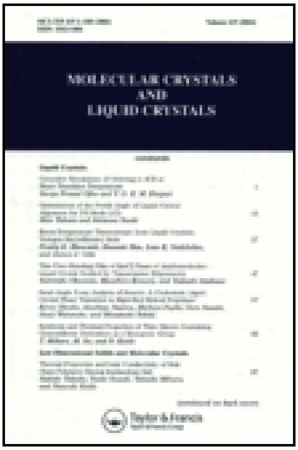

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The Raman Spectra of 4-Cyano-4′-pentylbiphenyl and 4-Cyano-4′-pentyl-d_{11}-biphenyl

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The Raman spectra of the solid, nematic, and isotropic liquid phases of 4-cyano-4′-pentylbiphenyl (5CB) and 4-cyano-4′-pentyl-d_{11}-biphenyl (5CB-d_{11}) are reported together with the method of synthesis of 5CB-d_{11}. A comparison of the spectra of the isotropic liquid phases of 5CB and 5CB-d_{11} has led to a partial assignment of these spectra. For each compound, the spectra of the fluid phases resembled each other, but differed from the corresponding spectrum of the solid phase. In particular, the cyano stretching vibration occurred as a doublet in the spectra of the solid phases of 5CB and 5CB-d_{11}, but as a single band in spectra of the fluid phases. The nematic to isotropic liquid transition temperature of 5CB-d_{11} was 1° lower than that of 5CB.

1 INTRODUCTION

A project was initiated† to study the thermal neutron scattering from aligned mesophases, with the object of obtaining information about the translational and rotational modes of individual molecules in various types of liquid crystals. To obtain meaningful data, it was essential that the flexible parts of the mesogenic molecules did not contain any hydrogens, since the incoherent scattering from these hydrogens would swamp any other scattering. In addition to this structural requirement, the compounds to be studied had desirably to be stable when exposed to atmospheric conditions for long periods of time. Furthermore, the experimental procedure would be greatly simplified if the chosen compounds possessed room temperature mesophases.

Attention was first directed towards the nematic mesophase, and the recently synthesised,[1] stable, room temperature nematic liquid crystal obtained from 4-cyano-4′-pentylbiphenyl (5CB) appeared to meet the above

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† Supported by the United Kingdom Atomic Energy Authority.

requirements. It was decided that the hydrogens in the alkyl chain of 5CB should be replaced by deuteriums, and the synthesis of 4-cyano-4′-pentyl-d_{11}-biphenyl (5CB-d_{11}) is discussed in section 2A.

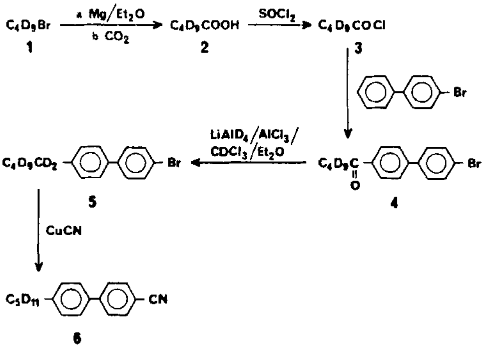
The thermal neutron scattering experiments on this material have been carried out by Leadbetter *et al.*[2] It was realised that 5CB and 5CB-d_{11} were also ideal nematogens for study by other spectroscopic techniques. For example, a study of the deuteron magnetic resonance spectrum of 5CB-d_{11} has been made by Luckhurst and co-workers.[3] In the present work, the Raman spectra of the various phases of 5CB and 5CB-d_{11} were obtained and they are presented and discussed in section 2B.

2 DISCUSSION AND RESULTS

2A The Synthesis of 5CB-d_{11}

The previous reported[1] method of preparation of 5CB was followed as far as possible; the synthetic route used is summarised in the scheme below. Each stage was carefully checked by carrying out at least two pilot preparations of the corresponding hydrogen-containing compound.

1-Bromobutane-d_9 was purchased from Merck, Sharp and Dohme of Canada and compounds **1**, **2**, and **3** were prepared by well established methods. To maximise the yield of compound **4** from a given amount of the acid chloride, **3**, an excess of 4-bromobiphenyl was used in the Friedel Crafts reaction.



In the previous[1] synthesis of 5CB, the ketone, **4**, was reduced by the Huang Minlon reaction, using 90% hydrazine hydrate. This method cannot readily be adapted for the reduction of $\gt C{=}O$ to $\gt CD_2$ because of the possibility of isotopic exchange. Nystrom *et al.*[4] have reported that alkyl aryl ketones can be reduced to the corresponding alkylarene using a mixture of lithium aluminium hydride and anhydrous aluminium trichloride in dry ether. It was found that a 1:3 molar ratio of $LiAlH_4:AlCl_3$ reduced the non-deuteriated ketone, **4**, to the corresponding product, **5**, but that the product contained approximately 20% of 4-bromo-4'-pent-1-enylbiphenyl, presumably formed by a β-elimination process. Many attempts were made, by varying the conditions of the reaction, to avoid the formation of the alkene, but all proved to be unsuccessful.

Albrecht *et al.*[5] have reported that 2,6-diacetyldibenzothiophene can be reduced to 2,6-diethyldibenzothiophene using lithium aluminium hydride, anhydrous aluminium trichloride, dry ether, and dry chloroform. This method was tried and found to be successful; only 2–3% of the alkene was obtained and was readily removed by crystallisation. Moreover, this procedure was readily adapted to the preparation of compound **5** by replacement of the two appropriate reagents by lithium aluminium deuteride and dry chloroform-d_1.

The cyanation of **5** was carried out using *N*-methyl-2-pyrrolidone as the solvent. This method is an improvement on the use of dimethylformamide, since the reaction time is reduced from 18 hours to 1 hour and the amount of amide formed is greatly lowered. The crude products (5CB or 5CB-d_{11}) were purified by column chromatography followed by vacuum distillation. The infrared, n.m.r. and mass spectra of the products were consistent with the structures of the required materials. The final samples of 5CB and 5CB-d_{11} were analysed by g.l.c. and found to have purities of >99%. The n.m.r. spectrum of 5CB-d_{11} indicated that the alkyl chain had an isotopic purity of >98%.

The melting points of 5CB and 5CB-d_{11} were identical (21–2°). However, the nematic-isotropic liquid (N-I) transition temperature of 5CB-d_{11} was 33.7 – 33.8°, 1° lower than the corresponding transition temperature of 5CB. The analytical data on the samples of 5CB and 5CB-d_{11} and the sharpness of their N–I transitions indicated that this small difference in the transition temperatures was unlikely to be due to impurities in the 5CB-d_{11}. However, the extreme sensitivity of N–I transition temperatures to impurities makes it impossible for this explanation to be eliminated. If, however, this small temperature difference is real,* it is probably due to the smaller polarisability of the deuteriated carbon chain compared with that of the protiated carbon chain. Verification of this possibility awaits the preparation of other mesogens with a high degree of deuteriation so that data can be compared for a range of materials and N–I temperatures.

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* *Note added in proof.* The possibility that the difference in N–I transition temperatures is solely due to the effect of deuteriation on the energy differences between trans and gauche conformers of the alkyl chains, as discussed by S. Marcelja, *J. Chem. Phys.*, **60**, 3599 (1974) would seem to be eliminated by our more recent observations that similar temperature effects result from deuteriation exclusively in aromatic rings.

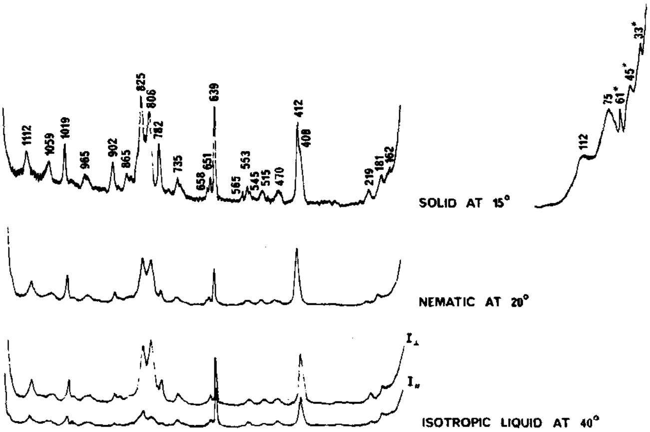

FIGURE 1 Raman spectra in the region $\Delta\nu = 50 - 1100\ \text{cm}^{-1}$ of the various phases of 4-cyano-4′-pentylbiphenyl.
Depolarisation ratios are given by $I_{\parallel}/I_{\perp}$.
* These bands are thought to be spurious.

2B Raman Spectra of 5CB and 5CB-d_{11}

The Raman spectra of the solid, nematic, and isotropic liquid phases of 5CB and 5CB-d_{11} are shown in Figures 1 to 5. Partial possible assignments of the spectra of the isotropic liquid phases of 5CB and 5CB-d_{11} are given in Table I. These possible assignments were based on the following: known Raman frequencies of functional groups,[6] a comparison of the Raman

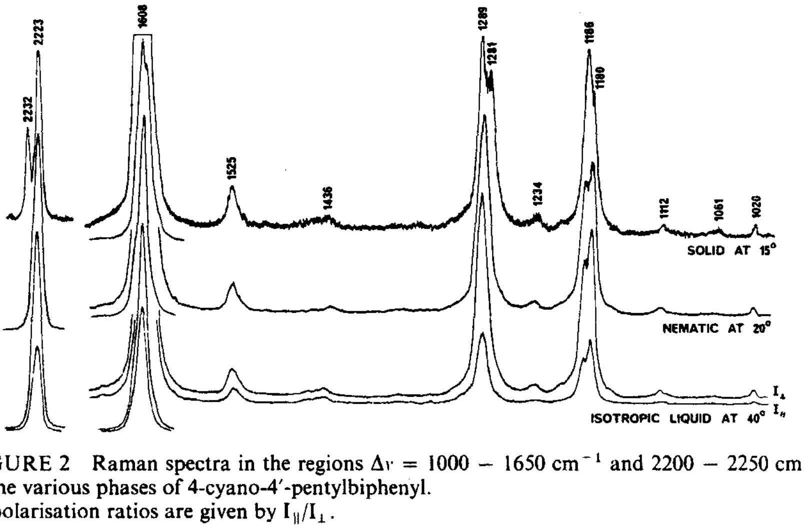

FIGURE 2 Raman spectra in the regions $\Delta\nu = 1000 - 1650\ \text{cm}^{-1}$ and $2200 - 2250\ \text{cm}^{-1}$ of the various phases of 4-cyano-4′-pentylbiphenyl.
Depolarisation ratios are given by $I_{\parallel}/I_{\perp}$.

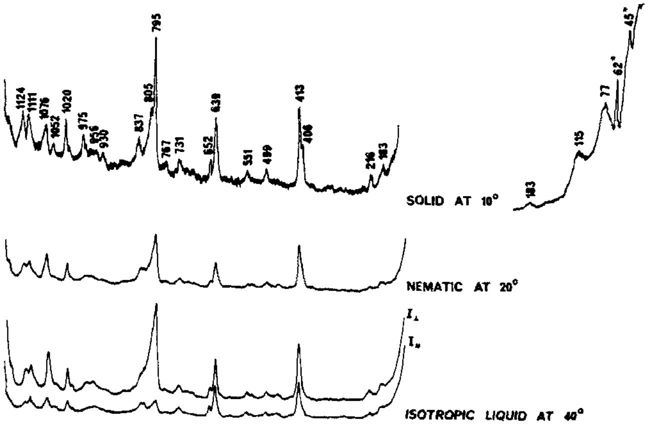

FIGURE 3 Raman spectra in the region $\Delta\nu = 50 - 1100 \text{ cm}^{-1}$ of the various phases of 4-cyano-4′-pentyl-d_{11}-biphenyl.
Depolarisation ratios are given by $I_\parallel/I_\perp$.
* These bands are thought to be spurious.

spectra of the isotropic liquid phases of 5CB and 5CB-d_{11}, and the depolarisation ratio of a given vibrational frequency. Each assignment is meant to indicate the probable major contribution to a particular Raman frequency.

Only a few of the bands in the Raman spectrum of 5CB are due to the vibrations of the alkyl chain. Deuteriation of the alkyl chain therefore produces only a small number of differences between the spectra of 5CB

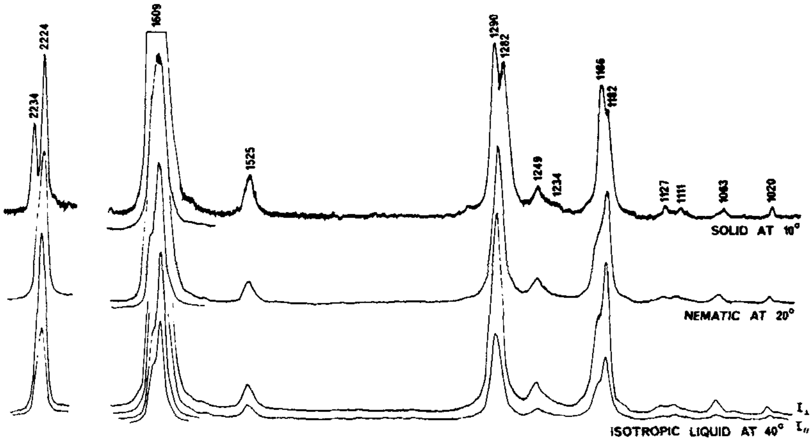

FIGURE 4 Raman spectra in the regions $\Delta\nu = 1000 - 1650 \text{ cm}^{-1}$ and $2200 - 2250 \text{ cm}^{-1}$ of the various phases of 4-cyano-4′-pentyl-d_{11}-biphenyl.
Depolarisation ratios are given by $I_\parallel/I_\perp$.

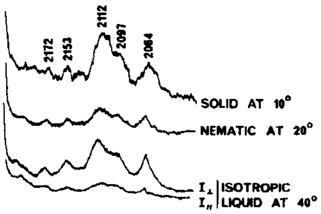

FIGURE 5 Raman spectra in the region $\Delta\nu = 2000 - 2200\ \text{cm}^{-1}$ of the various phases of 4-cyano-4′-pentyl-d_{11}-biphenyl.
Depolarisation ratios are given by $I_{\parallel}/I_{\perp}$.

TABLE I

Possible assignments for the Raman spectra of the isotropic liquid phases of 4-cyano-4′-pentylbiphenyl (5CB) and 4-cyano-4′-pentyl-d_{11}-biphenyl (5CB-d_{11})

5CB		5CB-d_{11}		
$\Delta\nu$	Intensity	$\Delta\nu$	Intensity	Possible Assignment
	F.S.D. = 10^3		F.S.D. = 10^3	
179	3	178	3	
216	3	213	3	
410	23	410	25	Ring vibration and/or ϕ—C wag
		468	2	
474	3			
		498	3	
509	3			
		541	2	
551	3	552	3	
639	23	637	18	Ring vibration
651	5	650	5	
		697	1	
		713	1	
		732	3	
738	4			
780	10	767	1	
		795	40	Ring breathing vibration
		801	sh.	
806	28			Ring breathing vibration
826	25			Alkyl chain vibration
		831	sh.	Alkyl chain vibrations
862	1			
886	1			
899	2			
		955	5	
967	3	971	4	
976	sh.			
		1007	2	
1018	10	1018	9	Aromatic C—H in plane deformation
		1052	1	

TABLE I (*Continued*)

5CB		5CB-d_{11}		
$\Delta\nu$	Intensity	$\Delta\nu$	Intensity	Possible Assignment
1062	3			Alkyl chain vibration
		1070	15	C—D deformation
1112	8	1112	9	
		1123	8	C—D deformation
	F.S.D. = 3 × 10^3		F.S.D. = 3 × 10^3	
1179	75	1181	69	Aromatic C—H in plane deformation
1185	60	1187	sh.	
1235	3	1235	v.w.	Ring vibration
		1248	12	ϕ—CD_2 stretch
1285	92	1287	90	C—C stretch of biphenyl link
1436	4			C—H deformations of pentyl chain
1445	3			
1452	2			
1527	10	1525	10	C—C stretch of aromatic rings
1606	>100	1607	>100	
1613	sh.	1613	sh.	
			F.S.D. = 10^3	
		2067	15	C—D stretching vibrations
		2098	15	
		2116	22	
		2150	5	
		2175	3	
			F.S.D. = 3 × 10^3	
2224	90	2224	80	C≡N stretch

and 5CB-d_{11}, and many of these can be readily interpreted. For example, the bands at 1436, 1445, and 1452 cm^{-1} in the spectrum of the isotropic liquid phase of 5CB are absent from the corresponding spectrum of 5CB-d_{11}. These bands can be assigned to the C—H deformations of the alkyl chain in 5CB. However, there is one difference, in particular, between the spectra of 5CB and 5CB-d_{11} which is difficult to explain. The band at 1249 cm^{-1} in the spectra of 5CB-d_{11} does not appear to correspond to any of the bands in the spectra 5CB. The following argument is proposed as a tentative explanation of this observation, but is by no means thought to be conclusive.

It seems reasonable to assign the band at 1249 cm^{-1} to a vibration of the deuteriated alkyl chain of 5CB-d_{11} and to assume that the corresponding band in the spectra of 5CB is masked by a much stronger band. The band at 1249 cm^{-1} may be due to the carbon–carbon stretching vibration of the methylene-d_2 carbon atom and the aromatic carbon atom, which has moved to a lower frequency because of the effect of deuteriation. A similar shift in frequency has been observed[7] in the Raman spectra of *p*-azoxyanisole and 4,4′-bis(methoxy-d_3)azoxybenzene, where the frequency of the C—O stretching vibration of the methoxy group decreases by 34 cm^{-1} as a result of deuteriation. If a frequency shift of this magnitude occurs in the Raman spectra of 5CB and 5CB-d_{11}, then the band at 1249 cm^{-1} in the spectra of 5CB-d_{11} should occur at 1283 cm^{-1} in the spectra of 5CB. However, this band cannot be detected because of the strong band at 1285 cm^{-1}. It is hoped that confirmation, or otherwise, of this explanation will be obtained from a Raman spectroscopic study of other deuteriated 4-*n*-alkyl-4′-cyanobiphenyls.

The Raman spectra of the nematic and isotropic liquid phases of 5CB resembled one another, but differed from the spectrum of the solid phase in the following manner. The bands at 1059, 902, 825, 112, and 75 cm^{-1} appeared to decrease in intensity when the crystalline lattice is destroyed. The three highest frequencies are probably due to vibrations of the alkyl chain in 5CB. This conclusion is confirmed by the absence of these bands from the Raman spectra of 5CB-d_{11}. The decrease in intensity of the bands at 1059, 902, and 825 cm^{-1} is associated with the formation of several conformations of the alkyl chain in the fluid phases, as opposed to the single, all-trans conformation present in the solid phase. This type of observation has also been made by Schnur[8] and Vergoten and Fleury.[9]

The bands at 112 and 75 cm^{-1} in the spectrum of the solid phase of 5CB are probably oscillatory lattice vibrations and as expected, they are absent from the spectra of the isotropic liquid and nematic phases of 5CB.

The above spectral changes were confirmed, where possible, by comparing the corresponding spectra of 5CB-d_{11}.

The cyano stretching vibration occurs as two bands at 2224 and 2233 cm^{-1} for the solid phases of 5CB and 5CB-d_{11}, but only as a single band at 2224 cm^{-1} in the corresponding spectra of the fluid phases. The bands at 1180 and 1286 cm^{-1} also appear to form doublets on the formation of the crystalline lattice. These effects are probably due to some feature of the crystal structure of 5CB, but until this structure has been elucidated it is not possible to provide a reasonable explanation for them. However, a preliminary study has revealed that the cyano stretching vibration occurs as a singlet for the solid phases of the 4′-heptyl-, -hexyl-, and -butyl-derivatives of 4-cyanobiphenyl. Furthermore, Gray *et al.*[1] have reported that the heptyl derivative possesses an unstable solid phase. An attempt will shortly be made to see if the cyano stretching vibration occurs as a doublet for the unstable solid phase of 4-cyano-4′-heptylbiphenyl.

It is intended that future work on 5CB and other 4-*n*-alkyl-4′-cyanobiphenyls will also include a Raman spectroscopic study of the aligned mesophases. The 4-*n*-alkyl-4′-cyanobiphenyls are especially suited to this type of study (as described by Priestley *et al.*[10]) since the molecules are essentially linear and contain a cyano group.

The synthesis of the following compounds is now nearing completion: 4-cyano-4′-pentylbiphenyl-d_8, 4-cyano-4′-octyl-d_{17}-biphenyl, 4-cyano-4′-octylbiphenyl-d_8, and 4-cyano-4′-octylbiphenyl-d_{25}. The N–I transition temperatures and Raman spectra of these compounds will then be available for comparison with the results reported here for 5CB and 5CB-d_{11}.

3 EXPERIMENTAL

Raman spectra were obtained by using a Spectra Physics 125 He–Ne laser. The light scattered at 90 degrees was analysed by a Spex 1401 double monochromator operated at a spectral slitwidth of approximately 2 cm^{-1}. This experimental arrangement limited the spectral region that could be studied to $\Delta\nu = 50 - 2300\ \text{cm}^{-1}$. The uncertainty in the recorded Raman frequencies was better than $\pm 2\ \text{cm}^{-1}$. Depolarisation ratios were obtained by rotating the plane of polarisation of the incident laser beam through 90 degrees.

Samples of 5CB and 5CB-d_{11} contained in capillary tubes were maintained in the isotropic liquid and solid phases by heating with warm air or cooling with cold gaseous nitrogen as required. The spectra of the nematic phases were obtained at room temperature.

The transition temperatures of the samples of 5CB and 5CB-d_{11} were determined by using a Nikon L–Ke polarising microscope in conjunction with a Mettler FP 52 heating stage and FP 5 control unit.

Pentanoic acid-d_9 **(2)** The Grignard reagent was prepared in the usual manner[11] using magnesium turnings (1.9 g, 0.08 mole), 1-bromobutane-d_9 (10 g, 0.068 mole), and anhydrous ether (70 ml). The ethereal solution of the Grignard reagent was slowly decanted into a mixture of solid carbon dioxide (30 g) and anhydrous ether (100 ml). The complex was decomposed with a mixture of 5 M hydrochloric acid (20 ml) and ice (50 g). Isolation and purification by the recommended procedure[11] gave 5.8 g, (75%) of product, b.p. = 182 – 3°.

Pentanoyl chloride-d_9 **(3)** Pentanoic acid-d_9 (5.6 g, 0.05 mole) was treated with an excess of freshly distilled thionyl chloride (5.5 ml). The excess of thionyl chloride was removed by careful rotary evaporation and the residue was used without purification, in the Friedel Crafts reaction.

4-Bromo-4′-pentanoyl-d_9-biphenyl **(4)** 4-Bromobiphenyl (13.2 g, 0.057 mole), pentanoyl chloride-d_9, anhydrous aluminium trichloride (8.6 g, 0.065 mole), and dry nitrobenzene (50 ml) were used in the method reported by Gray *et al.*[1] with the following modifications. The residue from the steam distillation was dissolved in benzene (500 ml) and this solution decolourised (animal charcoal). The benzene was removed by rotary evaporation; crystallisation of the crude product from ethanol gave 9.5 g (60% from the acid) of pure material, m.p. 98 – 9° (Lit.[1] 98 – 8.5°).

4-Bromo-4′-pentyl-d_{11}-biphenyl **(5)** A solution of anhydrous aluminium trichloride (21 g, 0.157 mole) in anhydrous ether (60 ml) was added dropwise to a mixture of lithium aluminium deuteride (3 g, 0.071 mole) and anhydrous ether (60 ml). A solution of 4-bromo-4′-pentanoyl-d_9-biphenyl (9.4 g, 0.029 mole) in chloroform-d_1 (120 ml) was then added over a period of 30 min. The reaction mixture was stirred and heated under reflux for 18 hours. The excess of reducing agent was destroyed by the careful addition of deuterium oxide (100 g), followed by a 38% solution of deuterium chloride in deuterium oxide (72 ml). The ethereal layer was washed successively with water (3 × 100 ml), brine (3 × 100 ml), and water (100 ml) and then dried (anhydrous sodium sulphate). The ether was removed, the residue was crystallised from ethanol and the required product, 6.7 g (74%), m.p. 95 – 7° (Lit.[1] 95 – 6°) obtained after vacuum desiccation.

4-Cyano-4′-pentyl-d_{11}-biphenyl **(6)** Cuprous cyanide (1.8 g, 0.02 mole) was added to a solution of 4-bromo-4′-pentyl-d_{11}-biphenyl (3.3 g, 0.011 mole) in *N*-methyl-2-pyrrolidone (10 ml). This mixture was stirred and heated under reflux for 1 hour. The cooled reaction mixture was poured into a solution of ferric chloride (4 g) in water (60 ml) and concentrated hydrochloric acid (2 ml). The organic product was extracted into ether (1 × 80 ml, 2 × 60 ml). This solution was treated with animal charcoal, dried (anhydrous sodium sulphate), and then evaporated to dryness. Any unreacted bromo compound was removed (first fraction) by column chromatography on silica gel with chloroform as eluant. The cyano compound was then eluted and further purified by vacuum distillation. This gave 1.5 g (55%) of pure material, b.p. 132°/0.03 mm Hg.

Acknowledgement

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References

1. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Raynes, *Liquid Crystals and Ordered Fluids* (Edited by J. F. Johnson and R. S. Porter), Plenum Press, New York, 1974, p. 617.
2. A. J. Leadbetter, F. P. Temme, A. Heidemann, and W. S. Howells, *Chem. Phys. Lett.*, **34**, 363, (1975).
3. J. W. Emsley, J. C. Lindon, and G. R. Luckhurst, to be published.
4. R. F. Nystrom, C. Rainer, and A. Berger, *J. Amer. Chem. Soc.*, **80**, 2896, (1958).
5. W. L. Albrecht, D. H. Gustafson, and S. W. Horgan, *J. Org. Chem.*, **37**, 3355, (1972).
6. F. R. Dollish, W. G. Fateley, F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley-Interscience, New York, 1973.
7. A. Mosley, *Ph.D. Thesis*, Department of Chemistry, University of Bradford, England, 1973.
8. J. M. Schnur, *Mol. Cryst. Liquid Cryst.*, **23**, 155, (1973).
9. G. Vergoten and G. Fleury, *Mol. Cryst. Liquid Cryst.*, **30**, 213, (1975).
10. E. B. Priestley, P. S. Pershan, R. B. Meyer, and D. M. Dolhin, *Raman Memorial Volume*, Vijnana Parishad Dusanshan Patrika, **14**, (3–4), 93 (1971).
11. H. Gilman and R. H. Kirby, *Org. Syn.*, *Coll. Vol. I*, 361.