, P. Boy, C. Combellas, and A. Thiebault, Chemical Physics **185**, 65 (1994).
[8] R. Cammi, B. Mennucci, and J. Tomasi, J. Phys. Chem. A **104**, 4690 (2000).
[9] C. Bosshard and G. Knöpfle, P. Prêtre, P. Günter, J. Appl. Phys. **71**, 1594 (1992).
[10] D. Matyushov and G. Voth, J. Phys. Chem. A **103**, 10981 (1999).
[11] J. Woodford, M. Pauley, and C. Wang, J. Phys. Chem. A **101**, 1989 (1997).
[12] R. Wortmann and D. Bishop, J. Chem. Phys. **108**, 1001 (1998).
[13] Y. Luo, H. Ågren and K. Mikkelsen, Chem. Phys. Lett. **275**, 145 (1997).
[14] Y. Alvarado, N. Cubillán, P. H. Labarca, A. Karam, F. Arrieta, O. Castellano, and H. Soscún, J. Phys. Org. Chem. **15**, 154 (2002).
[15] Y. J. Alvarado, H. Soscún, W. Velazco, P. H. Labarca, N. Cubillán, and J. Hernández, J. Phys. Org. Chem. **15**, 835 (2002).
[16] R. Le Fèvre, J. Orr, and G. Ritchie, J. Chem. Soc. B, 2499 (1965).
[17] R. Le Fèvre and E. Sullivan, J. Chem. Soc. B, 2873 (1954).
[18] M. Gussoni, M. Rui, and G. Zerbi, J. Mol. Struct. **447**, 163 (1998).
[19] R. Le Fèvre, Molecular Refractivity and Polarizability, Vol. 3 of Adv. Phys. Org. Chem. pp. 90, Academic Press, London 1965.
[20] C. Le Fèvre and R. Le Fèvre, J. Chem. Soc. B, 1577 (1954).
[21] H. Soscún, Y. Alvarado, J. Hernández, P. Hernández, R. Atencio, and A. Hinchliffe, J. Phys. Org. Chem. **14**, 709 (2001).
[22] J. Bertie and Z. Lan, J. Chem. Phys. **103**, 10152 (1995).
[23] C. Keefe, J. Mol. Spect. **205**, 261 (2001).
[24] K. Singer and A. Garito, J. Chem. Phys. **75**, 3572 (1981).
[25] L. Onsager, J. Amer. Chem. Soc. **58**, 1486 (1936).
[26] U. Hohm, D. Goebel, and S. Grimme, Chem. Phys. Lett. **272**, 328 (1997).
[27] D. Goebel and U. Hohm, J. Chem. Soc., Faraday Trans. **93**, 3467 (1997).
[28] J. Bertie and C. Keefe, Fres. J. Anal. Chem. **362**, 91 (1998).
[29] J. Bertie, Y. Apelblat, and C. Keefe, J. Mol. Struct. **550 – 551**, 135 (2000).
[30] H. Kagawa, A. Ichimura, N. Kamka, and K. Mori, J. Mol. Struct. (THEOCHEM), **546**, 127 (2001).
[31] A. Burnham, G. Alms, and W. Flygare, J. Chem. Phys. **63**, 3321 (1975).
[32] Y. Alvarado, P. H. Labarca, N. Cubillán, and J. Peña, unpublished data.
[33] P. Suppan, Spectrochim. Acta **24A**, 1161 (1968).
[34] K. Siglow and J. Neusser, J. Phys. Chem. A **105**, 7823 (2001).
[35] T. Ishida, F. Hirata, and S. Kato, J. Chem. Phys. **110**, 11423 (1999).
[36] Y. Alvarado, H. Soscún, and O. Castellano, unpublished data.
[37] P. Calaminici and A. Köster, J. Chem. Phys. **112**, 6301 (2000).
[38] A. Hinchliffe and H. Soscún, Asian J. Spect. **1**, 169 (1997).
[39] R. Doerksen and A. Thakkar, Int. J. Quant. Chem. **30**, 421 (1996).