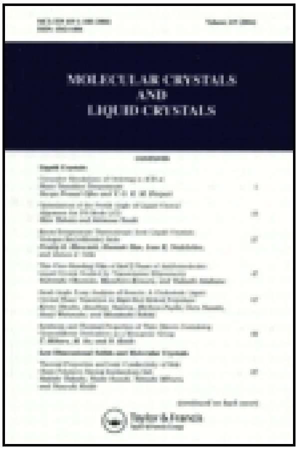

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# Effects of Branching of the Ester Alkyl Chain on the Liquid Crystalline Properties of Alkyl 4-(4-Alkoxybenzylideneamino)-benzoates

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The liquid crystalline properties of alkyl 4-(4-alkoxybenzylideneamino)benzoates, where the ester alkyl groups are propyl, isobutyl, neopentyl, racemic 2-methylbutyl, pentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, and 4-methylpentyl, have been studied by thermal microscopy and differential scanning calorimetry. The alkoxyl group includes all the members from methoxyl to decyloxyl in most of the series. Chain branching of the purely smectogenic five propyl, two butyl, and six pentyl esters produces nematic behavior. All the resulting nematogens but one are the 2-methyl derivatives in which two are neopentyl esters. The smectic B phases observed for many propyl esters are not found for the isobutyl and neopentyl esters. Similarly, the smectic B and C phases of the butyl esters are eliminated by a 2-methyl substituent. On the other hand, smectic B behavior not exhibited by the pentyl esters appears in a few early homologs and smectic C behavior is thermally enhanced in some higher homologs of the 3- and 4-methyl derivatives.

## INTRODUCTION

Extensive studies on the mesomorphic behavior of branched alkyl 4-(4-substituted benzylideneamino) cinnamates were carried out by Gray and Harrison.[1,2] Their results indicated that the nematic-isotropic (N-I) transition temperatures are very sensitive to the position of the branching methyl group. If this occupies the 1-position, nematic properties become monotropic or are completely destroyed relative to the normal alkyl ester. The branching methyl group located nearer the end of the chain has a much smaller influence. The smectic A-isotropic ($S_A$-I) transition temperatures are also decreased most by a 1-methyl substituent, but the effect is not so large as that on the N-I transition temperature. Our previous study on twenty-three alkyl 4-(4-phenylbenzylideneamino)benzoates revealed that the effects of chain branching on the liquid crystalline properties are far more complicated than the empirical correlations described by Gray and Harrison and vary widely with a small change introduced to the molecular structure.[3] Particularly, the nematic behavior produced by 2-methylation of the purely smectogenic butyl and pentyl esters contrasts with the trends cited above. Therefore, we extended the work to some alkyl 4-(4-alkoxybenzylideneamino)benzoate series. Namely, the effects of branching of the ester alkyl chain upon the liquid crystalline transition temperatures of the propyl, butyl and pentyl ester series were studied in a systematic manner.

## EXPERIMENTAL

The alkylation of 4-hydroxybenzaldehyde was carried out by the method of Gray and Jones.[4] The alkyl 4-aminobenzoates employed were those prepared for our earlier work.[3] The Schiff's bases were obtained by refluxing equimolar amounts of the aldehyde and the ester in ethanol. The determination of transition temperatures and the identification of mesophases were performed as described in our previous paper.[3]

## RESULTS AND DISCUSSION

### a) Normal Alkyl Esters

The melting points and liquid crystalline transition temperatures of the propyl ester series are summarized in Table I. Monotropic I-N transitions appear in the methoxy and ethoxy compounds. A metastable $S_A$ phase arises also in the latter compound. The other homologous members are purely smectogenic. In addition to a stable $S_A$ phase, a metastable $S_B$ phase is exhibited by many of them.

According to the work by Fishel and Patel,[5] the first member in the butyl ester series is nonmesogenic. All the other members are smectogenic. The ethoxy and propoxy compounds are monomorphous. The $S_A$ phase found in the former compound is metastable but that in the latter is stable. The butoxy to nonyloxy compounds are dimorphous. The texture appearing below the temperature range

TABLE I

Transition Temperatures for the Propyl 4-(4-Alkoxybenzylideneamino)benzoate Series

| Alkoxyl Group | Temperature (°C) of transition to | | | |
|---|---|---|---|---|
| | Smectic B | Smectic A | Nematic | Isotropic |
| Methoxyl | — | — | (43)[a)] | 93 |
| Ethoxyl | — | (68.5) | (85) | 93 |
| Propoxyl | — | 58 | — | 70.5 |
| Butoxyl | (47.5) | 55 | — | 90 |
| Pentyloxyl | (36.5) | 56.5 | — | 85 |
| Hexyloxyl | (38) | 61 | — | 91 |
| Heptyloxyl | (35.5) | 62.5 | — | 90.5 |
| Octyloxyl | (37.5) | 59.5 | — | 92 |
| Nonyloxyl | — | 60.5 | — | 93.5 |
| Decyloxyl | (40) | 52 | — | 95.5 |

a) Values in parentheses indicate monotropy.

of the $S_A$ phase was designated as smectic$_2$ by the authors. Since they identified the lowest temperature mesophase monotropically produced in the trimorphous decyl compound as $S_B$, the smectic$_2$ phase is supposed to be $S_C$ in the scheme developed by Sackmann and Demus.[6]

Table II presents the liquid crystalline behavior of the pentyl ester series. No mesophase is detectable for the methoxy compound. Both N and $S_A$ phases are observed with the next homolog, and then the propoxy to heptyloxy compounds are purely smectogenic. The last

TABLE II

Transition Temperatures for the Pentyl 4-(4-Alkoxybenzylideneamino)benzoate Series

| Alkoxyl Group | Temperature (°C) of transition to | | | |
|---|---|---|---|---|
| | Smectic C | Smectic A | Nematic | Isotropic |
| Methoxyl | — | — | — | 52 |
| Ethoxyl | — | 35 | 58.5 | 63 |
| Propoxyl | — | 45 | — | 58 |
| Butoxyl | — | 29 | — | 77.5 |
| Pentyloxyl | — | 47.5 | — | 74.5 |
| Hexyloxyl | — | 60 | — | 79 |
| Heptyloxyl | — | 57 | — | 79 |
| Octyloxyl | (35.5)[a)] | 51 | — | 83.5 |
| Nonyloxyl | (45) | 53.5 | — | 87.5 |
| Decyloxyl | (42.5) | 51 | — | 86 |

a) Values in parentheses indicate monotropy.

three members in this series exhibit a metastable $S_C$ phase in addition to an $S_A$ phase.

Including the methyl and ethyl ester series studied by Dave and Patel and by Fishel and Patel respectively,[5,7] the normal alkyl 4-(4-alkoxybenzylideneamino)benzoates are mostly purely smectogenic. Only the following four are exceptional: the methoxy compound in the propyl ester series and the ethoxy compounds in the ethyl, propyl, and pentyl ester series. They can exhibit N properties, but the transition is enantiotropic only in the last one.

b) Branching of the Ester Propyl Chain

In Figure 1, the transition temperatures are plotted against the number of carbon atoms in the alkoxyl group for the propyl and isobutyl esters. The melting points are denoted by crosses. The full circles represent enantiotropic liquid crystal-liquid crystal transition or the clearing point temperatures, while the open circles indicate that the transitions are monotropic. Numerical values for the latter series are given in Table III. In the methoxy compound, the I-N transition temperature is raised by the methylation. Although the melting point is drastically lowered, the mesophase remains metastable. As the branching has essentially no effect on the I-N transition temperature in the ethoxy compound, an appreciable destabilization of the crystalline phase makes the mesophase enantiotropic. It must be noted that the temperature range of stable existence is merely 5.5°C; how-

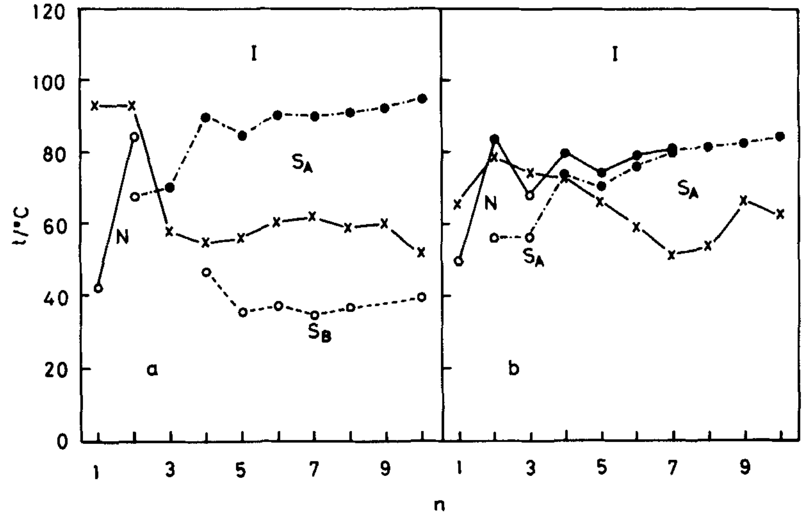

FIGURE 1 Plots of transition temperatures against the number of carbon atoms in the alkoxyl group for (a) propyl and (b) isobutyl 4-(4-alkoxybenzylideneamino)benzoates.

TABLE III

Transition Temperatures for the Isobutyl 4-(4-Alkoxybenzylideneamino)benzoate Series

| Alkoxyl Group | Temperature (°C) of transition to Smectic A | Nematic | Isotropic |
|---|---|---|---|
| Methoxyl | — | (50)[a] | 66 |
| Ethoxyl | (56.5) | 79 | 84.5 |
| Propoxyl | (56.5) | (68.5) | 74.5 |
| Butoxyl | 74 | 74.5 | 80 |
| Pentyloxyl | 66 | 71 | 75 |
| Hexyloxyl | 59.5 | 77 | 79.5 |
| Heptyloxyl | 52 | 81 | 82 |
| Octyloxyl | 54 | — | 82 |
| Nonyloxyl | 67 | — | 83 |
| Decyloxyl | 62.5 | — | 84.5 |

a) Values in parentheses indicate monotropy.

ever, the difference between the I-N and N-$S_A$ transition temperatures is as large as 28°C in the isobutyl ester and is markedly larger than 16.5°C in the propyl ester. This increase is mostly ascribed to the decrease of the $S_A$ thermal stability by the branching methyl group. The methylation results in the appearance of N phase in the purely smectogenic propoxy to heptyloxy compounds and the elimination of $S_B$ phase in the butoxy compound and higher homologs.

The temperature range of stable or metastable existence of N phase consistently decreases as the series is ascended: that is 12°C in the propoxy compound and 1°C in the heptyloxy compound. The $S_A$ phase in all the isobutyl esters is thermally less stable than that in the corresponding propyl esters in agreement with the trends described by Gray and Harrison. The extent of destabilization varies from 9.5°C in the heptyloxy compound to 15.5°C in the butoxy compound. The stability of the crystalline phase is affected in a complicated way by the branching methyl group. The melting point is raised in the propoxy, butoxy, and pentyloxy compounds, then is lowered in the next three homologs, and finally is raised again in the nonyloxy and decyloxy compounds. Therefore, the temperature range of the $S_A$ phase in the isobutyl ester series is merely 0.5°C in the butoxy compound, while it is as wide as 35°C in the corresponding compound of the propyl ester series. It is noted that the ranges in the two series are close to each other in the heptyloxy and octyloxy compounds.

Four members in the neopentyl ester series were found to be monotropically mesogenic. The N phases of the methoxy and ethoxy compounds in the propyl ester series are not extinguished by the introduction of two branching methyl groups even though the I-N transition temperatures are lower by ≧ 30°C than those of the corresponding isobutyl esters. The ethoxy compound remains monotropically smectogenic, the N-$S_A$ transition being located at 46°C. Thus, the effect of the second branching methyl group on the thermal stability of N phase is markedly different from that of the first one. Mesophases were also found for the hexyloxy and heptyloxy compounds. Neopentyl group promotes the crystal stability relative to propyl group; namely, the C-I transitions are at 66 and 72°C respectively, whereas both the N and $S_A$ stabilities are reduced and they become metastable with respect to the crystalline states. The I-N and N-$S_A$ transitions in the hexyloxy compound are at 57 and 52°C respectively; therefore, the N phase can exist in a range twice wider than that in the corresponding isobutyl ester. The same tendency is seen for the heptyloxy compound; that is, the I-N and N-$S_A$ transitions occur at 55 and 51°C respectively.

c) 2-Methylation of the Ester Butyl Chain

Figure 2 represents the plots of transition temperatures against the alkyl chain length for the butyl ester series together with that for the racemic 2-methylbutyl ester series. The temperatures of the branched alkyl esters are summarized in Table IV. The branching methyl group introduced to the ester butyl group produces a metastable N phase

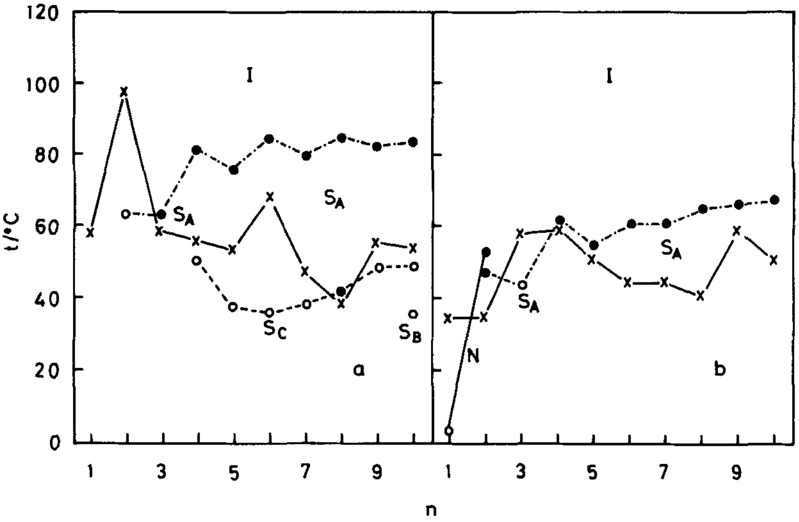

FIGURE 2 Plots of transition temperatures against the number of carbon atoms in the alkoxyl group for (a) butyl and (b) 2-methylbutyl 4-(4-alkoxybenzylideneamino)-benzoates.

TABLE IV

Transition Temperatures for the Racemic 2-Methylbutyl 4-(4-Alkoxybenzylideneamino)benzoate Series

| Alkoxyl Group | Temperature (°C) of transition to Smectic A | Nematic | Isotropic |
|---|---|---|---|
| Methoxyl | — | (3.5)[a] | 34.5 |
| Ethoxyl | 35 | 47.5 | 53 |
| Propoxyl | (43.5) | — | 58 |
| Butoxyl | 59.5 | — | 62 |
| Pentyloxyl | 50.5 | — | 55 |
| Hexyloxyl | 44.5 | — | 61 |
| Heptyloxyl | 44.5 | — | 61 |
| Octyloxyl | 40.5 | — | 65.5 |
| Nonyloxyl | 59 | — | 66.5 |
| Decyloxyl | 50.5 | — | 67.5 |

a) Values in parentheses indicate monotropy.

in the methoxy compound below 3.5°C. Nematic behavior arising in the second member is thermally stable. The melting point decrease as much as 63°C occurs by the substitution, giving an $S_A$ phase stable over the range of 12.5°C. In the propoxy compound, the methylation does not modify the thermal stability of the solid phase, while it decreases the $S_A$ stability by 20°C and makes the phase monotropic. In all the other members, the S phases with the exception of that of the A type are eliminated by the branching methyl group. The temperature range of the $S_A$ phase is appreciably diminished in the butoxy and pentyloxy compounds; that is, 2.5°C vs. 27°C in the former homolog and 4.5°C vs. 23°C in the latter. The methylation decreases both the melting and clearing points in the hexyloxy compound by 23.5°C; therefore, the range covered by the $S_A$ phase of the 2-methylbutyl ester is the same as that in the corresponding butyl ester. In the higher homologs, the change in the melting point by the substitution is generally small but the clearing point is lowered by 16 to 20°C.

### d) Methylation of the Ester Pentyl Chain

For this particular case, we studied all the derivatives in which a branching methyl group was moved progressively to the penultimate carbon of the ester pentyl chain. No mesomorphic properties arise in the 1-methylpentyl ester series except for the octyloxy to decyloxy compounds. The first mentioned melts at 21.5°C and gives a metastable $S_A$ phase when the melt is supercooled to 12.5°C. The I-$S_A$ transition is also found for the nonyloxy compound. It occurs at 31°C which is located 6°C below the melting point. The last member can exhibit a stable $S_A$ phase covering the temperature range from 31.5

to 34°C. On cooling, the $S_A$ phase is converted to an $S_C$ phase at 19°C.

The mesomorphic behavior of the 2-methylpentyl esters is presented in Table V. The plot obtained for the pentyl ester series is compared with that for this ester series in Figure 3. The 2-methylation considerably reduces the melting point of the methoxy compound and produces a metastable N phase below −2°C. The effects of the branching methyl group on the behavior of the ethoxy compound are complicated; namely, the thermal stability of the crystalline phase is enhanced by 10°C, those of the $S_A$ and N phases are diminished by 16.5 and 4°C respectively, extending the temperature range of the N phase to 17°C. The appearance of an N phase by 2-methylation is achieved for the propoxy to heptyloxy compounds. In all the cases, the upper limit of the $S_A$ phase is markedly lowered by the substitution. Not only the N phase but also the $S_A$ phase are monotropic in the propoxy compound. In the next homologous member, the former phase is stable but the latter continues to be metastable, then these mesophases become enantiotropic in the pentyloxy and hexyloxy compounds. Both the N and $S_A$ phases are again monotropic in the heptyloxy compound. The metastable $S_C$ phase found for the octyloxy to decyloxy compounds in the straight alkyl chain ester series can be observed also in the octyloxy and decyloxy compounds of the 2-methylpentyl ester series. However, the branching methyl group decreases the $S_A$-$S_C$ transition temperatures by about 10°C.

The liquid crystalline properties for the homologous series of the

TABLE V

Transition Temperatures for the 2-Methylpentyl 4-(4-Alkoxybenzylideneamino)benzoate Series

| Alkoxyl Group | Temperature (°C) of transition to | | | |
|---|---|---|---|---|
| | Smectic C | Smectic A | Nematic | Isotropic |
| Methoxyl | — | — | (−2)[a)] | 26.5 |
| Ethoxyl | — | (42) | 45 | 59 |
| Propoxyl | — | (31.5) | (37) | 41.5 |
| Butoxyl | — | (49) | 49.5 | 53 |
| Pentyloxyl | — | 38 | 43.5 | 47.5 |
| Hexyloxyl | (ca. 17)[b)] | 34 | 54 | 57 |
| Heptyloxyl | — | (55.5) | (56.5) | 57 |
| Octyloxyl | (26) | 33 | — | 60.5 |
| Nonyloxyl | — | 54 | — | 63 |
| Decyloxyl | (30.5) | 38.5 | — | 64.5 |

a) Values in parentheses indicate monotropy.

b) The phase is observable by a microscope but it is too unstable to be recorded on a differential scanning calorimeter.

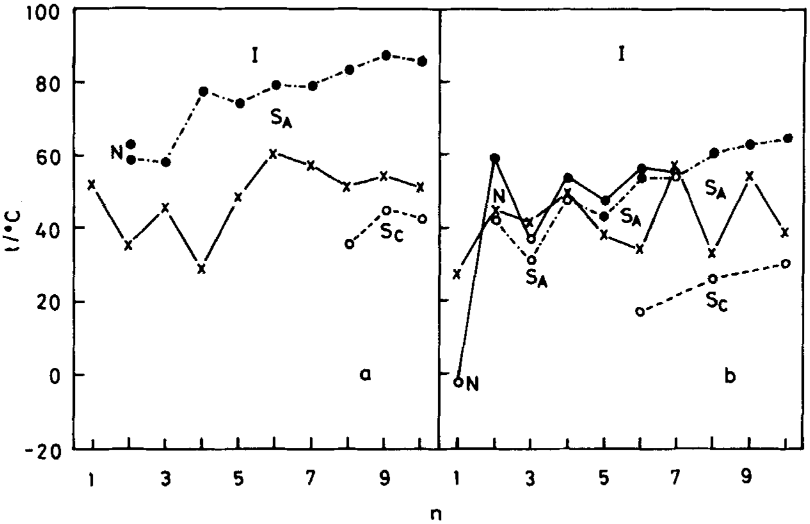

FIGURE 3 Plots of transition temperatures against the number of carbon atoms in the alkoxyl group for (a) pentyl and (b) 2-methylpentyl 4-(4-alkoxybenzylideneamino)-benzoates.

3-methylpentyl ester are given in Table VI. It is interesting to note that $S_B$ phases appear in the propoxy and butoxy compounds by this substitution. A 3-methyl group promotes also the $S_C$ thermal stability. This phase can exist stably in the octyloxy to decyloxy compounds. Moreover, it is monotropically produced in the hexyloxy and heptyloxy compounds.

The transition temperatures for the 4-methylpentyl esters are summarized in Table VII. The most remarkable change caused by the methylation is the emergence of an N phase in the methoxy compound. The monotropic I-N transition is at 16°C which is appreciably

TABLE VI

Transition Temperatures for the 3-Methylpentyl 4-(4-Alkoxybenzylideneamino)benzoate Series

| Alkoxyl Group | Temperature (°C) of transition to Smectic B | Smectic C | Smectic A | Isotropic |
|---|---|---|---|---|
| Propoxyl | (33)[a] | — | 39 | 51 |
| Butoxyl | 38 | — | 40 | 70.5 |
| Pentyloxyl | — | — | 47 | 59 |
| Hexyloxyl | — | (27) | 43 | 65 |
| Heptyloxyl | — | (42) | 51 | 62.5 |
| Octyloxyl | — | 36 | 49 | 67 |
| Nonyloxyl | — | 51.5 | 55.5 | 70 |
| Decyloxyl | — | 54.5 | 56.5 | 67 |

a) Values in parentheses indicate monotropy.

TABLE VII

Transition Temperatures for the 4-Methylpentyl 4-(4-Alkoxybenzylideneamino)benzoate Series

| Alkoxyl Group | Temperature (°C) of transition to Smectic B | Smectic C | Smectic A | Nematic | Isotropic |
|---|---|---|---|---|---|
| Methoxyl | — | — | — | (16)[a)] | 59 |
| Ethoxyl | (22) | — | 38 | — | 55.5 |
| Propoxyl | (33) | — | 51.5 | — | 53.5 |
| Butoxyl | (41.5) | — | 57 | — | 75 |
| Pentyloxyl | — | — | 59 | — | 67 |
| Hexyloxyl | — | — | 56.5 | — | 70 |
| Heptyloxyl | — | — | 66.5 | — | 70 |
| Octyloxyl | — | (49) | 52 | — | 71 |
| Nonyloxyl | — | 49.5 | 53.5 | — | 65.5 |
| Decyloxyl | — | 48 | 57.5 | — | 73.5 |

a) Values in parentheses indicate monotropy.

higher than that in the corresponding compound in the 2-methylpentyl ester series. Secondly, the observation of metastable $S_B$ phases for the ethoxy to butoxy compounds must be emphasized. The branching methyl group at the 4-position stabilizes the $S_C$ phases in the last three homologous members as much as the methyl group at the 3-position does. Nevertheless, this mesophase could not be observed for the hexyloxy and heptyloxy compounds.

Summarizing the above results, it is clear that 2-methylation favors the appearance of an N phase in all the examined series, especially in the propyl and pentyl esters, and reduces the stabilities of the $S_A$, $S_B$, and $S_C$ phases. In contrast to these effects, a methyl group occupying the 3- or 4-position of the pentyl group promotes the thermal stability of the $S_B$ phase in the low homologous members and that of the $S_C$ phase in the higher members.

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## References

1. G. W. Gray and K. J. Harrison, *Mol. Cryst. Liq. Cryst.*, **13**, 37 (1971).
2. G. W. Gray and K. J. Harrison, *Symp. Faraday Soc.*, No. 5, 54 (1971).
3. Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **104**, 353 (1984).
4. G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1954).
5. D. L. Fishel and P. R. Patel, *Mol. Cryst. Liq. Cryst.*, **17**, 139 (1972).
6. H. Sackmann and D. Demus, *Mol. Cryst.*, **2**, 81 (1966).
7. J. S. Dave and P. R. Patel, *Mol. Cryst.*, **2**, 115 (1966).