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## Liquid Crystals

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## Paramagnetic liquid-crystalline complexes based on novel enaminketone ligands

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Calamitic ligands having aminopropenone-3 ring substituted with alkyl-*trans*-cyclohexyl-phenyl and alkyl groups are low melting nematogens. Copper(II) complexed to the ligands gives thermally stable rod-like liquid crystals which exhibit an enantiotropic paramagnetic nematic phase. It is shown that modifications of the terminal groups as well as synthesis of asymmetric complexes enables us to extend the nematic range and depress the melting points.

Recently, novel types of organometallic liquid crystals [1] have been searched for intensively because of their unique properties, such as vivid colours, strong dichroism and paramagnetism. Since the magnetic properties of transition metal complexes depend mostly on the paramagnetic centre, major effort has been made to synthesize liquid crystals containing Cu(II), Co(II), VO(II), FeCl(II) and other ions (see [1] and references therein). It is well-known that the magnetic and optical properties of the complexes are also influenced by the environment of the central ion. However, so far rather few chemical structures of ligands are involved in the design of novel liquid-crystalline molecules. Particularly, in order to obtain stable calamitic complexes paramagnetic ions are chelated through the centres O, O<sup>-</sup> of  $\beta$ -diketones [2, 3] and N, O<sup>-</sup> of salicylaldimines [4-6]. In the present preliminary communication we report the synthesis and characterization of novel mesogens with copper(II) complexed to enaminketone ligands having O, N<sup>-</sup> chelating centres. It is apparent from our studies that enaminketones [7] are very promising ligands for the synthesis of rod-like thermally stable complexes having a wide mesogenic range and a low melting point.

Enaminketone complexes, synthesized previously from heterocyclic ligands [8], were not mesomorphic. This is probably due to the coordination of the copper ion by nitrogen atoms belonging to the hetero-rings of neighbouring molecules. In the present work we have designed calamitic complexes of the formulae (5) shown in figure 1, having typical mesogenic ( $R^1$ ) and terminal ( $R^2$ ) groups chosen to diminish the molecular interactions. For these reasons alkyl-*trans*-cyclohexylphenyl and alkyl substituents have been studied.

Complexes (5), for  $m=2$ ,  $n=3-12$  were synthesized following the route given in figure 1. Starting from methylketone (1) [9] the salt (2) was obtained by the Claisen formylation reaction. The solution of (2) when neutralized, gives 3-substituted-propen-

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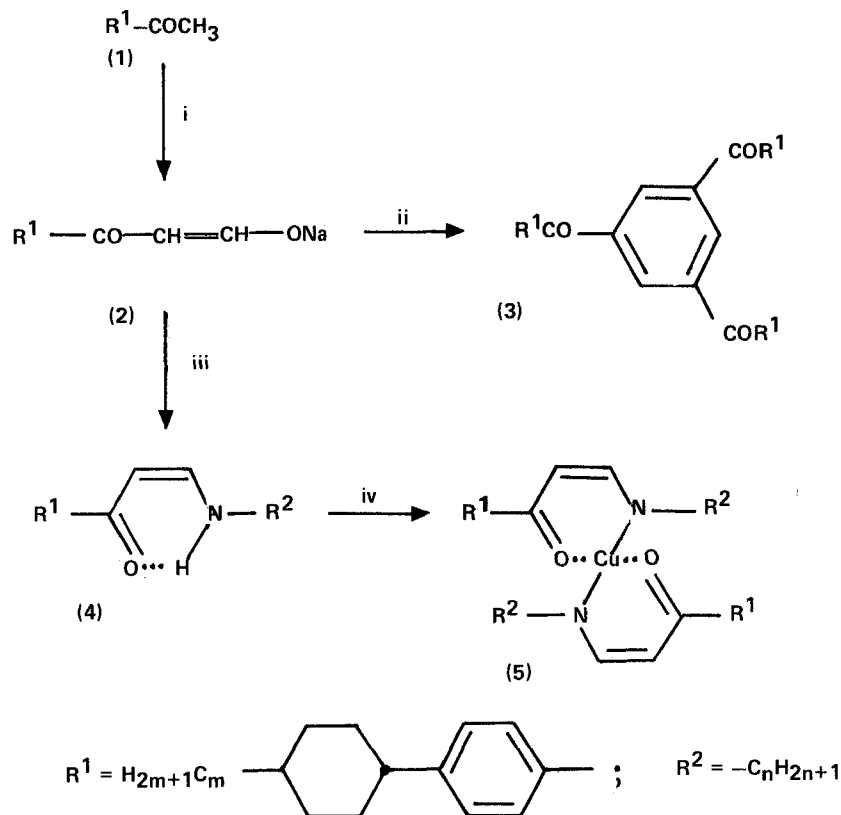


Figure 1. Synthetic scheme, reagents and conditions: (i)  $Et_2O$ , Na,  $HCOOEt$ , room temperature; (ii)  $HCl$  aq.,  $Et_2O$ ; (iii)  $HCl$  aq.,  $H_2N$ -alkyl,  $AcOH$ , 1 h at room temperature, 12 h at  $0^\circ C$ ; (iv)  $MeOH$ ,  $Cu_2(OAc)_4 \cdot 2H_2O$ , reflux, 5 min.

2-al-1; the ether extract of the latter, treated with *N*-alkylamine, yields a precipitate of a non-mesogenic by-product (3) ( $mp = 167^\circ C$ , discotic phases were not observed up to room temperature). Treating the filtrate with copper acetate we obtained complexes (5), for  $n = 8-12$ , without isolation of the parent ligands. Crystalline ligands (4) were obtained, for  $n = 3-7$ , when a mother solution of (2) was treated with an appropriate amine and frozen. From solutions of the pure ligands, copper complexes are obtained with a yield of 90 per cent. After crystallization from hexane they form thin, long brownish or green-brownish needles. Their purity was checked by DSC and microanalysis results were in agreement with the expected values. For example, for the complex  $n = 5$  ( $C_{44}H_{64}N_2O_2Cu$ ) analysis gave calculated: C, 73.74 per cent; H, 9.02 per cent; N, 3.91 per cent; found: C, 73.60 per cent; H, 9.13 per cent; N, 4.09 per cent, whereas for the parent ligand ( $C_{22}H_{33}NO$ ) analysis gave calculated: C, 80.66 per cent; H, 10.18 per cent; N, 4.28 per cent; found: C, 80.66 per cent; H, 10.38 per cent; N, 4.19 per cent. Molecular structures of the ligands and the complexes were confirmed by IR and NMR spectra. According to the same synthetic scheme we have synthesized some complexes,  $[R^1-CO-CH=CH-N-R^2]_2Cu$ , having other terminal substituents. In all cases elemental data were satisfactory. For example, for the complex having  $R^1 = H_{13}C_6O-C_6H_4-N=N-C_6H_4$ ,  $R^2 = C_9H_{19}$  analysis gave calculated: C, 70.85 per cent; H, 8.34 per

Mesomorphic transition temperatures and effective enthalpies† for ligands  $H_5C_2-C_6H_{10}-C_6H_4-CO-CH=CH-NH-C_nH_{2n+1}$  and their copper(II) complexes.

n	Ligand			Complex		
	$T_{CN}/^{\circ}C$	$\Delta H/kJ mol^{-1}$	$T_{NI}/^{\circ}C$	$\Delta H/kJ mol^{-1}$	$T_{NI}/^{\circ}C$	$\Delta H/kJ mol^{-1}$
3	56.1	(19.5)	101.7	(0.63)	163.5	(29.2)
4	59.0	(24.1)	78.6	(0.56)	138.4	(23.4)
5	64.0	(17.2)	89.4	(0.89)	125.5	(41.6)
6	67.9	(25.0)	80.7	(0.82)	115.3	(36.2)
7	64.1	(16.3)	86.1	(1.27)	113.9	(35.7)
8					112.9	(41.4)
9					124.3	(44.0)
10					120.7	(43.1)
12					122.5	(46.8)

† Effective enthalpies include pretransitional changes of the specific heat in the nematic phase. Data determined using a Perkin-Elmer DSC-7 calorimeter at a scanning rate of  $5^{\circ}C min^{-1}$  on heating 1.5 mg samples.

‡ Most stable crystalline phase.

cent; N, 8.27 per cent; found: C, 70.84 per cent; H, 8.42 per cent; N, 8.15 per cent; for  $R^1 = \text{H}_5\text{C}_2\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{O}-\text{C}_6\text{H}_4$ ,  $R^2 = \text{C}_{10}\text{H}_{21}$  analysis gave calculated: C, 71.79 per cent; H, 8.19 per cent; N, 2.99 per cent; found: C, 71.82 per cent; H, 8.24 per cent; N, 3.14 per cent; for  $R^1 = \text{H}_{23}\text{C}_{11}$ ,  $R^2 = \text{C}_6\text{H}_4-\text{COO}-\text{C}_2\text{H}_5$  analysis gave calculated: C, 68.31 per cent; H, 8.49 per cent; N, 3.46 per cent; found: C, 68.35 per cent; H, 8.45 per cent; N, 3.67 per cent.

As expected from their rod-like molecular shape, both ligands (4) and complexes (5) have liquid-crystalline properties revealing the nematic phase with marbled textures, although homeotropic textures can be easily obtained. Transition temperatures and enthalpies are collected in the table. Ligands have low melting points and, compared to the classical three-ring [10] or other enaminoketone [8] mesogens, about 80°C lower clearing temperatures. The latter feature results from the thermodynamic equilibria between conformers having an equatorially and axially substituted cyclohexane ring [11]. It is seen from the table that the transition temperatures of the complexes depend on the length of the *N*-alkyl chains. A destabilization of the nematic phase by the terminal substituents is striking. A similar effect of the pendant alkyl chains was found previously for copper  $\beta$ -diketonates [2] having the same substituents  $R^1$  and  $R^2$  as in (5). In  $\beta$ -diketonate complexes the alkyl chains are lateral substituents. By analogy, the phase transitions of the enaminoketone complexes (5) can be understood if we assume that the *N*-alkyl chains are not oriented along the molecular axis. This effect could be related to the non-planar surroundings of the nitrogen atom (X-ray studies are now being undertaken to verify this assumption). Tentative ESR studies show that another possibility, namely a remarkable twisting of the core of the complex, is less probable. ESR spectra reveal a single, rather wide, slightly asymmetric line in both isotropic and nematic phases. The location of this spectral line nearly corresponds to the *g* factor observed in isotropic solutions, where  $g = 2.111$ ,  $a = 190$  MHz. Almost identical values for planar complexes of salicylaldimines [4] with a similar type of copper(II) ion coordination, indicate a rather planar structure of enaminoketone complexes (5) in solution as well as in the mesophase.

Examining the optical properties of the complexes (5) we detect only slight dichroism (yellow/yellow-brownish colours) in the nematic phase. Refractive index anisotropy and mean refractive index of the complexes are similar to those of the parent ligands, as shown in figure 2. The agreement between the anisotropies confirms planar rather than tetrahedral Cu(II) coordination because in the case of tetrahedral complexes a distinct decrease in the anisotropy should be observed. The agreement between the mean values points to an additive behaviour of the optical polarizability rather than its remarkable enhancement due to complexation (cf. [12]). Conoscopic studies with He-Ne light, although difficult to perform due to strong non-linear phenomena, showed that the biaxiality of the complexes is negligible; the biaxial birefringence is lower than 0.003.

The thermal stability of the enaminone complexes is higher than that of related  $\beta$ -diketonates [2]; slight decomposition can be observed above 180°C. The temperature range of the nematic phase reaching 40°C and the relatively low melting temperatures make the examined series I ( $R^1 = \text{H}_5\text{C}_2-\text{C}_6\text{H}_{10}-\text{C}_6\text{H}_4$ ,  $R^2 = \text{C}_n\text{H}_{2n+1}$ ) comparable to the best series based on salicylaldimine ligands [5(a)]. The advantage of enaminoketones is that they provide an opportunity to introduce, in an easy way, a variety of terminal groups into the molecules. In order to check whether modifications of the terminal groups could change markedly the temperature characteristics of liquid-crystalline phases we have synthesized control series II and III of the copper(II)

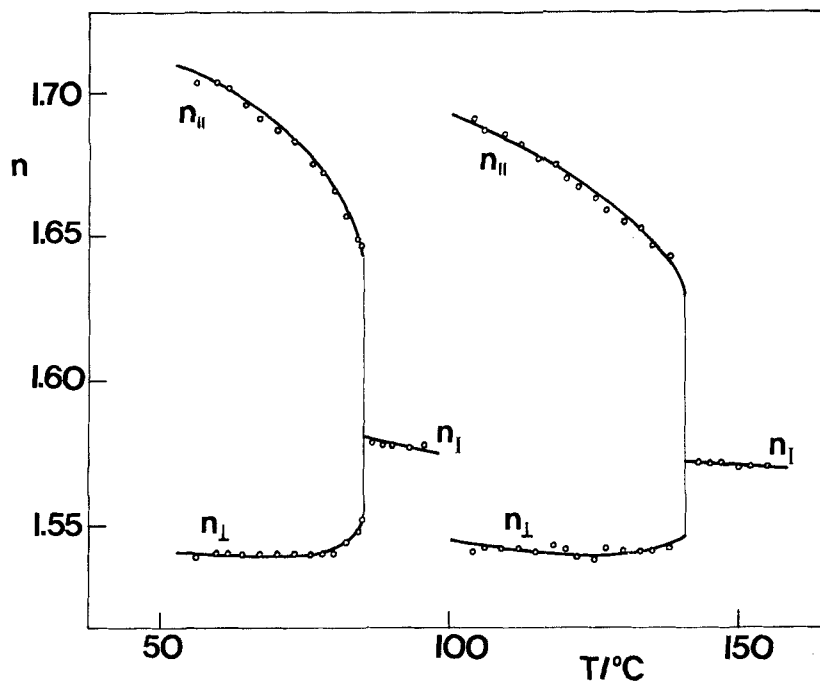


Figure 2. Refractive index  $n(\lambda=623\text{ nm})$  versus temperature of the ligand (left) and its copper(II) complex (right). Ligand:  $\text{H}_5\text{C}_2\text{-C}_6\text{H}_{10}\text{-C}_6\text{H}_4\text{-CO-CH=CH-NH-C}_7\text{H}_{15}$ .

complexes. It was found that for the series II ( $R^1 = \text{H}_{13}\text{C}_6\text{O-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4$ ,  $R^2 = \text{C}_n\text{H}_{2n+1}$ ) the nematic phase is extended to  $90^\circ\text{C}$ , although the melting points are still not below  $100^\circ\text{C}$ . For the series III ( $R^1 = \text{H}_{2m+1}\text{C}_m$ ,  $R^2 = \text{C}_6\text{H}_4\text{-COO-C}_2\text{H}_5$ ) the melting point is depressed to  $60^\circ\text{C}$ , however, only a very narrow or monotropic smectic A phase is observed.

Expecting that: (i) for asymmetric complexes having two different ligands in a molecule, a compromise between the clearing points of the symmetric complexes will be accompanied by remarkable depression of their melting points; (ii) for unresolved or eutectic mixtures of symmetric and asymmetric complexes further depression will be obtained, we have prepared some ternary mixtures of  $\text{A}_2\text{Cu}$ ,  $\text{ABCu}$  and  $\text{B}_2\text{Cu}$  complexes. Actually, low melting 1:2:1 mixtures have been obtained from equimolecular mixtures of ligands AH and BH. For example, for AH:  $\text{H}_{13}\text{C}_6\text{O-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{-CO-CH=CH-NH-C}_9\text{H}_{19}$  ( $\text{A}_2\text{Cu}$ :  $T_{\text{CN}} = 117^\circ\text{C}$ ,  $T_{\text{NI}} = 205^\circ\text{C}$ ) and BH:  $\text{H}_5\text{C}_2\text{O-C}_6\text{H}_4\text{-CH}_2\text{O-C}_6\text{H}_4\text{-CO-CH=CH-NH-C}_{10}\text{H}_{21}$  ( $\text{B}_2\text{Cu}$ :  $T_{\text{CN}} = 127^\circ\text{C}$ ,  $T_{\text{NI}} = 124^\circ\text{C}$ ) the resulting sample melts sharply to give a rather wide ( $76^\circ\text{C}$ ) nematic phase. The  $T_{\text{CN}} = 80^\circ\text{C}$ , is  $30^\circ\text{C}$  lower than the calculated eutectic temperature for the symmetric complexes. These examples convince us that by optimizing the type and length of the terminal substituents it will be possible to find broad, low temperature paramagnetic mesogens among enamino-ketone complexes.

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