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Liquid Crystals

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Novel family of liquid crystals based on a known biheterocyclic pigment material: mesomorphic derivatives of 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione†

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Presented at the Capri Symposium in Honour of George W. Gray, FRS held at the
Hotel Palatium, Capri, 11–14 September 1996

The chromophoric biheterocycle 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPPD) as a widely variable basic core structure has been introduced into liquid crystal research and the first eight calamitic examples of thermomesomorphic derivatives are presented and discussed.

1. Introduction

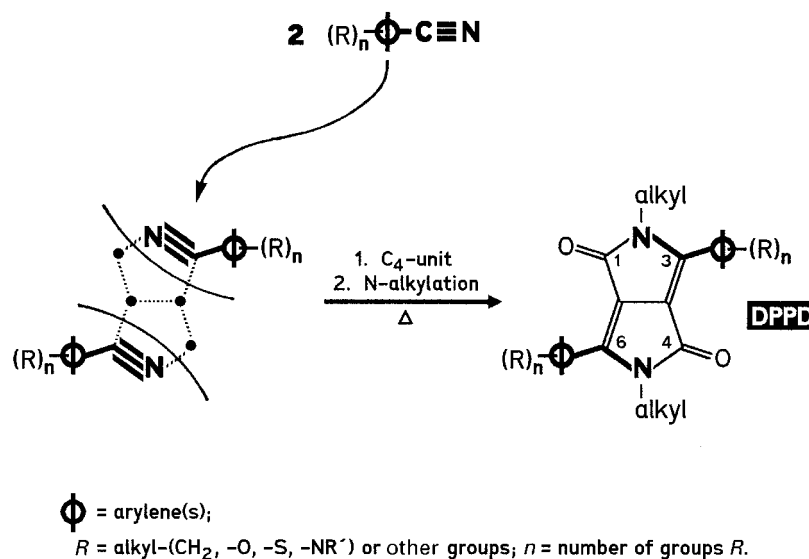
Derivatives of the 3,6-diaryl-substituted biheterocyclic compound 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPPD, figure 1) constitute a relatively new class of chemically stable fluorescent molecules of which the first examples were synthesized as long as 22 years ago [2]; however, most work with them dates only from recent years [3–9].

Although in the course of this activity DPPDs were studied from various scientific and technological aspects, e.g. their applications as photostable and weatherproof pigments—orange, red, or red-violet, etc. in colour—

laser, safety, and textile dyes, fluorescence dyes with large Stokes shifts, photosensitizers, or materials for the storage of digital data, etc. surprisingly thus far no reports regarding the relationship between low molar mass DPPDs and liquid crystalline properties are available in the literature.

The only connections of DPPDs with liquid crystals which have come to our knowledge are given in the references [7–9] dealing with (1) rational designs of multifunctional liquid crystalline conjugated polymers containing a *non*-thermomesomorphic DPPD derivative as photosensitizer [7,9] and (2) polarized light spectro-

Figure 1. Sketch of the two-step synthetic route to the tetrasubstituted 2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-diones (DPPD) from aryl nitriles and a C₄-unit (e.g. dialkyl succinates) on heating with base induction, followed by a classical N-alkylation reaction. This chromophoric biheterocycle is introduced here as a new core system in liquid crystal research.



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† See reference [1].

scopy of DPPDs with small substituents in an anisotropic environment, i.e. as additives in a macroscopically aligned lyotropic nematic liquid crystal [8].

In our opinion, the reason for this gap regarding this relationship between DPPD compounds and their mesomorphic behaviour lies clearly in the kind of substitution used in the aryl nitrile, the main starting material for the 3,6-diaryl DPPD derivatives (figure 1), hitherto characterized by only *short* substituents due to other interests (see above) in this fascinating chromophoric system.

2. Experimental

2.1. General

The chemical structures of all final products were confirmed by standard methods: elemental analyses, NMR spectroscopy (400 MHz, solvent: CDCl_3), as well

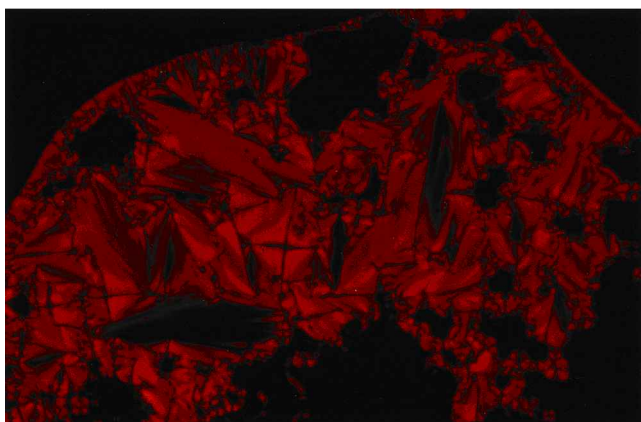
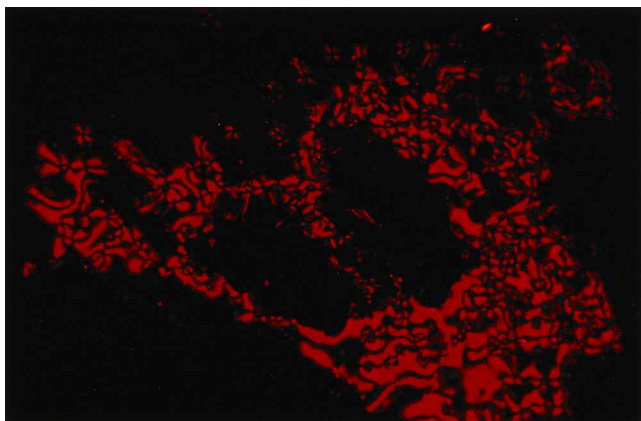


Figure 2. Characteristic textures of two examples of light red calamitic liquid crystals possessing the DPPD core shown in the table and figure 1: the schlieren texture (nematic, N phase between lipophilic glass plates: top) of **1a** at 113.3°C on heating into the isotropic liquid phase and the fan-like texture (smectic, SmA phase: bottom) of **1b** at 107.9°C on cooling from the isotropic liquid phase; heating or cooling rates 1 K min^{-1} .

as mass spectrometry (Varian MAT 711, 70 eV, $> 200^\circ\text{C}$, direct inlet).

Instruments for further studies and calculations included (1) Optical microscopy: Leitz Laborlux 12 Pol with a Mettler FP82 microfurnace and a FP80 control unit; (2) DSC: Mettler TA 3000/DSC-30 S with TA 72.5 software; (3) X-ray: Cu-K_α radiation, beam width 0.4 mm, sealed capillary; (4) semi-empirical calculations: MNDO94 3.0/AM1 procedure, standard parameter set of the Unichem 3.0 software package (Cray Research Inc.), Cray J 932/16-8192 computer, SCF field consistency achieved.

2.2. Preparation of the DPPD derivatives 1a–h

Starting from each 25 mmol of the respective aryl nitrile [10], the preparations of the red intermediate biheterocyclic product (yields: 12–35%) were carried out analogously to earlier descriptions [3]. Following an earlier procedure [3] for *N*-alkylations of analogous bis-lactams our preparations of **1a–h** ($\leq 50\%$ yield) were made on a 2 mmol scale. The phase transition data and types of mesophase are listed in the table; two texture photographs are shown in figure 2. Satisfactory elemental analyses and spectroscopic data for **1a–h** were obtained.

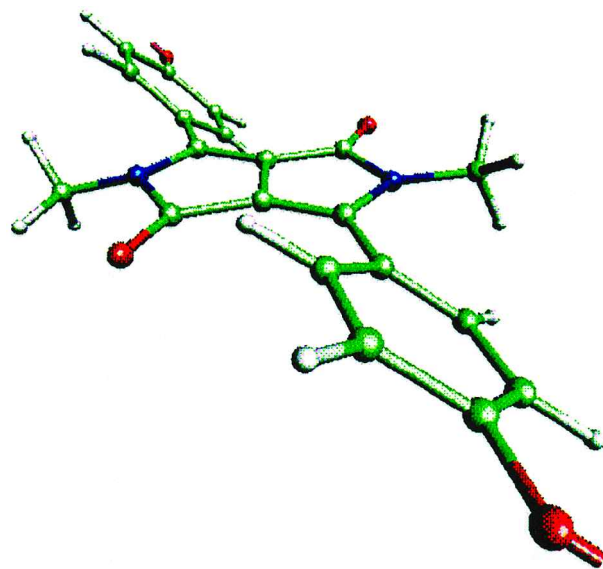


Figure 3. The ball-and-stick model of the new, light red DPPD liquid crystal **1c** [3,6-bis(4'-dodecyloxyphenyl)-2,5-dihydro-*N,N'*-dimethylpyrrolo [3,4-*c*]pyrrole-1,4-dione] (table), used here as an example from the 3,6-diaryl DPPD series to demonstrate the angle between the biheterocyclic molecular centre unit and the phenyl substituents attached to it; this was calculated (cf. §2.1) by us semi-empirically to be $30\text{--}40^\circ$. In its fully stretched form **1c** is about 43.6 Å long and 6.1 Å wide. However, to enable concentration on the angle situation in the model shown, the chains have been omitted.

The formulae and molar masses of the eight new *N,N'*-dialkylated thermotropic liquid crystal materials are:

- 1a** C₃₆H₄₈N₂O₄ (572·8), **1b** C₄₀H₅₆N₂O₄ (628·9),
1c C₄₄H₆₄N₂O₄ (685·0), **1d** C₄₄H₄₈N₂O₄ (668·9),
1e C₄₀H₄₀N₂O₂ (580·8), **1f** C₃₈H₄₈N₂O₂ (568·1),
1g C₅₄H₆₄N₂O₂ (773·1), **1h** C₅₆H₆₈N₂O₂ (801·2).

3. Results and discussion

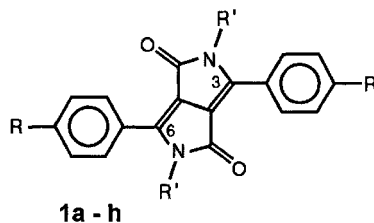
In an effort to test the suitability of the DPPD biheterocycle (see the structural formulae in the table and figure 1) as a liquid crystal core, we have begun work on this topic by synthesizing the eight bis-lactams **1a–h** starting from various 4-arylnitriles [10] with longer alkyl or alkoxy chains in their *para*-positions and diethyl succinate according to the literature [3], cf. §2. As expected, in comparison with other derivatives of this class of compounds [3, 5], the intermediate crude, as yet not *N*-alkylated products of cyclization

are extremely high melting, deep red solids. Their *N*-alkylation led to the new target compounds **1a–h** which crystallize in needles, are now light red in colour, have very much lower melting points than their precursors, and are indeed thermomesomorphic (table and figure 2).

Preliminary investigations of these first DPPD liquid crystal materials **1a–h** by three methods (optical microscopy, DSC and in part also X-ray diffraction) prove that they are always *mono*-thermomesomorphic and exhibit in six cases (**1a**, **1d–h**) a nematic phase and in the two cases **1b** and **1c** (carrying the longest alkoxy substituents) each a smectic A phase. Figure 2 depicts texture photographs of both types of mesophase observed so far with this new family of liquid crystal materials which, incidentally, have a distinct tendency for homeotropic alignment.

Whereas the group of three 3,6-diphenyl DPPD materials, **1a–c**, exhibit only narrow mesophases slightly above 100°C, the nematic phases of all the other five mesogens, **1d–h**, having two or even three—in part

Table. Phase transition temperatures* (°C) and enthalpies (ΔH in kJ mol⁻¹) for the first eight DPPD liquid crystal (LC) materials **1a–h**, light red in colour, synthesized in our laboratory.



| DPPD LC | R | R' | Cr | | M | Iso | |
|-----------|------------------------------------|-------------------------------|----|--------------------|-----|-------------------|---|
| 1a | H ₁₇ C ₈ O— | CH ₃ | • | 106·2/105·7 (59·2) | N | 114·0/113·7 (0·9) | • |
| 1b | H ₂₁ C ₁₀ O— | CH ₃ | • | 106·3/105·5 (68·9) | SmA | 119·0/117·9 (3·0) | • |
| 1c | H ₂₅ C ₁₂ O— | CH ₃ | • | 108·8/108·1 (81·9) | SmA | 122·7/121·6 (4·7) | • |
| 1d | H ₁₃ C ₆ O— | CH ₃ | • | 205·0/204·5 (44·3) | N | 335·0/336·7 (1·2) | • |
| 1e | H ₉ C ₄ — | CH ₃ | • | 220·0/219·0 (4·2) | N | 330·0/331·3 (0·1) | • |
| 1f | H ₇ C ₃ — | CH ₃ | • | 191·0/189·8 (23·3) | N | 358·0/356·2 (1·7) | • |
| 1g | H ₁₁ C ₅ — | CH ₃ | • | 248·5/248·5 (31·3) | N | 327·0/327·3 (0·3) | • |
| 1h | H ₁₁ C ₅ — | C ₂ H ₅ | • | 244·1/242·2 (37·7) | N | 349·4/347·1 (0·2) | • |

* Obtained by polarizing microscopy/DSC; Cr=crystalline, M=mesophase, N=nematic, SmA=smectic A, I=isotropic liquid.

aromatic—six membered rings in line at both positions 3- and 6-, prolonging the conjugation with the two double bonds of the DPPD core, are very much more stable. They appear mostly above 200°C and persist up to a clearing temperature close to 360°C (table).

Concerning the conjugation in **1a–h**, our semi-empirical calculations of the conformation in the 3,6-diphenyl DPPD part of the molecules (cf. the ball-and-stick model in figure 3) resulted in an energy minimum for an angle of 30–40° between the phenyl rings and the DPPD core.

Mesogen **1a** shows in an X-ray beam diffuse first order reflections which, however, are of greater sharpness than expected for typical nematic phases and seem to suggest a tendency to form a layered structure, found to be characteristic for the homologues **1b** and **1c**. The layer spacings for the latter two materials were found to be 32.06 and 35.42 Å, respectively.

The strong tendency to form ordered molecular structures is also reflected during the crystallization processes of all members of series **1**, as their melting points could be supercooled only by several degrees during cooling at a rate of 1 K min⁻¹ from their mesophases. The needle-like crystals are formed so quickly that the preparations crystallize entirely in less than 1 min. Interestingly, the melting points of **1a–c** are hardly different, whereas their clearing points go up steeply by about 9 K between **1a** and **1c** (table).

4. Conclusion

Certainly, the diverse possibilities of substitution of this interesting chromophoric DPPD system, offered in principle through the aromatic groups at positions 3 and 6 and the two lactam functions, indicate great promise for future development of not only further

coloured calamitic mesogens, but presumably also coloured phasmodic, disc-like, and polymer liquid crystal materials.

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References

- [1] Part 107 on liquid crystalline compounds; part 106: CHANDRASEKHAR, S., NAIR, G. G., RAO, S. S., PRASAD, S. K., PRAEFCKE, K., and BLUNK, D., 1997, *Liq. Cryst.*, **24**, 67–70.
- [2] FARNUM, D., METHA, G., MOORE, G., and SIEGAL, F., 1974, *Tetrahedron Lett.*, **15**, 2549.
- [3] POTRAWA, T., and LANGHALS, H., 1987, *Chem. Ber.*, **120**, 1075.
- [4] CLOSS, F., and GOMPPER, R., 1987, *Angew. Chem.*, **99**, 564; 1987; CLOSS, F., and GOMPPER, R., 1987, *Angew. Chem. Int. Ed. Engl.*, **26**, 552.
- [5] IQBAL, Z. A., JOST, M., KIRCHMAYR, R., PFENNINGER, J., ROCHAT, A., and WALLQUIST, O., 1988, *Bull. Soc. Chim. Belg.*, **97**, 615 and patents cited therein.
- [6] LANGHALS, H., and POTRAWA, T., 1990, *Chimia*, **44**, 62.
- [7] CHAN, W.-K., CHEN, Y., PENG, Z., and YU, L., 1993, *J. Amer. chem. Soc.*, **115**, 11735.
- [8] EDMAN, P., JOHANSSON, L. B.-A., and LANGHALS, H., 1995, *J. phys. Chem.*, **99**, 8504, and references cited therein.
- [9] BAO, Z., CHAN, W.-K., and YU, L., 1995, *J. Amer. chem. Soc.*, **117**, 12426.
- [10] 4-Alkoxybenzonnitriles: PARTRIDGE, M. W., 1949, *J. chem. Soc.*, 3043; SCHUBERT, H., and ZASCHKE, H., 1970, *J. prakt. Chem.*, **312**, 494. The other five aryl nitriles used here in our DPPD liquid crystal syntheses are commercially available, e.g. from E. Merck, Darmstadt, Germany.