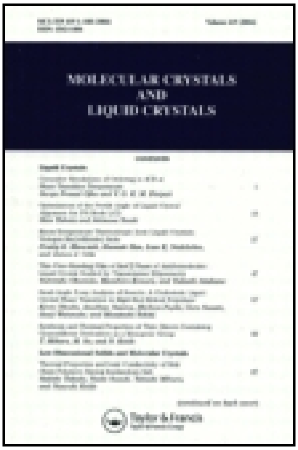

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Dipole Moments of 4-n Alkyl-4′-Cyanobiphenyl Molecules (from OCB to 12CB) Measurement in Four Solvents and Theoretical Calculations

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Dipole Moments of 4-n Alkyl-4′-Cyanobiphenyl Molecules (from 0CB to 12CB) Measurement in Four Solvents and Theoretical Calculations

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We report here a detailed description of our measurements on dielectric constants in nCB molecules highly diluted in four different solvents: cyclohexane, *n* hexane, benzene and carbon tetrachloride. From those experimental values we deduce at infinite dilution apparent values of molecular dipole moments μ. The study of the variation of μ versus the number *n* of carbon atoms in the alkyl tail shows that in the first two solvents variation for *n* greater than 6 is different from variation for *n* lower than 6; on the other hand no significant difference is observed in benzene and carbon tetrachloride. These results are commented upon and theoretical calculations are executed in order to search for a coherent explanation. Two kinds of calculation have been undertaken: molecular energies with Molecular Mechanics method and molecular dipole moments with D.I.D. method.

Keywords: cyanobiphenyls—dipole moment—dipole induced dipole.

1. INTRODUCTION

Many technical studies have been undertaken about nCB compounds since their discovery.[1] Among the various results already obtained, we have specially noted two interesting behaviours. Firstly, variation of physical properties versus the number *n* of carbon atoms of the alkyl chain shows an even-odd effect. Secondly, this variation is not monotonous: a significant difference is observed between the beginning and the end of the curve, the boundary being located at $n = 5$ or $n = 6$. The physical properties in accordance with these characteristic variations are varied: NMR measurements,[2] Kerr constants[3] or Transition temperatures.[4] These two behaviours, specially the second one, are probably of great interest because $n \geqslant 5$ is also the limit from which liquid crystal properties appear in nCB series.

For this reason we have undertaken a study of electro-optic properties of nCB compounds. Indeed, properties such as optical anisotropy, static Kerr constant and dipole moment can allow easily precise relative measurements because in nCB molecules the two aromatic rings and the $C \equiv N$ bound induce respectively a strong optical anisotropy and a strong dipole moment, and precise experimental values are necessary to expect a good and self consistent interpretation of experimental results. In a first work[5] we have measured molecular optical anisotropy of the whole nCB series in cyclohexane solution: experimental data show the two previously mentioned behaviours (even-odd effect and two different variations). Moreover comparison with calculated values of molecular optical anisotropy (by means of optical valency theory) indicates that trans conformations of the alkyl tail are favoured for $n \leqslant 5$. In a second work,[6] by means of more expanded calculations (D.I.D. and Molecular Mechanics methods), a conformational analysis allowed us to conclude more advanced hypotheses such as limitation of the alkyl tail size for $n > 6$. In a more recent paper published in this journal[7] we reported other experimental results on the nCB series: measured values in cyclohexane solution of molecular dipole moments and static Kerr constants.

The object of this last work was to examine variation of two new electro-optic parameters versus n, in order to complete our first observations:[5] in fact, a satisfying confirmation of the second characteristic behaviour (changing in the variation curve from $n = 6$) has been obtained, specially for dipole moments (interpretation of Kerr constant variations is more doubtful). The aim of the present work is to complete and to interpret our previous works. Firstly with an experimental study on dipole moments of nCB diluted in four different apolar solvents (from $n = 0$ to $n = 12$) we try to discuss the specificity of characteristic variations observed: an intrinsic (intramolecular) or a collective (intermolecular) effect? Secondly, by means of theoretical calculations, in the case of molecular dipole moments performed in cyclohexane solution, we compare experimental data to calculated ones in order to interpret the variation curves observed (with a method already used for molecular optical anisotropies[6]).

2. MATERIALS

The thirteen 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] nCB compounds were diluted in cyclohexane, n hexane, benzene and carbon tetrachloride solutions; the purity of the solvents 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 *n* hexane) and the obligation to measure with highly diluted solutions for extrapolation at infinite dilution have led us to 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. Details upon measurements are given in our previous study.[7] In the end of our study, densities were measured with a density meter DMA 45 from ANTON PARR.

3.2. Refractive index of solutions

Refractive indices n' 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). Details upon n' measurements are reported in our previous work[7] and mean value $a(n'^2)$ of the slope of n'^2 versus C is given in tables of section 4. 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 term $a(n'^2)$ being much smaller than $a(\epsilon_r)$ in dipole moment expression for infinite dilution solutions (see Table I).

Nevertheless, in order to reduce drawbacks of this lack of precision

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*:In some cases compounds purchased from HOFFMANN-LA ROCHE have been used with identical results.

we have assumed artificial regular values of $a(n'^2)$, based upon our average measurements (see Table I).

3.3. Dielectric constants 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, in a temperature controlled cell). The values of mean slope $a(\epsilon_r)$ of ϵ_r versus C are noted in tables of section 4 and its relative precision is 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 solution. 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.

4. EXPERIMENTAL RESULTS

Our experimental results are reported in Tables I_a to I_d $a(\epsilon_r)$ and $a(n'^2)$ being defined in section 3 (M is the molar weight of nCB compounds) μ_∞^2 is determined as follows.

μ_∞ is the apparent value of molecular dipole moment of solute for infinite dilution in 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:[8]

$$\mu_\infty^2 = 3kT\left\{\frac{9M}{4\Pi N d_o}\,\frac{[a(\epsilon_r) - a(n'^2)]}{(\epsilon_{r_o} + 2)^2}\right\} \qquad (1)$$

(k: Boltzmann constant. T: absolute temperature. N: Avogadro number d_o and ϵ_{r_o} are respectively the density and the relative dielectric constant of solvent).

In order to analyse our experimental results, we have presented in Figures 1_a to 1_d variations of μ_∞^2 of nCB versus n. All comments upon these curves are in the first part of discussion (section 6).

TABLE I

Square of the molecular dipole moment μ^2 (in D^2 or 10^{-36} u.e.s.c.g.s) deduced from experimental values extrapolated at infinite dilution in four different solvents ($\lambda = 5460$ Å; $t = 25$°C; $P = 1$ atm)

	Ia: in cyclohexane solutions				Ib: in *n* hexane solutions			
nCB	M	$a(n'^2)$	$a(\epsilon_r)$	μ^2	nCB	$a(n'^2)$	$a(\epsilon_r)$	μ^2
0CB	179.2	0.34	9.82	19.80	0CB	0.61	8.08	19.85
1CB	193.2	0.34	10.59	23.07	1CB	0.60	9.02	24.12
2CB	207.2	0.34	10.29	24.00	2CB	0.59	8.60	24.59
3CB	221.2	0.34	9.76	24.26	3CB	0.58	8.27	25.20
4CB	235.3	0.34	9.24	24.41	4CB	0.57	7.87	25.45
5CB	249.3	0.34	8.89	24.84	5CB	0.56	7.56	25.85
6CB	263.3	0.34	8.53	25.12	6CB	0.55	7.20	25.94
7CB	277.3	0.34	7.91	24.45	7CB	0.54	6.90	26.16
8CB	291.3	0.34	7.50	24.29	8CB	0.53	6.60	26.22
9CB	305.3	0.34	7.21	24.44	9CB	0.52	6.30	26.16
10CB	319.3	0.34	7.08	25.05	10CB	0.51	6.00	25.98
11CB	333.3	0.34	6.52	23.98	11CB	0.51	5.80	26.21
12CB	347.3	0.34	6.40	24.51	12CB	0.50	5.61	26.31

	Ic: in benzene solutions			Id: in carbon tetrachloride solutions			
nCB	$a(n'^2)$	$a(\epsilon_r)$	μ^2	nCB	$a(n'^2)$	$a(\epsilon_r)$	μ^2
0CB	0.31	12.76	20.37	0CB	0.58	21.20	18.95
1CB	0.30	14.13	24.40	1CB	0.58	23.61	22.82
2CB	0.29	13.57	25.13	2CB	0.57	22.30	23.09
3CB	0.28	12.31	24.29	3CB	0.57	20.20	22.27
4CB	0.27	11.89	24.98	4CB	0.56	19.12	22.40
5CB	0.26	10.93	24.30	5CB	0.56	18.96	23.52
6CB	0.25	10.56	24.80	6CB	0.56	17.87	23.38
7CB	0.24	10.01	24.75	7CB	0.55	16.33	22.44
8CB	0.23	9.63	25.01	8CB	0.55	15.84	22.84
9CB	0.22	8.96	24.36	9CB	0.54	14.81	22.34
10CB	0.21	8.79	25.02	10CB	0.54	14.39	22.67
11CB	0.20	8.35	24.80	11CB	0.53	13.89	22.84
12CB	0.18	7.99	25.31	12CB	0.53	13.36	22.86

5. THEORETICAL CALCULATIONS

5.1. General description

The general scheme of μ^2 calculations for a nCB compound can be described as following. Conformational energy E for all isomers is determined by using Molecular Mechanics (M.M.) method. Then μ^2 of each isomer is calculated with our Dipole Induced Dipole (D.I.D.) method. Finally μ^2 of the nCB molecule is the statistical mean value calculated in accordance with the following MAXWELL-BOLTZ-

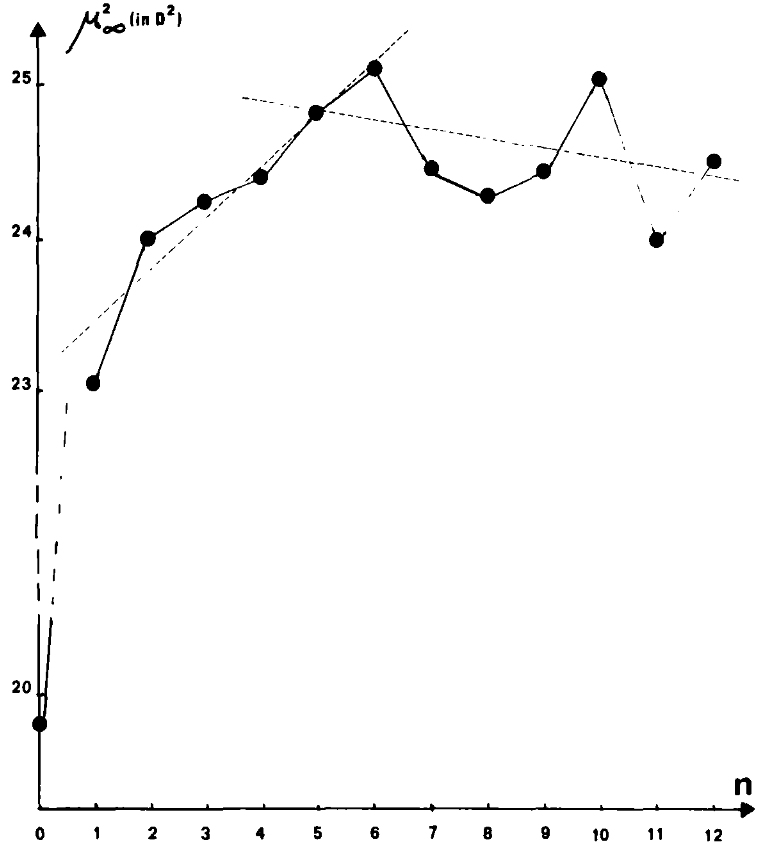

FIGURE 1a Variation of the experimental square of dipole moment μ^2 for nCB diluted in cyclohexane solutions versus the number *n* of carbon atoms in the alkyl tail.

MANN statistical relation.

$$\mu^2 = \sum_{i=1}^{1} (n_i/N)\mu_i^2, \quad \text{with} \quad n_i = n_j \exp(-\Delta E_{ij}/kT)$$

(n_i is the number of isomer i, μ_i^2 is the μ^2 value for isomer i, 1 is the number of different isomers in the nCB molecule, N is the total number of isomers in a molecule, ΔE_{ij} is the difference of molar energy between isomers i and j).

This general scheme and the two theoretical methods (M.M. and D.I.D.) have been already described in our previous work upon γ^2

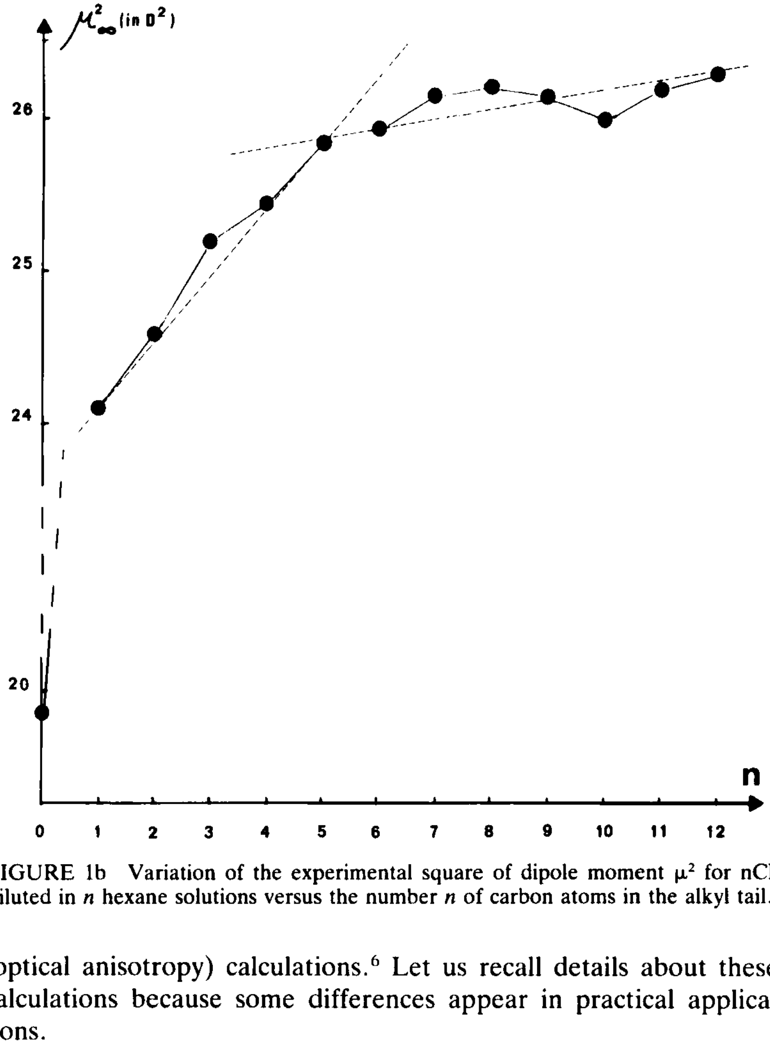

FIGURE 1b Variation of the experimental square of dipole moment μ^2 for nCB diluted in *n* hexane solutions versus the number *n* of carbon atoms in the alkyl tail.

(optical anisotropy) calculations.[6] Let us recall details about these calculations because some differences appear in practical applications.

5.1.1. Molecular Mechanics calculations

Molecular Mechanics is an inductive method in which a set of energy functions, deduced from experimental data, is used for the prediction of observable properties of series of molecules.[9] The four energy functions calculated are the following ones.

The compression energy (from bond length deformations), the bending energy and stretch bend energy (from bond angle defor-

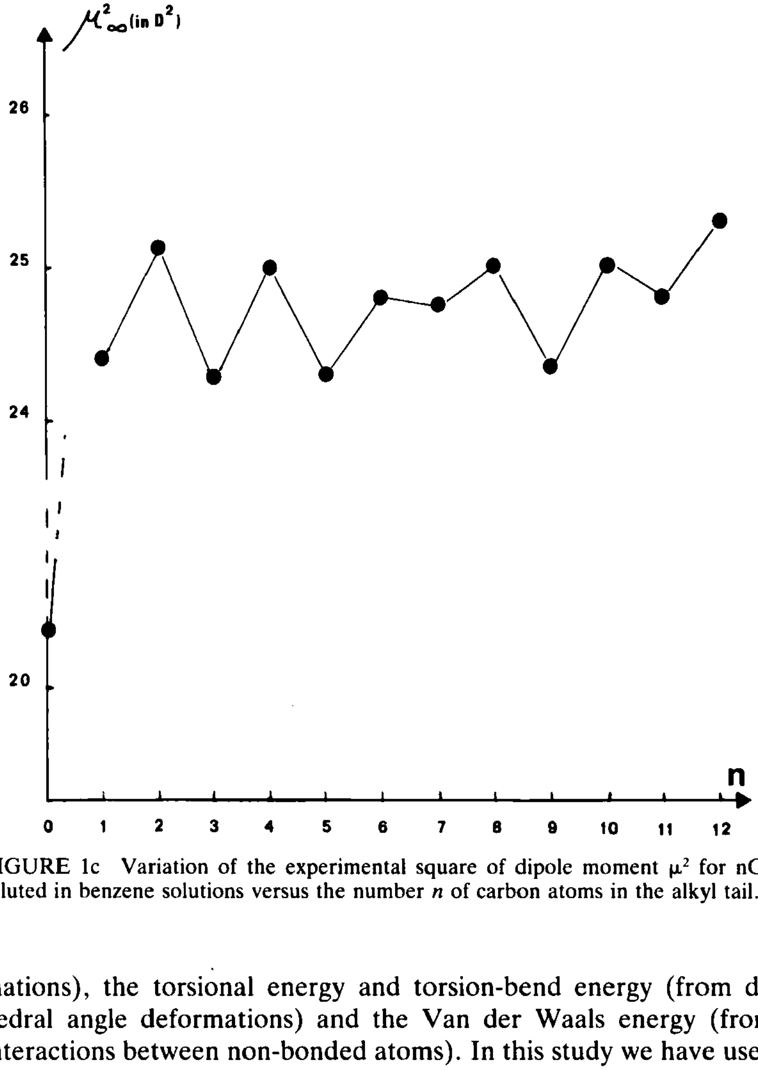

FIGURE 1c Variation of the experimental square of dipole moment μ^2 for nCB diluted in benzene solutions versus the number *n* of carbon atoms in the alkyl tail.

mations), the torsional energy and torsion-bend energy (from dihedral angle deformations) and the Van der Waals energy (from interactions between non-bonded atoms). In this study we have used the MM2 force field program of ALLINGER and YUH.[9b] Values of energetic parameters used are those of the MM2 program,[9b] some other parameters (connected with the triple bond $C \equiv N$ or with the bonds C—C in the two aromatic rings of nCB), not enclosed in original MM2 program, have been introduced, they are noted in Table II. Values of these parameters have been selected because a reasonable optimized geometry can be obtained for 0CB molecule in coplanar conformation. Indeed our previous conformation analysis[6] on

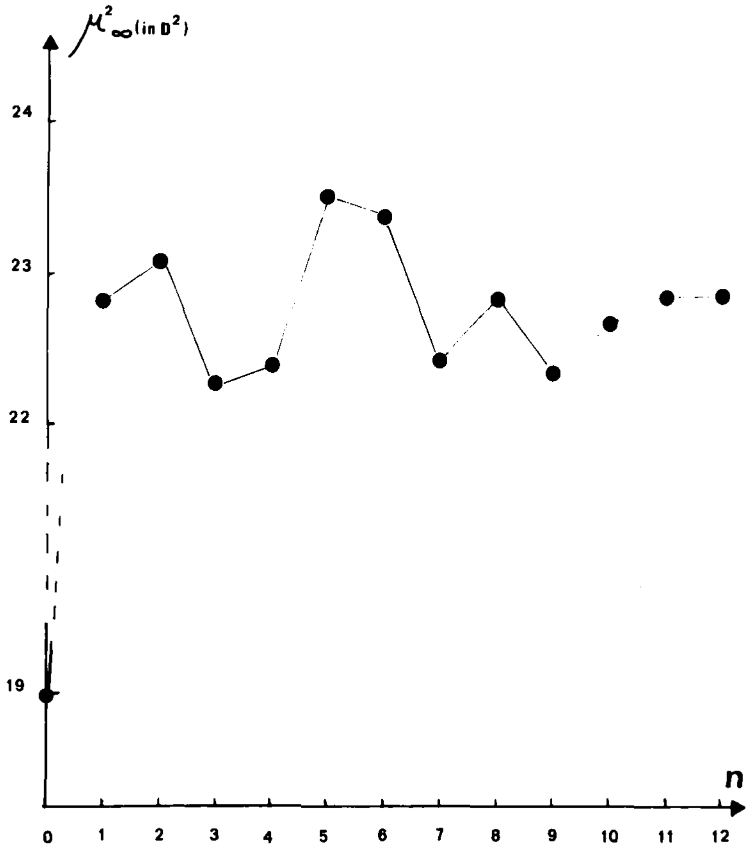

FIGURE 1d Variation of the experimental square of dipole moment μ^2 for nCB diluted in carbon tetrachloride solutions versus the number *n* of carbon atoms in the alkyl tail.

nCB molecules led us to admit that the two aromatic rings are coplanar in the first part of the series ($n \leq 6$) for compounds diluted in cyclohexane solutions. Moreover, a recent study[10] on 0CB give us the same result, this theoretical work was based on different calculations such as: Molecular Mechanics combined with V.E.S.C.F. calculations for the delocalized pi system (ALLINGER-SPRAGUE method using MMP1 program[11]), Van der Waals energy calculated for intermolecular interactions in cyclohexane solution and dipolar interaction energy calculated with a D.I.D. method. Thus, we assume a coplanar geometry for the aromatic core in our calculations. But

TABLE II

Set of new parameters introduced in our calculations to use MM2 program (all other parameters are enclosed in original program[9b])

IIa: Stretching parameters. K(s) = stretching constant (md/Å).
L(0) = minimum energy bond length (Å).

Bonds	K(s)	L(0)
C_{ar}—C_{sp}	10.0	1.430
C_{ar}—C_{ar}	8.0	1.393
C_{ar}—C_{sp3}	8.0	1.497
C_{ar}—C_{ar} (central bond)	8.0	1.485

(C_{ar} = aromatic carbon atom)

IIb: Bending parameters. K(B) = bending constant (md. Å/rad^2).
θ(0) = minimum energy angle (deg.).

Bond angles	K(B)	θ(0)
C_{ar}—C_{ar}—C_{sp}	0.38	120.0
C_{ar}—C_{sp}≡N	0.38	180.0
C_{ar}—C_{ar}—C_{ar}	0.38	120.0
C_{ar}—C_{ar}—H	0.38	120.0

IIc: Torsional parameters. V_1, V_2 and V_3 = first, second and third order torsional constants (Kcal/mole).

Dihedral angles	V_1	V_2	V_3
C_{ar}—C_{ar}—C_{ar}—C_{sp}	0.0	15.0	0.0
C_{ar}—C_{ar}—C_{sp}≡N	0.0	10.0	0.0
C_{sp}—C_{ar}—C_{ar}—H	0.0	15.0	0.0
C_{ar}—C_{ar}—C_{ar}—C_{ar}	−0.93	15.0	0.0
C_{ar}—C_{ar}—C_{ar}—H	0.0	15.0	−1.06

this choice induces a serious difficulty because the MM2 force field program is not theoretically suitable for delocalized pi systems: the MMP1 program, in particular is the more suitable in Molecular Mechanics methods. In spite of this theoretical objection, because it is the more suitable one for long practical studies, we have used MM2 program introducing parameters presented in Table II: those parameters allow us to obtain a reasonable conformation of the aromatic core in 0CB. A reasonable conformation means together with coplanar rings, values of bond lengths and of bond angles not far from usual values (1.40 Å and 120° for aromatic bonds for instance). We do not give details about the geometry because our object is the knowledge of conformational energy *E*. Moreover only energetic difference Δ*E* between trans and gauche conformers of the aliphatic chain is useful in this study.

5.1.2. Dipole Induced Dipole calculations

Our electrostatic calculations have been already described in details;[6,12] we recall briefly there our method and notice the different parameters required for the calculated results presented in this paper. In our model we consider a molecule composed of N bonds in which the intrinsic polarizabilities tensor and permanent dipole moment are α_i and μ_i. In an external electric field F, the total electric moment is, for the bond i:

$$M_i = \alpha_i^* F + \mu_i^* \quad \text{with:} \quad \alpha_i^* = \alpha_i + \sum_{i=j}^{N} \alpha_i T_{ij} \alpha_j^*$$

$$\text{and} \quad \mu_i^* = \mu_i + \sum_{i=j}^{N} \alpha_i T_{ij} \mu_j^*$$

These formula involve that all electrostatic interactions between the N bonds are taken into account. T_{ij} is the interacting field tensor for the bonds i and j:

$\overset{\rightleftarrows}{T}\,\vec{M} = \overrightarrow{\text{grad}}\,.\,\overrightarrow{\text{grad}}\,(\vec{M}/1)$, 1 being the distance between bonds i and j. Our calculation program can be summarized as following. In a molecule with a well known geometry, we assign to each bond intrinsic values (α and μ), the program calculates α^* and μ^* for the N bonds and deduces molecular polarizabilities and molecular permanent dipole moment. Then values of four molecular electro-optic behaviours are calculated with help of theoretical expressions: mean polarizability ($\bar{\alpha}$), permanent dipole moment (μ), polarizabilities anisotropy (γ^2) and specific KERR constant (Sk). Those four values are compared to experimental ones and adequate intrinsic bond parameters are deduced when a good accordance is observed, by means of an optimization program. Intrinsic bond parameters and molecules used for this optimization are noticed in Tables IIIa and IIIb. In Table IIIc, results obtained in three molecules, in order to test our method, are presented.

In conclusion of this section, three points must be noticed.

—Our calculated values are apparent values observed for compounds in cyclohexane solutions, thus, calculated data are consistent with our experimental observations on nCB series performed in cyclohexane solutions.

TABLE III

Basis of D.I.D. calculations

Table IIIa: Molecules used in the determination of intrinsic bond parameters. Comparison between experimental and calculated values

Molecule	$\bar{\alpha}$ (Å^3) exp.[a]	$\bar{\alpha}$ (Å^3) cal.	γ^2 (Å^6) exp.[b]	γ^2 (Å^6) cal.	μ (D) exp.[c]	μ (D) cal.	sK(10^{-14}uescgs) exp.[d]	sK(10^{-14}uescgs) cal.
Benzene	10.38	10.40	38.7	38.3	-	-	12	14
Naphthalene	16.50	16.85	178	170	-	-	50	39
Toluene	12.30	12.30	46	46.1	0.37	0.35	18	20
CN-Benzene	12.46	12.47	89	89.4	3.99	4.0	1600	1370

(For a, b, c and d, see references 13a, 13b, 13c and 13d).

Table IIIb: Calculated apparent intrinsic bond parameters (polarizabilities α and permanent dipole moment μ)

Bond	C_{ar}—C_{ar}	C_{ar}—H	C_{ar}—C	C≡N	C—C	C—H
$\alpha_{\parallel}$ (Å^3)	0.33	0.85	0.28	3.06	0.23	0.67
$\alpha_{\perp}$ (Å^3)	0.32	1.20	0.53	1.25	0.23	0.77
$\alpha_{\underline{\perp}}$ (Å^3)	0.51	1.20	0.53	1.25	0.23	0.77
μ (D)	-	0.5	-	3.25	-	0.3
l (Å)	0.70	1.10	0.75	1.16	0.77	1.10

//: parallel to the bond

$\perp$: perpendicular to the bond (in the symmetry plane)

$\underline{\perp}$: perpendicular to the symmetry plane

l is the location of the dipole moment and of the polarisability center (distance from the carbon atom)

ar = aromatic.

Table IIIc: Molecules used for test intrinsic parameters

Molecule	θ(°)	$\bar{\alpha}$(Å^3) exp.[a]	$\bar{\alpha}$(Å^3) cal.	γ^2(Å^6) exp.[b]	γ^2(Å^6) cal.	μ(D) exp.[c]	μ(D) cal.	sK(10^{-14}uescgs) exp.[d]	sK(10^{-14}uescgs) cal.
CN-Toluene	-	14.39	14.42	121	111	4.31	4.42	2030	1703
Biphenyl	0°		21.56		373				72
	30°	(20)	20.24	203	215			41	43
	90°		20.05		102				19
CN-Biphenyl	0°		23.98	642	600	4.64	4.42	2400	2780
	45°		22.53		315		4.25		1870
(OCB)	90°		22.30		227		4.22		1730

(θ = dihedral angle between the two aromatic rings).

—In our electrostatic calculations, "ideal" geometry is used (109°28′ and 120° for angles and usual values for bond lengths, see reference 14 for instance). Indeed, this simplification is adequate because some calculations made with real geometry (geometry obtained by energy minimization or by X RAY diffraction) have shown us that no significant relative differences were observed.

—In spite of some slight differences in the bond model (location in the bond of bond polarisabilities tensor and permanent dipole moment), our method is a D.I.D. one, similar to those now commonly used by other authors. For examples, BOYD[15] and MICOVIC[16] have used a D.I.D. method, with a bond centered model, in relation to M.M. (like in our present study). LADANYL and KEYES[17] have used a D.I.D. method with an atom centered model for γ^2 calculations of *n* alkanes.

5.2. Results

All calculations have been performed on a IBM 370/145 computer and final results are reported in Table IV and in Figure 2. Three different calculated values are presented. In first column μ^2 values calculated for only trans isomers are noted. In second column μ^2 statistical mean values calculated as indicated in section 5.1 are noted: all isomers (trans and gauche) are taken into account (see annex for

TABLE IV

Calculated results

nCB	μ^2 (D^2) Trans	μ^2 (D^2) Trans + Gauche	μ^2 (D^2) Trans + Gauche $R < 7.6$ Å
0	19.54	19.54	19.54
1	23.42	23.42	23.42
2	24.01	24.01	24.01
3	24.23	24.30	24.30
4	24.30	24.39	24.39
5	24.42	24.42	24.42
6	24.40	24.42	24.42
7	24.54	24.44	23.99
8	24.51	[24.4]	(23.99)
9	24.60	[24.4]	(23.84)
10	24.57	[24.4]	(23.81)
11	24.65	[24.4]	(23.78)
12	24.60	[24.4]	(23.58)

[ ] extrapolated results.

( ) approximative results (neglecting isomers with too high conformational energy. $\Delta E \geqslant 3.0$ Kcal/mole^{-1}).

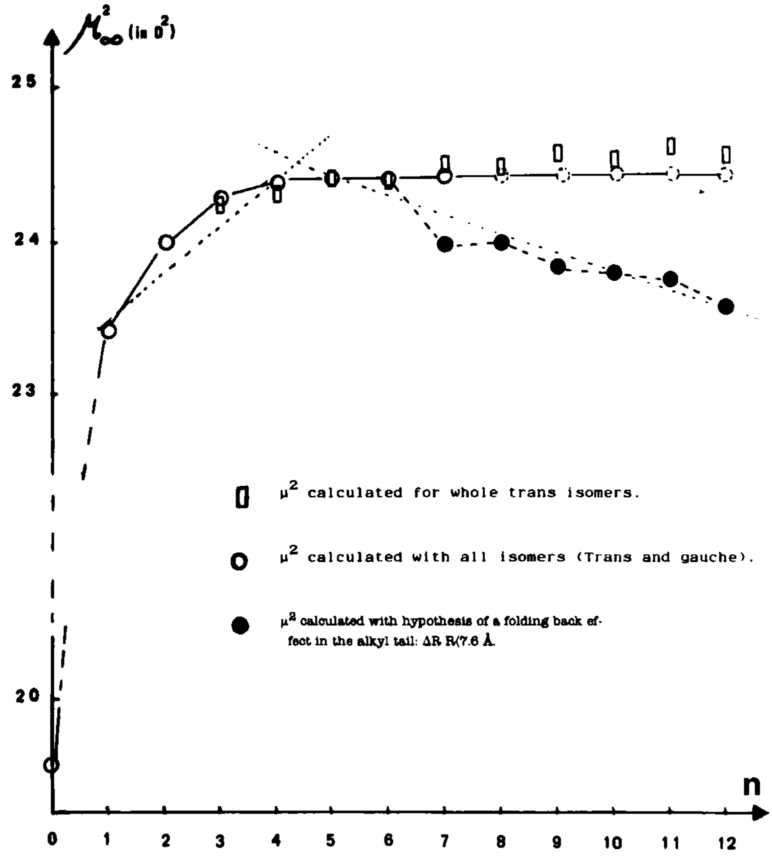

FIGURE 2 Variation of the calculated square of dipole moment μ^2 for nCB diluted in cyclohexane solutions versus the number n of carbon atoms in the alkyl tail.

details on 7CB for instance). In third column μ^2 statistical mean values calculated in the same way but not taking into account isomers with a length tail value ΔR greater than 7.6 Å (this limit value is the maximum ΔR value for 6CB; see annex for details about 7CB). Those last calculations have been made in relation with the first hypothesis noticed in comments of section 6.2.

All calculated results have been obtained by admitting in the whole nCB series the two following structural characteristics.

The aromatic core is coplanar (see section 5.1.1).

The tail is located in an average plane perpendicular to the phenyl plane in accordance with our first study[6] and with the present work:

MM2 program gives us $\Delta E \simeq 1.1$ Kcal.mole^{-1} between perpendicular position and coplanar one (the first being favoured).

6. DISCUSSION

6.1. Comments upon experimental results (Figures 1a to 1d)

The four following observations can be made by examination of Figures 1a to 1d.

Firstly, a general comparison between the four experimental curves shows significant differences in the absolute values of μ^2_∞, for instance, values in carbon tetrachloride solutions are lower than others for each nCB compound. The solvent effect, origin of these differences cannot easily be well explained and thus, this first observation is not very interesting for our study. Nevertheless, the relative strong decreasing of apparent μ^2_∞ values in carbon tetrachloride solutions shows the importance of permanent dipole moments in intermolecular interactions (dipole moments of C — Cl bonds interacting with $C \equiv N$ bonds).

Secondly, no significant regular even-odd effect (the first characteristic behaviour mentioned in section 1) can be observed except for measurements in benzene solutions (Figure 1c). Nevertheless we think that its existence is not doubtful in all cases because of the systematic irregular aspect of the experimental curves: the relative experimental error for μ^2_∞ (about 2.10^{-2}) probably hides this alternative phenomenon. In the case of benzene solutions the strong alternation in relation to the parity of n is induced certainly by special intermolecular forces (the singularity of this effect is the proof of a solvent effect); it cannot be hidden by experimental errors.

Thirdly, in the four cases, apparent μ^2_∞ values of 0CB is largely lower than those of other nCB molecules. This systematic particularity shows that this effect is probably mainly induced by intramolecular interactions: interactions between the beginning of the alkyl chain and the aromatic core seem to increase apparent μ^2_∞ values strongly. Comparison with calculated values gives us more complete informations in section 6.2.

Fourthly, two kinds of variation curves can be observed. In the case of measurements in cyclohexane and n hexane solutions, the variation versus n is different between the two parts of the series (it is the second characteristic behaviour previously mentioned in section 1). Until $n = 5$, values strongly increase, at the opposite from $n =$

5, μ_∞^2 values are slightly decreasing (Figure 1a) or stationary (Figure 1b) (those average variations are noted in dashed lines on Figures 1a and 1b). In the case of measurements in benzene and in carbon tetrachloride solutions, no significant changing between the two parts of the series can be observed in the variation curves. The following interpretation of this interesting observation can be proposed. The origin of the difference between the two cases is of course the solvent effect and more exactly the intermolecular interactions in the various solvents. Indeed, the nature of electrostatic interactions in cyclohexane and *n* hexane is very different from the one of electrostatic interactions in benzene and carbon tetrachloride. In the first case solvent molecules are composed of bonds with low polarisability anisotropy and low permanent dipole moments (see Table IIIb for C — C and C — H bonds); besides, molecular optical anisotropy γ^2 of cyclohexane and *n* hexane keep respectively the weak values 2.0 and 4.2 Å^6 [12]. At the opposite, in benzene γ^2 = 36 Å^6 [12] and in carbon tetrachloride C — Cl bonds have a strong permanent dipole moment in regard to other bonds (about 1.6 D[12]). So, it is not surprising that associative electrostatic effects are exalted in these two last solvents. Nevertheless, a question stands: is the aspect of variation curves in cyclohexane and *n* hexane induced by an intrinsic or an associative effect? In other words, in this case, can the intermolecular interactions be neglected in front of intramolecular effect? The answer to this question is important and can be partially given by analysing our theoretical calculations as noticed in section 6.2.

6.2. Comments upon calculated results (Figure 2)

Comparison of apparent values of μ_∞^2 in cyclohexane solutions calculated by means of D.I.D. and M.M. methods (Figure 2) to those previously measured (Figure 1a) can be an interesting store of information. Indeed the idea "apparent value in cyclohexane solutions" implies that solvent effects are practically negligible or identical for every nCB molecule. Thus, because calculated values are performed taking into account only intramolecular electrostatic forces, their study must indicate precision upon intramolecular or intermolecular effects as follows:

—a good accordance between experimental and calculated values shows that basic hypotheses are consistent: no special associative phenomena disturb results.

—at the opposite a discordance between experimental and calculated values shows the existence of not negligible and special associative effects.

In fact, in such a study upon an important series of similar molecules, in order to minimize disadvantage of imprecision about absolute values we consider only the relative variations of apparent values of μ^2. In this way we have analysed the third and fourth observations already commented in section 6.1.

The relative weak μ_∞ value of 0CB observed in Figure 2, as in Figure 1a, corroborates our previous interpretation of an intramolecular effect: electrostatic interactions between the first methyl group of the alkyl tail and the aromatic core are very much stronger than those between a simple C — H bond and the aromatic core (in 0CB). Thus, for two reasons, first because of the higher polarisabilities (see Table III6 for C_{ar}—C, C_{ar}—H and C — H bonds), second because of the shorter interaction distance of C_{ar}—C bond (0.75 Å instead of 1.10 Å for C_{ar}—H bond, in Table IIIb). Furthermore the relative difference of interaction distance is reduced for $n > 1$ and so the increasing of μ_∞^2 strongly diminishes from $n = 1$.

Comments about the more interesting observation, the fourth one, can be completed as follows. The general aspect of Figure 2 (curve in full line: variation of calculated statistical mean values of μ_∞^2 versus n) is not very different from the one of Figure 1a which confirms the generally weak importance of associative effects in cyclohexane solutions especially in the first part of the curve. Indeed, from $n = 1$ to $n = 5$ the average increasing is very similar to the one observed in experimental curve. The theoretical interpretation of this increasing is easy: from nCB to $(n + 1)$CB, a new electrostatic interaction between a methyl group and the aromatic core increases the molecular μ_∞^2 value. Moreover this phenomenon is in ratio to $1/l^3$ (l being the interacting distance, see detailed formula of the interacting field tensor[12]), thus, as observed in Figures 1a and 2 the increasing gradually diminishes. Nevertheless, in the second part (from $n = 5$ to $n = 12$), this explanation is not sufficient: the increasing number of gauche conformations gradually reduces the μ_∞^2 values (in Figure 2, this fact can be observed by comparing variations of μ_∞^2 for trans isomers to variations of statistical mean values of μ_∞^2) but cannot well explain the decreasing observed in Figure 1a from $n = 5$. This "anomaly," already more clearly observed on optical anisotropy variations in our previous study,[6] is necessarily induced by intermolecular effects. Furthermore, in this study on optical anisotropy[6] we have presented a first hypothesis in order to explain this aspect of the variation curve. This first hypothesis is a folding back of the alkyl chain induced by intermolecular forces in the solvent. The result of this hypothesis is presented on Figure 2 (curve in dashed lines): in this case isomers with an alkyl tail length ΔR greater than 7.6 Å are not included in calculations of statistical mean value of μ_x^2. As in our previous calculations on optical anisotropy this hypothesis can give a good explanation because the decreasing of μ_x^2 values so observed is in accordance with experimental results. Moreover, a similar folding back effect in long alkyl chains seems to have been observed in other compounds.[18] But in the case of nCB compounds, another hypothesis can be presented: if associative effects can alter the coplanar conformation of the aromatic core, a weak variation of dihedral angle between the two aromtic rings can induce a strong decreasing of μ_x^2 value as noticed in table IIIc for 0CB (this variation is even more exalted for $n \geqslant 1$). Thus, in accordance with this second hypothesis, a such associative effect from $n = 5$ is able to explain the decreasing observed. A recent work on crystalline structure of 4CB[19] have suggested us this last idea: indeed in crystalline phase, the value of dihedral angle between the two rings is 40°, this strong value implies a very strong influence of intermolecular forces on the dihedral angle value; moreover these intermolecular forces are probably induced by the alkyl tail because in 0CB the two rings are coplanar, even in cyclohexane solution.[10] At this time a study on this problem of dihedral angle value is in progress in our laboratory.

In conclusion, the present work allows us to precise the origin of the difference between the molecular physical properties of liquid crystalline molecules (from 5CB to 12CB) and those of other molecules of the nCB series: an associative effect induced by the alkyl tail. Now an interesting question is that concerning the exact process of this effect: a folding back of the tail (first hypothesis) or a rotation between the two aromatic rings (second hypothesis). Moreover we do not forget that our study is performed in cyclohexane solution and a more difficult question is that concerning associative effects in pure liquid crystalline phase.

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. Yamamoto, S. Ishihara, S. Hayakawa and K. Morimoto, *Phys. Lett.*, **A60**, 414 (1977).
4a. G. W. Gray and A. Mosley, J. C. S. Perkin II, 97, (1976).
4b. J. W. Park, C. S. Bak and M. M. Labes, *J. Amer. Chem. Soc.*, **97**, 4398 (1975).

4c. G. W. Gray, *J. Phys. (Fr)*, **36**, (C1), 337 (1975).
4d. G. W. Gray and A. Mosley, J. C. S. Chem. comm., 147 (1976).
4e. 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) and 8th International Liquid Crystal Conference, KYOTO (Japan), 30 June 4 July (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). J. R. Lalanne, J. C. Rayez, B. Duguay, A. Proutiere and R. Viani, *J. Chem. Phys.*, **81**, 1, 344 (1984).
7. E. Megnassan and A. Proutiere, *Mol. Cryst. Liq. Cryst.*, **108**, 245 (1984).
8. G. Hederstrand, *Zeit. Phys. Chem.*, **(B)Z**, 428 (1929).
9a. U. Burkert and N. L. Allinger, *Molecular Mechanics*, A. C. S. Monograh 177, Washington, D.C. (1982).
9b. N. L. Allinger and Y. H. Yuh, Molecular Mechanics: Q. C. P. E. Program No 395, updated as of January 1980. Indiana University, Chemistry Department.
10. S. Charbonnier, A. Proutiere, R. Viani, S. T. Beguemsi and Y. T. N'Guessan, 10th International Liquid Crystal Conference, York (Great Britain), 15–21 July (1984).
11. N. L. Allinger and Y. H. Yuh, Molecular Mechanics with delocalized pi systems: Q. C. P. E. Program No 318. Indiana university, Chemistry Department.
12. M. Camail, A. Proutiere and H. Bodot, *J. Phys. Chem.*, **82**, 24, 2617 (1978). A. Proutiere and M. Camail, Proceedings 6th International Conference on Thermodynamics, Merseburg (G.D.R.), 139 (1980).
13a. Handbook of Chemistry and Physics, 55th edition, Chemical Rubber Co. (1975).
13b. C. Clement, *J. Chim. Phys.*, **75**, 626 (1978).
13c. A. L. McClellan: Tables of Experimental Dipole Moments, Rahara Enterprises, El Cerrito, (1974).
13d. C. G. Le Fevre and R. J. W. Le Fevre, *Rev. Pur. App. Chem.*, **5**, 4, 261 (1955). A. Proutiere and M. Camail, *Mol. Phys.*, **29**, 5, 1473 (1975).
14. Tables of interatomic distances, No 11, Chemical Society, London (1958).
15. R. H. Boyd and L. Kesner, *J. Chem. Phys.*, **72**, 3, 2179 (1980).
16. L. D. Micovic, D. Jeremic and N. L. Allinger, *J. Am. Chem. Soc.*, **105**, 1716 (1983).
17. B. M. Ladanyi and T. Keyes, *Mol. Phys.*, **37**, 6, 1809 (1979).
18. A. Tchapla and C. Fabre, *Tetrahedron*, **38**, 14, 2147 (1982).
19. Structure of 4CB in crystalline phase: a work performed in our laboratory, not yet published.

ANNEX: DETAILS ABOUT 7CB CALCULATIONS

All calculated values used for evaluation of statistical mean value μ^2 for 7CB are noted in the following table.

Notation of isomers is made as following: the position of each carbon atom is noted respectively T, G_+ or G_- for a trans position, a positive gauche position (120°) or a negative gauche position ($-120°$); the latest letter corresponds to the position of the last carbon of the tail. ΔR is the distance between the first carbon atom (the aromatic carbon) and the last carbon atom of the alkyl tail.

ΔE is the difference of energy between considered isomer and trans one: $\Delta E = \Delta E_1 + \Delta E_2$. E_1 is the energy calculated with MM2 program for optimized geometry (see section 5.1.1). In fact, we have not made optimization of the aromatic core for practical reasons (time of calculations . . .). E_2 is the dipolar interaction energy calculated for "ideal geometry" (in accordance with our D.I.D. method) by means of the following formula: $E_2 = -\sum_{i\neq j} \mu_i^* T_{ij}\mu_j^*$ (see section 5.1.2 for definitions).

E_2 cannot be included in optimization program of MM2 because of too long calculation time, moreover final results obtained for ΔE are not far from those obtained with ΔE_1, as already noticed by BOYD[15] in his own work. μ^2 values are calculated with our D.I.D. program for ideal geometry (see section 5.1.2).

Calculated values of ΔR, ΔE and μ^2 for each isomer of 7CB molecule

ISOMERS	ΔR (Å)	ΔE (Kcal/mole)	μ^2 (D^2)
T T T T T	8.83	0.	24.54
T T T T G	7.69	0.86	24.19
T T T G T	8.08	0.88	24.63
T T T G G	6.82	1.39	24.27
T T G T T	7.27	0.78	24.23
T T G T G	6.82	1.49	24.30
T T G+T G−	7.69	1.91	24.59
T T G G T	6.34	1.32	24.10
T G G T T	6.34	1.22	23.97
T G T T G	6.81	1.54	24.13
T G−T T G+	6.34	1.64	24.15
T G T T T	8.08	0.85	24.50
T G T G T	7.68	1.73	24.62
T G+T G−T	8.08	1.93	24.50
G T T T G	6.82	1.14	24.79
G+T T T G−	7.27	1.34	24.70
G G T T T	6.83	0.91	23.72
G T T T T	7.69	0.43	24.74
G T T G T	6.83	1.04	24.40
G+T T G−T	6.35	1.31	24.10
G+T G+T T	6.82	1.06	24.80
G+T G−T T	7.69	1.46	25.26
T T G G G	6.82	2.01	24.65
T G T G G	5.81	2.20	24.40
T G+T G−G−	6.82	2.57	24.30
T G−G−T G+	6.81	2.31	24.47

ISOMERS	ΔR (Å)	ΔE (Kcal/mole)	μ^2 (D^2)
T G−G−T G−	5.24	2.53	23.92
T G G G T	6.34	1.90	24.16
T G G G G	6.82	2.68	24.65
G+T T G+G+	6.34	1.78	25.19
G+G+T T G−	5.25	1.74	23.62
G+G+T T G+	6.34	1.74	24.21
G G G T T	6.81	1.91	24.25
G+T T G−G−	5.26	1.60	24.50
G+T G+T G+	6.82	1.82	25.30
G+T G−G−T	6.82	1.92	25.36
G+T G−T G−	6.82	2.10	24.90
G+T G+T G−	6.82	2.04	24.81
G+T G−T G+	7.27	2.26	24.89
G+T G+G+T	5.26	1.48	24.79
G+G+T G−T	5.83	1.98	23.63
G+G+T G+T	6.83	1.43	24.10
G G G T G	5.24	2.95	23.76
G+T G−G−G−	6.34	2.98	24.97
G+G+G+T G−	6.34	3.18	23.91
G+T G+G+G+	5.26	2.98	(23.9)
G+G+T G+G+	6.34	2.98	(23.9)
G G G G T	6.82	2.97	(23.9)
G+G+T G−G−	6.34	3.18	(23.9)
G G G G G	6.34	3.83	(23.9)