

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Liquid-crystalline quinoline derivatives

Rino Leardini<sup>a</sup>; Daniele Nanni<sup>a</sup>; Antonio Tundo<sup>a</sup>; Giuseppe Zanardi<sup>a</sup>; Gian Franco Pedulli<sup>b</sup>

<sup>a</sup> Dipartimento di Chimica Organica, dell'Università, viale Risorgimento 4, Bologna, Italy <sup>b</sup> Istituto di Scienze Chimiche, Facoltà di Farmacia, via S. Donato 15, Bologna, Italy

**To cite this Article** Leardini, Rino , Nanni, Daniele , Tundo, Antonio , Zanardi, Giuseppe and Pedulli, Gian Franco(1987) 'Liquid-crystalline quinoline derivatives', *Liquid Crystals*, 2: 5, 625 – 631

**To link to this Article:** DOI: 10.1080/02678298708086321

**URL:** <http://dx.doi.org/10.1080/02678298708086321>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Liquid-crystalline quinoline derivatives

by RINO LEARDINI†, DANIELE NANNI†, GIAN FRANCO PEDULLI‡,  
ANTONIO TUNDO† and GIUSEPPE ZANARDI†

†Dipartimento di Chimica Organica dell'Università, viale Risorgimento 4,  
40136 Bologna, Italy,

‡Istituto di Scienze Chimiche, Facoltà di Farmacia, via S. Donato 15,  
40127 Bologna, Italy

(Received 5 December 1986; accepted 16 April 1987)

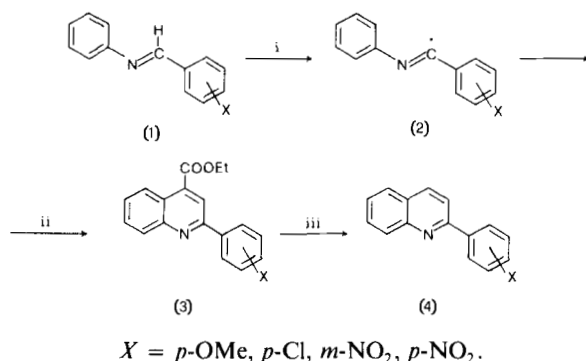
A number of novel liquid crystals have been synthesized. 2-Phenylquinolines with alkyl or alkoxyl substituents in positions 6 and 4' show a texture typical of nematic mesophases and are characterized by a greater thermal stability than Schiff bases bearing the same substituents. The possibility of lowering the melting temperatures by means of eutectic mixtures is discussed.

### 1. Introduction

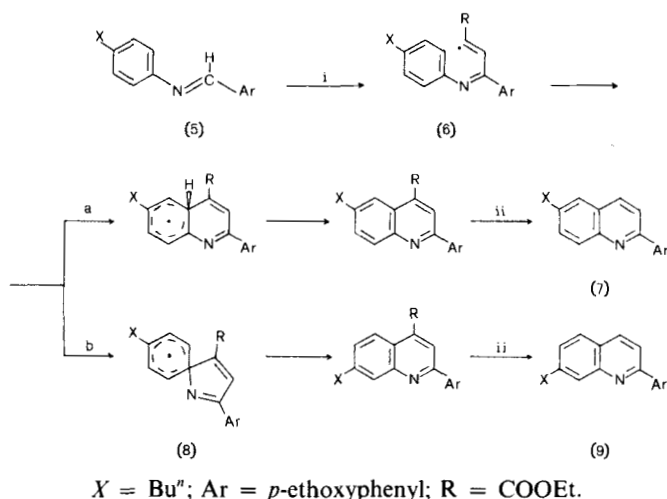
We have shown [1] that *N*-benzylideneanilines (Schiff's bases) (**1**) react with peroxides in the presence of monosubstituted acetylenes to give 4-substituted 2-phenylquinolines (**3**) in high yields, via the intermediacy of arylimido radicals (**2**). When the acetylene is ethyl propiolate, hydrolysis and decarboxylation afford 2-phenylquinolines (**4**) (scheme 1). Since Schiff's bases containing appropriate substituents at positions 4 and 4' are a well-known class of commercially available thermotropic liquid crystals, this reaction would be, in principle, a very convenient way of obtaining the corresponding substituted 2-phenylquinolines, for which liquid-crystalline behaviour would also be expected. However only a few examples of mesomorphic phenylquinolines are known [2, 3].

By repeating the reaction with *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (**5**) and ethylpropiolate, two isomeric compounds were obtained, i.e. 2-(*p*-ethoxyphenyl)-6-*n*-butylquinoline (**7**) and 2-(*p*-ethoxyphenyl)-7-*n*-butylquinoline (**9**). The former, as expected, showed liquid-crystalline properties, while the latter melted directly to an isotropic liquid. A rationale for this result was given in a subsequent paper [4] where evidence was provided that the vinyl radical (**6**), formed by attack of the intermediate imido radical to the alkyne, further reacts by giving both intramolecular homolitic aromatic substitution on the phenyl ring linked to the iminic nitrogen (path *a*), or an *ipso* cyclization followed by a rearrangement via cleavage of the C-N bond of the intermediate spirocyclohexadienyl radical (**8**) (path *b*, scheme 2). The latter route, leading to the 7-substituted quinolines, is favoured by a factor ranging from 1.3 to 3.4 depending on the substituent *X*; thus, high yields of 6-substituted 2-arylquinolines cannot be obtained using this reaction. Moreover, the two isomeric quinolines are not easily separated from their mixture.

However, since quinoline (**7**) prepared with this method showed liquid-crystalline behaviour, we attempted to synthesize other substituted 2-arylquinolines by using different reactions in order to explore the properties of these novel liquid crystals, which are potentially useful for many practical applications. Quinolines in fact do not



Scheme 1. Reagents: (i) di-isopropylperoxydicarbonate (DPDC); (ii)  $\text{HC}\equiv\text{C}-\text{COOEt}$ ; (iii)  $\text{H}_3\text{O}^+$ ,  $\Delta$ .



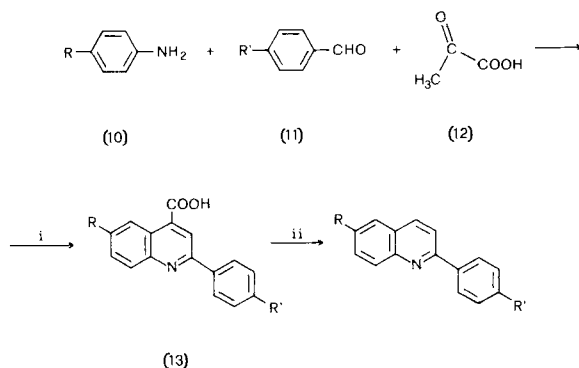
Scheme 2. Reagents: (i) DPDC,  $\text{HC}\equiv\text{C}-\text{COOEt}$ ; (ii)  $\text{H}_3\text{O}^+$ ,  $\Delta$ .

suffer the two main disadvantages of Schiff's bases, i.e. the photolability and that of undergoing easy hydrolysis when exposed to air.

## 2. Results and discussion

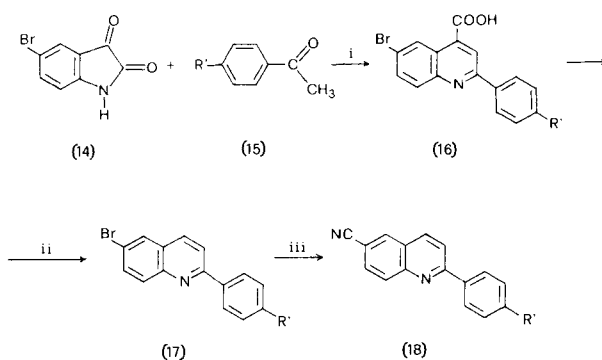
The majority of substituted quinolines were prepared by decarboxylation of the corresponding carboxylic acids (**13**), synthesized by reacting the appropriate substituted anilines (**10**) and benzaldehydes (**11**) with piruvic acid (**12**) [5, 6] (scheme 3). 2-Aryl-6-cyanoquinolines (**18**) were prepared by reaction of 2-aryl-6-bromoquinolines (**17**) with copper(I) cyanide; the latter were obtained by decarboxylation of the carboxylic acids (**16**), synthesized by reacting 5-bromoisatin (**14**) with the appropriate substituted acetophenone (**15**) [7, 8] (scheme 4).

The 6-substituted 2-arylquinolines prepared are reported in table 1 together with their melting ( $T_f$ ) and clearing ( $T_{NI}$ ) temperatures as well as the enthalpy of fusion ( $\Delta H_f$ ), determined by differential scanning calorimetry. 2-(*p*-Ethylphenyl)-6-ethoxyquinoline (**22**) melted to an isotropic liquid at 139°C; however, a monotropic transition was observed at 109°C by supercooling the isotropic liquid. All quinolines above their



(a) R = Bu<sup>n</sup>, R' = OMe; (b) R = Bu<sup>n</sup>, R' = OEt; (c) R = Bu<sup>n</sup>, R' = OBu<sup>n</sup>; (d) R = OEt, R' = Et; (e) R = OBu<sup>n</sup>, R' = Et; (f) R = OBu<sup>n</sup>, R' = Bu<sup>n</sup>; (g) R = OBu<sup>n</sup>, R' = Am<sup>n</sup>.

Scheme 3. Reagents: (i) EtOH, Δ; (ii) Cu, Δ.



(a) R' = OMe; (b) R' = OEt.

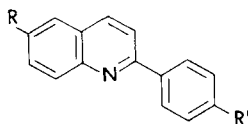
Scheme 4. Reagents: (i) EtOH, KOH, Δ; (ii) Cu, Δ; (iii) CuCN.

melting points exhibit the texture characteristic of a nematic mesophase when examined under a polarizing microscope [9]. By lowering the temperature this texture was observed until crystallization took place for compounds (19)–(24) and (26). With compounds (25) and (27) a second transition (a monotropic nematic to smectic transition) was detected at 76°C and 144°C, respectively. The nature of these smectic mesophases was not investigated.

It is worth noting that none of the 2,6-disubstituted quinoline-4-carboxylic acids, from which quinolines (19)–(27) were obtained by decarboxylation, showed liquid-crystalline behaviour. This may be due simply to steric reasons, as the presence of the carboxyl group prevents the molecules from achieving good alignment, or it may be the result of association of two carboxylic groups to give dimers where molecular linearity is completely lost [10].

The nematic ranges of the 2-arylquinolines and the known Schiff's bases containing the same substituents are shown in the figure. For the quinolines both the melting point and the nematic isotropic transition are higher, while the nematic ranges are fairly similar for the two series. The nematic–isotropic transition temperature is generally used as an index of the thermal stability of nematic mesophases [10]. The

Melting points and nematic–isotropic transition temperatures together with the enthalpy of fusion of 6-substituted 2-arylquinolines.



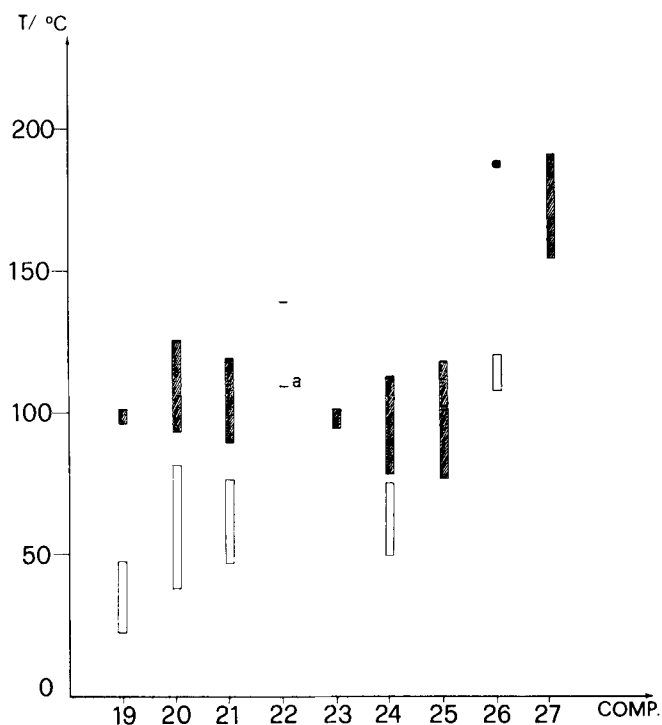
Compound	A	A'	$T_f/^\circ\text{C}$	$T_{NI}/^\circ\text{C}$	$\Delta H_f/\text{kJ mol}^{-1}\dagger$
19	Bu <sup>n</sup>	OMe	96	100	20.9
20	Bu <sup>n</sup>	OEt	93	124	24.7
21	Bu <sup>n</sup>	OBu <sup>n</sup>	89	118	25.9
22	OEt	Et	139	(109)‡	23.8
23	OBu <sup>n</sup>	Et	94	100	23.0
24	OBu <sup>n</sup>	Bu <sup>n</sup>	77	112	17.2
25	OBu <sup>n</sup>	Am <sup>n</sup>	77§	118	25.9
26	CN	OMe	187	188	28.4
27	CN	OEt	150	189	26.3

† Estimated error *ca* 10 per cent.

‡ Monotropic transition.

§ Smectic–nematic monotropic transition at 76°C.

|| Smectic–nematic monotropic transition at 144°C.



Nematic ranges of quinolines (19)–(27) (■) and of the corresponding Schiff's bases [3] (□). (a) monotropic transition.

results in the figure therefore indicate that 2-arylquinolines give rise to nematic phases characterized by a greater thermal stability than the Schiff's bases. This is in accord with expectations since, by replacing the central group  $N = CH$  with the closed ring of quinoline, the core rigidity of the nematogenic compound is increased.

The mesomorphic properties of 2-phenylquinolines may also be compared with those of liquid-crystalline 2-phenylnaphthalenes whose preparation has been described by two groups of authors [11, 12]. Disappointingly, all of the 2-phenylnaphthalenes reported have substituents either different from those of the presently investigated 2-phenylquinolines or, when they are the same, in different positions. If we choose substrates containing the same substituents, comparison can be made between quinolines (26) and (27) exhibiting nematic mesophases in the temperature range 187–188°C and 150–189°C respectively, and 2-(4'-cyanophenyl)-6-methoxynaphthalene and 2-(4'-cyanophenyl)-6-ethoxynaphthalene which are mesomorphic between 138 and 184°C and between 129 and 185°C respectively. From the similarity of the  $T_{NI}$  values it would seem that 2-phenylquinolines show comparable nematic thermal stabilities, albeit with reduced nematic ranges, to those of the 2-phenylnaphthalenes.

A convenient way of reducing the melting temperature of liquid crystals, and at the same time increasing the nematic range, is to make use of eutectic mixtures of structurally similar nematogens. Since the experimental determination of the eutectic composition for more than two nematogens is impractical, we have made use of the method proposed by Raynes *et al.* [13] based on an extension of the Schröder–van Laar equation [14]. Accordingly, the thermal behaviour of a mixture of  $N$  components is described by  $N$  simultaneous equations, one for each component, of the form

$$\ln x_j = \frac{\Delta H_f^j}{R} \left( \frac{1}{T_f^j} - \frac{1}{T_f^e} \right), \quad (1)$$

which, when solved with the condition

$$\sum_{j=1}^N x_j = 1,$$

provides the mole fraction  $x_j$  of component  $j$  and the melting temperature of the eutectic mixture  $T_f^e$ , as function of the latent heat of melting  $\Delta H_f^j$  and the melting point  $T_f^j$  of the pure component  $j$ . Once the composition of the eutectic is known the nematic–isotropic transition temperature  $T_{NI}^e$  can also be calculated by means of equation (2),

$$T_{NI}^e = \sum_{j=1}^N x_j T_{NI}^j, \quad (2)$$

where  $T_{NI}^j$  is the nematic–isotropic transition temperature of the pure component  $j$ . The simultaneous equations (1) have been solved by trial and error for the mixture of quinolines (19), (20) and (21). By using the data in the table, we obtained  $x_{19} = 0.36$ ,  $x_{20} = 0.32$ ,  $x_{21} = 0.32$ ,  $T_f^e = 48^\circ\text{C}$  and  $T_{NI}^e = 113^\circ\text{C}$ . The experimental melting and clearing points of this mixture were measured as  $52^\circ\text{C}$  and  $112^\circ\text{C}$  respectively, in good agreement with the predicted values, with a liquid-crystalline range of  $60^\circ\text{C}$ .

In conclusion, 6-substituted 2-arylquinolines represent an interesting new class of liquid crystals characterized by a good chemical stability, relatively low melting temperatures and large nematic ranges which might find useful applications as oriented solvents for physico-chemical studies and perhaps also in electro-optic devices.

### 3. Experimental

Experimental details on the preparation of the nine substituted 2-phenylquinolines are deposited as supplementary material with the British Library Document Supply Centre. Copies of these details which comprise 11 pages may be obtained from the British Library according to the procedure described at the end of the Journal and by quoting the number SUP 16504. We report here synthetic details for two typical members, i.e. 2-(*p*-anisyl)-6-*n*-butylquinoline (**19**) and 2-(*p*-anisyl)-6-cyanoquinoline (**26**).

#### 3.1. 2-(*p*-Anisyl)-6-*n*-butylquinoline-4-carboxylic acid (**13a**)

According to the procedure described by Doebner [5], *p*-*n*-butylaniline (7.5 g, 50 mmol) and *p*-anisaldehyde (6.8 g, 50 mmol) were refluxed for 4 hours with piruvic acid (4.4 g, 50 mmol) in absolute ethanol (100 ml). The solvent was removed under vacuum and the residue, washed with light petroleum (70–120) and diethylether, was recrystallized from ethanol (9.2 g, 55 per cent); m.p. 162–165°C, m/z 335 ( $M^+$ , 100), 292 (82), 249 (13), 248 (10), 204 (10) (found: C, 74.82; H, 6.35; N, 4.15.  $C_{21}H_{21}NO_3$  requires C, 75.20; H, 6.31; N, 4.18).

#### 3.2. 2-(*p*-Anisyl)-6-*n*-butylquinoline (**19**)

To a solution of the acid (**13a**) (7.5 g 22 mmol) in chloroform, copper bronze (7.5 g) was added; the solvent was removed under vacuum until the residue became a homogeneous powder and then it was warmed at 290–300°C for 30 min. The reaction mixture was chromatographed on silica gel; elution with light petroleum-diethylether (95:5 v/v) gave, after recrystallization from light petroleum-benzene (90:10 v/v), the quinoline (**19**) (2.0 g, 30 per cent); melting point and nematic–isotropic transition as well as the temperature enthalpy of fusion of quinolines (**19**)–(**27**) are reported in the table; m/z 291 ( $M^+$ , 100), 248 (90), 205 (46), 204 (37);  $\delta_H$  ( $CDCl_3$ ) 0.62–1.95 (7H, m, RH), 2.50–2.85 (2H, bt,  $ArCH_2$ ), 3.68 (3H, s, OMe), 6.72–7.05 (2H, bd, ArH), 7.25–8.20 (7H, m, ArH). (found C, 82.11; H, 7.32; N, 4.79.  $C_{20}H_{21}NO$  requires C, 82.44; H, 7.26; N, 4.81.)

#### 3.3. 2-(*p*-Anisyl)-6-bromoquinoline-4-carboxylic acid (**16a**)

According to the procedure described by Lindwall *et al.* [7], a mixture of 5-bromoisatin (3.5 g, 15 mmol), *p*-methoxyacetophenone (2.3 g, 15 mmol), 33 per cent aqueous potassium hydroxyde (14 ml) and ethanol (70 ml) was refluxed for 8 hours. The solvent was removed under vacuum and the oily residue poured into ice-water; the title compound was precipitated by addition of hydrochloric acid (20 per cent). The solid was filtered and recrystallized from ethanol-ethylacetate (90:10 v/v) (4.6 g, 85 per cent); m.p. 252–255°C, m/z 359 ( $M^+$  + 2, 98), 357 ( $M^+$ , 100), 344 (10), 342 (11), 316 (8), 314 (18), 271 (7), 269 (9), 190 (14). (Found C, 56.67; H, 3.40; Br, 22.40; N, 3.88.  $C_{17}H_{12}BrNO_3$  requires C, 57.01; H, 3.38; Br, 22.31; N, 3.91.) Compound (**16a**) was decarboxylated as reported for compound (**19**) to give 2-(*p*-anisyl)-6-bromoquinoline (**17a**).

#### 3.4. 2-(*p*-Anisyl)-6-cyanoquinoline (**26**)

Following the general procedure described in the literature [8], copper(I) cyanide (0.5 g, 6 mmol) was added to a solution of the quinoline (**17a**) (1.0 g, 3 mmol) in

*N,N*-dimethylformamide (20 ml) and the reaction mixture refluxed for 6 hours. After cooling, the inorganic residue was separated and washed several times with chloroform; the whole organic solution was treated under stirring for 30 min with water (500 ml). It was extracted with chloroform, the organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent removed under vacuum; the residue was chromatographed on silica gel: elution with light petroleum-diethylether (98 : 2 v/v) and recrystallization from light petroleum-benzene (90 : 10 v/v) gave the quinoline (**26**) (0.3 g, 35 per cent);  $m/z$  260 ( $\text{M}^+$ , 100), 245 (20), 217 (31), 216 (24);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 3.83 (3H, s, OMe), 6.85–8.25 (9H, m, ArH). (Found C, 77.90; H, 4.66; N, 10.70.  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}$  requires C, 78.44; H, 4.65; N, 10.76.)

All melting points are uncorrected. Column chromatography was performed on silica gel (Kieselgel 60, 70–230 mesh ASTM, Merck). Proton N.M.R. spectra were recorded on a Varian EM 360L instrument, using tetramethylsilane as an internal standard. Mass spectra were performed with a JEOL JMS-D100 spectrometer at an ionization energy of 70 eV. Calorimetric data were obtained by means of a Perkin-Elmer DSC-2 differential scanning calorimeter.

### References

- [1] LEARDINI, R., PEDULLI, G. F., TUNDO, A., and ZANARDI, G., 1984, *J. chem. Soc. Chem. Commun.*, p. 1320.
- [2] VOLOTIN, B. M., and SHISHOVA, R. S., 1979, *Zhidk. Krist.*, edited by Zhdanov, S. I. (Izd. Khimya), p. 285; 1980, *C.A.*, **92**, R155931c.
- [3] DEMUS, D., and DEMUS, H., 1976, *Flussige Kristalle in Tabellen*, Vols. 1, 2 (VEB Deutscher Verlag für Grundstoffindustrie).
- [4] LEARDINI, R., NANNI, D., PEDULLI, G. F., TUNDO, A., and ZANARDI, G., 1986, *J. chem. Soc. Perkins Trans. I*, p. 1591.
- [5] DOEBNER, O., 1887, *Chem. Ber.*, **20**, 277.
- [6] LUTZ, R. E., BAILEY, P. S., CLARK, M. T., CODINGTON, J. F., DEINET, A. J., FREEK, J. A., HARNEST, G. H., LEAKE, N. H., MARTIN, T. A., RAWLETT, R. J., JR., SALSBUURY, J. M., SHEARER, N. H., JR., DOYLE SMITH, J., and WILSON, J. W. III, 1946, *J. Am. chem. Soc.*, **68**, 1813.
- [7] LINDWALL, H. G., BANDES, J., and WEINBERG, I., 1931, *J. Am. chem. Soc.*, **53**, 317.
- [8] MOWRY, D. T., 1948, *Chem. Rev.*, **42**, 189.
- [9] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie).
- [10] GRAY, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chap. 1.
- [11] GRAY, G. W., and LACEY, D., 1983, *Molec. Crystals liq. Crystals*, **99**, 123.
- [12] LAUK, U., SKRABAL, P., and ZOLLINGER, H., 1981, *Helv. chim. Acta*, **64**, 1847; 1983, *Ibid.*, **66**, 1574; 1985, *Ibid.*, **68**, 1406.
- [13] HULME, D. S., RAYNES, E. P., and HARRISON, K. J., 1974, *J. chem. Soc. Chem. Commun.*, p. 98.
- [14] SCHRÖDER, I., 1893, *Z. phys. Chem.*, **11**, 449. VAN LAAR, J. J., 1903, *Arch. néerl. Sci.*, **8**, 264.