

Molecular Crystals and Liquid Crystals

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MESOMORPHIC TRANSITION METAL COMPLEXES

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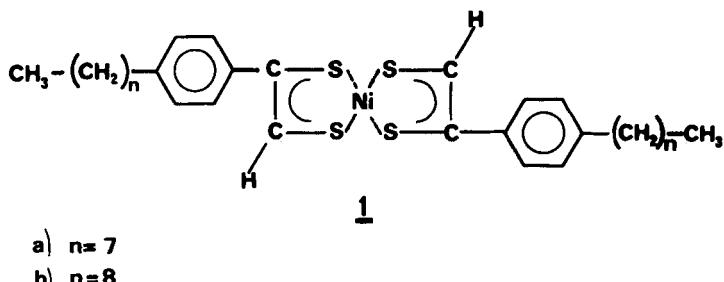
Abstract : The synthesis of two dithiolato nickel complexes carrying aliphatic substituents is described. Both compounds exhibit mesomorphic properties.

Among the many organic compounds which have been found to exhibit a mesomorphic behaviour, very few contain metals. The few known (1,2) main group organometallic liquid crystals are analogous to purely organic systems (carrying, for example, a trialkylsilyl substituent instead of an alkyl group). The only known transition metal compound with mesomorphic properties is a ferrocene Schiff base (3).

We have tried to find new types of transition metal complexes with liquid crystal properties in order to eventually introduce paramagnetic species. As a start in this direction, we have investigated the synthesis of the bis-(p-alkyl-styryl-1,2-dithiolato)nickel complexes 1. In general, dithiolato nickel complexes are square planar, and one can thus envision a planar terphenyl like structure for complexes of type 1.

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Since several terphenyl derivatives show liquid crystal behaviour, complexes 1 could also be expected to be mesomorphic. Indeed, these complexes exhibit a smectic C phase. ^(*)



The synthesis was carried out according to ref. (4) : acetylation of 1-phenyl-octane or 1-phenyl-nonane at -20°C in dichloromethane in the presence of aluminium chloride gave the p-alkyl-acetophenones (colorless oils) in 90% yields; each was mono-brominated with bromine in glacial acetic acid at 60°C . Recrystallization from methanol yielded 50% (p-bromoacetyl-phenyl-octane : mp $39-40^{\circ}\text{C}$; p-bromoacetyl-phenyl-nonane : mp 47°C). They were reacted with an excess of phosphorus pentasulfide in refluxing dioxane for one to three hours. The warm solutions were filtered and the filtrates treated with an excess of nickel chloride dissolved in water (reflux for two hours). After cooling to room temperature, the solutions were extracted with 1:1 hexane/benzene. The extracts were evaporated and the residues chromatographed on columns or plates of silica gel. The green p-alkyl-substituted styryl-dithiolato nickel complexes (5) show the following characteristics :

* We are most grateful to Prof. J. BILLARD for his help in the investigation of the liquid crystal properties.

^{1a} : Melting Points : C - S_C : 109° ; S_C - I : 184°
 Mass Spectrum (direct inlet, 200°) : 615 (M/e),
 492 (M - S₂Ni) , 460 (M - S₃Ni).

UV Spectrum (cyclohexane) : λ max, 265 nm (ϵ =45000),
 304 nm (ϵ =80000) , 580 nm (ϵ =2300), 830 nm (ϵ =43000)

^{1b} : Melting Points : C - S_C : 106°5 ; S_C - I : 188°
 UV Spectrum (cyclohexane) : λ max, 265 nm (ϵ =30000),
 304 nm (ϵ =70000) , 580 nm (ϵ =800) , 825 nm (ϵ =38000).

The melting points and transition temperatures of these compounds were determined with a differential scanning calorimeter (Perkin-Elmer, DSC.2) and the mesophases were identified by the examination of their structures under a polarizing microscope (Thermo Diavar, Reichert) equipped with a heating stage.

We are continuing this investigation to expand the liquid crystal range down to room temperature.

We thank Dr H. LEMAIRE for helpful discussions.

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