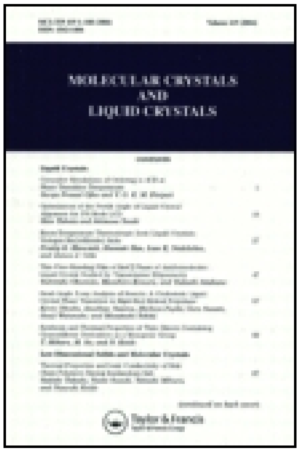

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Dipole Moments and Kerr Constants of 4-n Alkyl-4′-Cyanobiphenyl Molecules (From 1CB to 12CB) Measured in Cyclohexane Solutions

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Dipole Moments and Kerr Constants of 4-*n* Alkyl-4′-Cyanobiphenyl Molecules (From 1CB to 12CB) Measured in Cyclohexane Solutions

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We report here a detailed description of our measurements on dielectric and static Kerr constants in nCB molecules highly diluted in cyclohexane solutions. From previous experimental values we deduce at infinite-dilution apparent molecular values of dipole moment and Kerr constants. The study of the variation of those molecular values versus the number *n* of carbon atoms in the alkyl tail shows that for nCB with *n* greater than 6 the variation is different from those with *n* lower than 6; these significant differences are then succinctly commented upon.

1. INTRODUCTION

Since the discovery of cyanobiphenyl liquid crystals by Gray, Harrison and Nash[1], many technical papers about nCB have been published. In particular some authors have observed important alternations, with the number *n* of C—C bonds of the alkyl tail for various physical properties. This even-odd effect has been observed for instance by means of NMR measurements[2], Kerr constant measurements[3] or transition temperature measurements. Transition temperatures of nCB series have been measured by different authors[4] and those experimental results are reported in Figure 1. Examination of Figure 1 shows clearly two important phenomena. Firstly, values of transition temperature decrease strongly from $n = 1$ to $n = 6$ but from $n = 6$ to $n = 12$, values are stationary and even increase slightly. Secondly, in the last part of nCB series (from $n = 6$ or rather from $n = 5$ if we consider the beginning of the phenomena) a strong even-odd effect is easily observable. These two characteristic behaviors are probably of great interest in the study of nCB because liquid crystal properties appear from $n = 5$ which is precisely the limit observed for the two preceding behaviours. So, if we are able to explain this difference and this strong alternation in physical properties of nCB series we can reasonably think that this explanation can give important informations upon the phenomena which induce liquid crystal properties in nCB molecules for $n \geq 5$.

For this reason we have undertaken a study of electro-optic properties of nCB series. In a first work[5] we have measured molecular optical anisotropy of the whole nCB series, compounds being diluted in cyclohexane solutions: examination of experimental values shows the two previously mentioned phenomena (difference and alternation in the variation curve). Moreover, comparison with calculated values of molecular optical anisotropy indicates that trans conformations of

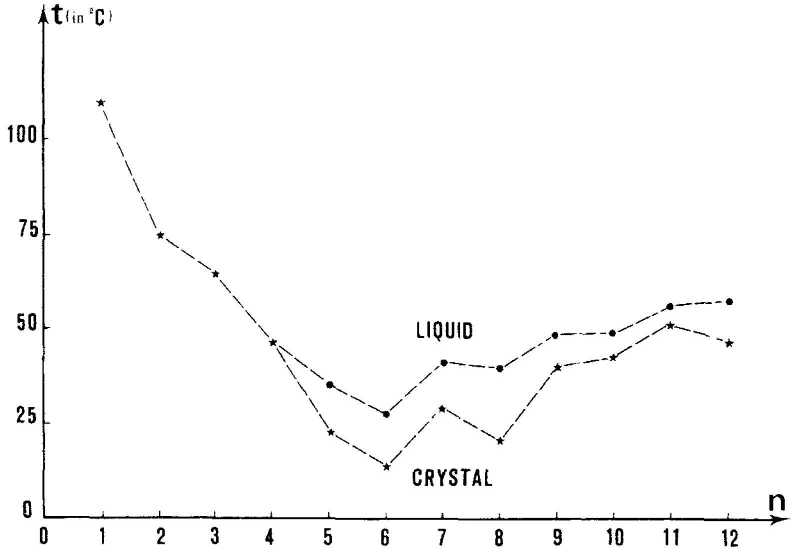

FIGURE 1 Variation of transition temperatures t of nCB versus the number n of carbon atoms in the alkyl tail.

the alkyl tail are favoured from $n = 3$ to $n = 5$. In a second work[6] by means of more expanded calculations a conformational analysis allowed us to conclude more precise hypotheses such as limitation of the alkyl tail size from $n = 6$.

The aim of the present work is to complete our previous studies on molecular optical anisotropy of nCB by means of measurements upon two different molecular electro-optic parameters: dipole moment and static Kerr constant.

2. MATERIALS

The twelve nCB compounds have been purchased from B. D. H., their purity being greater than 99.8%. All their physical properties can be found in already published data[4], for instance transition temperatures are reported in Figure 1. As in our previous studies, nCB compounds were diluted in cyclohexane solutions; the purity of the solvent was greater than 99%. The mole fractions of the solutions were in any case less than 10^{-2}, binary solutions being prepared gravimetrically. The weak solubility of nCB in cyclohexane and the obligation to measure with highly dilute solutions for extrapolation at infinite dilution have led us to use such concentrations.

3. EXPERIMENTAL

3.1. Density and concentration of solutions

Density d and mass concentration C of solutions are measured with precise gauged flask and balance at a stable temperature. The relative precision upon d and C is better than 10^{-3} in any case. An example of measurements is given in Table I for 6CB. In this table the mean value $a(d)$ of the variation of d relative to concentration variation is noted. The low precision of $a(d)$ is the result of weak differences in densities values and it is not important in our study because as mentioned in section 4, the term relative to $a(d)$ in the molar Kerr constant extrapolated to infinite dilution is negligible.

3.2. Refractive index of solutions

Refractive indices n' are measured with a PULFRICH refractometer (from Bellingham and Stanley). This apparatus allows measurements

TABLE I

Example of measurements for 6CB in cyclohexane solutions. Experimental values of density d, refractive index n', relative dielectric constant ϵ_r and Kerr constant B (in u.e.s.c.g.s.) versus the mass concentration c (in $g.g^{-1}$) ($\lambda = 5460$ Å, $t = 25\,°C$, $P = 1$ atm)

[a]	$C \times 10^2$	d	n'	ϵ_r	$B \times 10^9$
cyclohexane	0	0.7780	1.4262	2.024	6.28
Solution 1	0.330	0.7785	1.4268	2.050	33.0
Solution 2	0.420	0.7794	1.4271	2.058	40.9
Solution 3	0.606	0.7784	1.4273	2.073	56.3
Solution 4	0.773	0.7795	1.4274	2.087	69.2
Cyclohexane	0	0.7780	1.4268	2.022	6.20
$a(X)$[b]		0.19 ± 0.14	0.35 ± 0.05	8.31 ± 0.08	8190 ± 90

[a] The various solutions are noted in the chronological order of the experimentation. Measurements of cyclohexane properties are made at the beginning and at the end of the experimentation to insure good relative values, because the mean solvent values[7] are used as reference.

[b] $a(X)$ is the mean value of the variation of $X(d, n'^2, \epsilon_r$ or $B)$ relative to the variation of the concentration in $g.g^{-1}$: $\delta x/\delta c$ (for $a(X)$ calculations, only $\delta C = C$ is considered).

with a relative experimental error less than 10^{-4} (at 25 °C, in a temperature controlled cell). Values of n' measured on 6CB are reported in Table I and mean value $a(n'^2)$ of the slope of n'^2 versus c is given. Because of the weak variations between various solutions, this value is not precise but this is not an important disadvantage for our calculations in section 4: the terms containing $a(n'^2)$ being much smaller than others [$a(\epsilon'_r$ and $a(B)$] in dipole moment and molar Kerr constant expressions for infinite dilution solutions.

3.3. Dielectric constant of solutions

Relative dielectric constants ϵ_r of solutions are measured with a dipolmeter DM 01 (from W. T. W.). Relative experimental error is less than 10^{-3} (at $25\,°C \pm 0.2\,°C$, in a temperature controlled cell). Experimental values of 6CB given in table I indicate for the mean slope $a(\epsilon_r)$ a precision of about 10^{-2}. In spite of the low concentrations used in our solutions, we have obtained this satisfying precision for the two following reasons. Firstly, in order to reduce important experimental errors like bubbles or impurities in the cell or other aberrations in the signal of the apparatus, we have repeated many times carefully measurements for each solutions. Secondly, contrary to previous parameters d, c and n', because of the strong molecular dipole moment of nCB (see section 4) the values of the measured parameters are sufficiently important to allow a satisfying precision.

3.4. Kerr constant of solutions

The Kerr constants B defined by $B = (n_{\parallel} - n_{\perp})/\lambda E^2$ ($n_{\parallel}$ and $n_{\perp}$ are refractive indexes parallel and perpendicular to the electrostatic field E. λ is the wavelength of the light source) are measured with an apparatus already described.[5,8] Relative experimental error is less than 10^{-2} (at 25 °C ± 0.5 °C). Experimental values of 6CB given in Table I indicate for the mean slope $a(B)$ a good precision of about 10^{-2} obtained mainly because Kerr constants of nCB are very strong in regard to Kerr constant of cyclohexane. The amplitude of the birefringence optical signal of our Kerr apparatus being proportional to the quantity BE^2, in spite of the high dilution of solution, precise measurements are possible with electric field values from 13 to 19 KV per cm.

4. RESULTS AND DISCUSSION

Our experimental results are reported in Table II, $a(d)$, $a(n'^2)$, $a(\epsilon_r)$ and $a(B)$ being defined in section 3 (M is the molar weight of nCB compounds) μ^2_∞ and mK are determinated as follows.

TABLE II

Square of the molecular dipole moment μ^2 (inD^2 or 10^{-36} u.e.s.c.g.s) and molar Kerr constant mK (in u.e.s.c.g.s) calculated from experimental values extrapolated at infinite dilution in Cyclohexane solutions (λ = 5460 Å; t = 25 °C; p = 1 atm)

Compounds	M	$a(d)$	$a(n'^2)$	$a(\epsilon_r)$	$a(B)\,10^9$	μ^2_∞	$\mathrm{mK}_\infty 10^{11}$
1CB	193.2	0.07	0.28	10.43	10538	22.8_4	622
2CB	207.2	0.00	0.28	10.01	10190	23.4_8	645
3CB	221.2	0.13	0.32	9.49	9555	23.6_3	646
4CB	235.3	0.05	0.32	8.98	9408	23.7_4	676
5CB	249.3	0.00	0.37	8.70	8535	24.1_7	651
6CB	263.3	0.19	0.35	8.31	8190	24.4_2	659
7CB	277.3	0.05	0.31	7.75	7833	24.0_3	664
8CB	291.3	0.00	0.32	7.37	7689	23.9_1	684
9CB	305.3	0.25	0.36	7.06	7555	23.8_3	705
10CB	319.3	0.05	0.32	6.89	7354	24.4_2	718
11CB	333.3	0.00	0.32	6.42	7040	23.6_9	717
12CB	347.3	0.10	0.32	6.22	6910	23.8_7	734

μ_∞ is the apparent value of molecular dipole moment of solute for infinite dilution in cyclohexane solution. Using the Lorenz–Lorentz and Clausius–Mossotti formula and writing refractive index n' and relative dielectric constant ϵ_r of a solution as functions of solvent parameters, solute parameters and of weight fraction C, we obtain easily the following relation called the Hederstrand formula[9]:

$$\mu_\infty^2 = 3kT\left\{\frac{9M}{4\pi N_{d_0}}\frac{\left[a(\epsilon_r) - a(n'^2)\right]}{(\epsilon_{r_0} + 2)^2}\right\} \tag{1}$$

(k: Boltzmann constant. T: absolute temperature. N: Avogadro number. d_0 and ϵ_{r_0} are respectively the density and the dielectric constant of cyclohexane).

mK_∞ is the apparent value of molar Kerr constant of solute for infinite dilution in cyclohexane solution. Using the theoretical expression of the Kerr constant B, if we write constant B of a solution as a function of solvent parameters, solute parameters and of weight fraction C, we can show that:

$$\mathrm{mK} = \mathrm{mK}_0\frac{M}{M_0}\left[\frac{a(B)}{B_0} - \frac{a(d)}{d_0} + 1 - \left(\frac{n_0'^2 - 1}{n_0'^2 + 2}\right)\frac{a(n'^2)}{n_0'^2} - \left(\frac{\epsilon_{r_0}}{\epsilon_{r_0} + 2}\right)\frac{a(\epsilon_r)}{\epsilon_{r_0}}\right] \tag{2}$$

(The molar Kerr constant of cyclohexane being

$$\mathrm{mK}_0 = \frac{2B_0\lambda n_0' M_0}{d_0(n_0'^2 + 2)^2(\epsilon_{r_0} + 2)'}$$

with B_0, n_0', M_0, d_0 and ϵ_{r_0} as previously defined, relative to cyclohexane.)

Relation (2) differs from the Lefevre expression[10] by last term:

$$\left(\frac{2\epsilon_{r_0}}{\epsilon_{r_0} + 2}\right)\frac{a(\epsilon_r)}{\epsilon_{r_0}}.$$

We have already given details of our calculations in earlier works.[5,7,11] In order to analyse our experimental results, we have presented in

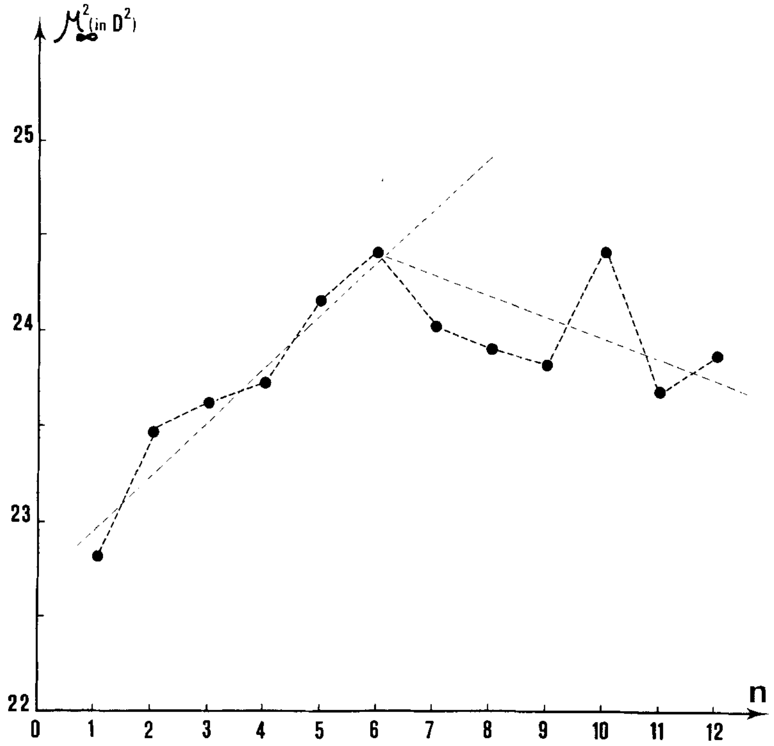

FIGURE 2 Variation of the square of dipole moment μ^2 for nCB diluted in cyclohexane solutions versus the number n of carbon atoms in the alkyl tail.

Figures 2 and 3 variations of μ^2_∞ and mK_∞ of nCB versus n. Figure 2 shows that variation curve of the apparent molecular dipole moment involves the two characteristic phenomena mentioned in section 1. The first phenomenon, difference between the molecules with $n \leq 6$ and the molecules with $n \geq 6$, is unambiguous because of the relative precision on μ^2_∞ values in regard to the observed difference in the curve. The increasing of μ^2_∞ from 1CB to 6CB is regular and reaches

$$7.10^{-2}\left(=\frac{\mu^2_\infty(6\text{CB})-\mu^2_\infty(1\text{CB})}{\mu^2_\infty(1\text{CB})}\right),$$

at the opposite μ^2_∞ values for $n > 6$ are stationary or slightly decreasing. Thus the experimental error less than 2.10^{-2} for μ^2_∞ values, is consistent with our interpretation. In addition to that, because our analysis is based upon relative values measured in compounds of the

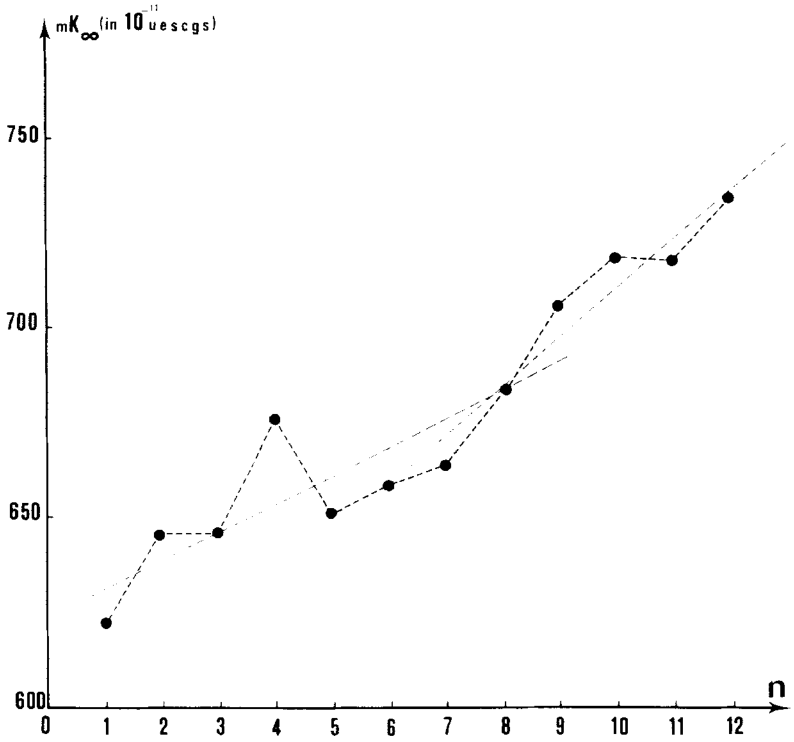

FIGURE 3 Variation of the molar Kerr constant mK for nCB diluted in cyclohexane solutions versus the number *n* of carbon atoms in the alkyl tail.

same chemical series, absolute experimental or theoretical errors like those inherent in relation (1) deduced from rough theoretical calculations, are not inconvenient. The second phenomenon, alternation in relation to the parity of *n*, is less evident because the amplitude of the even-odd effect is not regular and its mean value is not significantly larger than the relative experimental error ($1.6.10^{-2}$ against 2.10^{-2}). In spite of the imprecision of the observed even-odd effect, we think that its existence is not doubtful because of the systematic aspect of this part of Figure 2.

Figure 3 shows that variation curve of the apparent molar Kerr constant involves only the first characteristic phenomenon. The value of the relative increasing is about 5.10^{-2} from 1CB to 6CB and about 12.10^{-2} from 6CB to 12CB, this difference is unambiguous in regard to the relative experimental error (less than 2.10^{-2}) even though the exact separating place between the two different parts is not well located (from 5CB to 7CB). Another difference in the aspect of the curve between the two parts of the series can also be noticed: an alternation is observed in the first part (from $n = 1$ to $n = 5$); but any even-odd effect can be observable in the second part of the series (involving the liquid crystalline molecules) this effect being probably hidden by too much important experimental error. Yet, an interesting fact must be noted: although in the cases of dipole moments and of optical anisotropies (see references 5 and 6) the molecular values become stationary with a strong even-odd effect from 6CB to 12CB, in the case of molar Kerr constants, molecular values are increasing without a noticeable even-odd effect. At first sight this fact can seem inconsistent if we consider the theoretical expression (3) of the molar Kerr constant[5,7,10]:

$$\mathrm{mK} = \frac{2\pi N}{9}\left[\frac{1}{45\,kT}\left(3\alpha^0_{ij}\alpha_{ij} - \alpha^0_{ii}\alpha_{jj}\right) + \frac{1}{45k^2T^2}\left(3\alpha^0_{ij}\mu_i\mu_j - \alpha^0_{ii}\mu_j\mu_j\right)\right] \tag{3}$$

(α^0_{ij}, α_{ij} and μ_i are respectively the optical polarisability, the electrical polarisability and the permanent dipole moment component along i molecular axis)

If we admit $\alpha^0_{ij} \simeq \alpha_{ij}$, the first term is proportional to the molecular optical anisotropy γ^2. Nevertheless, a more precise examination show that the first term is very much smaller than the second one (less than about 5.10^{-2} in our previous calculations[5,6]). Moreover the second term is not simply proportional to μ^2 and γ^2. So it is not surprising that the variation of mK differs from the variation of μ^2 and γ^2 and indeed, this fact must be considered like an important and interesting one because it is the proof that our mK measurements can give independent informations by comparison of experimental and calculated values like in our previous study about optical anisotropy.[5,6]

In conclusion, an analysis of our measurements shows that variation of apparent molecular dipole moments and molar Kerr constants in cyclohexane solution versus the length of the alkyl tail confirm unambiguously the difference between the molecular physical properties of liquid crystalline molecules (from 5CB to 12CB) and those of other molecules of the nCB series. Moreover a more thorough study, like comparison with calculated values, must give fuller information about conformation of these molecules.

References

1. G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.*, **9**, 130, (1973).
2. A. Pines, D. J. Ruben and S. Allison, *Phys. Rev. Lett.*, **33**, 1002 (1974).
3. R. Yama Moto, S. Ishihara, S. Hayakawa and K. Morimoto, *Phys. Lett, A*, **60**, 414, (1977). No quantitative comparison is possible between values measured by Yamamoto et al. and those measured in our present work, because Kerr constants of Yamamoto are performed on pure liquid crystals and, consequently, relation (2) (see Section 4) can not be used. However Yamamoto have observed that Kerr constants tend to decrease with increasing n; our own measurements (see a(B) in Table II) confirm this variation.
4. (a) G. W. Gray and A. Mosley, *J.C.S. Perkin II*, **97**, (1976).
4. (b) J. W. Park, C. S. Bak and M. M. Labes, *J. Amer. Chem. Soc.*, **97**, 4398 (1975).
4. (c) G. W. Gray, *J. Phys. (Fr)*, **36**, (C1), 337 (1975).
4. (d) G. W. Gray and A. Mosley, *J.C.S. Chem. Comm.*, 147 (1976).
4. (e) M. G. Pellatt, B. D. H. Chemicals Ltd, Appendix 3b of the Liquid crystals Information booklet, (1982).
5. J. R. Lalanne, B. Lemaire, J. Rouch, C. Vaucamps and A. Proutiere, *J. Chem. Phys.*, **73**, 4, 1927 (1980).
6. A. Proutiere, R. Viani, J. R. Lalanne, B. Lemaire, J. C. Rayez and B. Duguay, 9th International Liquid Crystal Conference, Bangalore (India), 6–10 December (1982).
7. A. Proutiere, J. G. Baudet and M. Camail, *J. Chim. Phys.*, **11–12**, 1439 (1974) (and many other literature data).
8. A. Proutiere and J. G. Baudet, *C.R. Acad. Sci. Paris*, **267**, 682 (1968).
9. G. Hedestrand, *Zeit. Phys. Chem. (B) Z*, 428 (1929).
10. C. G. Lefevre and R. J. W. Leffevre, *Rev. Pur. App. Chem.*, **5**, 4, 261 (1955).
11. A. Proutiere and B. Choteau, *Mol. Phys.*, **35**, **2**, 397 (1978).