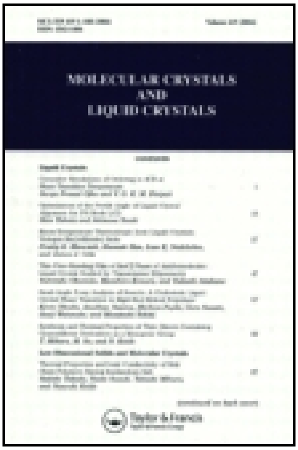

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Thermotropic Transition Metal Complexes Discogens and Their Smectogenic Intermediates

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Thermotropic Transition Metal Complexes Discogens and Their Smectogenic Intermediates

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The series of the first thermotropic transition metal complexes discogens is completed: *bis*(*p*-*n*-alkylbenzoyl)methanato copper (II) including one derivative possessing two sorts of side chains. The symmetrical and unsymmetrical members of this series exhibit the same very organized discophase. The intermediates for the synthesis, the *bis*(*p*-*n*-alkylbenzoyl)methanes with two identical or different side chains, containing more than 18 carbon atoms exhibit the same very organized optically biaxial and positive smectic phase. The existence of another smectic phase stable at lower temperatures is established for a symmetrical term of this series.

I. INTRODUCTION

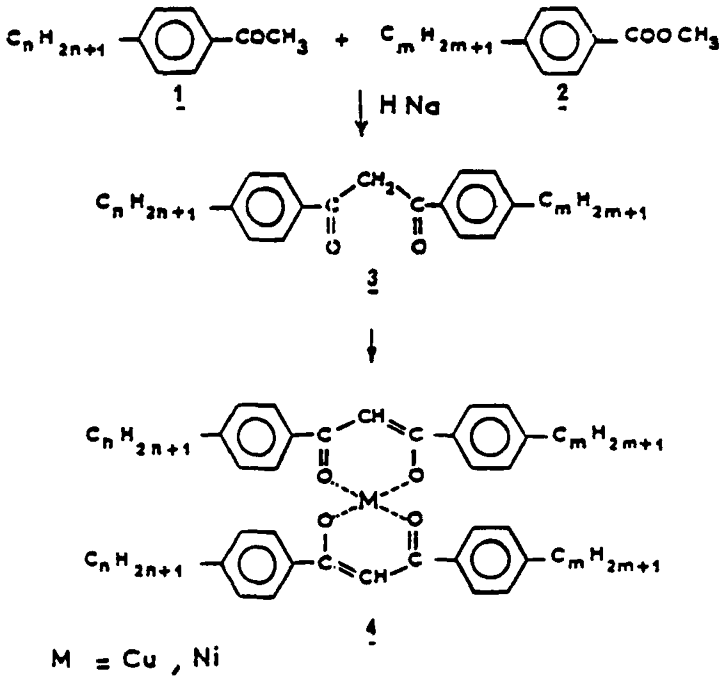
The first described organometallic discogen is only lyotropic.[1] We have previously reported the synthesis and the properties of a thermotropic transition metal complex discogen: the *bis*(*p*-*n*-decylbenzoyl)methanato copper (II)[2] having a twofold molecular symmetry. A few months ago, a metallophtalocyanine was published.[3] We will report here data for other compounds of this series including a derivative exhibiting two different sorts of side chains.

The intermediates for the synthesis, the *bis*(*p*-*n*-alkylbenzoyl)methanes with two identical or different alkyl chains, exhibit smectic mesophases.

II. SYNTHESIS

The organometallic derivatives *4* are elaborated as follows: to a solution of the appropriate *bis*(*p*-*n*-alkylbenzoyl)methane *3* dissolved in tetrahydrofurane, we add a solution of the respective transition metal halides dissolved in ethanol. The pH is adjusted at 7 or 8 with sodium acetate dissolved in water-ethanol 50:50 or with ammonia. After 2 to 20 h at room temperature, we filter and then recrystallize the complex *4*.

The *bis*(*p*-*n*-alkylbenzoyl)methanes *3* are obtained by a method derived from these of Burn, Holton and Webb:[4] reaction of *p*-alkylbenzoic acid methyl ester *2* dissolved in dimethoxy ethane on *p*-alkyl acetophenone *1* with sodium hydride.



All compounds and complexes were characterized by the usual analytical methods.

III. *BIS*(*p*-*n*-ALKYLBENZOYL)METHANES

The obtained colorless *bis*(*p*-*n*-alkylbenzoyl)methanes *3* are studied with a calorimeter (Perkin-Elmer, DSC.2C) and observed with a polarizing microscope (Leitz, Panphot) having a heating attachment (Mettler, FP.52). The transition temperatures and molar enthalpy changes are reported in Table I.

Only the derivatives having more than 18 carbon atoms on the side chains exhibit stable mesophase. For these compounds the clearing enthalpy changes are larger than the melting enthalpy changes. This situation observed for discogens[5] is exceptional for the calamitic mesogens—only one case is previously reported.[6] Among the three isomeric[7] compounds having 20 carbon atoms on the side chains, the *3d* (n = 8, m = 12) have a mesophase stable at room temperature and the symmetrical *3e* have the most elevated melting and clearing temperatures and also the highest molar enthalpy changes. Therefore, only this last compound *3e* exhibits two different stable mesophases. But we cannot observe the second transition with the microscope. For the compound *3f* a monotropic second mesophase can be observed on cooling. By cooling, the liquids give lamellar textures with uniform birefringences. These phases are optically biaxial with one optical axis nearly perpendicular to the walls of the preparation and with positive optical sign. To distinguish from lamellar crystals, we press over cover slips with a fine steel needle and this induces curvilinear nearly parallel defects. There are highly viscous fluid birefringent phases. Some Grandjean's terraces can be observed on preparations with one free surface. The structure is probably layered. Orientational effect on glass surfaces treated with polysilanes[8] is never observed. After cooling, a single domain of *3e* ($n = m = 10$) gives birefringent crystals with rectilinear parallel

TABLE I

Transitions of the *bis*(*p*-*n* alkylbenzoyl)methanes *3*

Number	n	m	Crystal-crystal		Melting		Mesophase mesophase		Clearing	
3a*	7	7			53.5	*15.9*			(47)	
3b	9	9			64	*28.4*				
3c	7	13			39	*15.7*			47.5	*18.5*
3d	8	12			−5	*11.6*			55	*27*
3e	10	10	−22	*1.5*	41	*24*	50	*1.95*	66	*30.7*
3f	12	12			61	*31.2*			69	*34.7*

In this table (and in Table II) the temperatures are in Celsius degrees and in *italic;* the molar enthalpy changes are in kJ/mole.

The values between brackets concern virtual transition.

*The melting point and the enthalpy have been measured on impure compounds.

limits. Only two extinction angles can be observed for these crystals. Only two orientations exist for these crystals. The difference between the two extinction angles depends on the initial mesomorphic area; the crystals obtained by cooling of a single liquid crystalline domain are oriented by the mesophase. These compounds exhibit positive biaxial mesophases that are very organized and probably layered.

To identify total miscibilities are searched. The binary isobaric phase diagrams are built from microscopic observations of contact preparations.[9] The compounds *3c* and *3e* are totally miscible in the mesomorphic state of *3e* stable at upper temperatures. The compounds *3c*, *3d* and *3f* are totally miscible in the mesomorphic state. Consequently the mesophases of *3c*, *3d* and *3f* have the same nature as the one of *3e* stable between 50 and 66°C. But in the binary phase diagram of the mixtures of *3e* and *3f*, the coexisting curves of the liquid and mesomorphic phases exhibit a minimum at 60.6°C. In such a case, the contact method cannot clearly give information on the total miscibility in the highly viscous liquid crystalline state. In the phase diagram of *3d* and *3f*, the coexisting curves of the liquid and mesomorphic phases exhibit a minimum at 54°C. But the liquid state of *3d* can be supercooled and the mesophase in pure *3d* is induced by the mesophase containing *3f*; this way, the isomorphy can be established. For two compounds exhibiting sufficiently different clearing temperatures, in spite of the minimum induced by the nonidealities of the solutions, the contact method can give useful data. Extrapolation of the coexisting curves for liquid and mesomorphic phases in the binary phase diagram of *3b* and *3f* gives a virtual clearing temperature at 47°C for *3b*.

The biaxial character of the mesophase M common to *3c*, *3d*, *3e* and *3f* establishes that this phase M is different to smectic B. We have used for reference compound the *trans-trans*-4'-*n*-butylbicyclohexyl-4-carbonitrile exhibiting two mesophases (smectic H stable between 28 and 54°C and nematic stable between 54 and 79°C) identified by isomorphy (Figure 1) with the *trans-trans*-4'-*n*-propylbicyclohexyl-4-carbonitrile (melting point: 58°C, smectic H monotropic between 19 and 48°C, smectic G monotropic between 48 and 57°C and nematic to 81.5°C[10]). The binary phase diagram of the mixtures of *3e* with the *trans-trans*-4'-*n*-butylbicyclohexyl-4-carbonitrile proves that M is different to smectic H. The binary phase diagram of *3e* with the *bis*(4'-*n*-decylbenzylidene)-1,4-phenylenediamine (crystal 73 S_G 120 S_F 150 S_I 156 S_C 191 S_A 192°C liquid[11-13] proves that M is different to smectic G. We have also used for reference compound the *n*-propanoyl-2-*n*-nonyl-7-fluorene[14] which exhibits two smectogenic phases (smectic E stable between 65 and 92°C and smectic A stable between 92 and 111°C, identified by isomorphy with the ethyl-4,4'-terphenyl dicarboxylic acid ester[15]) (Figure 2). From the phase diagram of the mix-

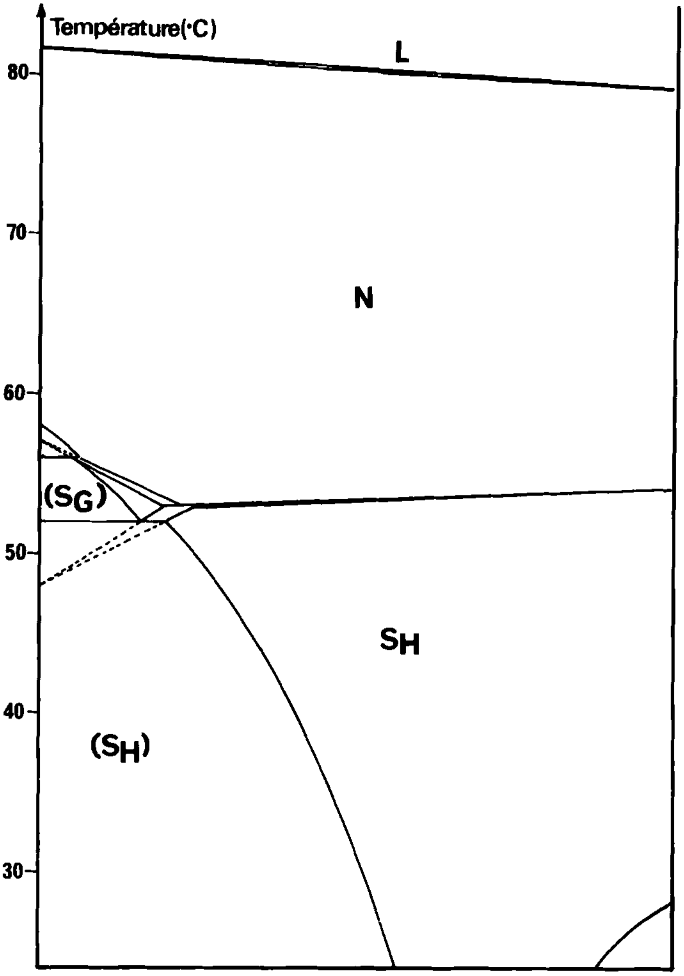


FIGURE 1 Phase diagram of the mixtures of two *trans-trans*-4′-*n* alkylbicyclohexyl-4-carbonitriles: butyl derivative on the right and propyl on the left.

tures of *3e* with the *n*-propanoyl-2-*n*-nonyl-7-fluorene (Figure 3) we can, tentatively, identify M as smectic E. This result is to be confirmed by X-ray investigation.

4. ORGANOMETALLIC DERIVATIVES

The organometallic derivatives *4* are studied by the same way. The nickel complex *4* ($n = m = 10$) (melting at 83°C) is not mesogenic. An iron

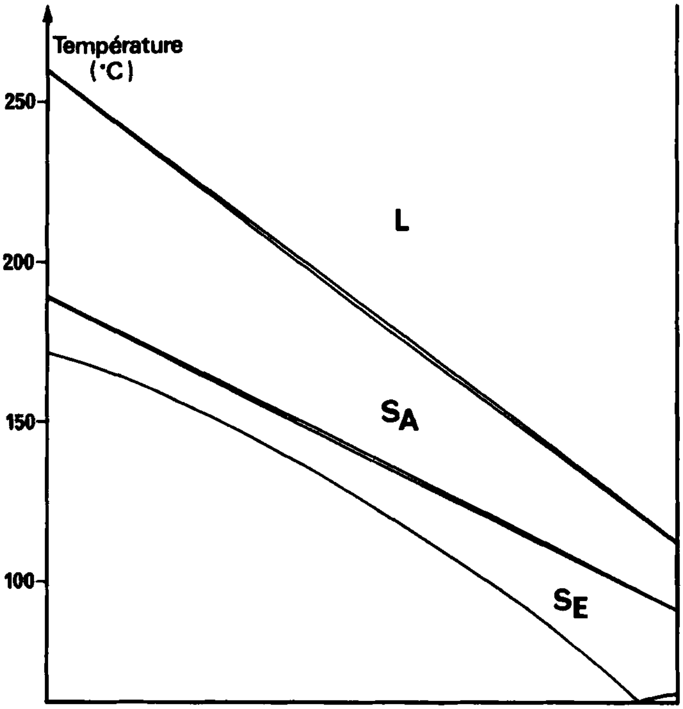


FIGURE 2 Binary phase diagram of the mixtures of the *n*-propanoyl-2-*n*-nonyl-7-fluorene on the right and the ethyl-4-4′-terphenyl dicarboxylic acid diester on the left.

complex is described elsewhere.[16] The transition temperatures and molar enthalpy changes of the copper (II) complexes *4* are reported in the Table II.

These three green derivatives exhibit mesophases. The thermograms of the *4c* (*n* = 7, *m* = 13) compound show sharp peaks. It is a pure compound; only one of the two possible isomers is present. Only this compound *4c* has a clearing enthalpy change larger than the melting enthalpy change. Among the two isometric compounds *4c* (*n* = 7, *m* = 13) and *4e* (*m* = *n* = 10), the most symmetrical has the most elevated melting and clearing temperatures and molar enthalpy changes. By cooling, the liquids give small birefringent domains without acicular form and sometimes with schlieren texture. By pressing over the cover slips with a sharp steel needle, curvilinear defects appear inside these highly viscous fluid birefringent phases. No orientational effect on glass surfaces treated with hexaphenol[17] is observed.

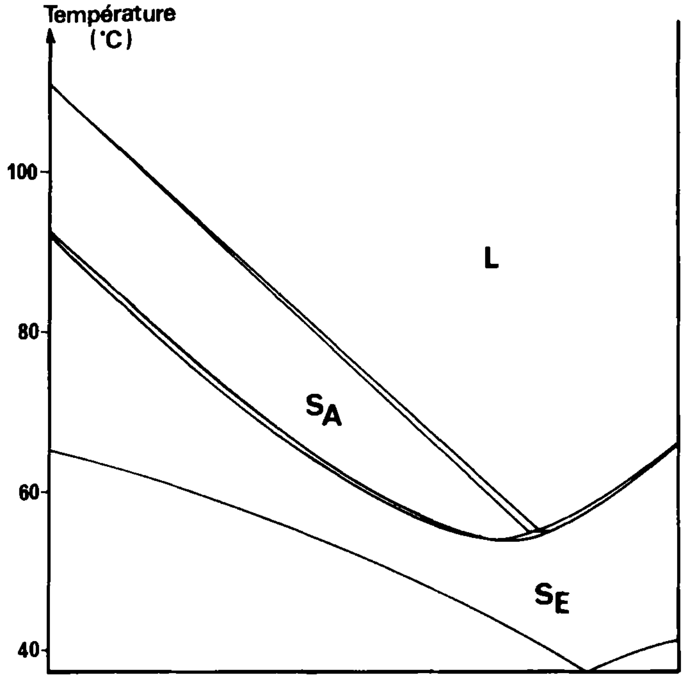


FIGURE 3 Binary phase diagram of the mixtures of the *n*-propanoyl-2-*n*-nonyl-7-fluorene on the left and *3e* (Table I) on the right.

The phase diagrams of the mixtures of first *4c* and *4e* and then *4e* and *4f* prove that these compounds are totally miscible in their mesomorphic state. Consequently, the mesophases of *4c* ($n = 7$, $m = 13$), *4e* ($m = n = 10$) and *4f* ($m = n = 12$) have the same nature. No total miscibilities are found in this mesomorphic state for *4e* and *3e* or 2,2′,6,6′-tetradodecylphenylbipyran-4-ylidène,[5] *n*-octanoic acid rufigallol hexaester,[18] hexaheptyloxy-2,3,6,7,10,11-triphenylene,[19] undecanoic acid

TABLE II

Transitions of the *bis*(*p*-*n* alkylbenzoyl)methanato copper (II) *4*

Number	*n*	*m*	Melting		Clearing	
4c	7	13	71	*23.2*	122	*23.7*
4e	10	10	85.5	*95*	128.5	*31.6*
4f	12	12	95.1	*116.6*	113.4	*19.4*

2,3,6,7,10,11-hexahydroxy-triphenylène hexaester,[20] octanoic acid hexahydroxy benzene hexaester,[21] 4′-*n*-nonyloxybenzoic acid 2,3,6,7,10,11-hexahydroxytriphenylene hexaester,[20] hexa-2,3,6,7,10,11-(4′-*n*-octylbenzoyloxy)triphenylene.[20] Consequently, the mesophase of the compounds *4c*, *4e* and *4f* is different from the discophases of the cited compounds and particularly different of D_B and D_E.[22] The mesophases exhibited by the transition metal complexes of Table II with a flat central core[23] and four flexible side chains have large clearing molar enthalpy changes. The structure of this very organized discophase is to be studied. Preliminary X-ray diffraction results indicate a lamellar mesophase with 29 Å lamellar thickness for *4e*.[24]

5. CONCLUSION

Pure *bis*(*p*-*n*-alkylbenzoyl)methanato copper (II) with four equal side chains or with two sorts of side chains have been elaborated. Three compounds studied of this series exhibit a very organized discophase stable in a temperature range larger than 18°C.

The intermediates for the synthesis, the *bis*(*p*-*n*-alkylbenzoyl)methane having more than eighteen carbon atoms in the side chains, exhibit a very organized optically biaxial and positive mesophase which is possibly smectic E (stable at room temperature for *3d*). The calorimetric measurements establish the existence of another mesophase in the compound *3e* stable at lower temperatures, similarly to one previously reported.[25]

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