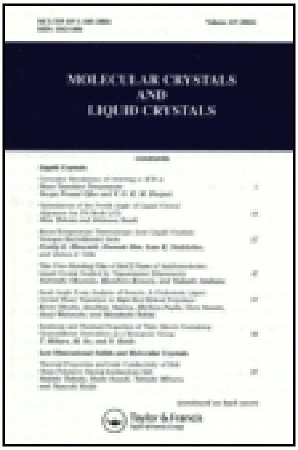

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Preparationof 4-Alkyl-4′-Cyanostilbenes :A New Series of Liquid Crystal Compounds

R. J. Cox [a] & N. J. Clecak [a]

[a] IMB Research Laboratory, San Jose, California, 95193

Version of record first published: 21 Mar 2007.

To cite this article: R. J. Cox & N. J. Clecak (1976): The Preparationof 4-Alkyl-4′-Cyanostilbenes :A New Series of Liquid Crystal Compounds, Molecular Crystals and Liquid Crystals, 37:1, 263-267

To link to this article: http://dx.doi.org/10.1080/15421407608084361

Mol. Cryst. Liq. Cryst., 1976, Vol. 37, pp. 263–267

Printed in Holland

The Preparation of 4-Alkyl-4'-Cyanostilbenes

A New Series of Liquid Crystal Compounds

R. J. COX and N. J. CLECAK

IMB Research Laboratory, San Jose, California 95193

(*Received March 19, 1976; in final form July 17, 1976*)

This paper describes the preparation of a series of 4-alkyl-4′-cyanostilbenes in which the alkyl group ranges from C_4 to C_{10}. The paper includes the description of the synthesis and a preliminary determination of the transition temperatures of the compounds.

INTRODUCTION

The 4-alkyl and 4-alkoxy-4′-cyanobiphenyls prepared by Gray[1] are of great interest, and have been the object of a good deal of study, particularly with regard to their use in electronic devices using the twisted nematic effect.[2] This is mainly due to their improved properties over the compounds previously suggested for use in such devices. They have increased chemical stability over Schiff bases such as MBBA and improved photochemical stability over chlorostilbenes. They are colorless in contrast to azoxy compounds and, in addition several are liquid crystalline at room temperature. We decided to extend this series and to prepare the stilbenes, the analogous compounds containing an ethylenic linkage, and to investigate their liquid crystal properties. The synthesis of the materials, along with some transition temperatures and preliminary microscopic investigations will be the subject of this communication. Detailed thermal investigations and comparison to the biphenyl compounds will be reported later.

COMPOUND PREPARATION

The preparation of stilbenes is a very common reaction and we followed a standard method[3] shown in Figure 1 in which we substituted a para-alkyl benzylhalide for benzylchloride, and para-cyanobenzylideneaniline for the unsubstituted Schiff base. This reaction gave a number of products, none of which was a stilbene, nor was the reaction successful using paracyanobenzaldehyde instead of the Schiff base. The use of butyl lithium however, in place of sodamide as the base, allowed the reaction to go quite cleanly and in fair yields. Unfortunately, the *cis* isomer was produced in quite large percentages and the yields of isolated product were lowered by the separation of the *cis* and *trans* isomers. The only manner in which we could routinely separate the two was by repeated crystallization from methanol in which the *trans* isomer is less soluble. Although we attempted a number of chromatographic techniques in only one case was this successful.

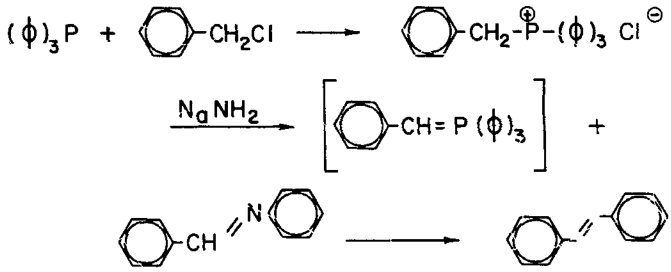

FIGURE 1 Standard synthesis of *trans* stilbenes.

The other major problem that confronted us was the preparation of pure para alkylbenzyl halides uncontaminated by the ortho isomer. The lower members of the series could be prepared by the reaction of formaldehyde and sodium bromide with the alkyl benzene,[4] carefully vacuum fractionating the mixture of ortho and para isomers on an annular spinning band column. This method was difficult when the separation of the heptyl compound was attempted, and became impossible with the higher members of the series. The temperatures necessary to get the compounds through the column caused decomposition of the benzyl bromides, which combined with foaming problems made an effective separation impractical. We attempted to carry the reaction through with the isomer mixture in the hope of separation either at the phosphonium bromide or the stilbene stage, but both isomers remained, and with about 30% ortho compound increasing the difficulties of the *cis*/*trans* isomer problem in the stilbene, the situation seemed hopeless. The use of chloromethyl methyl ether as a chloromethylating agent for aromatic compounds is well known[5] particularly with regard to its reaction with polystyrene in the Merrifield solid state synthesis. The reaction does not seem to have been applied to monoalkylbenzenes although there was no reason to believe it would not be successful. We did not use chloromethyl methyl ether for this reaction for two reasons. First, we had been using the benzyl bromides and felt that they might form the phosphonium salt more readily than the chlorides, and secondly, chloromethyl methyl ether is on the OSHA list and was not available to us. We therefore, substituted bromomethyl methyl ether, a readily available compound which turns out not to be on the list. To our surprise this did not form any benzyl bromide, and could be recovered unchanged from the reaction mixture. We did find, however, that chloromethyl ethyl ether, also not on the list, gave the desired benzyl chloride in good yields at 0°C after about two hours reaction time. This compared to nearly 20 hours at 90–100°C for the formaldehyde sodium bromide reaction. We also found that in this case the isomer ratio was in favor of the para subsitution by about 9 to 1, and that with this isomer ratio, without further separation, we could complete the synthesis successfully to isolate useable quantities of the pure para-*trans*-stilbene. The isomer ratio both of the ortho and para-benzyl halides and the *cis* and *trans*-stilbenes was determined by NMR spectroscopy. The difference between the chemical shifts of the benzylic protons of ortho and para substituted benzyl halides (447 Hz and 443 Hz respectively) allowed the differentiation of these isomers. The upfield resonances at 640 to 700 Hz, typical of the ethylenic protons in *cis* stilbenes, were used to distinguish the *cis* and *trans* stilbenes. The successful synthesis of the alkyl cyanostilbenes is shown in Figure 2.

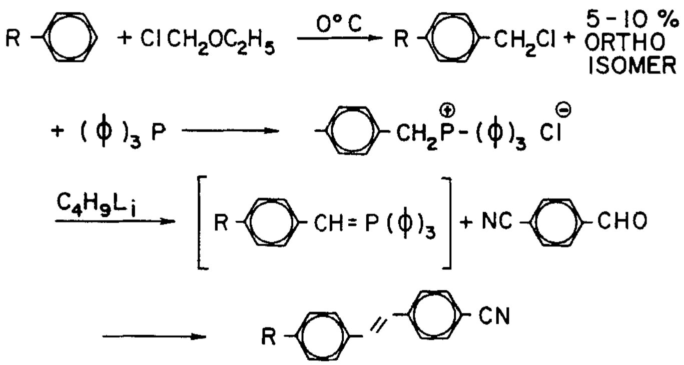

FIGURE 2 Synthetic route for the preparation of 4-alkyl-4'-cyanostilbenes.

A plot of the chain length vs. transition temperatures in Figure 3 shows the usual odd-even effect found in such series of compounds. Table I gives the transition temperatures, yields and combustion analysis for the new liquid crystal compounds.

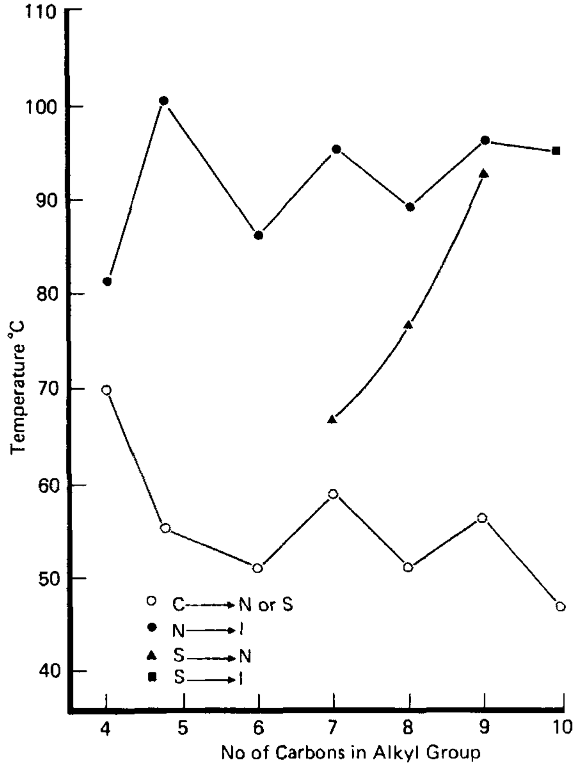

FIGURE 3 Plot of transition temperatures vs. alkyl chain length in 4-*n*-alkyl-4′-cyanostilbenes.

TABLE I

Physical properties and yields of *trans*-4-alkyl-4′-cyanostilbenes

					Combustion analysis[a]					
					Calculated			Found		
Alkyl Group	% yield	C-N or S °C	N-S C	S or N-I °C	C	H	N	C	H	N
n-C_4H_9	12	70.5	—	82.3	87.4	7.3	5.4	87.5	7.3	5.6
n-C_5H_{11}	10	55.1	—	101.0	87.3	7.6	5.1	86.9	7.7	5.0
n-C_6H_{13}	37	51.2	—	86.1	87.2	7.9	4.8	87.2	7.9	4.9
n-C_7H_{15}	35	59.5	64.6	95.0	87.1	8.3	4.6	86.4	8.1	4.5
n-C_8H_{17}	8	51.1	78.7	89.4	87.0	8.5	4.4	86.8	8.5	4.2
n-C_9H_{19}	26	56.2	94.4	96.7	86.9	8.8	4.2	86.9	8.8	4.2
n-$C_{10}H_{21}$	30	47.2	—	95.1	86.8	9.1	4.1	86.7	9.0	4.0

[a] Childers Microanalytical Laboratories, Milford, N.J.

EXPERIMENTAL

Satisfactory elemental analysis were obtained for all new compounds. The transition temperatures and tentative identification of the mesophases were determined by optical microscopy.

Alkyl benzene (0.5 moles) and chloromethyl ethyl ether (0.82 moles) were dissolved in either carbon tetrachloride or carbon disulfide (150 ml.) and stannic chloride (0.15 moles) was added slowly at 0°C. The reaction mixture was stirred for about 2 hours at this temperature and was then poured into ice water and phase separated. The organic phase was dried and evaporated. The oil that remained was either distilled or could be used directly in the next reaction. This para-alkylbenzyl halide was heated with equimolar quantities of triphenylphosphine for about $\frac{1}{2}$ hour at 140–160°C. The reaction mixture was poured into ether or petroleum ether, the solution filtered and the solid phosphonium chloride isolated and dried under vacuum. The salt was slurried in or dissolved in dry benzene, an equimolar solution of 5 M *n*-butyl lithium was added under a nitrogen blanket and the resultant phosphorylid stirred at room temperature for one hour.

The addition of an equimolar quantity of *p*-cyanobenzaldehyde caused an immediate disappearance of the dark colored ylid and the reaction mixture was stirred for an additional 2 hours. It was then poured into water, phase separated, the organic phase evaporated and the oily product slurried in methanol in order to isolate the trans-stilbene. Recrystallization from methanol was repeated until both the NMR and TLC indicated no cis isomer to be present. The purity was established by combustion analysis and by TLC (three solvents—chloroform, benzene, and petroleum ether). In each case only a single spot could be observed.

References

1. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Nash, *Liquid Crystals and Ordered Fluids.* Vol. 2 ed. J. F. Johnson and R. S. Porter (Plenum Press 1974), pp. 617.
2. M. Hareng, S. Le Berre, and L. Thirant, *Appl. Phys. Letters*, **25**, 386 (1974).
3. Newer Methods of Preparative Organic Chemistry, ed. W. Foerst. (Academic Press, 1963), Vol. 5, p. 48.
4. P. Mamalis, J. Green, D. J. Outred, and M. Rix, *J. Chem. Soc.*, **3915** (1962).
5. S. V. Rogozkin, V. V. Koshak, V. A. Davankov, and L. A. Maslova, *Vsokomolekul Soedin*, **8**, 1275–8 (1966).