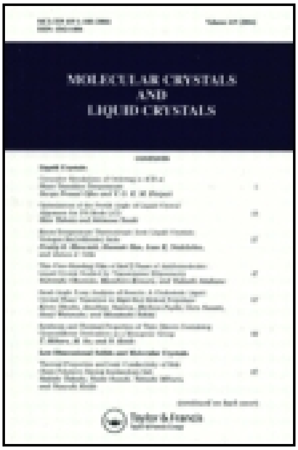

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Static and Dynamic Depolarized Rayleigh Scattering of Cyano Biphenyl Series in Dilute Solutions and Intrinsic Molecular Even-Odd Effect in Liquid Crystals

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Static and Dynamic Depolarized Rayleigh Scattering of Cyano Biphenyl Series in Dilute Solutions and Intrinsic Molecular Even-Odd Effect in Liquid Crystals

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We report here a detailed description of our experimental work about both static and dynamic investigations of depolarized Rayleigh scattering and Kerr effect in diluted solutions of the cyanobiphenyl series, and show how a carefully performed conformational analysis can lead to a possible interpretation of the intrinsic molecular even-odd effect experimentally evidenced.

1 INTRODUCTION

Recently, there has been considerable interest in the structure of compounds which possess a liquid crystalline phase. Of course, many of the technics of chemical physics have been used to try to determinate the structure of such

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materials when molecules are "isolated", or, more precisely, highly diluted in non-interacting solvent. Two of them, namely the measurements of the spectrum width and of the integrated intensity of depolarized Rayleigh light scattered from such binary solutions, seem to be well adapted to the studies of electronic properties and structure of the molecules. Six years ago, solutions of M.B.B.A. in carbon tetrachloride have been intensively studied[1,2] and, recently, depolarized Rayleigh light scattered by same compounds of the well-known cyano-biphenyl series, has been investigated.[3] Our availability of investigating a large number (thirteen) compounds of the homologous series of 4-*n* alkyl-4′ cyanobiphenyl (n.C.B.), $O \leqslant n \leqslant 12$,[4] lead us to the study of both static and dynamic depolarized Rayleigh scattering of such materials in cyclohexane, highly diluted, solutions.

Preliminary and incomplete results have been recently reported elsewhere.[5] In this communication, we give a more detailled presentation of our work, which, we hope, will lead to other possible investigations in the field of Chemical Physics.

In Section 2, we describe the studied compounds and the preparation of solutions. In Section 3, we briefly outline the main theoretical considerations necessary to interpret our depolarized Rayleigh investigations, the results of which are quickly recalled and discussed. In Section 4, we present the Kerr effect measurements performed on cyanobiphenyl ($n = 0$) and the results of dielectric permittivity investigation, and, in Section 5, we finally give the whole results of a comparison between experimentally measured and numerically calculated values of the molecular optical anisotropies of these compounds, trying to propose some possible origins of the even-odd effect which seems to exist in such "isolated" molecules.

2 MATERIALS

The thirteen compounds have been purchased from B.D.H. ($n = 5, 6, 7, 8$), or obtained from private source.[5] All their physical properties can be found in already published data.[3,4] Table 1 reports the eventual existence of stable liquid crystal phases.[4]

The thirteen compounds have been found to be stable and quite totally transparent for the three laser wavelengths used in our experiments (green line of Ar^+, red ones of Kr^+ and He-Ne lasers). All have been carefully purificated (some hours at 50°C in cyclohexane/charcoal bath) before being solubilized in cyclohexane (Eastman Kodak for U.V. spectroscopy grade). The mole fractions of the solutions were, in any case, less than 10^{-2}, i.e. near one order of magnitude smaller than the ones cited in Ref. 1. We shall see in Section 3 why this point will be of some importance. All investigations have

TABLE I

The stable liquid crystal properties of the 4-n alkyl-4′-cyanobiphenyl series (n.C.B) $O \leqslant n \leqslant 12$.

Number n of carbon atoms in the alkyl tail	0	1	2	3	4
Liquid crystal properties	no stable properties	no stable properties	no stable properties	no stable properties	no stable properties
Number n of carbon atoms in the alkyl tail	5	6	7	8	9
Liquid crystal properties	nematogen	nematogen	nematogen	nematogen + smectogen A	nematogen (range 1.5K) + smectogen A
Number n of carbon atoms in the alkyl tail	10	11	12	×	×
Liquid crystal properties	smectogen A	nematogen (range 0.5K) + smectogen A	smectogen A	×	×

been performed at (25.0 ± 0.1)°C. Binary solutions were prepared gravimetrically and carefully filtered to remove dust.

3 THEORETICAL CONSIDERATIONS AND RESULTS OF DEPOLARIZED RAYLEIGH SCATTERING INVESTIGATIONS

3.1 Integrated intensity measurements

The theory of depolarized Rayleigh scattering has been intensively given previously.[6] Let us only recall the definitions essential for analysing our data.

The integrated intensity I_{VH} of depolarized scattered light by liquids is given by:

$$I_{\mathrm{VH}} \propto \rho L(\eta)\gamma^2 g_2 \tag{1}$$

where ρ is the number density of particles; $L(\eta)$ a local-field and geometrical conditions correction parameter; γ the "apparent" optical polarizability anisotropy of the molecules, η the refractive index, and g_2 a "static" parameter, taking into account orientational pair correlations, and which takes the simplified form:

$$g_2 = 1 + \sum_{i \neq 1}^{N} \frac{\langle Y^{(2)}_{00}(1) \times Y^{(2)}_{00}(i)\rangle}{\langle Y^{(2)}_{00}(1) \times Y^{(2)}_{00}(1)\rangle} \tag{2}$$

where the summation is performed over (N − 1) molecules of the scattering volume. The spherical harmonics $Y^2_{00}(i)$ describe the orientation of the molecule *i*.

Because of the high dilution of our solutions, all orientational correlations between solute molecules can be neglected. Moreover, the use of a quite totally isotropic solvent molecule (cyclohexane) leads to an important reduction of these correlations between solute and solvent particles. And we can simply take:

$$g_2 \# 1 \tag{3}$$

We have used the classical Lorenz-Lorentz model in the evaluation of $L(\eta)$ parameter. In another way, it is well known that γ^2 includes contributions from collisions and radial fluctuations, but the very high values of molecular polarizability anisotropies of the studied compounds do considerably reduce such contributions, as it will be shown in Rayleigh line width study.

Our experimental set-up has been previously described.[5] Let us here simply recall that it allows relative determinations of γ^2 with a whole relative experimental error never larger than 10^{-2}. The experimental results are reported in Table II.

It must be noted that, for $n \leqslant 5$, when the molecules do not give rise to stable nematic or smectic phases, γ^2 increases very quickly with *n*, without any strong even-odd effect. In another way, for $\geqslant 6$, large oscillations occur and a strong even-odd effect is observed.

3.2 Line-width measurements

Let us consider a collection of *N* identical anisotropic molecules, labelled by the index *i* and embedded in a laser electric field **E**. Let us call $\alpha_i(t)$ the first order polarizability tensor of molecule *i* at time *t*. This tensor will be assumed to be symmetric, since the studied molecules do not show any optical activity. If we assume, as in Lorenz-Lorentz model, that the local field effectively seen by the molecule is collinear to **E**, the scattered field correlation function $C_E(\mathbf{q}, t)$, in the VH geometry,[7] is given by:

$$\begin{aligned} C_E(\mathbf{q}, t) &= \langle E_{\mathrm{VH}}(\mathbf{q}, t)\, E_{\mathrm{VH}}(-\mathbf{q}, 0)\rangle \\ &\propto \langle \alpha^{21}(\mathbf{q}, t)\alpha^{21}(-\mathbf{q}, 0)\rangle \sin^2\theta/2 + \langle \alpha^{31}(\mathbf{q}, t)\alpha^{31}(-\mathbf{q}, 0)\rangle \cos^2/2 \end{aligned} \tag{4}$$

TABLE II

Experimental values of γ^2 for thirteen 4-*n* alkyl-4′-cyanobiphenyls; $t = (25.0 \pm 0.1)^\circ C$; $\lambda = 647.1$ nm. All the values are extrapolated at zero value of the concentration, in cyclohexane solutions.

Number *n* of carbon atoms	0	1	2	3	4	5	6
γ^2 (in 10^{-48} cm^6)	642 ±3	698 ±3	716 ±4	773 ±4	796 ±4	868 ±4	891 ±4
Number *n* of carbon atoms	7	8	9	10	11	12	
γ^2 (in 10^{-48} cm^6)	852 ±4	900 ±4	790 ±4	964 ±5	840 ±4	958 ±5	

where α^{kl} denotes the kl component of the "apparent" (or effective) polarizability tensor:

$$\alpha^{kl}(\mathbf{q}, t) = \sum_{i=1}^{N} \alpha_i^{kl}(t) \exp\left[j\mathbf{q} \cdot \mathbf{r}_i(t)\right] \tag{5}$$

$\mathbf{q}$ is the transfer wave vector given, in the quasi elastic approximation, by:

$$|\mathbf{q}| = \frac{4\Pi\eta}{\lambda} \sin \theta/2 \tag{6}$$

and θ the scattering angle. $\mathbf{r}_i(t)$ describes the location of molecule i at time t.

A theoretical calculation of the field correlation function defined by Eq. (4) needs the precise knowledge of the various physical processes that can couple to α. From symmetry arguments in tensorial analysis, it can be shown that only molecular reorientations can influence α^{21}, whereas hydrodynamic modes can couple to α^{31}.[8] Among them, the most relevant is the 1-component of the linear momentum density. In this respect, by measuring the scattered light in the VH geometry, one can study the coupling between the orientational motion of molecules and the transverse shear waves. This has been done for number of viscous liquids,[9–12] M.B.B.A.[13] and 4-cyano-4′*n* pentyl biphenyl.[14]

In the limiting case of dilute samples, the above coupling does not take place and one is only left with the orientational motion of molecules. Then, the field correlation function behaves like second order spherical harmonics $Y^{(2)}.\ (\theta, \psi)$,[15] and can be calculated if the probability density $f_0[\Omega_0, \Omega(t)]$ that the molecule having the orientation Ω_0 at time 0 will have orientation $\Omega(t)$ at time t, is known. Various physical models have been proposed for f.

In the case of rotational diffusion, f obeys a diffusion equation:

$$\dot{f} = D_{\text{rot}} \cdot \nabla^2 f \tag{7}$$

where D_{rot} is the rotational diffusion coefficient and ∇^2 the angular part of the Laplace operator. Solution of Eq. (7) leads to:

$$f[\Omega_0, \Omega(t)] = \sum_{m,1} Y_{lm}(\theta, \phi)\exp\{-1(1+1)D_{\text{rot}}t\} \tag{8}$$

keeping the term $l = 2$, one obtains:

$$C_E(\mathbf{q}, t) \propto \exp(-6D_{\text{rot}} \cdot t) \tag{9}$$

i.e. the field correlation function is an exponential, decaying with a time constant $\tau_2 = 1/6\, D_{\text{rot}}$. The same results holds for Raman scattering, N.M.R. relaxation.... If, on the other hand, one performs experiments sensitive to $l = 1$ (dielectric relaxation, infrared spectroscopy ...) one would measure a correlation time $\tau_1 = 1/2\, D_{\text{rot}} = 3\tau_2$. Other models have also been proposed: jump diffusion, J and M diffusion[16] ... In all cases, the long time behaviour of the field correlation function is exponential, but relation (9) does not more hold. From Wiener-Kintchin theorem, the frequency spectrum $S(\mathbf{q}, \omega)$ of the scattered light is proportional to the real part of the Fourier transform of $C_E(\mathbf{q}, t)$, ω being the difference between the actual frequency of the scattered light and the laser frequency. From the above results, it follows that:

$$S(\mathbf{q}, \omega) \propto \frac{1/\tau}{\omega^2 + (1/\tau)^2} \tag{10}$$

i.e. the frequency spectrum is a Lorentzian centred at zero (laser) frequency, the half width at half height (H.W.H.H.) of which is $\Gamma = 1/\tau$. Therefore, measurements of either the scattered field correlation function using, for instance, Intensity Light Beating Spectroscopy,[17] or the scattered light frequency spectrum, provide essentially the same result, i.e. the orientational motion correlation time τ_2.

The experimental set-up has been described elsewhere.[5] Let us simply recall here that the fineness coefficient of the spectrometer is about 50, leading to a resolution better than 150 MHz for a Fabry-Perot spacing of 2 cm. The spectral profiles of the VH scattering of cyclohexane and liquid crystal solutions (concentrations of 1.06 10^{-2} g × cm^{-3} and 2.52 10^{-2} g × cm^{-3}) have been recorded.

As previously stated, cyclohexane is a quasi isotropic molecule. Then, depolarized scattering mainly arises from translational fluctuations and collision induced scattering. Using a very small spacing between the plates of the Fabry–Perot spectrometer, we have evaluated an order of magnitude of the characteristic time τ_c. We have found $\tau_c \sim 3$ psec, a value not too far from the one calculated by:

$$\tau_c = \frac{\Pi\sigma}{6}\left[1 - \frac{2}{\Pi}\,\mathrm{ar\,tg}\left(\frac{2\varepsilon}{kT}\right)^{1/2}\right] \tag{11}$$

Such a relation has been already proposed[18] for particles interacting via a Lennard-Jones potential, with the following values of characteristic parameters:[19]

$$\varepsilon/k = 324\,\mathrm{K} \quad \text{and} \quad \sigma = 0.61\,\mathrm{nm}.$$

For very diluted solutions, the VH interferograms, taken at large spacing of the plates, can be accurately fitted by the sum of a flat background and a sharp Lorentzian line.

The following results must be pointed:

— the integrated intensity of the background is the same (to within the experimental error) to that arising, at the same spacing, from pure cyclohexane.

— the integrated intensity of the sharp Lorentzian line is proportional to the concentration of the solute.

— the sharp line can be very well fitted by a single Lorentzian.

— τ_2 is found to be independent of the solute concentration.

Figure 1 gives the obtained experimental results. It must be noted that, when $\eta \leqslant 5$, i.e. when molecules do not exhibit any stable nematic or smectic property, H.W.H.H. is found to decrease very quickly when n increases. Such a strong decrease seems to be rubbed for $\eta > 7$. Such a behaviour can be compared with interest to the one exhibited by "static" depolarized scattering (Table II). One must also note that, from the above reported results, the orientational correlations between solute molecules are very small, or don't exist, since the integrated intensity and the correlation time of the sharp line are respectively proportional to the concentration and independent of it.

Moreover, values of reorientational correlation time have been already reported for liquid n-alkanes.[20] As expected, the variation of τ with n strongly differs in this cited work ($\tau \propto n^{4.3}$) and in ours ($\tau \propto n^{0.5}$ for n $1 \leqslant n < 7$; τ approximately constant for $n > 7$). In Debye "picture", such a result could indicate a quite constant molecular volume for $n > 7$, in agreement with the possible structures proposed in Section 5.

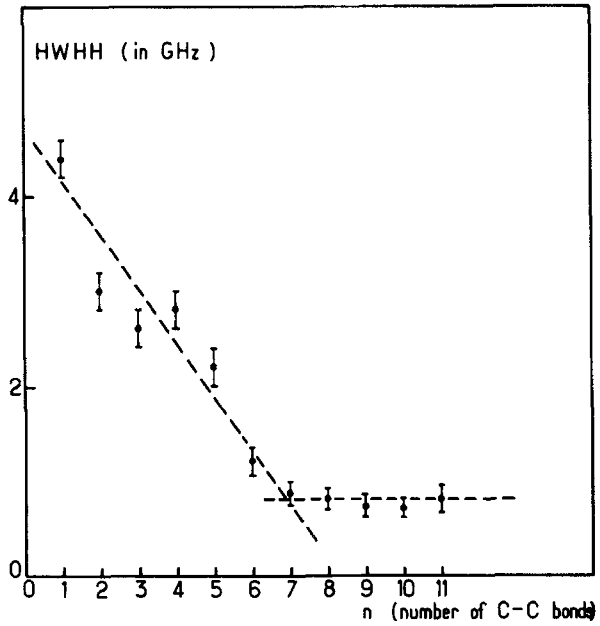

FIGURE 1 Variation of H.W.H.H. of n.C.B./cyclohexane versius the number *n* of carbon atoms in the tail; $\lambda = 546.1$ nm; $t = (25.0 \pm 0.1)$°C.

4 KERR EFFECT AND DIPOLE MOMENT MEASUREMENTS

Let us now describe how both measurements of Kerr constant B, optical molecular anisotropy, and permanent dipole moment μ can lead to the determination of the three principal molecular polarizabilities of *p*-cyanobiphenyl "core" of such compounds.

4.1 The measurement of Kerr constant B: practical aspect and experimental value

Our first experimental apparatus for electric birefringence measurements has been already described[21]: photometric relative measurements of optical intensities lead to experimental values of Kerr constant. The wavelength used in the present work is $\lambda = 6328$ Å, so the light source has been replaced by a C.W. He–Ne laser (from C.I.L.A.S., type 510). The optical arrangement has been changed in consequence as partially described in a preceding paper[22] (see Figure 2).

The study of *p*-cyanobiphenyl is made upon three different solutions;

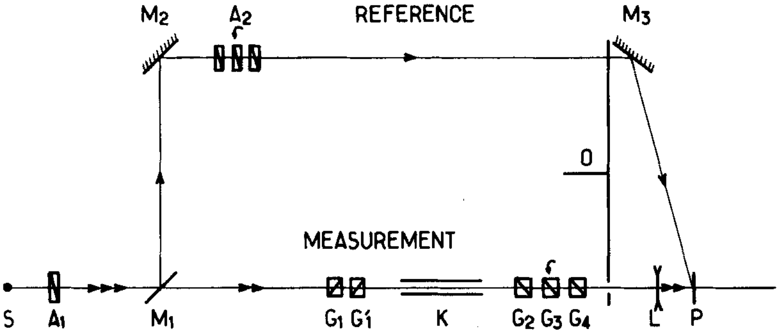

FIGURE 2 Optical device for Kerr constant measurement. S: Laser He-Ne; $\lambda = 632.8$ nm; $P \sim 1$ mw. O, A_1 and A_2: adjustable attenuators M_1: beam splitter; M_2 and M_3: mirors K: Kerr cell G_1; G_1'; G_2; G_3; G_4: Glazebrook polarizers L: Divergent lens; P: photomultiplier tube.

before and after the solution measurements, two measurements are made on pure solvent, because the cyclohexane Kerr constant is the reference value for B. So, it is important to get good precision on this latter value and also to make sure that the reference value remains constant during all the experiments. For each value of electric field E applied in the Kerr cell, there is an angular position β of the Glazebrook prism G_3 (see Figure 2) for which both light intensities of the measuring and of the reference beams are the same. Light intensity measurements are always made with three different values of electric field E, along with the three corresponding values of angle β:

$$E_0 = 0 \text{ and } \beta_0; \quad \simeq \quad E_m \simeq 13 \text{ kV and } \beta_m; \qquad E_M \simeq 19 \text{ kV and } \beta_M$$

According to the chosen method (22), light intensity is given by: $I = C/\cos^4 \beta$ (C is constant, light intensity unit is that of the reference beam). The light intensity, corresponding to the electric birefringence, is, for an applied field E:

$$A^2 = I - I_0 = C_1 B^2 E^4 \tag{12}$$

where C_1 is a constant.

Kerr constant being defined by: $B = (\eta_{\parallel} - \eta_{\perp})/\lambda E^2$, where $\eta_{\parallel}$ and $\eta_{\perp}$ are the refractive indexes in the Kerr cell for the components of the light parallel and perpendicular to the field E.

So, for the two values of the field:

$$A_M = (I_M - I_0)^{1/2} = C_2 B E_M^2 \quad \text{and} \quad A_m = (I_m - I_0)^{1/2} = C_2 B E_m^2 \tag{13}$$

The use of two different values of the electric field leads to a constant B which does not depend on an absolute electric field value, so experimental error is less important.

$$\Delta A = A_M - A_m = C_2 B(E_M^2 - E_m^2) \tag{14}$$

practically, ΔA is measured in the solution and in the solvent, so the Kerr constant B of a solution is a function of the solvent as following:

$$B_{(\text{solution})} = \frac{\Delta A_{(\text{solution})}}{\Delta A_{(\text{solvent})}} \cdot B_{(\text{solvent})} \tag{15}$$

where $B_{(\text{solvent})} = B_{(\text{cyclohexane})} = 5.38 \times 10^{-9}$ e.s.u. (this value is deduced from $B = 6.24 \times 10^{-9}$, measured at $\lambda = 5460$ Å and 25°C).[23]

Table III reports experimental values of all previously defined parameters.

Table III

Experimental Kerr constant B of OCB in cyclohexane solutions. C: weight fraction of solute; $\lambda = 632.8$ nm; $t = (25.0 \pm 0.1)$°C; $p = 1$ atm. n° is the chronological order of the experimentation.

n°	$10^3 \times C$ g × cm^{-3}	I_0	I_m	I_M	ΔA	$B \times 10^9$e.s.u.
n° 0	0	1.09	1.40	1.98	0.38	5.38
n° 1	2.30	1.49	5.27	15.1	1.75	24.9
n° 2	4.24	1.48	10.0	36.7	3.02	43.0
n° 3	6.71	1.13	21.9	87.2	4.71	67.1
n° 4	0	1.13	1.43	1.99	0.37	5.38

4.2 Experimental determinations of refractive index and dielectric constant

Refractive indexes η are measured with a Pulfrich refractometer (from Bellingham and Stanley). This apparatus allows measurements with a relative experimental error less than 10^{-4} (at 25°C, in a temperature-controlled cell).

Relative dielectric constants ε_r are measured with a dipolemeter DM 01 (from W.T.W.). Relative experimental error is less than 10^{-3} (at 25°C, in a temperature controlled cell).

Experimental values of B/Bc and ε_r are given in Figure 3 for the different solutions.

4.3 Experimental value of specific Kerr constant Sk extrapolated at infinite dilution

Earlier stages of our research[23] demonstrated that, by means of an empirical

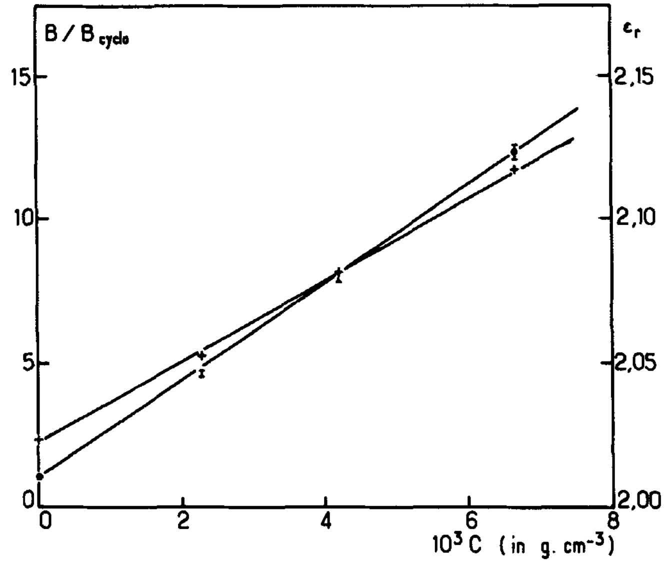

FIGURE 3 Variations of B/B cyclo and εr with the concentration of cyano biphenyl in cyclohexane. $t = (25.0 \pm 0.1)°C$; $\lambda = 632.8$ nm.

expression of B, it was possible to use with success simultaneously experimental data of depolarized Rayleigh light scattering and those of Static Kerr effect. The expression used is:

$$B = \frac{3\pi}{\lambda n}\frac{N\rho}{M}\left(\frac{n^2+2}{3}\right)^2\left(\frac{\varepsilon_r+2}{3}\right)(\theta_1+\theta_2) \tag{16}$$

N is the Avogadro constant and M the molar weight. With Einstein notation:

$$45kT\theta_1 = 3\alpha^0_{ij}\alpha_{ij} - \alpha^0_{ii}\alpha_{jj} \quad \text{and} \quad 45k^2T^2\theta_2 = 3\alpha^0_{ij}\mu_i\mu_j - \alpha^0_{ii}\mu_j\mu_j \tag{17}$$

Where k is the Boltzmann constant, T the absolute temperature; α^0_{ij}, α_{ij} and μ_i are respectively the optical polarisability, the electrical polarisability and the permanent dipole moment component along i axis of the molecule. The previous expression differs from the classical one by the term:

$$\left(\frac{\varepsilon_r+2}{3}\right)^2 \tag{18}$$

More information about this difference can be found elsewhere.[24] Specific Kerr constant is given by:

$$\mathrm{Sk} = \frac{2\pi N}{9M}(\theta_1+\theta_2)$$

If we write constant B of a solution as a function of solvent parameters, solute parameters and of weight fraction c, we can easily show that the specific constant Sk_∞ of the compound diluted in cyclohexane is given by:

$$\mathrm{Sk}_\infty = \mathrm{Sk}_0\left(\frac{a(B)}{B_0} - \frac{a(\rho)}{\rho_0} + 1 - \left(\frac{\eta_0^2 - 1}{\eta_0^2 + 1}\right)\frac{a(\eta^2)}{\eta_0^2} - \left(\frac{\varepsilon_{r_0}}{\varepsilon_{r_0} + 2}\right)\frac{a(\varepsilon_r)}{\varepsilon_{0r}}\right) \tag{19}$$

This expression differs from the Lefevre expression[25] by the last term:

$$\left(\frac{2\varepsilon_{r0}}{\varepsilon_{r0} + 2}\right)\frac{a(\varepsilon_r)}{\varepsilon_{r0}}$$

Sk_0, B_0, ρ_0, n_0 and ε_{0r} are measured parameters of cyclohexane.

For a parameter X, $a(X) = \left(\dfrac{\mathrm{d}X}{\mathrm{d}c}\right)_{c \to 0}$. Finally we obtain:

$$\mathrm{Sk}_\infty = 2.40 \times 10^{-12}\ \text{e.s.u.}$$

Relative experimental error is less than 4×10^{-2}.

4.4 Experimental value of dipole moment μ_∞ extrapolated to infinite dilution

Using the well known formula of Lorenz–Lorentz and Clausius–Mossotti, and writing refractive index η and dielectric constant ε_r of a solution as functions of solvent parameters, solute parameters and of weight fraction c, we show easily that the permanent dipole moment of *p*-cyanodiphenyl μ_∞ diluted in cyclohexane is:

$$\frac{\mu_\infty^2}{3kT} = \frac{9M}{4\pi N\rho_0}\,\frac{(a(\varepsilon_r) - a(n^2))}{(\varepsilon_{r0} + 2)^2} \tag{20}$$

This relation is also called the Hedestrand formula.[26] M is the molar weight of solute, other parameters have same significance as in previous relation. Finally, we obtain:

$$\mu_\infty = 4.64D$$

Relative experimental error is less than 2×10^{-2}.

5 CONFORMATIONAL ANALYSIS

5.1 General formulation[27,28]

We define a traceless tensor:

$$\beta = \sqrt{3/2}\,(\alpha_m - \bar{\alpha}_m M) \tag{21}$$

where α_m is the polarizability tensor of the molecule as a whole (the 4′-cyanobiphenyl group and its aliphatic tail), M is the identity matrix of order 3, and $\bar{\alpha}_m$ is the trace of tensor α_m. It can be shown that the molecular optical anisotropy can be written as:

$$\gamma^2 = \text{trace}\,(\beta\beta) = \sum_{s,t} \beta_{s,t}^2 \tag{22}$$

It is assumed that the polarizability α_m of the molecule, as a whole, is the sum of the tensors of the contributions of its individual bonds or atomic groups evaluated in the same reference system. This tensor sum depends, of course, on the conformations of the aliphatic tail.

5.2 Chain Model and Conformational Equilibrium

We have assumed the tetrahedral geometry of the CH_2 groups of the tail. Furthermore, the conformational equilibrium of the tail is described according to the rotational isomeric state model (R.I.S.M.), in which a conformation of the chain is characterized by a series of rotation angles associated with successive bonds of the skeleton.[27] Each C—C bond i of the tail can rotate about the preceding one (see Figure 4), and its position is defined by its dihedral angle ϕ_i, with respect to the preceding bond pair. For each bond i, three positions are allowed, corresponding to $\phi_i = 0$ (trans state t) and $\phi_i = \pm 120°$ (gauche states g^+ and g^-). The trans form of an elementary unit i of three bonds is chosen as a reference state and an energy difference $\Delta U^{(i)}$ is attributed to each gauche form. In addition, interdependence of internal rotations is taken into account by associating a supplementary energy of about 1900 cal.mole^{-1} to the units of four bonds of the g^+g^- or g^-g^+ type.

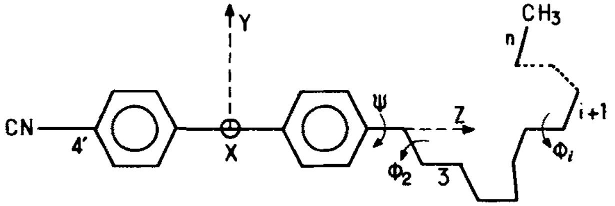

FIGURE 4 Structure of 4-n alkyl-4′cyanobiphenyls (n.C.B.) $0 \leqslant n \leqslant 12$; $0xyz$: principal reference system; ψ, ϕ_i: internal rotation angles.

5.3 Matrix representation of optical anisotropy[27,28]

For each conformation of the tail, β is formulated as the sum of $\beta_1, \beta_2, \ldots, \beta_{n+1}$, representing the contributions of the respective groups, each being expressed in the reference system of the skeleton bond of the same index. In these notations, n is the number of C—C bonds of the tail. Then β, for the molecule as a whole, expressed in the reference system of the first group is:

$$\beta = \beta_1 + T_1\beta_2 T_1^T + T_1 T_2 \beta_3 T_2^T T_1^T + \cdots = \sum_{i=1}^{n+1} \theta_i \tag{23}$$

with:

$$\theta_i = \left(\prod_{q=0}^{i-1} T_q\right)\beta_i\left(\prod_{q=0}^{i-1} T_q\right)^T \tag{24}$$

where T_q is the matrix transformation from the coordinate system of group $q + 1$ to that of group q, which depends on the rotation angle ϕ_q of bond $q + 1$, $\{T_q(\phi_q)\}$.

We define the column vector:

$$\gamma_i = \beta_i^c = \begin{pmatrix} \beta_{11} \\ \beta_{12} \\ \beta_{13} \\ \beta_{21} \\ \beta_{22} \\ \beta_{23} \\ \beta_{31} \\ \beta_{32} \\ \beta_{33} \end{pmatrix}_i$$

where the index i has to be applied to each element of the column and $\gamma = \beta^c$.

Using the identity:

$$\theta_i^c = \left(\prod_{q=0}^{i-1} T_q\right) \otimes \left(\prod_{q=0}^{i-1} T_q\right)\gamma_i \tag{25}$$

we can write:

$$\gamma = \sum_{i=1}^{n+1}\left(\prod_{q=0}^{i-1} (T_q \otimes T_q)\gamma_i\right) \tag{26}$$

where $\otimes$ represents the matrix tensor product (27) and finally, for a given conformation of the tail, we have:

$$\gamma^2 = \sum_{i=1}^{n+1} \gamma_i^T\gamma_i + 2\sum_{1 \leqslant i < j \leqslant n+1} \gamma_i^T\left(\prod_{q=1}^{j-1} (T_q \otimes T_q)\right)\gamma_j \tag{27}$$

5.4 Conformational averages

Considering the conformational equilibrium of a chain, it can be required to average γ^2 over conformations of the tail ($\langle\gamma^2\rangle$). From equation (27), Flory has derived the general formula of $\langle\gamma^2\rangle$ as:

$$\langle\gamma^2\rangle = 2Z^{-1}J^* \prod_{i=1}^{n+1} P_i J \tag{28}$$

where:

$$P_i = \begin{pmatrix} U_i & (U_i \otimes \gamma_i^T)\,\|T_i \otimes T_i\| & \frac{1}{2}\gamma_i^2 U_i \\ 0 & (U_i \otimes E_9)\,\|T_i \otimes T_i\| & U_i \otimes \gamma_i \\ 0 & 0 & U_i \end{pmatrix}_{33\times 33} \tag{29}$$

$$Z = (1, 0, 0,) \prod_{i=2}^{n} U_i \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

$$U_i = \begin{pmatrix} 1 & \sigma_i & \sigma_i \\ 1 & \sigma_i & \sigma_i\omega \\ 1 & \sigma_i\omega & \sigma_i \end{pmatrix}, \quad U_1 = U_n = U_{n+1} = M_3 \text{ identity matrix of order 3}$$

$$\sigma_i = \exp(-\Delta U^{(i)}/RT), \qquad \omega = \exp(-1900 + 600)$$

R is the perfect gas constant, T is the absolute temperature, M_9 is the matrix identity of order 9:

$$J = \begin{pmatrix} \mathrm{O} \\ \vdots \\ \mathrm{O} \\ \mathrm{H} \end{pmatrix}_{33\times 1}, \qquad H = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

$$J^* = (H^*, 0, \ldots, 0)_{1\times 33}, \qquad H^* = (1, 0, 0)$$

and finally:

$$\|T_i \otimes T_i\| = \begin{pmatrix} T_i(0) \otimes T_i(0) & 0 & 0 \\ 0 & T_i(+120) \otimes T_i(+120) & 0 \\ 0 & 0 & T_i(-120) \otimes T_i(-120) \end{pmatrix} \tag{30}$$

5. The optical anisotropy of the 4-*n* alkyl-4′ cyanobiphenyls

Assuming the symmetry of the bond polarizability tensor of C—C and C—H bonds, only the optical anisotropies of these bonds γ_{CC} and γ_{CH} are required in the evaluation of tensors β_i for $i \geqslant 2$. Definition of β_1 needs, in addition, the three principal polarizabilities of the cyanobiphenyl "core" previously determined. Furthermore, β_1 depends on the dihedral angle ψ of plane (Y, Z) relative to the plane of the two first bonds of the tail (see Figure 4). It follows that, in the reference system of bond 1:

$$\beta_1 = \sqrt{\tfrac{3}{2}}\begin{pmatrix} \begin{array}{l} \chi_{11} + \frac{2}{3}(\gamma_{CC} - \gamma_{CH}) - \bar{\alpha} \\ - \bar{\alpha} \end{array} & 0 & 0 \\ 0 & \begin{array}{l} \alpha_{22}\cos^2\psi + \alpha_{33}\sin^2\psi \\ - \frac{1}{3}(\gamma_{CC} - \gamma_{CH}) - \bar{\alpha} \end{array} & (\alpha_{22} - \alpha_{33})\sin\psi\cos\psi \\ 0 & (\alpha_{22} - \alpha_{33})\sin\psi\cos\psi & \begin{array}{r} \alpha_{22}\sin^2\psi + \alpha_{33}\cos^2\psi \\ - \frac{1}{3}(\gamma_{CC} - \gamma_{CH}) - \bar{\alpha} \end{array} \end{pmatrix} \quad (31)$$

For all the calculations, we have assumed that γ_{CH} does not vary along the tail and that it is equal to its aliphatic value ($0.22\ 10^{-24}$ cm^3).

The mathematical method described in the preceding sections can be applied in two situations. In the first case, it allows the calculation of the optical anisotropy γ^2 for every conformation of the tail defined by the set of its internal rotation angles ϕ_i. In the second case, it can be used to calculate the conformational average $\langle\gamma^2\rangle$ for any conformational equilibrium of the tail, defined by the statistical weights σ_i.

6 RESULTS AND DISCUSSION

Preliminary results of the conformational analysis have already been published.[5] Let us therefore quickly recall their main features:

— when n is less than 6, experimental results have been interpreted by assuming all *trans* conformation of the alkyl tail and regular increase of the anisotropy $\gamma_{C\text{—}C}$ along the chain.

— for n larger than 6, the experimentally evidenced oscillations of γ^2 and the decrease of the mean slope of the variations of γ^2 with n, suppose the presence of *gauche* isomers in the tail. We have found that the even–odd effect seems reliable with the position of the "freedom" point in the tail (see Table II in Ref. 5). Such results were obtained with the two following hypotheses:

$$-\psi = 0$$

— invariance of $\gamma_{C\text{—}C}$ for a bond in a fixed position along the tail from one compound to another.

We have tried to check the importance of these two hypotheses.

— for testing the value of ψ, we have used the opposite value $\psi = 90°$.

The results of the new calculation lead to large incoherent fluctuations of the γ_{C-C} values for the various bonds. So, it has not been possible to keep such a hypothesis and we have concluded to a preferential orientation corresponding to planar configuration.

— we have no more supposed the invariance of γ_{C-C} at a fixed position along the tail, but assumed a single mean value for all C—C bonds in the trans conformation of each compound. For the five first compounds, these mean values are reported on Table IV.

TABLE IV

Calculated mean values γ_{C-C} of the optical anisotropy of C—C bonds in the trans conformation of the alkyl tail versius n.

n	1	2	3	4	5
Values of γ_{C-C} (in 10^{-24} cm^3)	1.50	1.50	1.55	1.65	1.85

The important point is that a regular increase of γ_{C-C} occurs when the chain length increases, in agreement with the conclusion of the first calculation. Such an effect is probably the consequence of intramolecular internal field, as already suggested.[5]

For $n \geqslant 6$, the results are reported in Table V.

TABLE V

Conformational analysis results for $6 \leqslant n \leqslant 12$ t: trans; g: gauche; solid line: "freedom" position along the alkyl tail; numbers: computed values of γ_{C-C} (in 10^{-24} cm^3).

i	1	2	3	4	5	6	7	8	9	10	11	12
$n = 6$	1.95	1.95	1.95	1.95	1.95	1.85						
	t	t	t	t	t	t, g						
$n = 7$	1.85	1.85	1.85	1.85	1.65	1.22	1.22					
	t	t	t	t	t, g	t, g	t, g					
$n = 8$	1.95	1.95	1.95	1.95	1.95	1.85	1.22	1.22				
	t	t	t	t	t	t, g	t, g	t, g				
$n = 9$	1.65	1.65	1.65	1.55	1.22	1.22	1.22	1.22	1.22			
	t	t	t	t, g	t, g	t, g	t, g	t, g	t, g			
$n = 10$	1.95	1.95	1.95	1.95	1.95	1.95	1.85	1.22	1.22	1.22		
	t	t	t	t	t	t	t, g	t, g	t, g	t, g		
$n = 11$	1.85	1.85	1.85	1.85	1.65	1.22	1.22	1.22	1.22	1.22	1.22	
	t	t	t	t	t, g	t, g	t, g	t, g	t, g	t, g	t, g	
$n = 12$	1.95	1.95	1.95	1.95	1.95	1.95	1.85	1.22	1.22	1.22	1.22	1.22
	t	t	t	t	t	t	t, g	t, g	t, g	t, g	t, g	t, g

As indicated in Table V, the experimental values can be described according to the following scheme: the preferential conformation of any of the alkyl tails can be divided in two parts. A stabilized trans sequence similar to that of short compounds ($n \leqslant 5$) exhibiting perturbed values of γ_{CC} is followed by a totally disordered sequence with gauche isomers. Unperturbed values of $\Delta U^{(i)}$ (650 cal. mole^{-1}) and γ_{CC} (1.22 10^{-24} cm^3) can be attributed to each bond of this flexible part.

In this case, we have distinguished the first bond which can rotate, and a less perturbed γ_{CC} than in trans sequence is found. The positions along the tail where gauche isomers appear in flexible conformations are depending on the compound. The positions of these "freedom" points, which would be reliable to the even–odd effect, are mentioned in Table V and indicated by a solid line. It must be noticed that this interpretation does not depend on the exact values of γ_{CC} for the bonds included in the trans part of the tail, but only of the optical anisotropy of the trans sequence as a whole.

The main point is that *the position of the "freedom" line does not depend* upon the chosen hypothesis needed for the determination of $\gamma_{C—C}$ in the whole trans sequence (compare Table V and Table II in Ref. 5).

7 CONCLUSION

To summarize, when the number *n* of C—C bonds in the alkyl tail is less than six, one must note a quickly increasing anisotropy of the first order polarizability of the molecule connected to a whole *trans* sequence of the C—C bonds. Our experimental results cannot indicate if $\gamma_{C—C}$ is increasing, in each compounds, from the aromatic core towards the end of the tail, or if a mean value of anisotropy must be affected uniformly in the chain for each compound.

When $n \geqslant 6$, a "freedom" frontier between all trans and disordered sequences is evidenced, and its position seems to be independent of the distribution of $\gamma_{C—C}$ values along the tail.

Such a behaviour seems to be strongly connected to the even–odd effect reported here.

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