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The dielectric relaxation mechanism and internal rotation in biphenyl derivatives

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Abstract. The dielectric relaxation mechanism of 2,2'- and 3,3'-dibromodiphenyl has been examined from measurements at different frequencies and temperatures. All dielectric measurements have been done on diluted solutions in p-xylene. A simple dielectric absorption band was observed in both cases. It was found that the Gouillon–Rivail model provides a good description of the dielectric relaxation mechanism.

1. Introduction

Molecular dynamics investigations, by means of dielectric relaxation measurements in molecules in which internal rotation is possible, continue to be undertaken by a number of research workers [1–9], using both theoretical and experimental approaches; however, the dielectric relaxation of molecules, for which the possibility of rotation of larger molecule fragments could occur, has so far not been extensively studied.

The theoretical calculations [10] reveal that symmetrically substituted biphenyls (figure 1) in the 3,3' position are characterised by a potential energy curve with two minima for the dihedral angles between the phenyl rings close to 40° and 140°. In the case of 2,2' derivatives with bulky substituents, it is more probable that the potential energy curve for the rotation of the phenyl rings has one broad minimum corresponding to a perpendicular arrangement of the phenyl rings; such a picture has been confirmed electrochromographically [11].

The aim of the present work is to measure the dielectric absorption of 2,2'- and 3,3'-dibromodiphenyls (DBDP) in a non-polar solvent, at four temperatures. It should be noted that the conformational aspects of adjacent aromatic systems (to which the dynamics is related) are still an object of debate among researchers using linear and non-linear dielectric methods [12, 13].

2. Experimental details

The 2,2'- and 3,3'-DBDP were synthesised in our laboratory. The p-xylene used as a solvent was dried over metallic sodium and distilled. Its purity was checked by measuring the static dielectric permittivity at 298 K. The measurements of the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric permittivity in the range of 1.8–18 GHz were

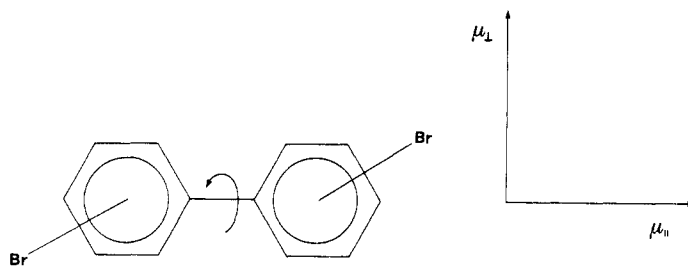


Figure 1. Symmetrically substituted biphenyls.

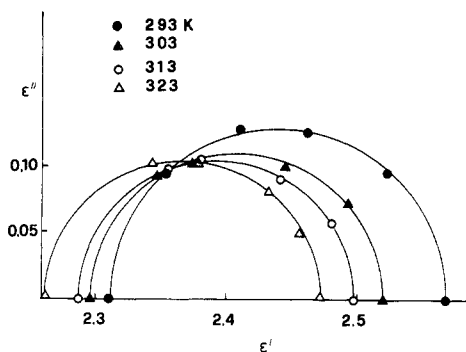


Figure 2. Cole-Cole diagrams observed for 2,2'-DBDP, in p-xylene at a weight fraction $W = 0.050$.

performed by means of a dielectrometer designed and made in our laboratory. The method used in our experiment is based on complex reflection coefficient measurements. The dielectrometer is fully controlled by a Commodore 128 microcomputer. The measuring method used has been described in our previous papers [14–16]. The static dielectric permittivity was measured at 1.59 kHz using a TESLA BM 484 semi-autobalance bridge. All measurements were made at four temperatures ($T = 293, 303, 313$ and 323 K), the temperature being controlled by means of a Unipan PID (proportional-integral-differential) programmable temperature controller with a precision of 0.01 K over the entire measurement range. The experimental error in the dielectric parameters was $\pm 0.5\%$ and $\pm 1.5\%$ for ϵ' and ϵ'' , respectively.

3. Results and discussion

The experimental results obtained from the dielectric relaxation measurements for 2,2'- and 3,3'-DBDP are shown as Cole-Cole plots in figures 2 and 3 and the parameters calculated are collected in table 1. In figure 3 ϵ_0 is the low-frequency limit of relative permittivity and ϵ_{∞} is the high-frequency limit of relative permittivity. From figures 2 and 3 one can see that in both systems the dielectric absorptions have a Debye-like pattern, which may point to the same dielectric relaxation mechanism for the molecules examined. It was also observed that the dielectric increment ($\Delta\epsilon = \epsilon_0 - \epsilon_{\infty}$), after

Table 1. Dielectric parameters observed for 2,2'- and 3,3'-DBDP in p-xylene. ϵ_0 and ϵ_∞ are, respectively, low-frequency limit of relative permittivity and high-frequency limit of relative permittivity. The activation enthalpy (in kJ mol^{-1}) was 9.02 ± 1.5 and 5.9 ± 1.5 for 2,2' and 3,3' isomers, respectively. It was calculated according to the Eyring–Kauzmann equation (3).

Isomer	T (K)	$\epsilon_{0,\text{obs}}$	$\epsilon_{\infty,\text{obs}}$	τ_{obs} (ps)
2,2'-DBDP $W = 0.050$	293	2.566	2.310	35.0
	303	2.520	2.297	29.9
	313	2.498	2.286	24.2
	323	2.471	2.256	19.6
3,3'-DBDP $W = 0.052$	293	2.544	2.323	23.6
	303	2.515	2.306	21.0
	313	2.491	2.293	19.0
	323	2.460	2.290	17.4

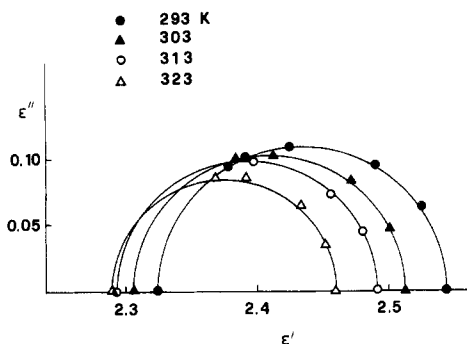


Figure 3. Cole–Cole diagrams observed for 3,3'-DBDP in p-xylene at a weight fraction $W = 0.052$.

correction for solution density variations with temperature, is linearly dependent upon the reciprocal temperature (figure 4).

In order to describe the dielectric absorption, the following equation can be used:

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + i\omega\tau) \quad (1)$$

and the dielectric relaxation times (τ) were calculated by means of the following equation:

$$\tau = \epsilon''(\omega)/(\epsilon'(\omega) - \epsilon_\infty)\omega. \quad (2)$$

In this equation, the value of ϵ_∞ has been obtained by extrapolation of the Cole–Cole semicircle to the value $\epsilon''(\omega) = 0$.

A comparison of the relaxation time for 2,2'- and 3,3'-diphenyl derivatives revealed that τ for 2,2'-DBDP exceeds that for 3,3'-DBDP. Similar results were reported by Jakusek [17] for 2,2'- and 3,3'-difluorodiphenyl in p-xylene, i.e. 20.2 and 16.8 ps at 298 K. However, the difference between τ for 3,3'-DBDP and 2,2'-DBDP is much more pronounced than in the literature [17].

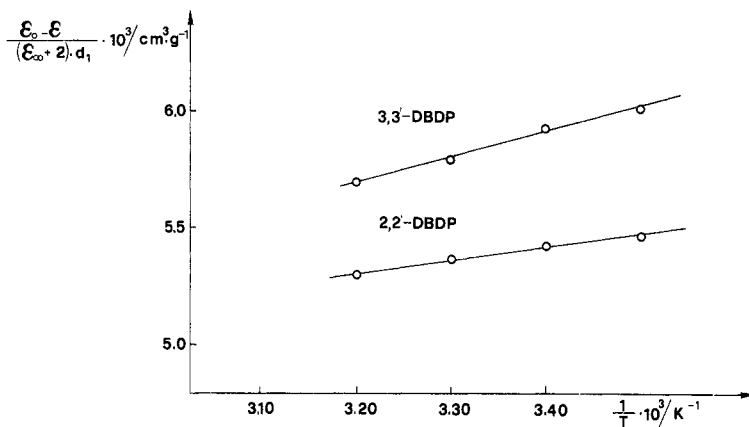


Figure 4. Dielectric increment, after correction for solution density variation with temperature, as a function of the reciprocal temperature.

The correlation between the relaxation time and energy of activation is estimated from the Eyring–Kauzman relation [18]

$$\ln(\tau T) = h/k - \Delta S_E^*/R + \Delta H_E^*/RT \quad (3)$$

where τ is the macroscopic dielectric relaxation time; h and k are, respectively, the Plank and Boltzmann constants; ΔH_E^* is the molar activation enthalpy barrier; ΔS_E^* is the corresponding entropy variation. T (temperature) is in K.

The Debye-like pattern can be observed in several situations.

(i) It is observed if we assume the presence of rigid configurations; that the reorientation of the molecules has a diffusion character and that the resultant dipole moment is located along one of the main axes of molecule.

(ii) The single relaxation time is also observed, when a molecule exists in a form of several conformers of long lifetime, and somewhat different dipole moment correlation function. It seems that the distribution of the relaxation time is not observed when their ratio is less than 3, because of the limitation in the dielectric absorption method. In practice, we observe in such a case a monodispersive character of the dielectric absorption due to a reorientation of the effective dipole moment situated in a molecule of geometry between those of the respective conformers.

(ii) If one takes into account the models of Fong [19] and Goulon–Rivail [20], the Debye-like relaxation is theoretically possible when the dipole moment may be changed in a dynamic sense, not only by molecular reorientation as a whole, but also by additional internal molecular rotation. The relaxation in such a case can be described by the following relation:

$$1/\tau = 1/\tau_{\text{or}} + 1/\tau_{\text{k}} \quad (4)$$

where τ_{or} is the correlation time corresponding to overall molecular rotation and τ_{k} is the ‘chemical relaxation time’ describing the internal rotation. The intramolecular rotation is able to modulate considerably the experimentally observed relaxation when the value of $\tau_{\text{k}} \ll \tau_{\text{or}}$. In order to analyse the situation in our systems we first estimated the main axes of inertia of the molecules and the orientation of the resultant dipole

moment about these axes. We performed the calculations on the assumption of three possible mutually oriented angles of the phenyl rings, i.e. 45, 90 and 135°, known from the electron diffraction and theoretical data. From the calculations it follows that the resultant dipole moment is not located along the main axes of the molecule. However, the value of the dipole moment components situated along the axes perpendicular to the shortest one, are very small in comparison with the dipole moment of that axis. Thus only the component perpendicular to the longest molecular axis should contribute to the dielectric increment. From the comparison of the moment of inertia about the longest molecular axis with the relaxation time observed one can conclude that these two molecules behave like rigid molecules. This has also been reported by Khwaja and Walker [21], who have examined the mono-substituted diphenyls in polystyrene matrices. However, in the case of 3,3'-DBDP one could expect some influence of the absorption by the rotation of phenyl rings about the 1-1 bond.

According to (4) such an influence can be estimated if the correlation time τ_{or} is known. However, this value cannot be obtained experimentally. If we assume that the 2,2' isomer is a rigid unit, because of large steric hindrance, while the 3,3' isomer has some freedom of rotation around 1,1 bonding, so the correlation time τ_{or} may be equal to the relaxation time observed for the 2,2' isomer. Under this assumption the τ_k value could be estimated for the 3,3' derivative from (4). The value of 72.46 ps at 293 K was found. This indicates that the contribution of the intramolecular rotation to the dielectric relaxation may be neglected in this system. In the case of 2,2'-DBDP the rigidity is doubtless, rather because of a larger hindrance in comparison to 3,3'-DBDP. If the 3,3'-DBDP occurs as several conformations (which seems to be the case, as can be seen from the results of non-linear dielectric experiments [12]), the relaxation time values allow us to state only that exchange rate of one conformation to another is much lower than overall molecular rotation. For that reason the kinetic process (τ_k) is not active in the dielectric relaxation.

In the light of the above analysis the correlation between the relaxation time and the moment of inertia, as well as the linear dependence of the dielectric increment on reciprocal temperature, indicate that in the systems under study we are dealing with the reorientation of the rigid molecules, in the sense of the dielectric absorption method. In the case of 2,2'-DBDP such a conclusion is fully justified. This conclusion has also been confirmed by correlation between the relaxation time at 293 K and the energy of activation ΔH_E^* , as well as by correlation between τ_{obs} and the dipole moment value. In the case of 3,3'-DBDP we cannot prove whether we are dealing only with the reorientation of rigid molecules at an almost perpendicular arrangement of the phenyl rings, as might be suggested by the dipole moment values.

Acknowledgments

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