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Angle of Twist in 4-*n* alkyl-4′-cyanobiphenyl Molecules ($0 \leq n \leq 12$). Study by Infrared and Raman Spectrometry.†

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We report infrared and Raman experiments performed on the *n*CB series (4-*n* alkyl-4′-cyanobiphenyl, $0 \leq n \leq 12$). The thirteen molecules are studied in solution ($CC\ell_4$, C_6H_6 or C_6H_{12}) and in crystalline phases, our attention is mainly focused on the value of the angle of twist θ between the aromatic rings. In $CC\ell_4$ solutions, measurements of relative integrated Raman intensities in the 1600 cm^{-1} region indicate a nearly planar conformation in the whole series: $\theta \simeq 0$. Comparison between infrared spectra registered on solutions and on crystals in the range 400–600 cm^{-1} shows frequency shifts related to θ variations or to changes in the alkyl residue. Analysis of the out of plane bending vibrations located from 461 to 482 cm^{-1} in the *n*CB series (B_{3u} mode in solid biphenyl at 461 cm^{-1}) shows that in solid phase various twisted conformations can be observed: θ value varies from 0 (in 0CB) to about 40° (in 3CB or 4CB).

Keywords: 4-n alkyl-4′-cyanobiphenyl, infrared, Raman

1. INTRODUCTION

The number of papers in the scientific and technical literature dealing with liquid crystals is considerable, but the main effort has been in the characterization and description of the properties at the macroscopic level. Because macroscopic properties depend on microscopic behavior, study of molecular conformation must give useful informations: such molecular studies on the *n*CB series (4-*n* alkyl-4′-cyanobiphenyl with $0 \leq n \leq 12$) are the aim of our work on that subject from several years.[1–6] The flexibility of the alkyl chain and the angle of twist θ between the aromatic rings are the two characteristic variables of their molecular geometry. The first time we were interested in the conformational study of the alkyl residue

†A part of this work was presented at the Fifth European Winter Liquid Crystal Conference, Borovetz, 25–30 March 1987.

by using several electro-optic experiments (Rayleigh Light scattering, static Kerr effect, dipole moment measurements), Dipole Induced Dipole calculations and Molecular Mechanics calculations. We concluded particularly that, in solution, experimental observations could be explained by the hypothesis of a folding back effect of the alkyl tail in the second part of the *n*CB series ($n > 5$).[1-4] Nevertheless this conclusion was based on a preliminary hypothesis: because we have observed that the aromatic core was nearly coplanar in the first part of the series ($n < 5$) we assumed that $\theta \simeq 0$ in the whole series. Subsequently we confirmed this coplanarity for 4-cyanobiphenyl ($n = 0$) both in solution and in solid phase.[5] More generally, in biphenyl derivatives, θ is known to be quite sensitive to the molecular environment and its determination in various phases is yet a topical and often difficult problem.[7-10] At this time, for *n*CB molecules in crystalline phase, only θ values of 3CB[11] and 4CB[12] have been determined. In order to tackle this problem we have recently done a critical analysis of various methods used.[6]

In the present work we apply two of those methods based on vibrational spectroscopic measurements to *n*CB molecules in solution and in solid phases. The first method derived from the works of Schmid *et al.*[13-16] consists in the measurement of the integrated Raman intensity of the ν_8 vibration ($\sim$1600 cm^{-1}). This intensity is enhanced by a preresonance effect and depends thus on the length of conjugation of the electronic π system. This method can give a quantitative estimate of θ in solution. The second method derived from the works of Barrett *et al.*[17] and of Almennigen *et al.*[9] is the analysis of infrared frequency shifts $\Delta\nu$ in a low frequencies range (400–600 cm^{-1}). Force field calculations and experimental observations indicate that frequency of an out of plane bending vibration (B_{3u} mode in solid biphenyl, at 461 cm^{-1}) is strongly sensitive to θ variations. Comparison between infrared spectra performed on solution and on solid phases for the whole *n*CB series shows characteristic $\Delta\nu$ values between the two phases and allows to deduce a qualitative estimate of θ value in solid.

2. EXPERIMENTAL

Materials. The thirteen *n*CB compounds have been purchased from B.D.H. or Hoffmann-La Roche, their purity being greater than 99.8%. Solvents (Carbon tetrachloride, benzene or cyclohexane) were of spectroscopic grade. All compounds have been studied without further purification.

Raman spectrometry. Spectra of carbon tetrachloride solutions have been recorded on a T800 Coderg spectrometer using an argon ion laser from Spectra Physics (488 nm).

Infrared spectrometry. Spectra of solution state (in carbon tetrachloride, cyclohexane or benzene) and those of solid state (in KBr disks or in thin layers obtained from evaporation of solutions on KBr windows) have been recorded on a Fourier Transform i.r. spectrometer (Bruker IFS 85).

3. INTEGRATED INTENSITY OF THE RAMAN ν_8 BAND

3.1 Principle of the method

We have already described and discussed this method in a previous work.[6] In brief the intensity of the ν_8 vibration (Ca 1600 cm^{-1}) observed in Raman spectra of aromatic compounds is strongly exalted by preresonance Raman effect and thus its integrated intensity S is very sensitive to conjugation. Consequently, in biphenyl molecules the dihedral angle θ, related to conjugation in the aromatic core, can be easily evaluated from S measurements through some practical formulae. Those semi-empirical formulae first elaborated by Schmid *et al.*[13-16] are

$$\mathrm{Cos}^2\,\theta = (S(\theta) - S(90))/(S(0) - S(90)) \tag{1}$$

and

$$S = a\,L^4,\ a = \text{constant} \tag{2}$$

$S(\theta)$, $S(0)$ and $S(90)$ are the integrated intensities corresponding to θ, $\theta = 0$ and $\theta = 90°$ respectively. L is the length of conjugation. In our own method,[6] those parameters are determined as follows for biphenyl derivatives such as

$$X - C_6H_4 - C_6H_4 - Y$$

(e.g. X = CN and Y = $(CH_2)_{n-1} - CH_3$ in nCB molecules).

When $\theta = 0$, the conjugation length is supposed to be $L(0) = L(C_6H_5 - X) + L(C_6H_5 - Y) + \Delta L$, $L(C_6H_5 - X)$ and $L(C_6H_5 - Y)$ are the conjugation lengths of the two component molecules. ΔL is an empirical term taking into account the change of conjugation length between the biphenyl derivative and the two separate component molecules. Because ΔL concerns the common central part of biphenyl derivatives, its value is assumed to have the same constant value

$$\Delta L = L(\text{fluorene}) - 2\,L(C_6H_6)$$

In spite of the geometric distortion of the longitudinal axis, fluorene is taken as a reference because $\theta = 0$. Thus, from formulae (2) we obtain

$$S(0) = [S^{1/4}(C_6H_5 - X) + S^{1/4}(C_6H_5 - Y) + S^{1/4}(\text{fluorene}) - 2S^{1/4}(C_6H_6)]^4 \tag{3}$$

When $\theta = 90°$, S is assumed to be equal to the sum of the intensities in the separate molecules because in this case there is no intensity enhancement by conjugation:

$$S(90) = S(C_6H_5 - X) + S(C_6H_5 - Y) \tag{4}$$

When $0 \leq \theta \leq 90°$, S is deduced from formulae (1), (3) and (4):

$$S(\theta) = [S(C_6H_5 - X) + S(C_6H_5 - Y)]\sin^2\theta + [S^{1/4}(C_6H_5 - X) + S^{1/4}(C_6H_5 - Y) + S^{1/4}(\text{fluorene}) - 2S^{1/4}(C_6H_6)]^4\cos^2\theta \quad (5)$$

The main advantage of this method is that it needs Raman relative integrated intensity measurements only. These measurements are made on the biphenyl derivative ($S(\theta)$), on benzene ($S(C_6H_6)$) on fluorene (S(fluorene)) and on model molecules ($S(C_6H_5 - X)$ and $S(C_6H_5 - Y)$). The use of this method is limited to solutions because all intensities are relative to an internal reference: the Fermi doublet (762–790 cm^{-1}) of the solvent ($CC\ell_4$). Experimental $S(i)$ values are obtained from measured band area A using the value observed in fluorene by Schmid *et al.*[6] as a reference: S(fluorene) = 12.2 (a relative scattering coefficient). Because we only need relative parameters measured in identical conditions (about 0.05 $mol.l^{-1}$), we use, without any optical correction, the following formula,

$$S(i) = 12.2(Ac_0/A_0c)/(A'c_0'/A_0'c') \quad (6)$$

where A, A_0, A′ and A_0' are the band area respectively of ν_8 in i derivative, $CC\ell_4$ doublet in i solution, ν_8 in fluorene and $CC\ell_4$ doublet in fluorene solution. c, c_0, c′ and c_0' are the corresponding concentrations.

In our previous work on the subject[6] we have tested this method on seven biphenyl derivatives: θ values deduced from formula 5 (S values being deduced from measurements through formula 6) were consistent with values given by electro-optic methods.

3.2 Results on *n*CB series

We registered Raman spectra of benzene, fluorene and nCB ($0 \leq n \leq 12$) compounds diluted in carbon tetrachloride solutions. Relative integrated intensities of the ν_8 band deduced from formula 6 are reported in Table 1 (S observed). Relative integrated intensities measured by Schmid and Brosa[13] for four benzene derivatives and fluorene used in our calculations are also reported in Table 1. The Schmid's value S(fluorene) = 12.2 is used as a reference. Moreover we performed calculations of $S(\theta)$ in nCB for various θ values through formula 5 as follows. In the whole series $S(C_6H_5 - X) = S(C_6H_5—CN) = 2.30$.

For $n = 0$ $\quad S(C_6H_5 - Y) = S(C_6H_6) = 0.40$

For $n = 1$ $\quad S(C_6H_5 - Y) = S(C_6H_5—CH_3) = 0.94$

For $n = 2$ $\quad S(C_6H_5 - Y) = S(C_6H_5—C_2H_5) = 1.08$

For $n = 3$ $\quad S(C_6H_5 - Y) = S(C_6H_5—CH_2C_6H_5) = 1.13$

For $n \geq 4$ $\quad S(C_6H_5 - Y) = 1.13 + 10\% = 1.24$

TABLE 1

Raman data for the ν_8 vibration of fluorene and benzene derivatives (used in S calculations) and of nCB molecules, in carbon tetrachloride solutions (C ≃ 0.05 mol.ℓ^{-1}). S = relative * integrated intensity

Molecules	ν_8 (cm^{-1})	S observed		S calculated (formula 5)	
		Schmid (Ref. 13–16)	This work (formula 6)	$S(0)$	$S(90)$
C_6H_6	1587/1606		0.40		
C_6H_5—CH_3	1605	0.94			
C_6H_5—C_2H_5	1602	1.08			
C_6H_5—$CH_2C_6H_5$	1585/1604	1.13			
C_6H_5—CN	1597	2.30			
Fluorene	1614	12.2*	12.2*		
0CB	1604/1613		28.2	28.2	2.7
1CB	1612		40.8	38.7	3.2
2CB	1613		41.6	40.9	3.4
3CB	1613		41.6	41.7	3.4
4CB	1613		44.0	43.3	3.4
5CB	1613		42.0	43.3	3.5
6CB	1613		43.2	43.3	3.5
7CB	1613		43.1	43.3	3.5
8CB	1613		43.6	43.3	3.5
9CB	1613		44.3	43.3	3.5
10CB	1613		43.3	43.3	3.5
11CB	1612		44.0	43.3	3.5
12CB	1613		43.0	43.3	3.5

*S observed are referred to the Schmid's value in fluorene.[13-16] Error on S values is about 10%.

The last two approximations are very rough but practically give S values probably not far from the reality. Indeed $(S/a)^{1/4}$ is the conjugation length L and comparison between C_6H_5—CH_3, C_6H_5—C_2H_5 and C_6H_5—$CH_2C_6H_5$ indicates a very slight increasing of L versus n, thus we decided to limit this increasing at $n = 4$ with a S value corresponding to the highest admissible value (10% is the relative experimental error). In addition a value of $S(C_6H_5 - Y)$ lower than 1.24 should give systematically nonrealistic cosine values.

S values calculated for $\theta = 0$ and 90° in nCB molecules are reported in Table 1. In Figure 1 values of S observed are compared to values of S calculated with various θ values in the nCB series. The comparison clearly shows that in all nCB compounds, diluted in carbon tetrachloride solutions, the aromatic core is coplanar ($\theta \simeq 0$), the uncertainty being lower than $\Delta\theta = 10°$ (see Figure 1).

4. INFRARED FREQUENCY SHIFTS BETWEEN SOLID AND SOLUTION

4.1 Principle of the method

We have already noticed that a large percentage of frequencies are modified when the dihedral angle θ is different in the solid state and in solution.[6] Barrett and Steele,[17] using a force field model could compute absolute values of frequencies

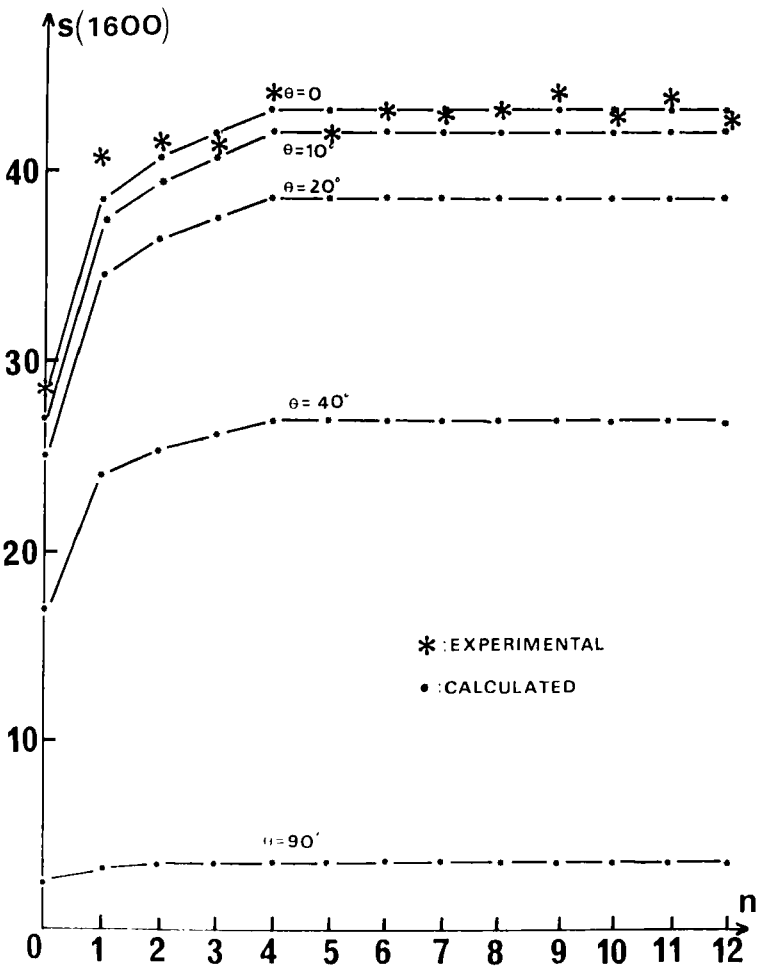

FIGURE 1 Relative integrated intensities $S(1600)$ of the ν_8 Raman band in nCB diluted in $CC\ell_4$ solutions.

in biphenyl and in 4,4′-dihalobiphenyls which were in good agreement with the experimental values. They also estimated frequency shifts due to the variations of θ. The most characteristic mode seems to be the B_{3u} vibration at 461 cm^{-1} (458 cm^{-1} in Reference 17) in solid biphenyl. This vibration is an out of plane bending of the ring and it is located in a region which is generally free from unwanted absorption bands. It shifts at 489 cm^{-1} in solution ($\Delta\nu$ = 28 cm^{-1}). The force field calculations of Barrett and Steele give also a strong shift (from 431 to 449 cm^{-1}) when $\Delta\theta$ = 30°. Almennigen *et al.*[9] recently performed frequency calculations on the same compounds and the variations of $\Delta\nu$ versus $\Delta\theta$ are sometimes different from those calculated by Barrett and Steele, but concerning the frequency shift of the above B_{3u} band it is of the same sign and of the same order of magnitude in both papers.

Thus the method consists in deducing $\Delta\theta$ variations from $\Delta\nu$ observed between solid and solution phases. The main practical difficulty is in some cases the assignment of the B_{3u} vibration (in D_2h symmetry) which can be a B_3, B_1 or B vibration (in D_2, C_{2v} or C_2 symmetry). This assignment, made in an empirical way, is based on similarities in intensity, frequency and sharpness (compared to the well known case of biphenyl); moreover it is often easy because other neighbouring bands are generally far from the interesting frequency range. The Figure 2 illustrates the method in four 4-substituted biphenyls: large positives $\Delta\nu$ values indicate strong $\Delta\theta$ values[6] (from solid to solution phase) and in fluorene $\Delta\nu$ is negligible in accordance with $\Delta\theta = 0$.

4.2 Results on *n*CB series

We registered infrared spectra of the thirteen *n*CB molecules in the range 400–4000 cm^{-1} both in solution and in solid phases. Solid phases were studied either on KBr pellets or on thin crystalline layers prepared by evaporation of solutions

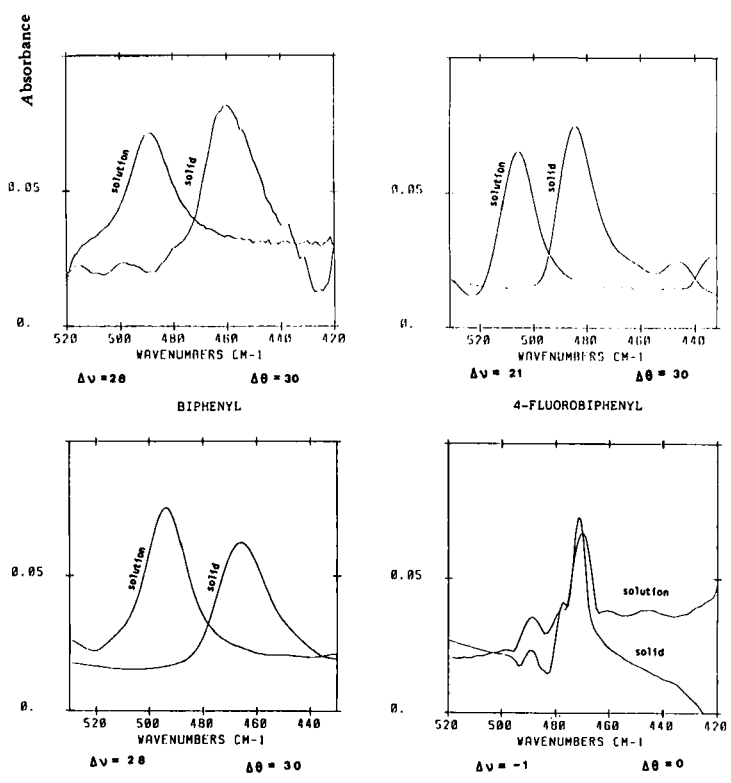

FIGURE 2 Infrared frequency shifts $\Delta\nu$ (cm^{-1}) observed in fluorene and biphenyl derivatives (comparison with dihedral angle changes $\Delta\theta$ (degrees) from solid to carbon tetrachloride solution).

on KBr windows. The last process, more practical, allows to obtain easily a stronger absorption which is necessary to study the very low intensities observed in the characteristic 400–500 cm^{-1} region. Comparison between the two kinds of spectra does not show any significant difference neither in sharpness nor in frequency for the concerned region. Solution phases were studied in cyclohexane, carbon tetrachloride or benzene as solvents, in regard to the studied parameter ($\Delta\nu$ from solid to solution) no significant difference were observed between the various solutions (less than about 1 cm^{-1}). Thus because band intensities are very low in the 400–500 cm^{-1} region we adopted the best solvent (benzene) in order to perform an homogeneous comparative analysis in the whole series.

Spectra of solids and benzene solutions (about 0.1 mol l^{-1}) are presented in Figures 3 and 4 respectively from 440 to 600 cm^{-1}. The right sides (440–500 cm^{-1}) of the figures concern the range where the vibration sensitive to θ variations, here

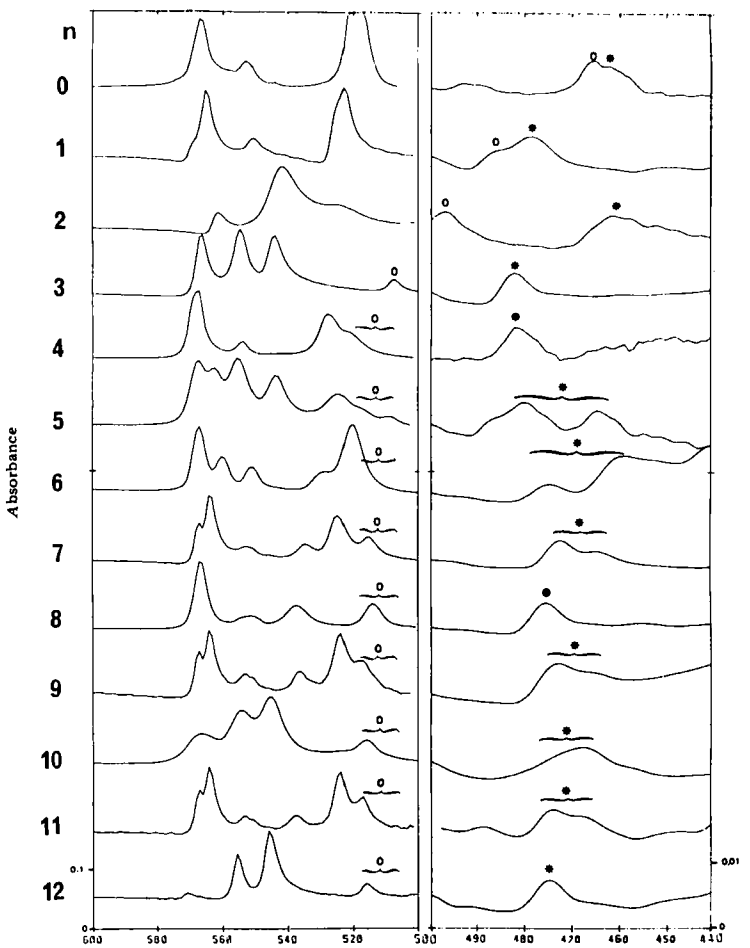

FIGURE 3 Infrared spectra observed in solid *n*CB compounds (440–600 cm^{-1}).

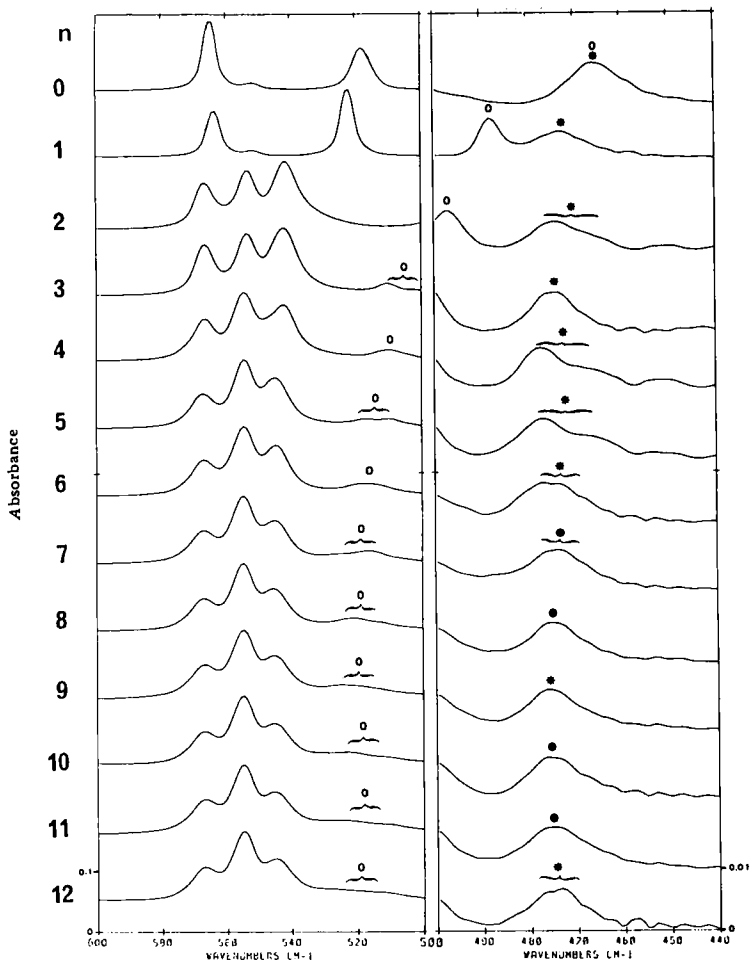

FIGURE 4 Infrared spectra observed in *n*CB compounds diluted in benzene solutions (440–600 cm^{-1}).

above mentioned, is observed. Absorbances of this part are extended in regard to the left part (about ten times more). The left sides (500–600 cm^{-1}) do not concern the interesting vibrations but are reported in order to allow a more easy assignment by a comparative analysis. In our empirical assignment intended to choose the band of which the frequency shift was really characteristic of θ changes in the 440–500 cm^{-1} range, we encountered two main difficulties. The first one is the presence at the beginning of the series (n = 0, 1 and 2) of two bands noticed 0 and * in Figures 3 and 4. Examination of the two parts of Figures 3 and 4 shows that the frequency of one band (noticed 0) is very sensitive to the alkyl residue $\nu(0)$ increases strongly from 466 cm^{-1} (n = 0) to about 510–520 cm^{-1} (n = 4) both in solid and solution, then from n = 5 to n = 12, $\nu(0)$ is nearly stationary. Consequently only the band noticed * must be considered in our method. The second difficulty is the frequent existence of doublets (bracketed together in Figures 3 and 4) in place of

the band noticed * in both phases. Because we were not able to do an exact assignment, we decided to consider the mean frequency value of those doublets in our following analysis. This disadvantage is partially palliated because in some separated doublets (for instance $n = 5$) similar situations are observed in both phases and thus the comparison of mean values of $\nu(*)$ between the two phases indicates probably a frequency shift not far from the reality. In Table 2, frequencies of the characteristic bands * are reported and comparison is made between frequency shifts $\Delta\nu$ and $\Delta\theta$ variations in some known cases: $\theta \simeq 0$ in 0CB (from other i.r. and Raman studies and Molecular Mechanics Calculations),[5,6] $\theta = 43°$ in 3CB (from X-Ray experiments),[11] $\theta = 40°$ in 4CB (from X-Ray experiments)[12] and $\theta = 27°$ in 12CB (from an X-Ray study of our group in progress). $\Delta\theta$ values from solid to solution phases, referred to the results obtained with the Raman method in carbon tetrachloride solutions ($\theta \simeq 0$ in all cases, see part 3.2) are 0, $-43°$, $-40°$ and $-27°$ respectively. Those $\Delta\theta$ values are in qualitative accordance with the $\Delta\nu$ values observed: as expected significant negative $\Delta\nu$ values are observed in 3CB, 4CB and 12CB (-7, -7 and -4 cm^{-1}), the less important frequency shift corresponding to the lowest $\Delta\theta$ value (in 12CB). At the opposite a slightly positive value ($\Delta\nu = +3$ cm^{-1}) is observed when $\Delta\theta \simeq 0$ in 0CB. In the cases of 0CB, 3CB and 4CB the corresponding regions of infrared spectra are presented in Figure 5; comparison with Figure 2 illustrates the coherence of $\Delta\nu$ variations versus $\Delta\theta$ changes. Nevertheless positive $\Delta\nu$ values observed are not consistent with $\Delta\theta$ values, indeed our Raman study (part 3.2) indicates $\theta = 0$ for all nCB compounds in solution and thus $\Delta\theta$ cannot takes positive values. This fact is certainly due to a positive frequency shift induced by change in phase. Comparison of experimental (28 cm^{-1}) and calculated (18 cm^{-1}) $\Delta\nu$ values in the work of Barrett and Steele[17] on biphenyl (B_{3u} band in solid) tends to confirm that point of view (calculated $\Delta\nu$

TABLE 2

Infrared frequencies (cm^{-1}) of the out of plane bending vibration of the ring (*) and dihedral angle θ observed for nCB in solid and solutions phases (in benzene).
$\Delta\nu = \nu$(solution) $- \nu$(solid). $\Delta\theta = \theta$(solution) $- \theta$(solid).

n	ν(solid)	ν(solution)	$\Delta\nu$	$\Delta\nu - 9$	$\Delta\theta$(degrees)
0	463	466	3	−6	0[6]
1	478	473	−5	−14	(−30)
2	461	474/466	9	0	(0)
3	481	474	−7	−16	−43[11]
4	482	477/473	−7	−16	−40[12]
5	479/465	477/467	0	−9	(−10 to −20)
6	475/465	476/474	5	−4	(0)
7	473/465	476/474	6	−3	(0)
8	475	475	0	−9	(−10 to −20)
9	474/466	475	5	−4	(0)
10	472/467	476	5	−4	(0)
11	473/468	476	4	−5	(0)
12	475	474/468	−4	−13	−27[+]

[+] from a crystallographic study of our group in progress.
( ) roughly assumed values.

values of Almennigen *et al.*[9] leads to the same conclusion). For this reason, we decided to correct $\Delta\nu$ value with an arbitrary frequency shift equal to 9 cm^{-1} in the whole series. This rough correcting value is the highest positive $\Delta\nu$ value observed in the series (2CB) which is not inconsistent with the difference $\Delta\nu$(observed) $-$ $\Delta\nu$(calculated) $=$ 10 cm^{-1} previously noticed in biphenyl. The corrected values ($\Delta\nu - 9$), presented in Table 2, allowed us to make rough estimates of $\Delta\theta$. Because $\Delta\nu \simeq 0$ in 0CB in spite of $\Delta\nu$ (corrected) $= -6$ cm^{-1}, we considered that for $0 > \Delta\nu > -6$ cm^{-1}, $\Delta\theta$ must be nearly equal to zero. Those roughly assumed values of which the absolute values are the values in solid phase are reported in last column of Table 2. It may be noticed that, contrary to solution phase, *n*CB molecules in solid phase present various θ values from 0 to about 40°. The diversity in the sharpness of the solid spectra observed in Figure 4 and at the opposite the similarity of the solution spectra visible in Figure 5, especially for 500–600 cm^{-1} are probably partially related to diversity and similarity of θ values. But the differences in crystalline symmetries must also be considered for a complete analysis.

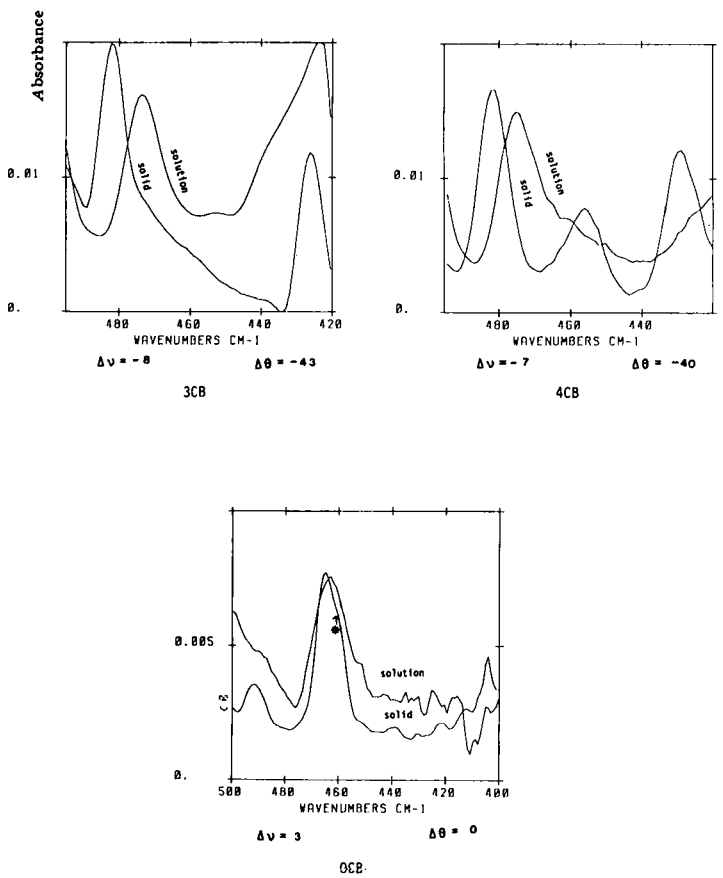

FIGURE 5 Infrared frequency shifts $\Delta\nu$ (cm^{-1}) observed in three *n*CB compounds (comparison with dihedral angle changes $\Delta\theta$ (degrees) from solid to carbon tetrachloride solution).

5. CONCLUSION

Two methods of estimation of the dihedral angle θ have been applied to thirteen molecules of the *n*CB series. The values of θ in solution have been obtained from measurements of the intensity of the Raman ν_8 band. This method is fast and simple and gives reliable results because intensities are quite sensitive to θ and because the *n*CB derivatives composed an homogeneous series, $\theta \simeq 0$, within about 10° have been observed in the whole series. Estimates of θ in solid phase have been obtained from measurements of the infrared frequency shift between solid and solution phase for the out of plane bending vibration of the ring located between 461 and 482 cm^{-1}. Those θ values, roughly estimated in most cases show that in the crystal lattice θ varies from nearly 0 to about 40° without any visible correlation with the alkyl residue length. In conclusion results on solutions by the Raman method corroborate our previous hypothesis about a folding back effect of the alkyl tail[1-4] (because experimental observations cannot be explained by strong θ values from $n = 5$). Moreover results obtained with the comparative infrared method suggest us to extend this study to liquid-crystal mesophases, not only to precise θ values but also to study the alkyl tail conformation. About this last point, similar comparative spectrometric studies have been already undertaken with some success.[18-20]

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