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Enaminoketones as calamitic liquid crystals with a novel hydrogen-bonded rigid core

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A series of compounds having an aminopropenone-3 group between two aromatic rings has been synthesized and thermally stable enantiotropic mesogens with properties typical of three ring liquid crystals were obtained. The mesomorphic properties of the molecules result from the presence of a rigid calamitic core stabilized by a hydrogen-bonded *cis-s-cis* quasi-ring form of the enaminoketone group.

Many investigations have been devoted recently to liquid crystals based on novel molecular structures. Such structures often lead to unique physical properties of the mesogenic phases making them suitable for applications in liquid crystal displays. Conventional liquid crystals have a properly terminated rigid core composed of aromatic and/or aliphatic rings [1]. There are a few examples of the ring formation involving intermolecular hydrogen bonding, as in dimers of 4-substituted benzoic acid derivatives [2(a)] or 5-substituted 2-oxypyridines [2(b)]. Different molecules may also form a rigid core mesogenic complex due to hydrogen bonds between the sterically matched donors and acceptors in mixtures of non-mesogenic components [3].

A new approach to the synthesis of mesogenic materials is in designing rigid molecular cores containing quasi-rings stabilized by intramolecular hydrogen bonding. Previous attempts have led to strongly bent rather than calamitic structures [4]. In this preliminary communication we report the first calamitic liquid crystals with an autonomous, well documented quasi-ring made by a *cis-s-cis* enaminoketone group [5] capable of giving an almost linear molecular geometry. We have synthesized several molecules incorporating this group connected with one or two aromatic rings. In the first case the liquid-crystalline behaviour is often observed thus supporting the ring-like structure of the enaminoketone moiety. In the second case mesogenic properties are strongly pronounced as reported here for some three ring compounds having structure:

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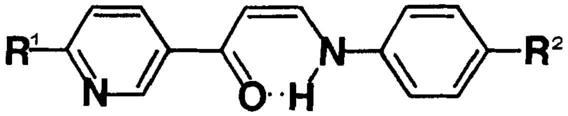

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with terminal alkyl or alkyloxy groups R^1 and R^2. The pyridine ring is employed to enhance the transverse dipole movement and to lower the melting point.

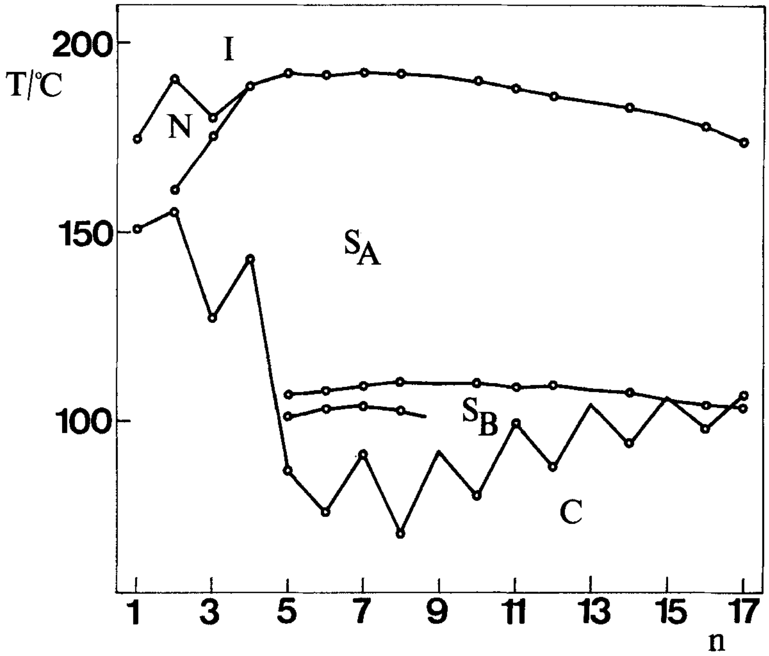
Enaminoketonic mesogens were synthesized by reacting hydroxymethylene derivatives of 5-substituted 3-acetylpyridines with 4-substituted anilines. For example, to obtain 1-(4′-methoxyphenylamino)-3-[5″-(2″-methylpyridyl)]-propen-1-one-3 ($R^1 = H_3C$, $R^2 = OCH_3$) 10 mmols of anisidine in methanol (20 ml) and acetic acid (10 ml) in methanol (5 ml) were subsequently added to a solution of the sodium salt of 3-oxo-3-[5′-(2′-methylpyridyl)]-propionic aldehyde [6] (10 mmols) in methanol (20 ml). After 12 h the yellow microcrystals were filtered off and recrystallized from ethanol. Yield 1·8 g (68 per cent); mp 151°C, clp 174·5°C. The NMR, IR and microanalytical properties are consistent with the molecular structure. ^{1}H NMR ($CDC1_3$): $\delta = 2{\cdot}61$ (s, 3 H, CH_3), 3·80 (s, 3 H, OCH_3), 5·92 (d, $J = 7{\cdot}7$ Hz, 1 H, $\underline{\mathrm{HC}}$–CO), 6·97 (AB, $J = 9{\cdot}1$ Hz, 4 H, $H^{2'}$, $H^{3'}$, $H^{5'}$, $H^{6'}$), 7·23 (d, $J = 8{\cdot}1$ Hz, 1 H, $H^{3''}$), 7·44 (dd, $J = 12{\cdot}4$; 7·7 Hz, 1 H, $\underline{\mathrm{HC}}$ NH), 8·10 (dd, $J = 8{\cdot}1$; 2·1 Hz, 1 H, $H^{4''}$), 9·02 (d, $J = 2{\cdot}1$ Hz, 1 H, $H^{6''}$), 12·21 (d, $J = 12{\cdot}4$ Hz, 1 H, NH). The value of $J_{C^1HC^2H} = 7{\cdot}7$ Hz strongly confirms the *cis* substitution around the C^1=C^2 bond; $\delta_{NH} = 12{\cdot}21$ ppm is typical for enaminoketones in the *cis-s-cis* configuration stabilized by an intramolecular hydrogen bond [7]. However, the formation of a ring structure should be strongly hindered sterically for additional substituents of the enaminoketonic group. Eventually we find that although unsubstituted compounds are mesogenic over a wide range of temperatures, the methyl derivatives are not. In this light we see that liquid-crystalline properties of the only known mesogenic enaminoketone which has two 2-methyl-aminopropenone-3 groups and four phenyl rings [8], result from the extreme molecular elongation rather than from the formation of hydrogen-bonded rings.

All of the compounds synthesized with one enaminoketonic group placed between two aromatic rings when studied by both polarization microscopy and DSC proved to be mesogenic. The pyridyl series with $R^1 = H_3C$ and $R^2 = OC_nH_{2n+1}$ has a particularly strong tendency to form the smectic A phase preceding more ordered phases. As shown in the figure the series exhibits rather rare polymorphism with a hexatic S_B to a crystal S_B transition, which will be described elsewhere. The clearing points of 185 ± 10°C are typical for three ring calamitic mesogens with terminal alkyl and alkyloxy groups. This coincidence as well as a high temperature mesomorphism point to:

(i) a remarkable thermal stability of the *cis-s-cis* enaminoketone group;
(ii) the absence of other molecular conformers, *trans-s-trans* and *trans-s-cis* [5], in the smectic, nematic and isotropic phases;
(iii) a very slight bend of the molecule at the nitrogen atom of the enaminone ring.

The second conclusion may be drawn also from the sharp peaks observed in DSC thermograms. Compounds with terminal alkyl instead of alkyloxy groups behave similarly, but the clearing points are lowered by about 20°C.

Concluding, we wish to emphasize that it is possible to obtain calamitic mesogenic molecular cores of pronounced rigidity, stabilized by intramolecular hydrogen bonding. In order to take advantage of the fairly easy synthesis and strong thermal stability the *cis-s-cis* enaminoketone moiety is used. The relevant compounds are considerably dichroic (colourless/yellow) and have a high dipole movement of about 1×10^{-29} C m. The new compounds may be used in the synthesis of organometallic mesogens which are attracting increasing interest in recent years for their colours and paramagnetism [9]. Unfortunately, pyridyl ligands are useless as they yield complexes



Phase behaviour for the homologous series of compounds for $R^1 = H_3C$ and $R^2 = OC_nH_{2n+1}$ as obtained by optical miscroscopy and DSC. Note the terminated first order transition line between two smectic B modifications, hexatic S_B and crystal S_B. Unidentified tilted phases are observed for $n = 4$ and 5, below 110°C and 90°C, respectively.

with a high melting point; for instance, the copper (II) complex for $R^1 = H_3C$ and $R^2 = C_4H_9$, melts above 225°C.

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References

[1] Demus, D., 1988, *Molec. Crystals liq. Crystals*, **165**, 45; 1989, *Liq. Crystals.*, **5**, 75.

[2] (a) Demus, D, and Zaschke, H., 1984, *Flüsssige Kristalle in Tabellen II* (VEB Deutscher Verlag für Grundstoffindustrie), p. 56; (b) *Ibid.*, p. 368.

[3] Briene, M. J., Gabard, J., Lehn, J. M., and Stibor, I., 1989, *J. chem. Soc. Chem. Commun.*, 1868.

[4] Godquin-Giroud, A. M., and Billard, J., 1983, *Molec. Crystals liq. Crystals.*, **97**, 287.

[5] Frejamanis, J. F., 1974, *Chemistry of Enaminoketones, Enaminoimines, Enaminothiones* (in Russian) (Izd. Zinatie).

[6] Benary, E., and Psile, H., 1924, *Berichte*, **57**, 828.

[7] Dudek, G. O., and Volpp, G. P., 1963, *J. Am. chem. Soc.*, **85**, 2697.

[8] Benicewicz, B. C., Huang, S. J., and Johnson, J. F., 1981, *Molec. Crystals liq. Crystals*, **72**, 9.

[9] Adams, H., Bailey, N. A., Bruce, D. W., Dhillon, R., Dunmur, D. A., Hunt, S. E., Lalinde, E., Maggs, A. A., Orr, R., Styrings, P., Wragg, M. C., and Mailtis, P. M., 1988, *Polyhedron*, **7**, 1861.