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## Dielectric relaxation and internal rotation in cyanodiphenyls

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**Abstract.** Dielectric relaxation measurements were carried out on three isomers 2,3'-dicyanodiphenyl, 3,3'-dicyanodiphenyl and 4-cyanodiphenyl in p-xylene in the temperature range 293–323 K for static frequencies up to 10 GHz. The analysis of the dielectric dispersion of these compounds was carried out and the mechanism of the internal rotation for these molecules has been proposed.

### 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 [1–12], using both theoretical and experimental approaches. The contribution of our laboratory to the elucidation of this interesting problem has shown that, in general, the Goulon–Rivail [4] model can be effectively employed to describe the dynamics of the dielectric relaxation process. This was found to be common to many molecular structures whose internal rotation does not possess the same characteristics (e.g. bipyridyls, dipyridylethylenes, phenylpyridines and dibenzoyl). A common peculiarity of these substances arises from the presence of group moments rotating with respect to each other.

Cyanodiphenyls may also contain two such rotating groups. However, in this case, the partial moment of the phenyl rings derives essentially from the mesomeric effect. Thus, taking into account that this phenyl group moment is modified with a change in the dihedral angle between the two rotating planes, one can predict a peculiar behaviour for this type of molecule. Greater knowledge would improve our understanding of the molecular dynamics.

With this aim, the dielectric dispersion of 2,3'-dicyanodiphenyl (2,3'-DCDP), 3,3'-dicyanodiphenyl (3,3'-DCDP) and 4-cyanodiphenyl (4-CDP) was measured in a non-polar solvent at four temperatures and at various frequencies in the gigahertz region. It should be noted that the conformational aspect (to which the dynamics are strictly related) of adjacent aromatic systems are still an object of debate [12–17].

### 2. Experimental details

The compounds 2,3'-DCDP, 3,3'-DCDP and 4-CDP were synthesized in our laboratory and

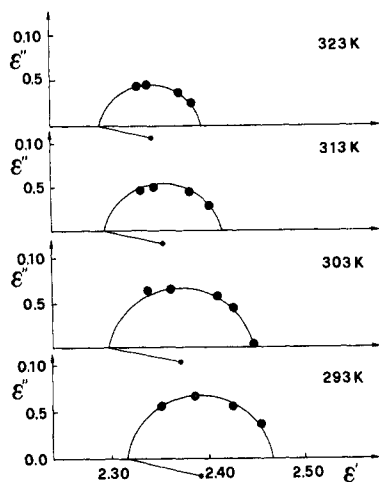


Figure 1. Cole-Cole plots for 2,3'-DCDP in *p*-xylene at a concentration of  $0.276 \text{ mol dm}^{-3}$ .

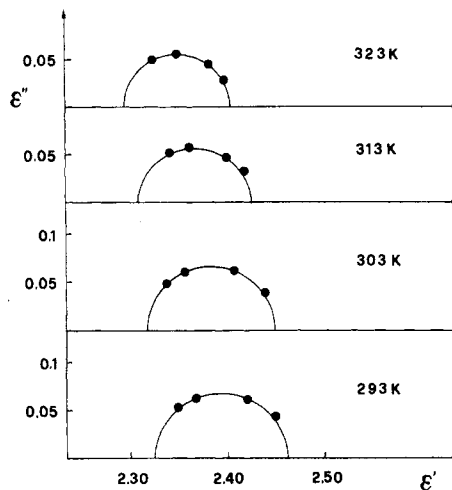


Figure 2. Cole-Cole plots for 3,3'-DCDP in *p*-xylene at a concentration of  $0.296 \text{ mol dm}^{-3}$ .

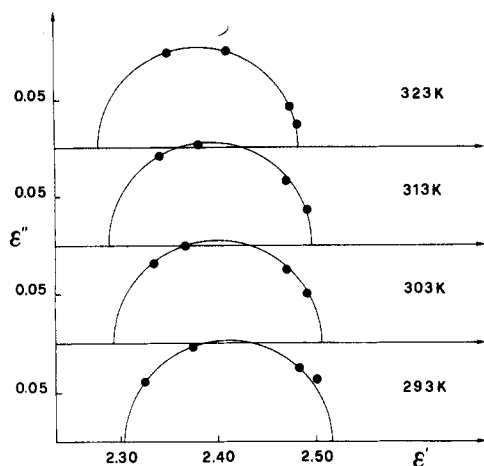
purified by means of microdistillation under vacuum. The *p*-xylene used as a solvent was dried over metallic sodium and distilled. Its purity was checked by measuring the static dielectric permittivity at 298 K. The measurement of the real part  $\epsilon'$  and the imaginary part  $\epsilon''$  of the complex dielectric permittivity in the range 2–10 GHz was performed by means of an Orion coaxial slotted line EZ Or-1 for 2–4 GHz and an HP slotted line 817a for 4–10 GHz. The static dielectric permittivity was measured at 1.59 kHz using a Tesla BMM-484 semiautobalance bridge. All measurements were made at four temperatures (293, 303, 313 and 323 K), the temperatures being controlled by means of a Unipan proportional–integral–differential temperature controller with a precision of 0.01 K over the entire measurement range. The experimental errors in the dielectric parameters were  $\pm 2\%$  and  $\pm 3\%$  for  $\epsilon'$  and  $\epsilon''$ , respectively.

### 3. Results and discussion

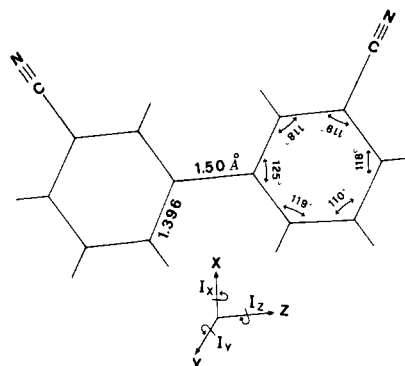
The results obtained from the dielectric relaxation measurements for 2,3'-DCDP, 3,3'-DCDP and 4-CDP are shown as Cole–Cole plots in figures 1, 2 and 3, respectively. From figure 1, one can see that the relaxation times of 2,3'-DCDP display a certain distribution. In this case, the equation

$$\epsilon(i\omega) = \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty})/[1 + (i\omega\tau_0)^{1-\alpha}] \quad (1)$$

can be used, where  $\alpha$  is the distribution parameter for the dielectric relaxation times, the values of which are shown in table 1. It should be noted that the value of  $\alpha$  clearly decreases with increasing temperature. Such a distribution of relaxation times in this molecule could be due to the overlapping of two or more bands. However, as far as the interpretation of the mechanism of the dielectric relaxation process in the molecules is concerned, one can say that, as in previous similar situations, it is quite difficult to justify the presence of more than two absorption bands as components of the complex band observed experimentally. In theory these two overlapping absorptions may be due to



**Figure 3.** Cole-Cole plots for 4-CDP *p*-xylene at a concentration of  $0.284 \text{ mol dm}^{-3}$ .



**Figure 4.** Molecular diagram for 3,3'-DCDP.

**Table 1.** Dielectric parameters for 2,3'-DCDP, 3,3'-DCDP and 4-CDP in *p*-xylene at concentrations of  $0.276 \text{ mol dm}^{-3}$ ,  $0.296 \text{ mol dm}^{-3}$  and  $0.284 \text{ mol dm}^{-3}$  respectively. The activation enthalpies  $\Delta H_E^*$  were  $4.4 \pm 1.8 \text{ kJ mol}^{-1}$ ,  $4.0 \pm 1.6 \text{ kJ mol}^{-1}$  and  $8.7 \pm 1.8 \text{ kJ mol}^{-1}$  for 2,3'-DCDP, 3,3'-DCDP and 4-CDP, respectively and were calculated according to Eyring's equation.

Isomer	$T$ (K)	$\tau_{\text{obs}}$ (ps)	$\alpha$	$\epsilon_0$	$\epsilon_\infty$
2,3'-DCDP	293	28.32	0.11	2.466	2.319
2,3'-DCDP	303	26.03	0.11	2.440	2.297
2,3'-DCDP	313	24.05	0.09	2.411	2.296
2,3'-DCDP	323	22.09	0.07	2.397	2.287
3,3'-DCDP	293	24.45	0.02	2.472	2.326
3,3'-DCDP	303	22.55	0.02	2.448	2.314
3,3'-DCDP	313	21.02	0.01	2.425	2.301
3,3'-DCDP	323	20.00	0.01	2.404	2.292
4-CDP	293	44.75	0.01	2.530	2.315
4-CDP	303	39.86	0.01	2.525	2.283
4-CDP	313	34.01	0.01	2.498	2.280
4-CDP	323	30.03	0.01	2.470	2.254

(i) the two components (along the mutual perpendicular molecular rotation axes) of the molecular electric dipole moment, assuming the molecule to be rigid, or

(ii) a fast interconversion between two rotamers stabilized by the conjugation which may give rise to the appearance of an additional mechanism.

In 2,3'-DCDP the component of the dipole moment perpendicular to the longest axis of the molecule is not equal to zero. In the case of 3,3'-DCDP and 4-CDP the dielectric absorption shows an almost Debye-like pattern (see figures 2 and 3) which is different

from that for 2,3'-DCDP; however, for 4-CDP, only the dipole moment component parallel to the longest axis exists and, for 3,3'-DCDP, only the non-zero dipole moment component is perpendicular to the longest axis.

If we assume the presence of rigid configurations, we can obtain  $I_1$  (the moment of inertia connected with rotation around the  $x$  and  $y$  axes) and  $I_2$  (the moment of inertia connected with the  $x$  and  $z$  axes) (figure 4) by using the relationships

$$I_1 = (I_x + I_y)/2 \quad I_2 = (I_x + I_z)/2 \quad (2)$$

where  $I_x$ ,  $I_y$  and  $I_z$  are the moments of inertia for the rotation around the axes  $x$ ,  $y$  and  $z$ , respectively. On this basis, one can expect the existence of two different dielectric relaxation times  $\tau_1$  and  $\tau_2$ . The calculation of the moment of inertia gives  $I_1 = 1600 \times 10^{-47} \text{ kg m}^2$  and  $I_2 = 961 \times 10^{-47} \text{ kg m}^2$ ; so one can easily obtain the ratio of the relaxation times:

$$\tau_1/\tau_2 = (I_1/I_2)^{1/2} = (1600/961)^{1/2} = 1.29 \quad (3)$$

which appears to be almost the same for all isomers examined. This is the theoretical ratio calculated from the assumption that these molecules are rigid. Taking into account that, for 4-CDP, only one dipole moment component  $\mu_{\parallel}$  occurs and assuming that the mesomeric moment is negligible, one can see that the value of  $\tau_{4\text{-CDP}}$  is almost equal to  $\tau_1$ ; then the value of  $\tau_2$  can be calculated. This value (see table 1) is much higher than the values of the observed relaxation times for 2,3'-DCDP and 3,3'-DCDP. The ratios  $\tau_{4\text{-CDP}}/\tau_{2,3'\text{-DCDP}}$  and  $\tau_{4\text{-CDP}}/\tau_{3,3'\text{-DCDP}}$  at 293 K are 1.58 and 1.83, respectively. If we compare the above ratios with the ratio obtained from the moment of inertia calculations, we can easily see that the molecules investigated do not behave like rigid molecules. There is some additional motion.

Taking into consideration all the points discussed above, it seems that our results can be investigated by means of the Goullon-Rivail theory which for internal rotation considers the possibility of jumps from one potential well to another.

For molecules having two non-symmetrical rotating groups (two components of the molecular dipole moment) this model predicts two relaxation times  $\tau_1$  and  $\tau_2$ ;  $\tau_1$  is connected with the reorientation of the component  $\mu_{\parallel}$  of the dipole moment which does not change during the internal rotation,  $\tau_2$  is described by the following relationship:

$$1/\tau_2 = 1/\tau_{\text{or},2} + 1/\tau_k \quad (4)$$

where  $\tau_2$  is the relaxation time connected with the component  $\mu_{\perp}$  of the dipole moment which changes its direction during the reorientation of the polar groups and  $\tau_k$  is the 'chemical relaxation time' and should describe the internal rotation. If one knows  $\tau_{\text{or},2}$ , the relaxation time connected with the reorientation of the rigid framework of the molecule about  $z$  axis (see figure 4), it is possible to calculate  $\tau_k$ . The value of  $\tau_{\text{or},2}$  may be obtained from

$$\tau_1/\tau_{\text{or},2} = (I_1/I_2)^{1/2} \quad (5)$$

where  $\tau_1$  describes the reorientation of the molecule about the axes perpendicular to the long molecular axis. If one assumes that the value of the relaxation time obtained for 4-CDP is very close to  $\tau_1$  ( $\tau_{4\text{-CDP}} \approx \tau_1$ ) (which seems reasonable), it is possible to estimate the value of  $\tau_{\text{or},2}$ . The values of  $\tau_{\text{or},2}$  together with  $\tau_k$  and  $\tau_2$  are shown in table 2.

According to the model chosen, a single-domain absorption for 3,3'-DCDP and 4-CDP should be observed, and indeed our independent experimental data show only Debye-like absorption in both cases. However, the relaxation times differ from each other.

**Table 2.** Dielectric relaxation times for 2,3'-DCDP, 3,3'-DCDP and 4-CDP in *p*-xylene at concentrations of 0.276 mol dm<sup>-3</sup>, 0.296 mol dm<sup>-3</sup> and 0.286 mol dm<sup>-3</sup>, respectively.

Isomer	<i>T</i> (K)	$\tau_{or,2}$ (ps)	$\tau_k$ (ps)	$\tau_{2,calc}$ (ps)	$\tau_{obs}$ (ps)
2,3'-DCDP	293	21.0	73.0	16.4	28.32
2,3'-DCDP	303	20.1	71.6	15.6	26.03
2,3'-DCDP	313	17.8	54.2	13.4	24.05
2,3'-DCDP	323	16.4	38.5	11.5	22.09
3,3'-DCDP	293	18.0	44.5	12.7	24.45
3,3'-DCDP	303	16.7	35.8	11.6	22.55
3,3'-DCDP	313	15.4	26.7	9.6	21.02
3,3'-DCDP	323	14.6	21.5	8.5	20.00
4-CDP	293				68.0
4-CDP	303				61.0
4-CDP	313				53.0
4-CDP	323				44.0

Taking into consideration all the points discussed above and also the decrease in the effective dipole moment with increasing temperature (particularly for 2,3'-DCDP and 3,3'-DCDP) and a fair activation enthalpy (table 1), one could say that the molecular dynamics of these molecules are a modulation of the overall reorientation by fast interconversion.

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