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

Effect of Substituent Location on the Thermodynamic Properties of Cholesteryl Halobenzoates and Halocinnamates

Edward M. Barrall Ii [a] , Karin E. Bredfeldt [a] & Marcel J. Vogel [b]
[a] IBM Research Laboratory, San Jose, California
[b] Adv. Systems Dev. Div. Laboratory, Los Gatos, California
Version of record first published: 28 Mar 2007.

To cite this article: Edward M. Barrall Ii , Karin E. Bredfeldt & Marcel J. Vogel (1972): Effect of Substituent Location on the Thermodynamic Properties of Cholesteryl Halobenzoates and Halocinnamates, Molecular Crystals and Liquid Crystals, 18:3-4, 195-207

To link to this article: http://dx.doi.org/10.1080/15421407208083594

Molecular Crystals and Liquid Crystals. 1972. Vol. 18, pp. 195–207

Printed in Great Britain

Effect of Substituent Location on the Thermodynamic Properties of Cholesteryl Halobenzoates and Halocinnamates†

EDWARD M. BARRALL II and KARIN E. BREDFELDT

IBM Research Laboratory
San Jose, California

and

MARCEL J. VOGEL

Adv. Systems Dev. Div. Laboratory
Los Gatos, California

Received October 5, 1971

Abstract—A series of substituted aromatic esters of cholesterol has been examined by DSC. Temperatures and heats of transition were measured. A special modification of the cholesteric mesophase was noted in the 3-chloro and 4-bromo benzoate esters by microscopy. A series of statements has been formulated from these observations which permit the prediction of transition temperatures as well as entropies as a function of the modification of a parent compound whose properties are known within the cholesteryl ester series.

1. Introduction

Much effort has been expended in liquid crystal research to formulate some general rules about the effects of substituent groups on the mesophase transition temperature and range (number of degrees between solid → mesophase and mesophase → isotropic liquid transitions). These efforts extend back to the beginnings of liquid crystal studies in the late nineteenth century through the efforts of Gray *et al.*[1–5] up to the most recent efforts of the mid-twentieth century.[6–9] The problem is obviously quite complex, since no general rules have been forthcoming.[9] On the other hand, with the advent of recent calorimetric studies on smectic, nematic and cholesteric materials some quite general rules concerning the interaction between functionality and total transition entropy have been derived.[10–20] There are notable exceptions, but the family of

† Part XXIX of a series on Order and Flow in Liquid Crystals.

liquid crystal forming materials containing the cholesterol ring system are the best behaved. These materials show a great dependence of transition entropy on intuitively easy to understand geometric considerations.[10]

However, knowing the entropy of transition is not a material aid in predicting the effects of substituent groups on the temperatures of transition of the various phases. This was demonstrated by an earlier paper in this series on the thermodynamic properties of Marker's acid.[21] Marker's acid is the acid positional analog of cholesteryl formate; as such the entropies of both the solid → cholesteric and cholesteric → isotropic liquid transitions could be predicted with some certainty from a consideration of the length of the group pendant from the cholesterol ring. However, no statement could be made as to the temperatures of these transitions with the exception that they should be " higher " in Marker's acid than in the formate ester. This statement was predicated on the known effects of hydrogen bonding in acids. Indeed, the cholesteric → isotropic liquid entropy change indicated that the acid was dimerized in the mesophase via hydrogen bonding.

The generality of the geometric chain length rule was again demonstrated in a study by Davis, Porter, Steiner and Small of C_{18} aliphatic esters of cholesterol.[22] Esters with unsaturation at C_9; C_9, C_{12}; and C_9, C_{12}, C_{15} were compared to cholesteryl stearate. If it was assumed that the double bond at C_9 prohibited chain order beyond this point, the transition entropies of all the unsaturated C_{18} esters should be comparable to cholesteryl nonanoate. In addition, the unsaturated esters should exhibit not only a cholesteric but also a smectic mesophase as does a n-C_9 aliphatic ester. Experiment has demonstrated these interpretations to be true. However, no general rule could predict the transition temperatures with any degree of accuracy. It could be proposed that the transition temperatures should be lower than cholesterol stearate by analogy with other olefin/paraffin systems but not on such firm grounds as the entropy consideration.

From the work of Ennulat and Elser[6-9] and the Marker's acid study,[21] several productive generalities are beginning to emerge in the area of predicting transition temperatures. To test these concepts, the entropies and temperatures of transition of a series of

substituted benzoate (2-chloro, 3-chloro, 4-chloro and 4-bromo) esters and the 4-chlorocinnamate ester of cholesterol have been measured. In this way it is possible to alter the geometrical hindrance and polarity of the acid carbonyl via rotational hindrance and electron withdrawing or donating effects in the benzene ring. The data from these measurements along with earlier results should urnish a test of transition temperature relationships.

2. Experimental

Samples of cholesteryl 2-chloro, 3-chloro, 4-chloro- and 4-bromobenzoate and 4-chlorocinnamate were obtained from van Schuppen Chemical, Veenendaal, Holland. These samples were recrystallized three times from c.p. ethanol (benzene-free) and dried for 24 hours at 10^{-5} Torr. The boundaries of the solid and mesophase transitions were explored by hot stage microscopy prior to scanning calorimetry.

The temperatures and heats of transition were measured with a Perkin–Elmer DSC-1B differential scanning calorimeter (DSC). Samples of about four milligrams were weighed to four significant figures and encapsulated between metal plates in Perkin–Elmer volatile sample sealed containers under nitrogen. The technique has been described in detail elsewhere.[23] The DSC was calibrated with the heats and temperatures of fusion of 99.999% gallium, indium, lead and tin. All heats of transition were determined on heating. In the case of cholesteryl 3-chlorobenzoate, where the transition to the solid phase was monotropic, the mesophases were formed by cooling the melt and reheating. Advantage was taken of the tendency of the mesophase to supercool into the solid phase range. All temperature corrections, purities[23] and heat calculations were made using computer programs developed at IBM. The data was acquired directly by an IBM 1800 computer with the analog to digital interface using an IBM program developed for the DSC.

3. Results

The esters of 2-chlorobenzoic, 4-chlorobenzoic, and 4-chlorocinnamic acids exhibit the customary sequence of reversible

transitions on heating:

$$\text{Solid} \rightleftarrows \text{Cholesteric} \rightleftarrows \text{Isotropic Liquid.}$$

The cholesteric mesophase exhibits the usual streaked texture on heating and focal conic texture on cooling on the hot stage microscope. The two other esters studied show a more complex mesophase pattern. Two distinct forms of a clearly cholesteric mesophase develop on both heating and cooling (the 3-chlorobenzoate is monotropic). The other esters measured, as noted in Table 1, exhibited

TABLE 1 Thermodynamic Properties of Some Substituted Aromatic Esters of Cholesterol†

Graphical code	Compound	T_m‡ °C	ΔH kcal/mole	ΔS cal/mole/°K	
1	Cholesteryl 2-Chlorobenzoate				
	Solid → Cholesteric	96.03	7.01	19.0	
	Cholesteric → Isotropic liquid	144.8	0.11	0.27	
2	Cholesteryl 3-Chlorobenzoate				
	Solid → Isotropic liquid	144.4	7.28	17.4	
	Cholesteric I → Cholesteric II	137.4	0.041	0.10	0.46
	Cholesteric II → Isotropic liquid	142.0	0.15	0.36	
3	Cholesteryl 4-Chlorobenzoate				
	Solid → Cholesteric	165.0	7.10	16.2	
	Cholesteric → Isotropic liquid	240.0	0.16	0.31	
4	Cholesteryl 4-Bromobenzoate				
	Solid → Cholesteric I	175.3	6.44	14.4	
	Cholesteric I → Cholesteric II	241.8	0.058	0.11	0.43
	Cholesteric II → Isotropic liquid	245.3	0.17	0.32	
5	Cholesteryl 4-Chlorocinnamate				
	Solid → Cholesteric	146.2	5.12	12.2	
	Cholesteric → Isotropic liquid	262.4	0.20	0.37	
6	Cholesteryl Benzoate[10]				
	Solid → Choesteric	145.8	5.30	12.2	
	Cholesteric → Isotropic liquid	180.7	0.17	0.38	
7	Cholesteryl Cinnamate[10]				
	Solid → Cholesteric	162.6	6.87	15.8	
	Cholesteric → Isotropic liquid	215.2	0.17	0.35	

† All compounds were 99.89 mole% pure or better by DSC.
‡ Vertex of corrected DSC endotherm.

two distinct forms of the cholesteric mesophase in sequence on heating. The lower temperature mesophase forms a streaked texture against a *bright* background between crossed polarizers. At the indicated temperature, the bright background rapidly darkens (range about 0.1 °C) and the streaks increase in thickness. The conversion of the streaked cholesteric mesophase to the isotropic liquid is indicated by a complete vanishing of rotated polarized light. On cooling, the usual focal conic cholesteric texture develops. At the background darkening temperature observed above, the moss-like texture rapidly rearranges into large leaf-shaped plates (very similar to a smectic mesophase). However, the mesophase is *not* smectic since the conoscopic interference figure remains characteristic of the cholesteric (negative in sign), and a slight shearing of the sample between the cover slip and slide results in the streaked structure seen above. This latter effect has been noted previously for well-known cholesteric mesophases on cooling and shearing (cholesteryl myristate).[25,26] The undisturbed texture is easily converted to streaks with a slight movement of the cover slip. The smectic mesophase is too viscous to shear with gentle pressure. Thus, these esters develop a unique mesophase variation of the cholesteric form. The forms are clearly recognizable on DSC curves by well-defined, sharp endotherms. On the basis of purity analyses and sharpness of *all* DSC endotherms, the authors do not believe that the two forms of the cholesteric are due to the presence of impurities. It is interesting to note that Leclerq, Billard and Jacques have noted multiple cholesterol mesophases in alkoxy-biphenylcarboxylic acid enantiomers.[24] Racemic mixtures were noted as nematic. The transitions of the 4-bromobenzoate ester may be summarized as:

$$\text{Solid} \leftrightharpoons \text{Cholesteric I} \leftrightharpoons \text{Cholesteric II} \leftrightharpoons \text{Isotropic Liquid}.$$

The 3-chlorobenzoate ester is:

$$\begin{array}{ccc} \text{Solid} & \longrightarrow & \text{Isotropic Liquid} \\ \uparrow & & \updownarrow \\ \text{Cholesteric I} & \rightleftharpoons & \text{Cholesteric II} \end{array}$$

The direction of the arrows is intended to describe monotropy and not equilibrium.

4. Discussion

Examination of Table 1 and Fig. 1 shows that the transition temperatures for the solid → isotropic liquid or solid → cholesteric mesophase do increase in a regular fashion as the chlorine group is moved from ortho to meta to para on the benzoic acid ring. It is possible to ascribe this effect to steric hindrance and also to acid carbonyl polarity. The *p*Ka's of the corresponding acids, 2.92, 3.82, and 3.98,[27] show a regular variation. However, a correlation based only on *p*Ka does not prove to be consistent. *p*-Chlorocinnamic acid has a *p*Ka of 4.41 and, thus, should have a higher transition temperature than the *p*-chlorobenzoate ester. This is not the case, see Fig. 1. As noted previously,[10] geometric considerations appear to dominate the thermal properties. The *o*-chloro substitution decreases the freedom of rotation of the benzene ring. Examination

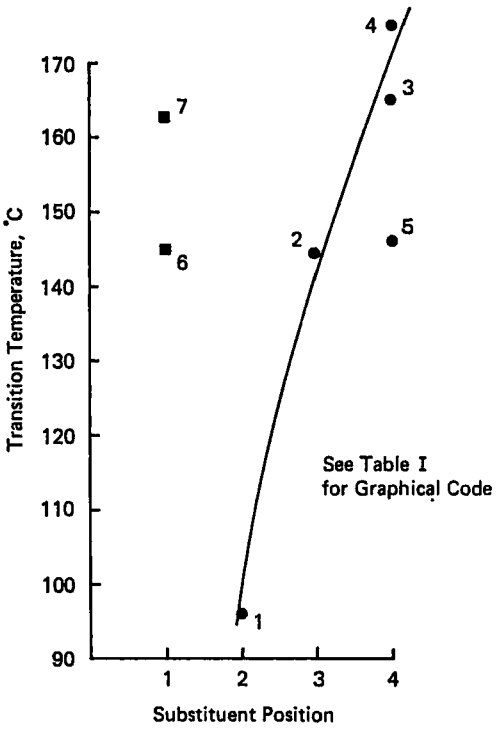

Figure 1. Effect of substituent position on the solid to mesophase or solid to isotropic liquid transition temperature.

of a model of the molecule indicates that the ring may not be able to assume any position in the plane of the cholesterol molecule. This would have a tendency to increase intermolecular distances in the solid, introduce some disorder in the solid and inhibit short-range electronic forces. Any or all of these effects would tend to reduce the melting point.

An examination of the transition entropy for the solid, Table 1 and Fig. 2, shows that for the *o*-, *m*-, *p*-benzoate esters the entropy of solid to mesophase or liquid transition *decreases* in that order. This evidence rules out solid phase disorder—or increased intermolecular distance as an active factor in producing the low melting *o*-chlorobenzoate ester. It is also instructive to note that although the entropy of the *p*-chloro ester is low, it is not as low as the unsubstituted benzoate ester.

From the above considerations and those considerations given in earlier work,[10,21] it is possible to describe the melting of the solid

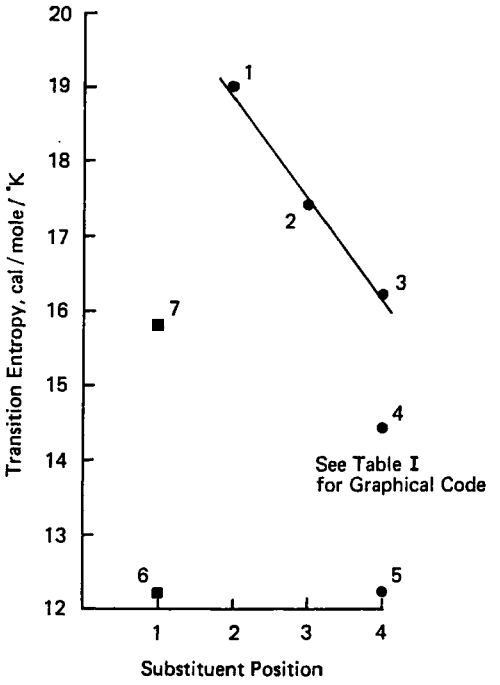

Figure 2. Effect of substituent position on the solid to mesophase or solid to isotropic liquid transition entropy.

phase of the chlorobenzoate esters as follows. Substitution in the ortho position inhibits the rotational freedom of the benzene ring in such a way that ring alignment is reduced. This causes the short-range electronic interactions *between* benzoate esters to be reduced. This produces an aromatic ester lacking the aromatic ring interactions. Lacking these interactions, the *o*-chloro ester molecules should align in the solid phase in an ordered fashion similar to the aliphatic ester of chain length between C_5 and C_6. According to data known on the pentanoate ($T_m = 92.9\,°C$, $\Delta S = 14.5$ cal/mole/°K[28] and the hexanoate ester ($T_m = 102.6\,°C$, $\Delta S = 19.1$ cal/mole/°K,[28] this postulated material should melt at $\sim 96\,°C$ with $\Delta S = \sim 18$ cal/mole/°K. This is in excellent agreement with the *o*-chlorobenzoate ester shown in Table 1 ($T_m = 96.03\,°C$, $\Delta S = 19.0$ cal/mole/°K).

The *m*-chlorobenzoate ester should behave in a typically aromatic nature since rotational freedom of the benzene ring and short-range electronic interactions are not decreased by the substitution. This should produce an ester with a melting point near the benzoate ester. This is the case, see Table 1. The asymmetric substitution of the *m*-chloro ester should furnish an additional ordering feature in the solid phase, thus, increasing the transition entropy over that observed for the benzoate ester. This is the case as shown in Table 1.

The *p*-chloro and *p*-bromobenzoate esters should show increased electronic interaction due to the *p*-halogen, and a solid phase melting point well above that of the benzoate ester. On geometric and electronic grounds, the melting point and transition entropy should be very near that of the cinnamate ester. This is the case. The electronic assumptions concerning the donating nature of the *p*-halogen is in the correct order with bromo substitution having the greater contribution as evidenced by the higher melting point.

Substitution of a halogen at the 4- position of the cinnamate ester would be expected to produce a cancellation of donating and withdrawing effects. The *p*-chlorocinnamate ester should be almost identical to cholesteryl benzoate in melting temperature and entropy. This is the case as shown in Table 1.

The mesophase transition entropies are relatively insensitive to substitution on the benzene ring. The entropy appears to be only mass of the acid substituent sensitive. No evidence for side chain effects is apparent. The cholesteric to isotropic liquid transition

temperature varies over a wide range, but never out of the temperature range characteristic of aromatic cholesteryl esters.[10] Ortho and meta substitution are characterized by relatively low mesophase transition temperatures. Para substitution results in an increased mesophase transition temperature in all cases studied. This may be due to increased ring dipole. The double bond in the cinnamate ester would be expected to have the same effect.

5. Conclusions

This study has demonstrated that transition temperatures, both for the solid and mesophase, are sensitive to positional substitution in aromatic cholesteryl esters. A series of observations on the chloro benzoate and *p*-chloro cinnamate esters indicates that the effects of substitution are phase sensitive, i.e., different rules must be employed when considering the implication of a certain group in the solid phase and in the mesophase. Although much more work is necessary, the following statements for predicting transition temperature and entropy are derived from this study. These comparisons are made to the unsubstituted parent compound, in this case, cholesteryl benzoate. The cinnamate is regarded as a substituted benzoate.

Solid Phase

(1) Inhibition of ester pendant rotation (ring in this case) results in a decreased transition temperature. Aromatic esters will behave as aliphatic esters of the corresponding length, as a corollary.

(2) Meta substitution has no effect on the transition temperature.

(3) Meta substitution, because of increased asymmetry, increases the transition entropy.

(4) Para substitution results in stronger ring interactions than in the parent compound. Therefore, the transition temperature is higher as is the entropy of transition compared to the unsubstituted parent compound.

(5) If opposed by a counter electron donating or withdrawing group, the effects of para substitution are negated. The substituted compound will melt as does the parent compound with both groups omitted. (The *p*-chloro cinnamate should be compared to the benzoate ester.)

(6) Alterations of the parent compound at either the 1 or 4 position have the same effects.

MESOPHASE

(1) Ortho substitution decreases the mesophase entropy and temperature of the parent compounds. This is due to steric factors.

(2) Meta substitution has the same effect as ortho substitution on the transition temperature. However, increased asymmetry without steric hindrance in the liquid phase results in an increased entropy of transition.

(3) Para substitution increases the transition temperature, but has little effect on the transition entropy.

(4) Alteration of the parent compound at the 1 or 4 positions is essentially equivalent with respect to effects on temperature and entropy of transition.

(5) Rule 5 of the solid phase list does not apply. One or four opposition is additive rather than subtractive. Therefore, transition temperatures are higher in such compounds.

(6) One or four substitution does not significantly alter the transition entropy.

These statements have been derived on the basis of experience with cholesteryl esters and lack the broad basis in experiment to qualify as " rules " in their present form. However, the sequence is self-consistent and is not contradicted by any cholesteryl esters which have been studied. It is hoped that these observations will prove of general use. As the body of thermodynamic information continues to grow, it should be possible to formulate a general theory which will relate structure and thermodynamic properties.

Appendix

The publication of the Series on Order and Flow in Liquid Crystals has now reached Part 29 with this paper. Since these papers have appeared in a number of journals and occasionally the part number has been omitted, the authors would like to take this opportunity to list all parts of the series in summary.

SERIES ON ORDER AND FLOW OF LIQUID CRYSTALS

I. Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **66**, 1826 (1962).
II. Porter, R. S. and Johnson, J. F., *J. Appl. Phys.* **34**, 51 (1963).
III. Porter, R. S., and Johnson, J. F., *J. Appl. Phys.* **34**, 55 (1963).
IV. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **68**, 2810 (1964).
V. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **70**, 385 (1966).
VI. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *J. Chromatog.* **21**, 392 (1966).
VII. Porter, R. S., Barrall, E. M., II and Johnson, J. F., *J. Chem. Phys.* **45**, 1452 (1966).
VIII. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **71**, 1224 (1967).
IX. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *Mol. Cryst.* **3**, 103 (1967).
X. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **71**, 895 (1957).
XI. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *Mol. Cryst.* **3**, 299 (1968).
XII. Torgalkar, A., Porter, R. S., Barrall, E. M., II and Johnson, J. F., *J. Chem. Phys.* **48**, 3897 (1968).
XIII. Porter, R. S., Barrall, E. M., II and Johnson, J. F., *Thermal Analysis*, Vol. I, ed. Schwenker, R. F. and Garn, P. D., Academic Press, N.Y., 1969, p. 597.
XIV. Barrall, E. M., II, Johnson, J. F. and Porter, R. S., *Thermal Analysis*, Vol. I, ed. Schwenker, R. F. and Garn, P. D., Academic Press, N.Y., 1969, p. 555.
XV. Sakamoto, K., Porter, R. S. and Johnson, J. F., *Mol. Cryst. and Liq. Cryst.* **8**, 443 (1969).
XVI. Porter, R. S., Barrall, E. M., II and Johnson, J. F., *Accounts Chem. Res.* **2**, 53 (1969).
XVII. Stein, R. S., Rhodes, M. B. and Porter, R. S., *J. Colloid Sci.* **27**, 336 (1968).
XVIII. Rhodes, M. B., Porter, R. S., Chu, W. and Stein, R. S., *Mol. Cryst. and Liq. Cryst.* **10**, 295 (1970).
XIX. Barrall, E. M., II, Johnson, J. F. and Porter, R. S., *Mol. Cryst. and Liq. Cryst.* **8**, 27 (1969).
XX. Vogel, M. J., Barrall, E. M., II and Mignosa, C. P., *Liquid Crystals and Ordered Fluids*, ed. Johnson, J. F. and Porter, R. S., Plenum Press, N.Y., 1970, p. 333.
XXI. Johnson, J. F., Porter, R. S. and Barrall, E. M., II, *Mol. Cryst. and Liq. Cryst.* **8**, 1 (1969).
XXII. Barrall, E. M., II and Vogel, M. J., *Thermochemica Acta* **1**, 127 (1970).
XXIII. Davis, G. J., Porter, R. S. and Barrall, E. M., II, *Mol. Cryst. and Liq. Cryst.* **10**, 1 (1970).
XXIV. Davis, G. J. and Porter, R. S., *Mol. Cryst. and Liq. Cryst.* **6**, 377 (1970).

XXV. Young, W. R., Barrall, E. M., II and Aviram, A., *Analytical Calorimetry*, Vol. II, ed. Porter, R. S. and Johnson, J. F., Plenum Press, N.Y., 1970, p. 113.
XXVI. Davis, G. J., Porter, R. S., Steiner, J. W. and Small, D. M., *Mol. Cryst. and Liq. Cryst.* **10**, 331 (1970).
XXVII. Vogel, M. J., Barrall, E. M., II and Mignosa, C. P., *Mol. Cryst. and Liq. Cryst.* **15**, 49 (1971)., also *IBM J. Res. & Dev.* **15**, 52 (1970).
XXVIII. Davis, G. J., Porter, R. S. and Barrall, E. M., II, *Mol. Cryst. and Liq. Cryst.* **11**, 319 (1970).
XXIX. Barrall, E. M., II, Bredfeldt, K. E. and Vogel, M. J., this paper.

REFERENCES

1. Vorländer, D., *Krystallinisch-flüssig Substanzen* Vol. 12, 9–10 Heft, F. Enke, Stuttgart (1908).
2. Kast, W., *Ann. Physik* **83**, 391 (1927).
3. Gaubert, P., *Compt. rend.* **156**, 149 (1913).
4. Gray, G. W., Jones, B. and Marson, F., *J. Chem. Soc.* 1956, 1417.
5. Gray, G. W., *Mol. Cryst.* **1**, 333 (1966).
6. Elser, W., *Mol. Cryst. and Liq. Cryst.* **8**, 219 (1969).
7. Elser, W., *Mol. Cryst.* **2**, 1 (1967).
8. Elser, W., Pohlmann, J. L. W. and Boyd, P. R., *Mol. Cryst. and Liq. Cryst.* **11**, 279 (1970).
9. Ennulat, R. D., *Mol. Cryst. and Liq. Cryst.* **8**, 247 (1969).
10. Barrall, E. M., Johnson, J. F. and Porter, R. S., *Mol. Cryst. and Liq. Cryst.* **8**, 27 (1969).
11. Johnson, J. F., Porter, R. S. and Barrall, E. M., II, *Mol. Cryst. and Liq. Cryst.* **8**, 1 (1969).
12. Davis, G. J., Porter, R. S. and Barrall, E. M., II, *Mol. Cryst. and Liq. Cryst.* **10**, 1 (1970).
13. Arnold, H., *Mol. Cryst.* **2**, 62 (1966).
14. Arnold, H., *Z. phys. Chem.* (*Leipzig*) **226**, 146 (1946).
15. Arnold, H. and Roediger, P., *Z. phys. Chem.* **231**, 407 (1966).
16. Arnold, H., El-Jazairi, E. B. and Konig, H., *Z. phys. Chem.* **234**, 401 (1967).
17. Arnold, H. and Roediger, P., *Z. phys. Chem.* **239**, 283 (1968).
18. Arnold, H., Jacobs, J. and Sonntag, O., *Z. phys. Chem.* **240**, 177 (1969).
19. Arnold, H., Demuo, D., Koch, H. J., Nelles, A. and Sackmann, H., *Z. phys. Chem.* **240**, 185 (1969).
20. Arnold, H., *Z. Chem.* **4**, 211 (1964).
21. Young, W. R., Barrall, E. M., II and Aviram, A., *Analytical Calorimetry*, Vol. 2, ed. R. S. Porter and J. F. Johnson, Plenum Press, 1970, p. 113.
22. Davis, G. J., Porter, R. S., Steiner, J. W. and Small, D. M., *Mol. Cryst. and Liq. Cryst.* **10**, 331 (1970.)
23. Barrall, E. M., II and Diller, R. D., *Thermochem. Acta* **1**, 509 (1970).
24. Leclerq, M., Billard, J. and Jacques, J., *Mol. Cryst. and Liq. Cryst.* **8**, 367 (1969).
25. Barrall, E. M., II, Porter, R. S. and Johnson, J. F., *Mol. Cryst.* **3**, 103 (1967).

26. Sakamoto, K., Porter, R. S. and Johnson, J. F., *Mol. Cryst. and Liq. Cryst.* **8**, 443 (1969).
27. *Handbook of Chemistry and Physics*, ed. C. D. Hodgman, Chemical Rubber Publishing Co., Cleveland, Ohio, 44th ed., 1963, p. 1753.
28. Barrall, E. M., II and Johnson, J. F., *Liquid Crystals and Liquid Crystalline Solutions*, ed. P. A. Winsor and G. W. Gray, 2nd edition, Van Nostrand, London, in press.