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Infrared and Far-Infrared Studies on the Nematogenic Homologous Series Trans-4-Alkyl-(4-Cyanophenyl) Cyclohexanes

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Infrared (4000–650 cm^{-1}) and far-infrared (650–20 cm^{-1}) spectra of the nematogenic homologous series trans-4-alkyl-(4-cyanophenyl) cyclohexanes (ethyl, propyl, butyl, pentyl and heptyl) have been examined in the solid and liquid crystalline states. An attempt has been made to correlate the variation in the intensities and frequency shifts with the molecular structures. The gradual shift towards smaller wavelength in the —C≡N stretching vibration and the relative alternation in the intensity of this frequency as the chain length increases may be correlated with odd-even effects in homologous liquid crystals and with the increase in thermal stability, as the spectra reveal an increase in the dipole–dipole interaction between the neighbouring molecules. A strong feature centred around 90 cm^{-1} is assigned to hindered rotation about the long axis of the molecule. Absolute orientational order parameter S has been evaluated for the series by a study of the temperature variation of —C≡N vibration in homeotropically oriented sample. The results are in very good conformity with those of NMR and optical methods.

INTRODUCTION

Molecular spectroscopic studies viz., Infrared and Raman, have gained much interest in recent years to study the structure and physical properties of liquid crystals. In particular the vibrational spectroscopic studies are quite helpful in gaining a better understanding of the molecular and structural characteristics of mesogenic materials. We

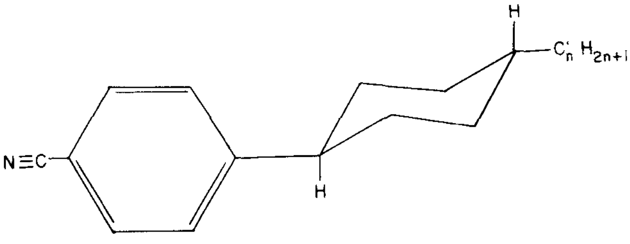

FIGURE 1 Structure of a typical compound.

present in this paper near and far infrared spectroscopic studies of liquid crystals in solid and liquid crystalline phases of materials comprising of cyclohexane rings in the rigid core which have not been investigated extensively. When the Benzene (more polarizable) rings are replaced by cyclohexane (much less polarizable) most of the physical properties differ considerably. In view of this, we have studied the homologous series trans-4-alkyl-(4-cyanophenyl) cyclohexane which contains cyclohexane along with one cyano group. Figure 1 shows the structure of a typical compound.

EXPERIMENTAL

(a) Materials:

The samples of asymmetrical trans-4-alkyl-(4-cyanophenyl) cyclohexane series with $n = 2, 3, 4, 5$ and 7 used in our study are manufactured by E. Merck, Darmstadt and were recrystallised before use. The observed transitions of the homologous series are:

(1) $n = 2$, ethyl:
Melting point: +40 °C
Clearing point: + 4 °C
} Monotropic

(2) $n = 3$, propyl:
Melting point: 42 °C
Clearing point: 45 °C

(3) $n = 4$, butyl:
Melting point: 41 °C
Clearing point: 39 °C
} Monotropic

(4) $n = 5$, pentyl:
Melting point: 30 °C
Clearing point: 55 °C

(5) $n = 7$, heptyl:
Melting point: 30 °C
Clearing point: 57 °C

(b) Data collection

The near infrared spectra were obtained with a Perkin–Elmer spectrophotometer equipped with interchangeable LiF, NaCl and KBr prisms and providing a spectral region of 600–4000 cm^{-1}. The spectra were recorded by taking the sample between AgCl plates. The accuracy was ± 10 cm^{-1} at 2000 cm^{-1} and ± 4 cm^{-1} at 600 cm^{-1}. The far-infrared spectra were recorded in a Polytec Fourier far-infrared spectrometer providing a recording spectral range of 20–650 cm^{-1}. The range was covered by using two different beam splitters. One had a usable transmittance range of 20–180 cm^{-1} and the other 200–650 cm^{-1}. The spectra were obtained with a resolution of 5 cm^{-1}. The liquid crystalline sample with homeotropic configuration was obtained by randomly rubbing the surface of the window by chamois leather. The sample thickness for all the samples was maintained to be 20 μ by using mylar spacers. The spectra of $—C{\equiv}N$ stretching vibration at various temperatures were recorded using Perkin-Elmer IR spectrometer and SPECAC P/2 21.000 variable temperature cell (−190 °C to 250 °C). Typical near infrared spectra at different temperatures for $n = 5$ and $n = 7$ are shown in Figures 2 and 3. Figure 4 gives molecular band contours of $—C{\equiv}N$ stretching vibration for few temperatures for $n = 3$. Figure 5 represents the far infrared spectra for the materials.

RESULTS AND DISCUSSION

The vibrational assignments of the spectra arising from different molecular units are given in Tables I to V. Designations such as rocking, and twisting modes are only approximate as considerable coupling between these motions can occur in a complex molecule. The analysis reveals that there are no gross changes in either relative intensities or in frequencies between the members of the series except for the cyano $—C{\equiv}N$ stretching frequency. Also, we do not observe

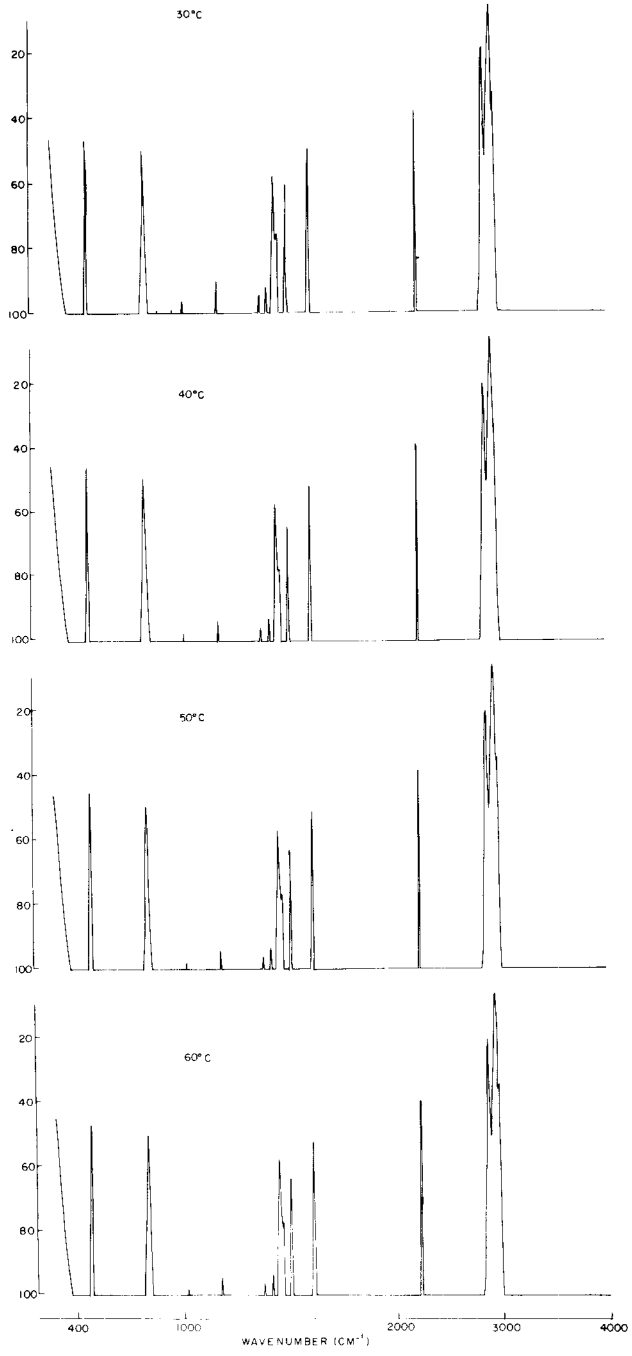

FIGURE 2 Typical near infrared spectra at different temperatures for $n = 5$.

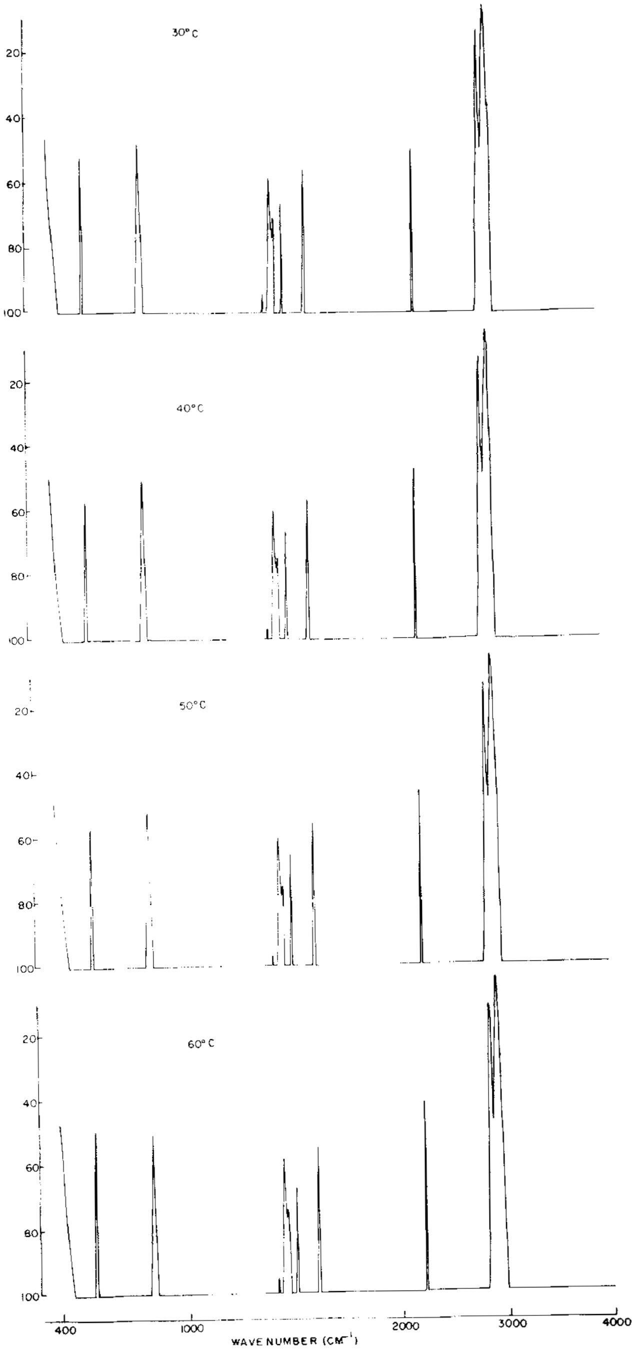

FIGURE 3 Typical near infrared spectra at different temperatures for $n = 7$.

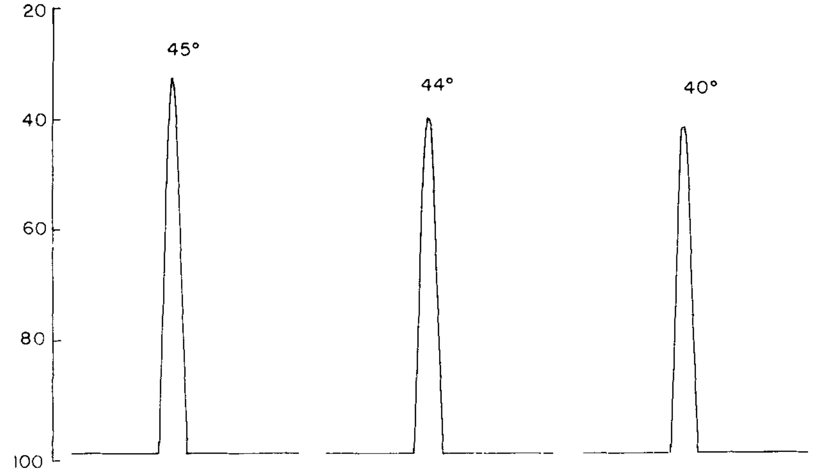

FIGURE 4 Molecular band contours of —C≡N stretching vibrations for few temperatures for $n = 3$.

much difference in the frequency assignment as we go from solid to liquid crystalline to isotropic phases as demonstrated earlier.[1-3] This suggests strong dependence of the molecular arrangement in liquid crystalline state on the previous history of molecular arrangement in the crystalline state. We have observed that the intensity of infrared bands between 400 to 1500 cm^{-1} decreases continuously as the crystal–nematic transition was approached from below. Whereas the intensity of bands between 1500 to 2300 cm^{-1} increases continuously indicating the increasing freedom of end groups which play an important role on the physical properties.

The spectra in the nematic phase was obtained by using homeotropically aligned samples. The flat baseline at wavelength shorter than 3 μ indicates that the alignment is very good. We have estimated the dichroic ratio defined by Fernandes and Venugopalan[4] as the ratio of the integrated intensity of the band in the liquid crystalline to that in the isotropic phase. The integrated absorption of the band has been evaluated using Ramsay's[5] procedure for several bands. It is found that the dichroic ratio R is less than unity for certain bands and is greater than unity for few other bands. This indicates that the transition moment of the former are along the long molecular axis and those of the latter being perpendicular to the long molecular axis.

We have observed that there are gradual shifts towards smaller wavelength in the —C≡N stretching vibration and the intensities alternate between even and odd members and also gradually increase

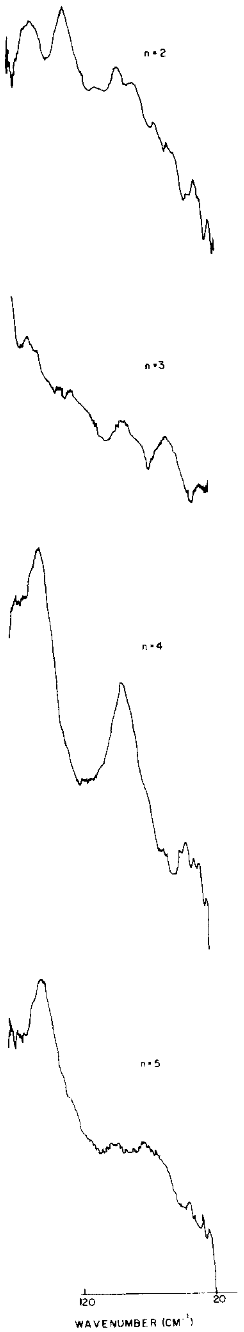

FIGURE 5 Typical far infrared spectra for $n = 2, 3, 4, 5$.

TABLE I

$n = 2$

Band Wavelength (μm)	Band Wave Number cm^{-1}	Intensity[a]	Assignment[b]
3.38	2962	vs	ν(C—H)
3.41	2934	vs	ν(C—H)
3.50	2860	vs	ν(C—H)
4.50	2220	s	ν(C≡N)
6.23	1605	s	βske (C=C)
6.66	1502	s	βske (C=C)
6.85	1460	vs	$\delta_{sy}(CH_2)$
6.92	1445	vs	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.06	1415	s	$\delta_{sy}(CH_2)$
12.12	825	vs	γ(C—H)
17.63	567	vs	$\varnothing$(C—C)

[a, b]—See footnote at the end of Table V.

with increase in chain length. This may be indicative of the familiar odd-even effect observed for several physical properties of liquid crystals which depend mainly on the symmetry and asymmetry of the end chains and are not influenced by the detailed structure of the central rigid core, as confirmed by the study of Boden et al.[6]

As regards the far infrared spectra, a strong feature centred around 90 cm^{-1} is assigned to the hindered rotation along the long axis of the molecule. Many of the other peaks are essentially due to internal

TABLE II

$n = 3$

Band Wavelength (μm)	Band Wave Number cm^{-1}	Intensity[a]	Assignment[b]
3.37	2965	vs	ν(C—H)
3.41	2930	vs	ν(C—H)
3.50	2860	s	ν(C—H)
4.50	2221	s	ν(C≡N)
6.21	1610	s	β_{ske}(C=C)
6.64	1505	s	β_{ske}(C=C)
6.80	1470	m	$\delta_{sy}(CH_2)$
6.92	1445	s	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.06	1415	m	$\delta_{sy}(CH_2)$
12.05	830	s	γ(C—H)
17.54	570	s	$\varnothing$(C—C)

[a, b]—See footnote at the end of Table V.

TABLE III

$n = 4$

Band Wavelength (μm)	Band Wave Number cm^{-1}	Intensity[a]	Assignment[b]
3.38	2958	vs	ν(C—H)
3.41	2935	vs	ν(C—H)
3.50	2860	vs	ν(C—H)
4.50	2223	s	ν(C≡N)
6.20	1612	s	β_{ske}(C=C)
6.64	1505	m	β_{ske}(C=C)
6.80	1470	m	$\delta_{sy}(CH_2)$
6.91	1448	s	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.05	1417	w	$\delta_{sy}(CH_2)$
12.05	830	m	γ(C—H)
17.7	565	w	$\emptyset$(C—C)

[a, b]—See footnote at the end of Table V.

vibrations. The 90 cm^{-1} band also shows a decreasing trend in frequency similar to —C≡N stretching frequency.

Finally we have evaluated the absolute orientational order parameter S for all the members of the series by estimating the dichroic ratio of —C≡N stretching which is a distinct and strong mode. We have used for our calculation the expression

$$S = \frac{1 - R}{1 - (3/2)\mathrm{Sin}^2\alpha}$$

TABLE IV

$n = 5$

Band Wavelength (μm)	Band Wave Number cm^{-1}	Intensity[a]	Assignment[b]
3.38	2960	sh	ν(C—H)
3.42	2922	vs	ν(C—H)
3.50	2855	vs	ν(C—H)
4.49	2227	s	ν(C≡N)
6.21	1610	m	β_{ske}(C=C)
6.64	1505	m	β_{ske}(C=C)
6.81	1468	sh	$\delta_{sy}(CH_2)$
6.90	1449	m	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.06	1416	w	$\delta_{sy}(CH_2)$
12.03	831	s	γ(C—H)
17.73	564	s	$\emptyset$(C—C)

[a, b]—See footnote at the end of Table V.

TABLE V

$n = 7$

Band Wavelength (μm)	Band Wave Number cm^{-1}	Intensity[a]	Assignment[b]
3.38	2960	sh	ν(C—H)
3.42	2925	vs	ν(C—H)
3.50	2855	vs	ν(C—H)
4.48	2230	s	ν(C$\equiv$N)
6.21	1610	m	$\beta_{ske}\cdot$(C=C)
6.64	1505	m	β_{ske}(C=C)
6.81	1468	sh	$\delta_{sy}(CH_2)$
6.90	1450	m	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.06	1415	vw	$\delta_{sy}(CH_2)$
12.05	830	m	γ(C—H)
17.73	564	s	$\varnothing$(C—C)

[a] sh—shoulder, vs—very strong, s—strong, m—medium, vw—very weak, w—weak.

[b] ν(C—H): C—H stretching, ν(C$\equiv$N): C$\equiv$N stretching, β_{ske}(C=C): C=C skeletal in plane deformation in benzene, $\delta_{sy}(CH_2)$: CH_2 symmetric deformation vibration, $\delta_{asy}(CH_3)$: CH_3 asymmetric deformation vibration, $\delta_{asy}(CH_2)$: CH_2 asymmetric deformation vibration, γ(C—H): C—H out of plane deformation, $\varnothing$(C—C): C—C out of plane ring deformation.

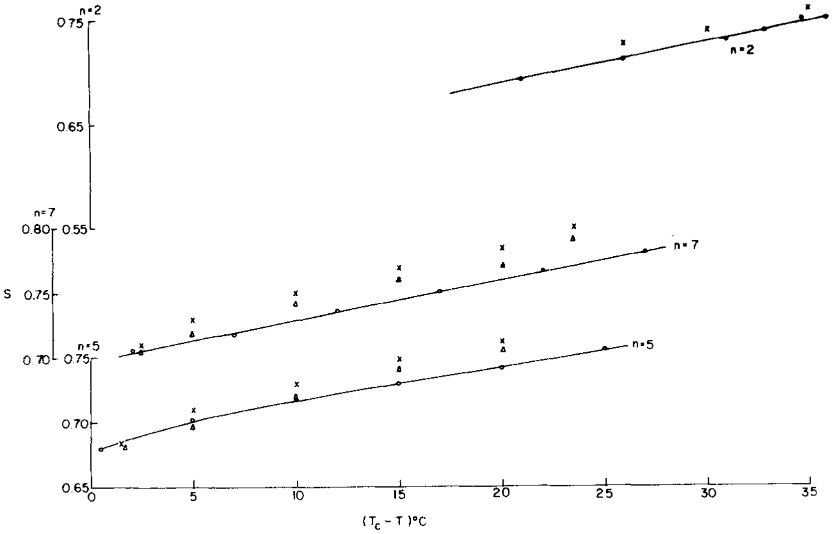

FIGURE 6 S factors for $n = 2, 5, 7$; ×—IR; △—optical; ○—NMR.

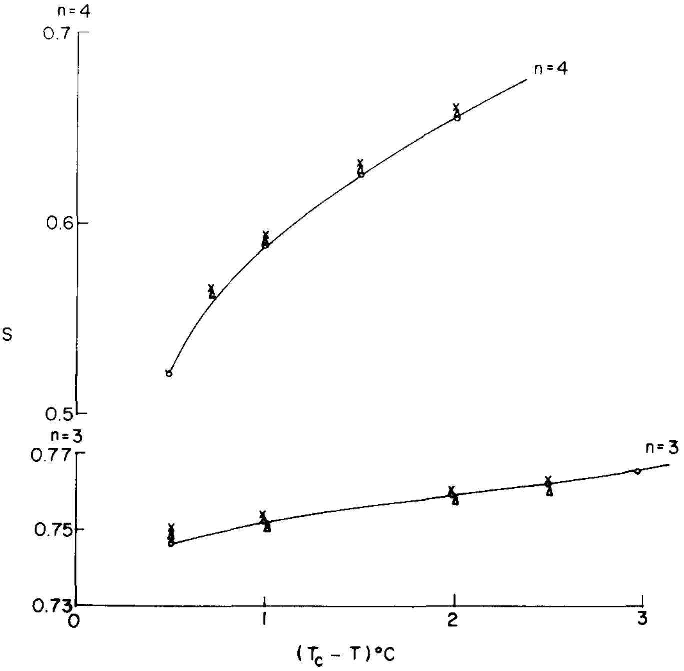

FIGURE 7 S factors for $n = 3,4$; ×—IR; △—optical; ○—NMR.

suggested by Fernandes and Venugopalan[4] for homeotropically aligned sample. Here R is the dichroic ratio, α is the angle between the long axis of the molecule and the transition moment of —C≡N stretching mode. As we see from Figure 4, the absorption strength increases with increase of temperature. There is a discontinuous change at transition to isotropic phase. α is taken to be 10° which is perceived to be the largest possible angle from molecular models.[7]

The values of S are plotted along with (Figures 6 and 7) some values of S factors obtained from NMR and optical studies.[8,9] We note that the results are in very good agreement with the values obtained by the other methods. The IR values are slightly smaller towards the crystal–nematic transition. This may be due to the magnetic field alignment caused in NMR measurements and surface orientation caused by rubbing, in prism experiments.

CONCLUSIONS

The results indicate that the vibrational spectroscopy can be usefully utilized to determine S factors. The study also throws light upon pre-transitional effects in addition to the information which it can provide regarding the molecular structural influence on physical properties.

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References

1. W. Maier and G. Englert, *J. Phys. Chem.*, (Frankfurt) **19**, 168 (1959).
2. V. D. Neff in "liquid crystals and plastic crystals", Vol. II (1974) Eds. G. W. Gray & P. A. Winsor, Ellis Horwood Ltd., Chichester.
3. C. Vergoten, G. Fleury, R. N. Jones and A. Nadean, *Mol. Cryst. Liq. Cryst.*, **36**, 327 (1976).
4. J. R. Fernandes and S. Venugopalan, *Mol. Cryst. Liq. Cryst.*, **35**, 113 (1976).
5. D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).
6. N. Boden, R. J. Bushby and L. D. Clark, *Chem. Phys. Letters*, **64**, 519 (1979).
7. W. Maier and A. Saupe, *J. Phys. Chem.*, **6**, 327 (1956).
8. M. M. M. Abdoh, N. C. Shivaprakash and J. Shashidhara Prasad, *J. Phys. Chem.*, **86**, 2349 (1982).
9. M. M. M. Abdoh, Srinivasa, N. C. Shivaprakash and J. Shashidhara Prasad, *J. Chem. Phys.*, **77**, 2570 (1982).