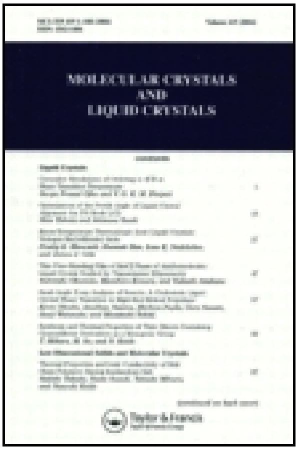

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Synthesis and Mesomorphic Properties of Axially Cyano-Substituted 1,3-Dioxane-5-Carboxylates

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Synthesis and Mesomorphic Properties of Axially Cyano-Substituted 1,3-Dioxane-5-Carboxylates

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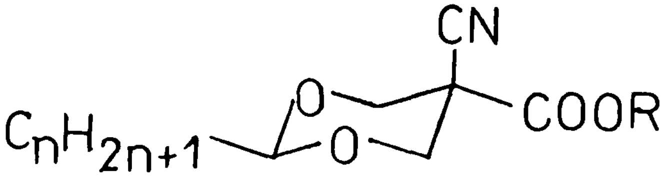
(*Received February 20, 1989; in final form May 30, 1989*)

Liquid-crystalline 1,3-dioxane derivatives incorporating a lateral cyano-group in position 5 were synthesized. The liquid-crystal phases between the transition temperatures were determined and compared with those of related materials. In spite of the lateral CN-dipole, the new compounds exhibit only small negative or even positive anisotropies of the dielectric constant. The $\Delta\epsilon$-values are only moderate due to compensation of dipole moments.

1. INTRODUCTION

Recently, Vorbrodt *et al.*[1-3] have described the liquid crystalline properties of *trans*-2,5-disubstituted 1,3-dioxanes and related compounds. Continuing research on new liquid crystalline heteroalicyclic compounds, we have synthesized *r*-2-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates (1) which† should exhibit a negative dielectric anisotropy due to the lateral CN-group.



1

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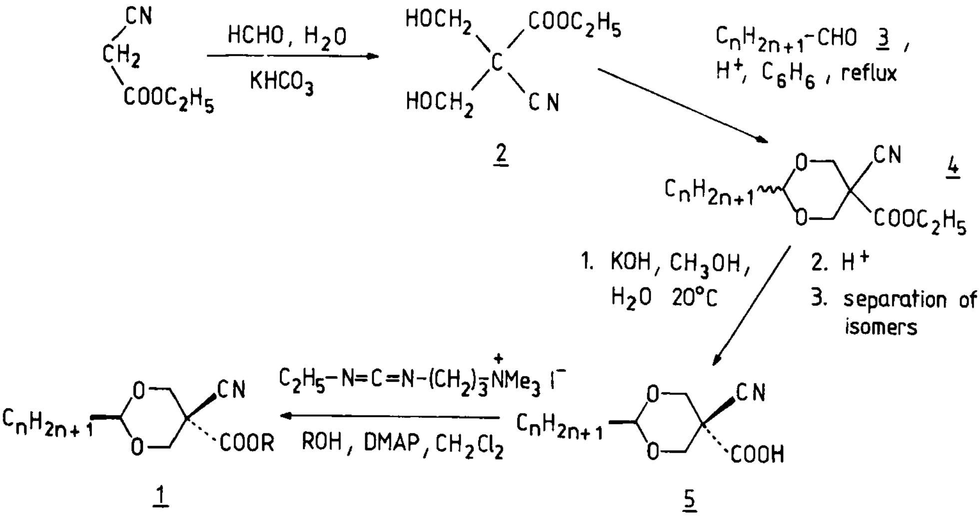
†The convention used here employs *r* to indicate the substituent to which stereochemical reference (c: *cis* or *t*: *trans*) is made (Ed).

2. SYNTHESIS

The *r*-2-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates (1) have been synthesized according to Scheme 1:



SCHEME 1 Synthesis of *r*-2-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates (1)

Ethyl *bis*-(hydroxymethyl)cyanoacetate (2) was obtained from ethyl cyanoacetate and formaldehyde. The acid catalyzed acetalization of (2) with various aldehydes (3) gave the ethyl 2-alkyl-5-cyano-1,3-dioxane-5-carboxylates (4) in good yields. These were saponified with potassium hydroxide in aqueous methanol at room temperature, and the corresponding acids were liberated by careful treatment with hydrochloric acid. After crystallization from hexane, the *r*-2-*n*-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylic acids (5) were obtained in stereoisomerically pure form. The esterifications of these carboxylic acids were performed using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide methiodide (DEC $\cdot$ CH_3I) as condensating agent in the presence of 4-dimethylaminopyridine (DMAP).[4] The final products were crystallized from methanol.

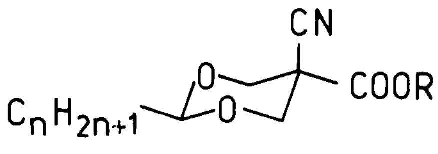
3. RESULTS AND DISCUSSION

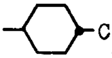
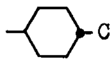
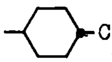
The liquid crystalline transition temperatures of the compounds (1) are listed in Tables I and II.

In accordance with experience,[5] the derivatives of cyclohexane (Table I) show smectic B phases, whereas smectic A and nematic mesophases were detected for the phenyl carboxylates given in Table II. In all cases the melting temperatures are rather high in comparison with simpler 1,3-dioxane-5-carboxylates.[6] However, the clearing temperatures of both classes of compounds are comparable.

TABLE I

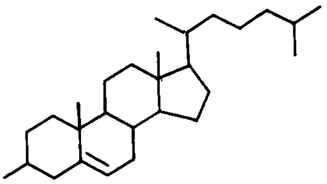
Transition temperatures (°C) for compounds (1) with non-aromatic substituents R



Comp.	n	R	cr	S_B	S_A	Ch	is
1.1	5	 C_5H_{11}	• 111	(• 91)	– –	– –	•
1.2	5	 C_3H_7	• 107	– –	– –	– –	•
1.3.	3	 C_5H_{11}	• 101.5	(• 67.5)	– –	– –	•
1.4	5	-Chol 1)	• 180	– –	• 219	– –	•
1.5	3	-Chol 1)	• 172	– –	• 185.5	• 215	•

1)

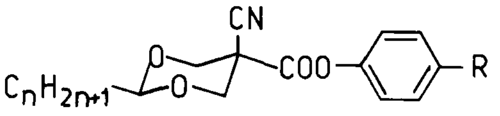
Chol =

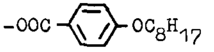
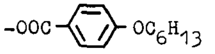
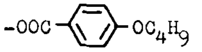
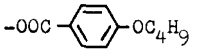
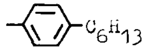
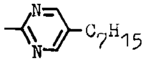
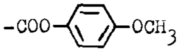
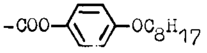
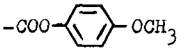


The same is also true based on the comparison of the 5-cyano-1,3-dioxane-5-carboxylates (1.1 and 1.2) with analogous cyclohexane carboxylates without lateral cyano-groups.[7,8] These results show that the axial CN-group in position 5 does not significantly disturb the molecular order in the liquid crystalline state, as has been observed in the case of laterally substituted benzene derivatives.[5,9–11] Thus, in this position, the enhanced effective size of the cyano-group compared with hydrogen apparently does not significantly influence the total molecular size. On the other

TABLE II

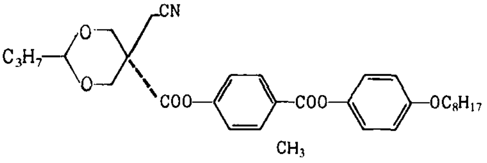
Transition temperatures (°C) for the 4-substituted phenyl *r*-2-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates



Comp.	n	R	cr		S_A	N	is
1.6	3		· 113		· 153	· 155	·
1.7	3		· 131		· 169	- -	·
1.8	3		· 146		- -	· 161.5	·
1.9	5		· 121		- -	· 160.5	·
1.10	5		· 135.5		· 137	· 156.5	·
1.11	3	$-OC_5H_{11}$	· 28		- -	- -	·
1.12	3	$-OC_8H_{17}$	· 84.5		(· 65.5)	- -	·
1.13	5	$-OCH_3$	· 63/68[1)]		- -	- -	·
1.14	5	$-OC_8H_{17}$	· 80.5		· 82	- -	·
1.15	5	$-C_3H_7$	· 63		- -	- -	·
1.16	5	$-C_8H_{17}$	· 62		(· 51)	- -	·
1.17	5		· 130		- -	(· 74)	·
1.18	3		· 102		· 146	- -	·
1.19	3		· 151		- -	- -	·
1.20	3		· 147/150[1)]		- -	· 168	·
1.21	3		· 129		· 175	- -	·
1.23	5		· 137.5		- -	· 161.5	·

[1)] different solid modifications

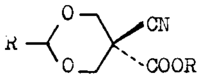
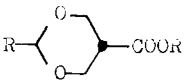
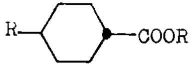
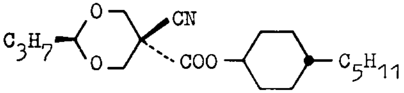
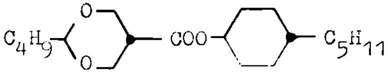
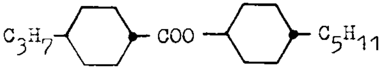
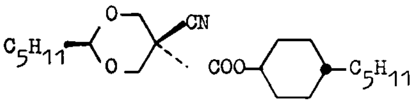
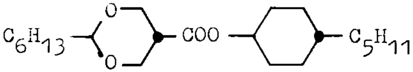
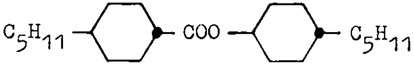
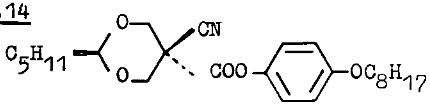
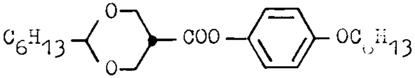
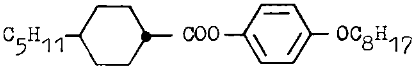
1.22



Cr 98/103[1)] S_A 100.5 is

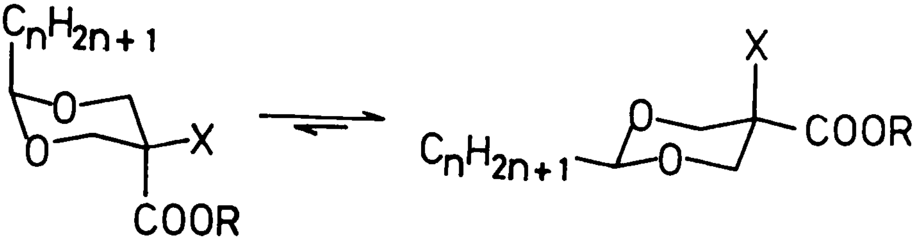
TABLE III

Comparison of the mesomorphic properties for related *r*-2-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates, *trans*-2-alkyl-1,3-dioxane-5-carboxylates[6] and *trans*-4-alkylcyclohexane carboxylates[7,8]

		
1.3  cr 101.5 (S_B 67) is	 cr <20 S_B 89 is	 cr 24 S_B 51.5 N 54 is
1.1  cr 111 (S_B 91) is	 cr <20 S_B 97 is	 cr 52 S_B 72 is
1.14  cr 80.5 S_A 82 is	 cr 82 S 93 is	 cr 31 S_G 32.5 S_B 48.5 N 80 is

hand, the strongly polar CN-group ($\mu = 3.6$ D)[12] should enhance the attractive intermolecular forces and in this way compensate the disturbance to the order caused by steric effects.

Furthermore, conformational considerations indicate that the conformational equilibrium between the two conformers *a* and *e* should be only slightly influenced by the introduction of the cyano group, since the conformational free energy difference of the CN-group attached to C-5 in 1,3-dioxanes is low ($\Delta G^\circ_{5-\mathrm{CN}} = -0.8$ kJ/mol)[13] and therefore this equilibrium is mainly determined by the carboxylate group ($\Delta G^\circ_{5-\mathrm{COOMe}} = -3.4$ kJ/mol) and the 2-substituent ($\Delta G^\circ_{2-\mathrm{Me}} = -17$ kJ/mol)[13].



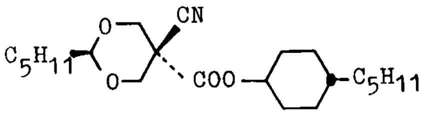
a

e

X = H

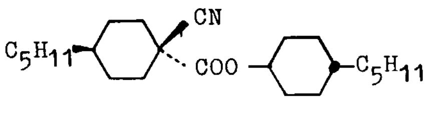
X = CN

This argument is supported by the fact, that the mesophase stability of compound (1.1) is greater than that observed for the analogous cyanocyclohexanecarboxylate (6).[14]



1.1

Cr 111 (S_B 91) is



6

Cr 11 S_B 10 N 32 is

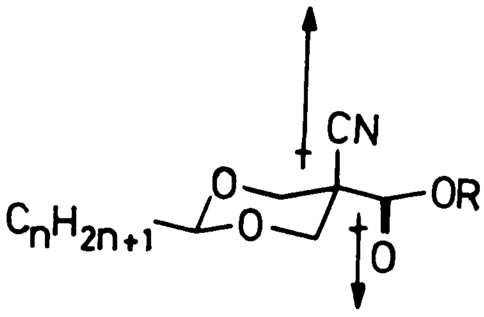
In compound (6), the conformational equilibrium is more significantly influenced by the introduction of the carbonitrile group, since this equilibrium is less biased by the alkyl substituent attached to the cyclohexane ring ($\Delta G^\circ_{\mathrm{Me}} = -7{,}1$ kJ/mol).[15]

In the case of the three ring compounds (1.6 – 1.10 and 1.17 – 1.23) the situation is more complex. There are also many cases in which the mesophase stability of the CN-substituted derivatives is strongly diminished. These are mainly compounds with additional strong polar groups (e.g., 1.17 and 1.19), where troublesome dipolar intermolecular interactions are likely to occur.

The dielectric anisotropies of four compounds have been determined by measuring $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ of the nematic mixture 5 consisting of four substituted phenyl benzoates.[16] The respective substances have been dissolved in this ester mixture to obtain the given mole fraction x_2. $\Delta\epsilon$ of the solute was calculated using the additivity of $\Delta\epsilon$ in the mixture ($\Delta\epsilon$ of the solvent at $T_{N/Is} - T = 30$ K was -0.33). The error increases strongly with decreasing x_2 ($x_2 = 0.02$: $\delta_\epsilon = \pm 1$; $x_2 = 0.05$: $\delta_\epsilon = \pm 0.05$). All $\Delta\epsilon$ values are given for $T_{N/Is} - T = 30$ K.

1.3 $\Delta\epsilon = -2.5$ ($x_2 = 0.05$)
1.8 $\Delta\epsilon = +5.7$ ($x_2 = 0.05$)
1.14 $\Delta\epsilon = -1.5$ ($x_2 = 0.063$)
1.18 $\Delta\epsilon = -1.4$ ($x_2 = 0.030$)
1.19 $\Delta\epsilon = +4.6$ ($x_2 = 0.020$)
1.22 $\Delta\epsilon = -3.8$ ($x_2 = 0.05$)

In comparison with the dielectric anisotropies of CN-substituted dialkyl bicyclohexyls[14] ($\Delta\epsilon = -7$ to -8), the $\Delta\epsilon$ values of the investigated substances are relatively high (less negative or even positive). Also for compound (6)[14] ($\Delta\epsilon = -4$), the high $\Delta\epsilon$ value (small negative number) indicates that there is intramolecular compensation between the dipole moments of the carbonitrile group and the carboxylate group.



A second carboxylate group which is not influenced by the CN-dipole, due to the larger distance from it (compound 1.22), decreases $\Delta\epsilon$. Contrary to this, a small positive dielectric anisotropy has been found in the cases in which the dipole moment of R (—OOC— or pyrimidine) acts in the direction of the benzene ring indicating that the overall component of the longitudinal dipole moment in the basic formula (1) is directed from R (positive) to the alkyl group (negative part).

4. EXPERIMENTAL

4.1. General remarks

The transition temperatures of the compounds given in Tables I and II were determined by hot-stage polarizing microscopy. The single component nature of the compounds was tested by thin layer chromatography. The structures of the compounds were checked by analysis of their ^{1}H-NMR, ^{13}C-NMR, IR and mass spectra. Representative examples of these are given below.

4.2. Ethyl *bis*-(hydroxymethyl)cyanoacetate

$KHCO_3$ (4 g) was dissolved in 30% aqueous formaldehyde (95 g), and ethyl cyanoacetate (56 g) was added dropwise to the stirred solution at −5°C. Stirring was continued at this temperature for 1 h. Afterwards, ammonium sulfate (20 g) was added and the reaction mixture was shaken three times with ether (total 400 ml). The combined organic layers were dried over anhydrous sodium sulphate for 1 h and the solvent was carefully evaporated at room-temperature. The resulting syrup slowly crystallized upon standing in the open air. The crystals were filtered off and the crude product used without further purification: m.p. 46–50°C.

4.3. Ethyl 2-alkyl-5-cyano-1,3-dioxane-5-carboxylates (4)

A mixture of ethyl *bis*-(hydroxymethyl)cyanoacetate (34.6 g: 0.2 mole), the corresponding aldehyde (0.2 mole, freshly distilled) and toluene-4-sulphonic acid (5 g) in benzene (1000 ml) was healed under reflux using a Dean-Stark-trap, until no water separated. After cooling to room-temperature, the mixture was washed with saturated aqueous $NaHCO_3$ (200 ml) and dried over Na_2SO_4. After removal of the solvent the crude product was crystallized from hexane.

comp.	n	m.p. (°C)	yield (%)	m/e
4.1	3	41.5	58	255
4.2	5	50.5	62	

4.1: IR (CCl_4, cm^{-1}): 1145, 1155, 1265, 1750, 2245, 2860, 2870, 2960
^{1}H-NMR (80 MHz, $CDCl_3$, ppm): 4.50 (t, J = 4.6 Hz, 1H, H-2); 4.36 (d, J = 12.0 Hz, 2H, H-4·6eq); 4.24 (q, J = 7.1 Hz, 2H, —OCH_2CH_3); 3.29 (d, J = 12 Hz, 2H, H-4, 6ax); 1.8 – 1.3 (m, 4H, —$(CH_2)_2$—); 1.31 (t, J = 7.1 Hz, 3H, —OCH_2CH_3); 0.89 (t, J = 6.5 Hz, 3H, —CH_3)
^{13}C—NMR (50 MHz, $CDCl_3$, ppm); 164.09 (C=O); 117.02 (CN); 102.75 (C—2); 69.74 (C—4, 6); 63.12 (OCH_2); 43.31 (C—5); 36.07 (CH_2); 16.67 (CH_2); 13.72 (CH_3); 13.65 (CH_3)

4.4. *r*-2-Alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylic acids (5)

A solution of potassium hydroxide (4.1 g, 0.06 mole) in a mixture of methanol (50 ml) and water (1 ml) was added to a stirred solution of ethyl 2-alkyl-5-cyano-1,3-dioxane-5-carboxylate (4) (0.05 mole) in methanol (100 ml) at 20°C. After 15 min the solvent was evaporated at 30°C. The residue was dissolved in ethyl acetate (200 ml), cooled to −20°C and shaken with hydrochloric acid (0.059 mol, 6.0 ml of a 32% solution) for one min. The precipitated KCl was filtered off and washed twice with cold ethyl acetate (100 ml). The solvent was evaporated at room temperature and the residue was treated with hexane (50 ml) and cooled to −20°C. The precipitate was collected, dissolved in chloroform (100 ml) and the solution filtered.

Afterwards, the solution was concentrated to approximately 20 ml and treated with pentane (50 ml). The crude products obtained were crystallized from chloroform/hexane (1:4) to yield the pure carboxylic acids (5).

comp.	n	m.p. (°C)	yield (%)
5.1	3	129.5	75
5.2	5	101	62

5.2: IR (nujol, cm^{-1}): 1725, 2230, 2670, 2730
^1H-NMR ($CDCl_3$, ppm): 8.54 (broad, 1H, —COOH); 4.56 (t, J = 4.0 Hz, 1H, H-2); 4.42 (d, J = 11.5 Hz, 2H, H-4, 6equ.); 4.00 (d, J = 11.5 Hz, 2H, H-4, 6 ax.); 0.6 – 1.8 (m, 11H, $—C_5H_{11}$)
^{13}C-NMR (20 MHz, $CDCl_3$, ppm): 167.6 (C=O); 116.6 (CN); 103.5 (C—2); 69.7 (2C, C—4, 6); 43.7 (C—5); 34.1, 23.2, 22.5, 13.9

4.5. *r*-2-Alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates (1.1–1.23)

These compounds were prepared according to a recently published procedure.[4]

1.18 ^1H-NMR (200 MHz, $CDCl_3$, ppm): 7.61 – 7.13 (m, 8H, H-arom.); 4.59 (t, J = 4.6 Hz, 1H, H-2); 4.56 (d, J = 11.5 Hz, 2H, H-4, 6eq); 4.13 (d, J = 11.5 Hz, 2H, H-4, 6ax); 2.63 (t, J = 7.5 Hz, 2H, ar—CH_2—); 1.78 – 0.84 (m, 18H, —CH_2—, —CH_3)

References

1. H.-M. Vorbrodt, S. Deresch, H. Kresse, A. Wiegeleben, D. Demus and H. Zaschke, *J. prakt. Chem.*, **323**, 902 (1981).
2. H.-J. Deutscher, H.-M. Vorbrodt and H. Zaschke, *Z. Chem.*, **21**, 9 (1981).
3. C. Tschierske and H. Zaschke, *J. prakt. Chem.*, **330**, 1 (1988).
4. C. Tschierske and H. Zaschke, *J. prakt. Chem.*, **331**, 365 (1989).
5. D. Demus and H. Zaschke, "*Flüssige Kristalle in Tabellen*," Vol 2, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1984).
6. D. Demus, H. Zaschke, H.-M. Vorbrodt, A. Hauser and J. Vogel, Patent DD 203543.
   D. Demus, H. Zaschke, H.-M. Vorbrodt, J. Vogel and A. Hauser, Patent DD 204 102.
7. H.-J. Deutscher, M. Körber and H. Schubert in "*Advances in Liquid Crystal Research and Applications*" (ed. L. Bata), Pergamon Press, Oxford and Akademiai Kiado, Budapest (1980) p. 1075.
8. H.-J. Deutscher, B. Laaser, W. Dölling and H. Schubert, *J. prakt. Chem.*, **320**, 191 (1978).
9. M. A. Osman, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 295 (1983).
10. S. M. Kelly and H. Schad, *Helv. Chim. Acta*, **67**, 1580 (1984); *Mol. Cryst. Liq. Cryst.*, **110**, 239 (1984).
11. M. A. Osman and T. Huynh-Ba, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 339 (1983); *Z. Naturforsch.*, **38B**, 1221 (1983); *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 345 (1983).
12. C. P. Smyth, "*Dielectric Behaviour and Structure*," McGraw-Hill, New York (1955).
13. E. L. Eliel, *Angew. Chem.*, **84**, 779 (1972).
14. R. Eidenschink, *Mol. Cryst. Liq. Cryst.*, **123**, 57 (1985).
15. J. A. Hirsch in "*Topics in Stereochemistry*," Vol. I (eds. N. L. Allinger and E. L. Eliel) Interscience Division, John Wiley & Sons Inc., New York, N.Y. (1967).
16. H. Kresse, *Advances in Liquid Crystals*, **6**, 109 (1983).