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Liquid Crystals

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The Synthesis, Polymerization and Second Order Non-Linear Optical Properties of Novel, Conjugated, Unsymmetrical Diacetylenes Showing Liquid Crystal Behaviour

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The synthesis, polymerization and second order non-linear optical properties of novel, conjugated, unsymmetrical diacetylenes showing liquid crystal behaviour

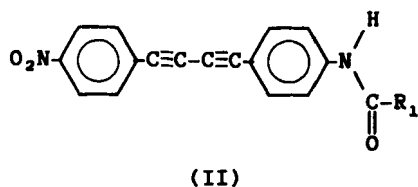
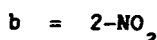
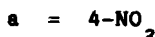
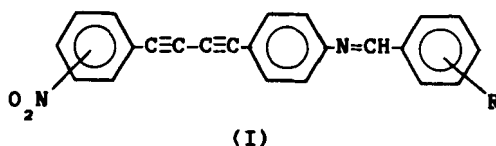
by J. TSIBOUKLIS, A. R. WERNINCK, A. J. SHAND and G. H. W. MILBURN
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A number of novel, conjugated, unsymmetrically disubstituted diphenyl-diacetylenes have been synthesized and polymerized in the liquid-crystalline phase to yield liquid-crystalline polymers. The efficiency of second harmonic generation is reported for both monomers and polymers.

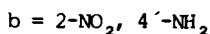
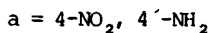
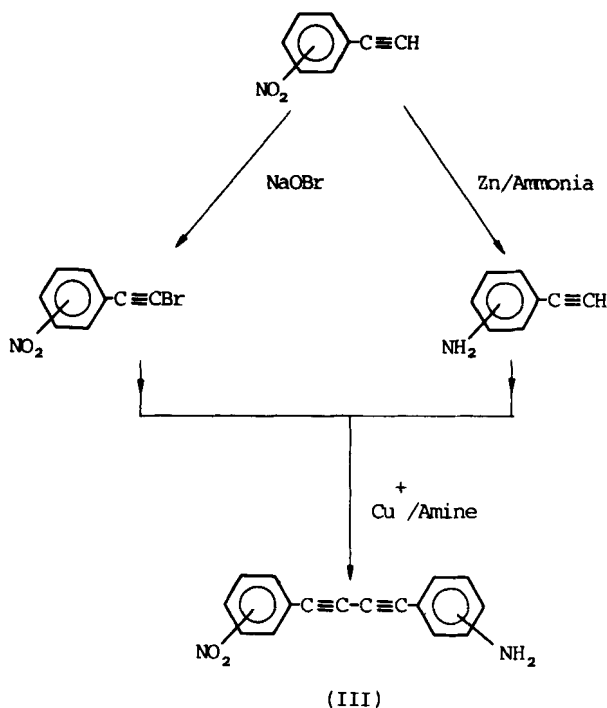
1. Introduction

It is well known [1, 2] that mesogenic diacetylene monomers form thermotropic liquid crystal phases which can undergo polymerization on thermal annealing. Pronounced second order non-linear optical properties have been shown by conjugated diacetylene monomers with an electron donating group at one end of the molecule and an electron withdrawing group at the other [3]. Centrosymmetric liquid-crystalline polymers formed from diacetylenes have been shown [4, 5] to possess third order non-linear susceptibilities, $\chi^{(3)}$, which are two orders of magnitude larger than quartz. As part of our work on the investigation of the non-linear optical properties of conjugated, unsymmetrically disubstituted diphenyldiacetylene monomers and polymers, we now report the synthesis of a number of compounds of structures (I) and (II) which exhibit liquid crystallinity.



2. Experimental

4-Nitro-4'-aminodiphenyldiacetylene (III a) and 2-nitro-4'-aminodiphenyldiacetylene (III b) were synthesized from the corresponding 4-nitro- or 2-nitrophenylacetylene [6] according to the scheme [7]



Reaction of (III a) or (III b) with aldehydes gave the corresponding imines (I), while reaction of (III a) with acyl halides gave the amides (II).

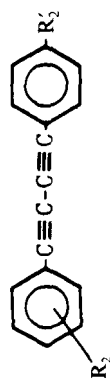
2.1. General method for the synthesis of (I)

A mixture of either (III a) or (III b) (0.5 g) and the appropriate aldehyde (1.0 g) in ethanol (2 cm³) was warmed on a water bath until no further colour change was observed. The product was filtered and recrystallized from ethanol.

2.2. General method for the synthesis of (II)

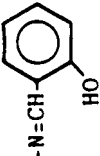
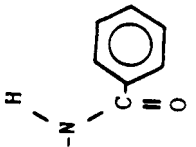
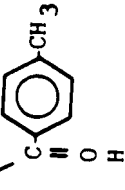
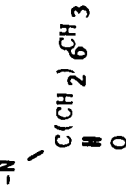
The appropriate acid chloride (5 cm³) was added to a mixture of (III a) (0.5 g) and 2M sodium hydroxide solution (10 cm³) and the solution stirred at room temperature for 30 min. On addition to ice, the crude product which separated was filtered, washed in turn with hot, saturated sodium hydrogen carbonate solution and water and finally recrystallized from dioxane: water (9:1). The compounds synthesized are given in table 1.

Table 1. Diacetylenes



Compound	R ₂	R ₁	Elemental Analysis; Found(Calc.)			ν(C≡C) /cm ⁻¹	Yield per cent	T _{CA} [†] /°C
			C	H	N			
Ia(i)	4-NO ₂	-N=CH-	75.71(75.79)	4.19(4.21)	7.33(7.37)	2200	92	215
Ia(ii)	4-NO ₂	-N=CH-	75.44(75.41)	3.84(3.82)	7.51(7.65)	2204	93	223
Ia(iii)	4-NO ₂	-N=CH-	72.72(72.73)	4.01(4.04)	7.09(7.07)	2200	87	238
Ia(iv)	4-NO ₂	-N=CH-	73.03(73.10)	3.51(3.55)	7.16(7.11)	2208	89	246
Ia(v)	4-NO ₂	-N=CH-	74.18(74.12)	3.53(3.53)	8.15(8.24)	2197	97	238
Ib(i)	2-NO ₂	-N=CH-	75.69(75.79)	4.20(4.21)	7.18(7.37)	2193	83	175

Table 1 (continued)

Compound	R ₂	R ₂ '	Elemental Analysis; Found(Calc.)			Yield per cent	T _{csA} [†] /°C
			C	H	N		
I b(ii)	2-NO ₂		75.40(75.41)	3.80(3.92)	7.61(7.65)	83	177
II(i)	4-NO ₂		75.43(75.40)	3.67(3.82)	13.14(13.11)	69	220
II(ii)	4-NO ₂		75.92(75.79)	4.23(4.21)	7.33(7.37)	74	251
II(iii)	4-NO ₂		74.98(75.00)	6.14(6.18)	7.49(7.28)	83	161

† Crystals to smectic transition temperature.

2.3. Instrumental

I.R. spectra were recorded as KBr discs on a Perkin-Elmer 598 spectrophotometer. CHN analyses were carried out using a Carlo-Erba 1106 elemental analyser equipped with a Spectra Physics SP4100 computing integrator.

Measurements of the thermal behaviour were carried out on a differential scanning calorimeter equipped with a Mettler DSC30 low temperature cell and a Mettler TC10A automated data processor and confirmed by differential thermal analysis (DTA) and thermogravimetry (TG) using a Stanton Redcroft STA-780 thermal analyser. The transition characteristics and texture of the liquid crystals were examined on a Nikon Optophot-Pol polarizing microscope equipped with a Linkam TH600 hot stage at $360\times$ magnification.

Molecular weight distribution studies [8] on the polydiacetylenes were performed by GPC in tetrahydrofuran solution (0.2 per cent by weight) on a column combination of $1\times 100\text{A}$ and $1\times 500\text{A}$ PL gel. Measurements were carried out at room temperature using a flow rate of $1.0\text{cm}^3\text{min}^{-1}$. A GPC calibration graph was obtained using a series of polystyrene standards.

The KCl disc technique used for the investigation of the second harmonic generation effect is to be reported elsewhere [9].

3. Results and discussion

All the compounds synthesized exhibit liquid crystallinity. A combination of D.S.C., D.T.A. and T.G. measurements demonstrated that the disubstituted diphenyl-diacetylene monomer crystals undergo liquid crystal phase transitions. Upon further heating, an irreversible polymerisation process takes place. A typical thermogram is

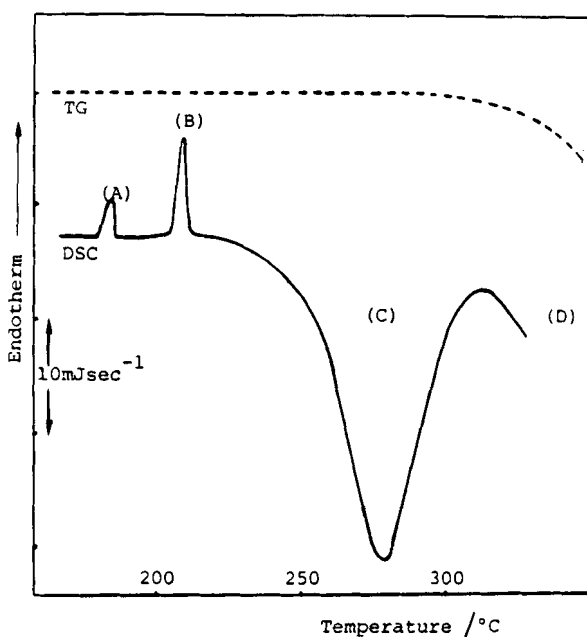
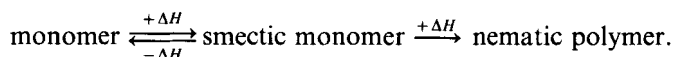


Figure 1. D.S.C. thermogram of the liquid-crystalline diacetylene, Ia(i); first heating; heating rate: $5^{\circ}\text{C min}^{-1}$.

shown in figure 1. The area and position of endotherm (A) depends on the heating conditions suggesting a crystal–crystal transition. Transition (B) is characterized by a relatively low enthalpy change ($\approx 20 \text{ kJ mol}^{-1}$) typical of a crystal \rightarrow liquid crystal phase transition.

The enthalpy of polymerization, computed from the area of exotherm (C), is large ($\Delta H_p \approx 240 \text{ kJ mol}^{-1}$) compared to the enthalpy change of $\approx 150 \text{ kJ mol}^{-1}$ observed for diacetylenes which polymerise in the solid state [10]. This high value may indicate that the polymers resulting from liquid-crystalline state polymerisation of diacetylenes do not have the one dimensional chain structure commonly observed in solid state polymerized diacetylenes. These liquid-crystalline polymers are under further investigation. Peak (D) is attributed to degradation.

Evidence for the formation of polymers was obtained by optical microscopy. On initial heating, the monomers underwent reversible transitions to smectic phases. Further heating gave random nucleation of separate nematic polymer phases resulting in the formation of orange/brown liquid-crystalline polymers of low solubility in common organic solvents;



The existence of nematic polymer phases in the liquid-crystalline polymers was confirmed by the observation of disclination structures containing both two and four brushes see (figure 2). All the diacetylenes prepared in this study behaved in a like manner. The average molecular weight of the slightly soluble polydiacetylenes with respect to polystyrene was of the order of 2500 g mol^{-1} .

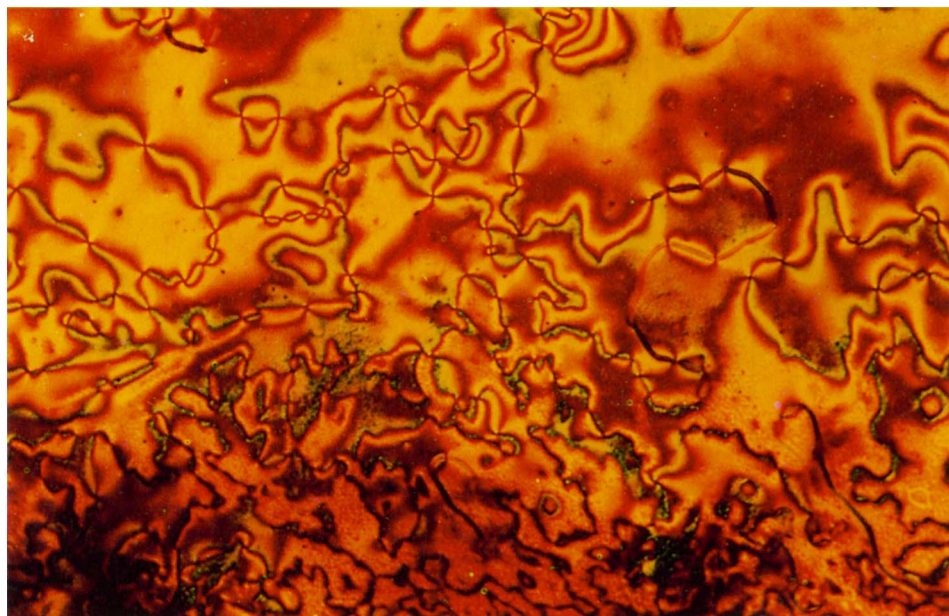
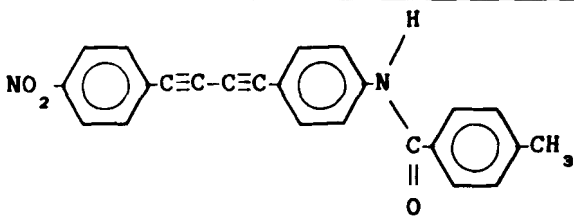
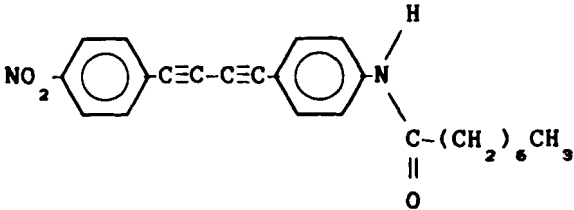
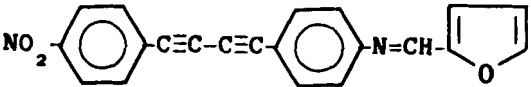
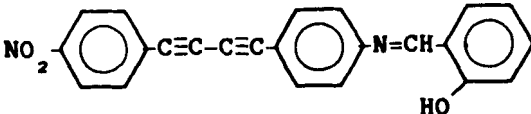


Figure 2. Photomicrograph ($\times 360$) of the nematic polymer from Ia(i) at 225°C between crossed polarizers.

Table 2. Second harmonic generation

Diphenyldiacetylene	Second harmonic generation signal
	0.01
	0.07
	0.10
	0.33
Standard	
2-methyl-4-nitroaniline	4.27
3-nitroaniline	0.59
2-chloro-4-nitroaniline	0.97
3-bromonitrobenzene	0.02

The efficiency of second harmonic generation was evaluated by means of the KCl disc technique [9]. This method is good for evaluating materials with second harmonic generation efficiencies several times greater than those already in use, but it is not capable of differentiating between compounds of similar second order non-linear optical responses. The advantage of the technique is that an evaluation of the second harmonic generation effect can be carried out instantaneously using a few milligrams of a micro-crystalline material. The method does not replace the well-established Maker fringe [11] or phase matching [12] experiments for determining the individual second order non-linear optical coefficients.

Table 2 compares the 532 nm second harmonic generation signal (mean of five measurements) of the diphenyldiacetylenes giving a detectable signal, with those of a series of standards of known second order non-linear optical coefficients. These results confirm that the second order non-linear optical effects increases with increasing conjugation of the molecule [13]. In agreement with previous results [7] none of the corresponding polymers showed activity.

4. Conclusion

The conjugated, mesogenic diacetylenes polymerize in the liquid-crystalline state, in a controlled manner to form nematic polymers. Although none of the polymers

exhibited detectable second order non-linear optical responses, the second harmonic signals of some of the monomers were of the same order of magnitude as those of nitrobenzenes.

We would like to thank Mrs. S. M. G. Guthrie and Dr. F. R. Cruickshank of the University of Strathclyde for evaluation of the non-linear optical properties of the materials synthesized and Dr. S. Holding of Rapra Technology Limited for carrying out the molecular weight determinations.

References

- [1] DESAI, K. N., MCGHIE, A. R., PANACKAL, A. A., and GARITO, A. F., 1985, *Molec. Crystals liq. Crystals Lett.*, **1**, 83.
- [2] OZCAYIR, Y., and BLUMSTEIN, A., 1986, *J. Polym. Sci. Polym. Chem.*, **24**, 1217.
- [3] FOUQUEY, C., LEHN, J. M., and MALTHETE, J., 1987, *J. chem. Soc. Chem. Commun.*, p. 1424.
- [4] GARITO, A. F., and WONG, K. Y., 1987, *Polym. J.*, **19**, 51.
- [5] GARITO, A. F., TENG, C. C., WONG, K. Y., and ZAMMANI KHAMIRI, O., 1984, *Molec. Crystals liq. Crystals*, **219**, 106.
- [6] DREWSEN, N. B., 1882, *Ber.*, p. 150.
- [7] TSIBOUKLIS, J., WERNINCK, A. R., SHAND, A. J., and MILBURN, G. H. W., *Chemtronics* (to be published).
- [8] HOLDING, S., Rapra Technology Ltd (personal communication).
- [9] BAILEY, R. T., BLANEY, S., CRUICKSHANK, F. R., GUTHRIE, S. M. G., PUGH, D., and SHERWOOD, J. N., 1988, *J. appl. Phys. B* (in the press).
- [10] PATEL, G. N., CHANCE, R. R., TURI, E. A., and KHANNA, Y. D., 1978, *J. Am. chem. Soc.*, **100**, 6644.
- [11] JERPHAGNON, J., and KURTZ, S. K., 1970, *J. appl. Phys.*, **41**, 1667.
- [12] BJORKHOLM, J. E., 1969, *I.E.E.E. JI quant. Electron.*, **5**, 26.
- [13] BUCKLEY, A., 1986, *Polymeric Materials, Science and Engineering* (ACS), p. 502.