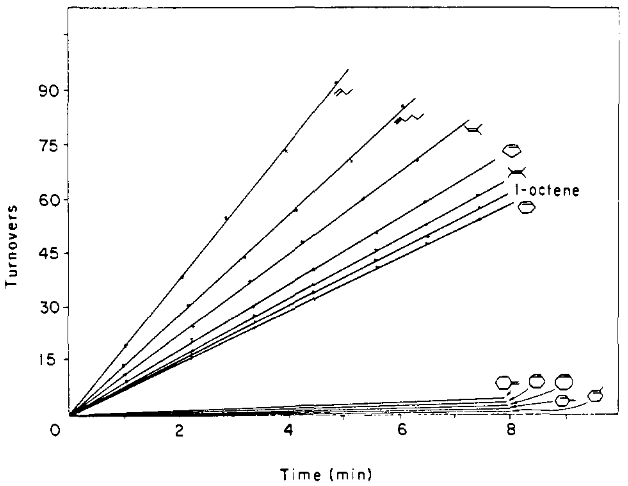

Figure 1. Rate of hydrogenation of olefins catalyzed by (Z-X)–ORh(allyl)H. Conditions: catalyst (50 mg, 0.01 mmol of Rh); (olefin) = 0.2 M in hexane; H_2 (1 atm); 20 °C.

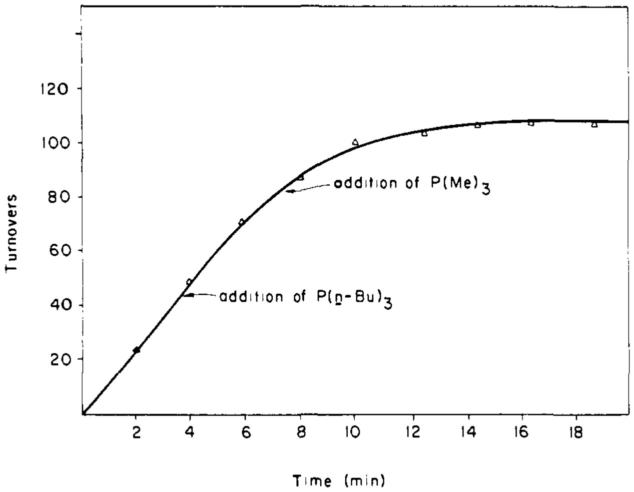

Figure 2. Hydrogenation of 1-butene by (Z-X)–ORh(allyl)H followed by sequential additions of P(n-Bu)$_3$ and PMe_3.

and are greater than that for 2,3-dimethyl-2-butene; for **2**, however, these rates decrease in the order 1-butene > 1-hexene > 1-octene, and transport limitations are such that locally highly substituted, but "small", 2,3-dimethyl-2-butene is hydrogenated *more readily* than is the "larger" long-chain primary olefin, 1-octene.[5] Consistent, too, with the notion of size/shape selectivity is the observation that **2** efficiently catalyzes benzene hydrogenation to cyclohexane at an appreciable rate (500 psig H_2, 120 °C, 203 (mol of product) (mol of Rh)$^{-1}$ h^{-1}), but under the same conditions toluene was hydrogenated only slowly (<20 (mol of product) (mol of Rh)$^{-1}$ h^{-1}).

Complex **2** coordinates 2 equiv of PMe_3 to give **5**, but n-Bu_3P (of larger cone angle:[6] $\theta_{PMe_3} = 118°$; $\theta_{PBu_3} = 132°$) is not coordinated by **2**. Therefore, a selective poisoning experiment could be used to substantiate the contention that the catalytically active rhodium complex is located *inside* the zeolite cavity. When excess n-Bu_3P and Me_3P were added sequentially to a reaction mixture during hydrogenation of 1-butene catalyzed by **2**, it was found that adding n-Bu_3P did not detectably alter the rate of hydrogenation of the olefin. However, introducing PMe_3 caused the hydrogenation rate to drop, almost immediately, to ca. zero (see Figure 2).

The work described herein presents a new approach to specific deposition and activation of metal complexes inside zeolite cavities. Deposition occurs protolytically most rapidly (and, therefore, can occur specifically) at hydroxylic sites (of the bulk zeolite material) of greatest acidity (which, apparently, are those inside the supercage). This approach, therefore, should be of general utility for deposition of protolytically labile complexes of any metallic entity into proton-exchanged zeolite species. Activation of the bound species as a catalyst can be accomplished under mild conditions which minimize degradation of the active site. Of particular interest to us is the possibility that the cage environment of the zeolite might impart an environmental effect to the reactivity of substrate molecules through specific substrate/environment interactions.

Acknowledgment. We acknowledge support for this research provided by the National Science Foundation.

Registry No. Rh(allyl)$_3$, 12082-48-3; 1-butene, 106-98-9; 2-methyl-2-butene, 513-35-9; 1-hexene, 592-41-6; 1-octene, 111-66-0; 2,3-dimethyl-2-butene, 563-79-1; 1-octene, 111-66-0; benzene, 71-43-2; toluene, 108-88-3; cyclohexene, 110-83-8; cyclopentene, 142-29-0.

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(5) Rates for olefin hydrogenation relative to that for 1-methylcyclohexene catalyzed by [Si]–ORh(allyl)H were as follows: cyclohexene, 1.18; 2,3-dimethyl-2-butene, 0.02. For the catalyst [Z-X]–ORh(allyl)H, these rates were as follows: cyclohexene, 57; 2,3-dimethyl-2-butene, 57. Relative rates for hydrogenation of the small olefin 1-butene with use of [Z-X]–ORh(allyl)H vs. [Si]–ORh(allyl)H were 0.54:1. For actual hydrogenation rates for a series of olefins catalyzed by [Si]–ORh(allyl)H, see ref 2; for those catalyzed by [Z-X]–ORh(allyl)H, see Figure 1.

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Discotic Mesophases Obtained from Substituted Metallophthalocyanines. Toward Liquid Crystalline One-Dimensional Conductors[1]

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A new type of liquid crystals, the discotic mesophases,[2] has recently been described.[3-8] They are observed with organic compounds whose structure is characterized by a flat aromatic core surrounded by several flexible hydrocarbon chains. The molecules are stacked in columns, the different columns forming a hexagonal array (see Figure 1). The spines formed by the superposition of the aromatic cores are isolated by the molten aliphatic tails. This led us to envisage a new class of one-dimensional conductor in which the conducting chains would be composed of the spine of the discotic mesophase. The columns are separated from each other by 10–20 Å of a nonpolar medium. This ensures a very good "insulation" of the various conducting chains. Metallophthalocyanines (PcM) seemed to us particularly suitable for that purpose, since their conducting properties are now well established[9-13] (see Figure 2). Columnar phases formed

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(1) Part 7 of Annelides. For the part 6 see: Markovitsi, D.; Knoesel, R.; Simon, J. *Nouv. J. Chim.*, in press.

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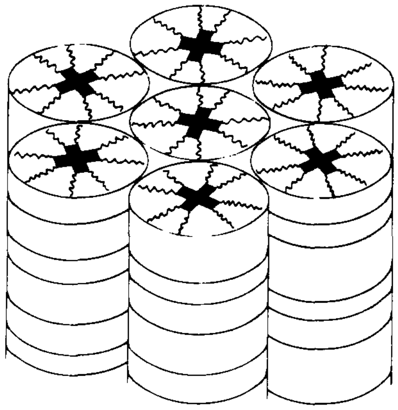


Figure 1. Characteristic structure of the discotic mesophases.

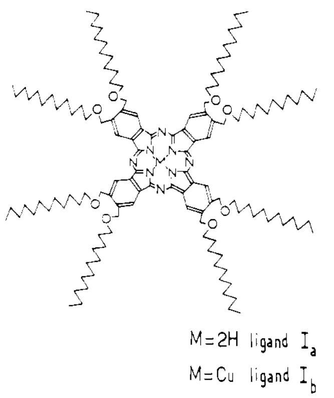
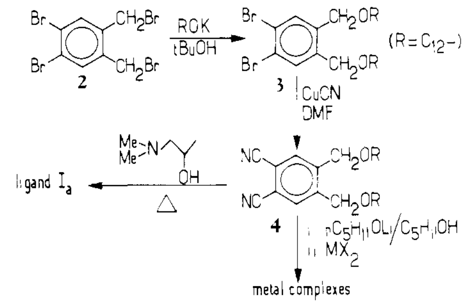


Figure 2. Octasubstituted metallophthalocyanines synthesized.

from metallophthalocyanines substituted with hydrocarbon chains should possess two interesting properties. First, the classical herring-bone structure found in the crystalline form of the PcM's is replaced in the columnar configuration by an untilted parallel stacking of the molecules. In the β form, the metal to metal distance is 4.85 Å; an untilted stacking should decrease this value up to approximately 3.4 Å, i.e., the characteristic van der Waals distance for aromatic compounds.[14–16] This should increase the cooperative properties between the metallophthalocyanine subunits (ferro- and antiferromagnetism, ferroelectricity, exciton transfer, semiconducting properties). Second, the molten paraffin chains surrounding the columns create an apolar medium that permits the dissolution of various organic dopants without disrupting the conducting chains.

To our knowledge, no other example of thermotropic liquid crystal formed from metallophthalocyanine derivatives has been published so far. A lyotropic mesophase obtained from aqueous solutions of tetracarboxylated copper phthalocyanine has been observed by polarizing microscopy,[17] but no further characterization has been made. A thermotropic discotic mesophase of uroporphyrin derivatives has been recently reported.[18] However, its thermal stability extends only over a very narrow range of temperature (0.1 °C). More generally, only a few transition-metal complexes showing mesomorphic behavior have been described in the literature.[19–21]

Scheme I



A general method has recently been proposed to synthesize octasubstituted phthalocyanines.[22] A close chemical pathway has been used to obtain the corresponding dodecyl derivative (Scheme I). The tetrabromo derivative **2** is obtained in two steps from *o*-xylene by reaction with bromine[23] and side-chain bromination of the methyl groups with *N*-bromosuccinimide[24,25] (**2**, overall yield 25%, mp 88 °C). The substitution of the bromomethyl groups with potassium dodecyle alcoholate must be carried out in a nonnucleophilic protic solvent (*t*-BuOH) to avoid side reactions (**3**, yield 60%, mp 42–43 °C). The corresponding dicyano derivative **4** is obtained in 60% yield by reacting **3** with CuCN in dimethylformamide (**4**, mp 82 °C). The free ligand I_a is synthesized by refluxing **4** in 1-(dimethylamino)-2-propanol[26] (yield 35% recrystallized from hexane). The metal complexes are obtained in two steps by treating **4** by the lithium salt of 1-pentanol to give the dilithium derivative of the phthalocyanine,[27,28] which is transformed into the divalent metallic complex by reaction with the corresponding anhydrous salt. The copper complex I_b may be also prepared directly from **4** by reaction with an excess of CuCN. The final products as well as the intermediates have all been characterized by microanalysis and ^{13}C NMR, ^1H NMR, and UV–visible absorption spectra. These determinations were in agreement with the proposed structures.[29]

The copper complex I_b has been studied by differential scanning calorimetry (DSC) and polarizing microscopy. On heating, a transition is observed at 53 °C. The solid crystalline phase present at room temperature is transformed into a viscous birefringent liquid. This mesophase is apparently stable up to about 300 °C, where the product starts to decompose. The structural parameters of this thermotropic liquid crystal have been determined at 80 °C from X-ray diffraction experiments. In the small-angle region, at least four sharp Bragg reflections are observed. Their spacings are exactly in the ratio $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$. This is in perfect agreement with a two-dimensional hexagonal lattice. Most of the discotic mesophases show this same arrangement of the columns.[3–8]

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(29) Anal. Calcd for **3**, $C_{32}H_{56}O_2Br_2$: C, 60.76; H, 8.92; O, 5.06; Br, 25.26. Found: C, 60.66; H, 8.79; O, 5.02; Br, 25.63. ^1H NMR (CCl_4, 60 MHz) δ 1.2 (br m, 46 H, paraffin), 3.3 (m, 4 H, OCH_2), 4.25 (s, 4 H, $PhCH_2O$), 7.4 (s, 2 H, Ph). Anal. Calcd for **4**, $C_{34}H_{56}O_2N_2$: C, 77.81; H, 10.75; N, 5.34. Found: C, 77.82; H, 10.91; N, 5.16. ^1H NMR (CCl_4, 60 MHz) δ 1.2 (br m, 46 H, paraffin), 3.35 (t, 4 H, OCH_2), 4.3 (s, 4 H, $PhCH_2O$), 7.55 (s, 2 H, Ph). Anal. Calcd for I_a, $C_{136}H_{226}O_8N_8$: C, 77.74; H, 10.84; O, 6.09; N, 5.33. Found: C, 77.68; H, 10.78; O, 6.37; N, 5.62. ^1H NMR (CCl_4, 60 MHz) δ 1.2 (br m, 184 H, paraffin), 3.65 (br s, 16 H, OCH_2), 4.8 (br s, 16 H, $PhCH_2O$), 8.4 (br s, 8 H, Ph); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.0 (Me), 22.6, 26.5, 29.3, 29.7, 29.8, 30.1, 31.9 (paraffin), 71.2 71.3 (OCH_2, OCH_2Ph), 122.5, 135.2, 138.8, 148.8 (Ph). Anal. Calcd for I_b, $C_{136}H_{224}O_8N_8Cu$: C, 75.52; H, 10.44; O, 5.92; N, 5.18; Cu, 2.94. Found: C, 75.19; H, 10.08; O, 5.91; N, 5.77; Cu, 3.05. ^1H NMR (CCl_4, 60 MHz) δ 1.2 (br m, 184 H, paraffin), other peaks not observed due to paramagnetic copper ion. The UV spectra of I_a and I_b are strongly concentration dependent. This indicates some aggregation process.

Moreover, the distance found between neighboring columns (d = 34 Å) is quite in accordance with the expected molecular parameters of the constituting molecules. In the large-angle region, X-ray diffraction measurements also show two broad and diffuse rings. The first one corresponds to a spacing of 5 Å, which is characteristic of paraffinic moieties in a disordered state. The second ring at 3.8 Å is presumably related to the stacking of the macrocyclic subunits within the columns. The density of the complex I_b has been measured by a flotation technique in binary mixtures water/dimethylformamide ($\rho = 0.98 \pm 0.01$ g cm^{-3}). Knowing the periodicity of the hexagonal lattic previously determined, it is possible to calculate the mean stacking distance of the molecules along the axis of the columns. The value of 3.7 Å which is found in that way is in good agreement with the distance obtained from the X-ray patterns. The structure of the mesophase seems to remain unchanged from about 60 to 300 °C. As far as we know no other discotic phase is stable over such an extended range of temperature.

In conclusion, a new type of discotic mesophase has been prepared and characterized. Metallophalocyanine subunits are used to constitute their rigid core. Doped liquid crystals have been prepared by recrystallizing the substituted phthalocyanine from heptane containing small amounts of iodine. Preliminary electron spin resonance measurements indicate a good mobility of the charge carriers inside each column. Conductivity studies are under progress to further elucidate the electrical properties of these new mesophases.

Acknowledgment. CNRS and PIRDES are acknowledged for their financial support. Mrs. Pouyet and Mr Schneider are thanked for their helpful assistance.

Registry No. Ia, 82731-99-5; Ib, 82732-00-1.

Electron Transmission Spectroscopy of 1,3,5-Hexatriene: Isomeric Differences in π^* Orbital Energies

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We report here the observation of a large (0.55 eV) difference in the energies of the second π^* anion states of *cis*- and *trans*-1,3,5-hexatriene. This finding is of particular interest since photoelectron spectroscopy indicates that each of the three π ionization potentials (IP) of the two isomers agree respectively to within 0.10 eV.[1] Similarly, optical spectroscopy has revealed little difference in those $\pi \rightarrow \pi^*$ excitation energies of the two isomers which have been observed.[2]

In the present investigation we employ electron transmission spectroscopy (ETS)[3] to determine the gas-phase electron affinities (EA) of *cis*- and *trans*-hexatriene.[4] In Figure 1 we display the electron transmission spectra of these compounds, plotting the derivative of the electron beam current passing through the gas cell as a function of electron impact energy. In the derivative format the vertical attachment energies, that is, –EA, correspond to the vertical midpoints between adjacent dips and peaks. Within the context of Koopmans' theorem these electron affinities correspond to the negatives of the energies of the unoccupied orbitals, in the same way that the IP's are related to the energies of the filled orbitals. The energy resolution in this study is ≈0.04 eV, and the relative EA's should be accurate to ±0.03 eV.[5]

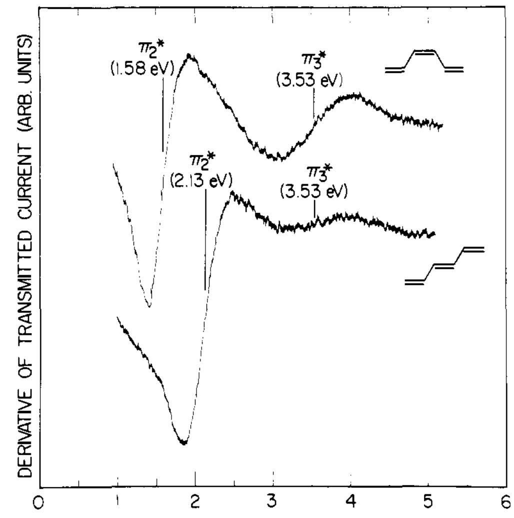

Figure 1. Derivative of transmitted current as a function of electron energy in *cis*- and *trans*-1,3,5-hexatriene. The vertical lines indicate the most probable attachment energies.

As shown in Figure 1, two anion states are observed in each molecule. From simple molecular orbital considerations one expects three low-lying π^* orbitals and hence three anion states. The energies of anion states in ethylene and butadiene[6] suggest that the ground-state anion of hexatriene is stable and hence inaccessible to study by ETS. We therefore assign the two observed features in the spectra to the second and third anion states, $^2B_1$ and $^2A_2$ for the cis species, assuming a planar C_{2h} structure, and ^2A_u and ^2B_g for the trans C_{2v} structure.

The most striking difference between the ET spectra of the two isomers is that the energy of electron attachment into the b_1 orbital of the cis isomer is 0.55 eV lower than that of the corresponding a_u orbital of the trans isomer.[7] To aid in the interpretation of these results it is useful to refer to the π^* MO's of the cis isomer (Chart I).[8]

Of the three π^* MO's, the $b_1(\pi^*_2)$ orbital has the largest charge densities on the C_2 and C_5 atoms. We propose therefore that the stabilization of the π^*_2 orbital of the cis isomer relative to that of the trans isomer is due to the C_2–C_5 bonding interaction. However, since the second π MO's also have substantial coefficients on C_2 and C_5, this picture would lead one to expect a sizable energy difference in the second π IP's of the two isomers, in contradiction to experiment. This objection is resolved, we contend, by noting that the anion wave functions are much more diffuse than those in the neutral molecule, greatly enhancing long-range interactions.

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† John Simon Guggenheim Memorial Fellow.

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