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PRELIMINARY COMMUNICATION

A liquid-crystalline cyclam derivative

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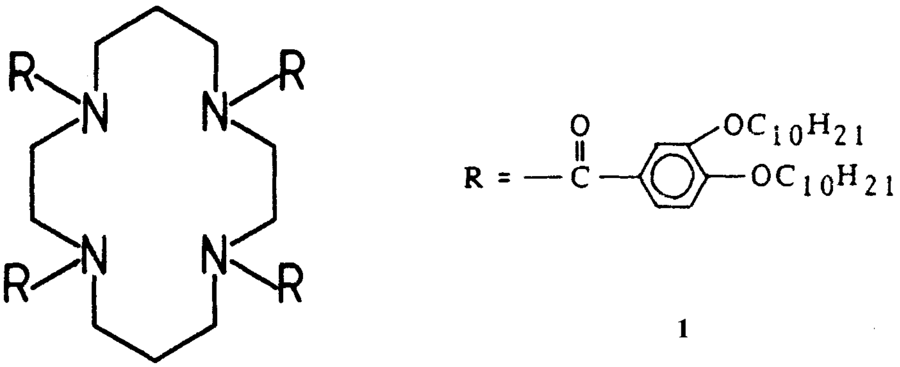
The first example of a liquid-crystalline tetraacylated cyclam (1,4,8,11-tetraazacyclotetradecane) derivative is described. Its mesomorphic behaviour, presumably discotic, is characterized by means of polarizing microscopy and D.S.C. measurements.

The first liquid crystals with saturated macrocyclic cores were described by Lehn *et al.* [1], they form columnar mesophases of the D_{hd} type. With respect to the hexacyclene (1,4,7,10,13,16-hexaazacyclooctadecane) derivative described this work was continued by Ringsdorf *et al.* [2], who also introduced some new types of substituents. All of those examples of the one chain type, i.e. where one side chain is connected to the macrocyclic core by amide groups, show discotic phases exhibiting mostly D_{hd} mesomorphism. With a cyclam core no liquid crystallinity could be observed by the authors. The relevant tetrasubstituted alkanoyl- and alkoxybenzoyl derivatives are crystalline while the 3,5-bis(alkoxy)benzoyl- and the 3,4,5-tris(alkoxy)-benzoyl derivatives are described as glassy [2]. In this preliminary communication, the 3,4-bis(alkoxy)benzoyl substituent was chosen for a reason, which will be discussed later, and gave the mesomorphic compound **1**.



1

The synthesis was performed by treating the azacrown (R = H, Fluka) with 4·5 equivalents of 3,4-didecyloxybenzoylchloride in dimethylformamide in the presence of dimethylaminopyridine for 12 h at 80°C, in analogy with the literature [2]. The reaction product was purified by recrystallization twice from acetone, followed by column chromatography (MPLC). The purity of the resulting white solid (yield: 51

per cent) was checked by GPC and elemental analysis: $C_{118}H_{200}N_4O_{12}$ (1866, 94). Calculated: C 75·92 per cent, H 10·80 per cent, N 3·00 per cent, O 10·28 per cent; found: C 75·84 per cent, H 10·79 per cent, N 3·15 per cent, O 10·22 per cent. The spectral data (IR, ^{1}H N.M.R. and MS) are in agreement with the assigned structure. ^{1}H N.M.R. ($CDCl_3$): δ (ppm) = 0·88 (t; 24 H), 1·27 (m; 96 H), 1·44 (m; 16 H), 1·79 (m; 16 H), 2·09 (m; 4 H), 3·51 (m; 8 H), 3·72 (m; 8 H), 3·99 (t; 16 H), 6·81, 6·91 (m; 12 H). The peaks of the aromatic protons at 6·81 and 6·91 ppm, those of the cyclam protons at 3·72, 3·51 and 2·09 are remarkably unresolved and broad. MS: 1865.

The equipment used in the characterization was as follows; IR: Bio Rad/Digilab FTS 40. ^{1}H N.M.R.: Bruker 500 MHz. MS: Varian. GPC: Waters ALC 200, two 0·5 m PL-gel columns (Polymer Laboratories, 5 μm particle diameter, 10 and 20 nm pore width, eluent: THF, elution rate 0·5 ml/min. MPLC: Labomatic Labomat VS-200, UV detector, 1 × 539 mm column (Labochron-gel, 20–45 μm particle size, 60 Å pore width), eluent: hexane/ethylacetate 1 : 1. D.S.C.: Perkin–Elmer, DSC 7; temperatures were taken from peak maxima; the values given are average values of at least three measurements (with different heating and cooling cycles). Polarizing microscopy: Leitz, Laborlux 12-Pol, Mettler hot stage FP 82, photoautomat Wild MPS 45/51 S. Both D.S.C. measurements and polarizing microscopy of the dry product were performed as described previously [15]. As could be seen by repeated water vapour development during the first observations under the microscope, compound **1** is hygroscopic. To obtain a really dry product the compound was freeze dried from benzene solution and kept under an inert gas atmosphere.

D.S.C. measurements and polarizing microscopy reveal a multiple transition behaviour. The second and subsequent heating cycles of the D.S.C. measurements (2°C/min; cf. figure 1 (*a*), especially after quenching to room temperature, exhibit a broad peak at 71·8°C (ΔH = 4·34 kJ mol^{-1}) and an unresolved double peak at 93·5°C and 95·8°C (ΔH = 7·05 kJ mol^{-1}). On heating the sample after several days (cf. figure 1 (*c*)) the shoulder at 95·8°C does not appear. Furthermore an unpronounced shoulder can be observed at 75·7°C. In all heating runs a sharp peak appears at 132·4°C (ΔH = 4·80 kJ mol^{-1}). On cooling (2°C/min; cf. figure 1 (*b*)) a sharp endotherm is observed at 130·6°C (ΔH = $-$4·80 kJ mol^{-1}). In the region between 88°C and 62°C several broad and very small peaks appear. It is not clear whether this indicates very slow multiple transition processes and why this occurs only on cooling.

Under the polarizing microscope, on cooling below 130°C, a mesophase appears with pseudo focal conic fan-shaped or streak-like domains and homeotropic areas (cf. figure 2 (*a*)). On further cooling, the fan-shaped texture of the focal conic domains disappear at 82°C and concentric arcs can be observed (cf. figure 2 (*b*)). At 78°C the concentric arcs disappear and crossed stripes are formed in the homeotropic areas (cf. figure 2 (*c*)). On heating, the rings reappear between 94°C and 96°C. On further heating the pseudo focal conic texture shows very pronounced linear streaks (cf. figure 2 (*d*)). The clearing point is 132°C.

The structure of the mesophase between 95·8°C and 132·4°C is still unknown. It should be discotic columnar considering the texture and in analogy to the mesogens with larger azacrown cores. Below this mesophase crystallinity could not be observed. The formation of concentric arcs in the pseudo focal conic texture until now is known only for S_E phases [3] or from, to our knowledge the still unidentified, discotic phases of certain triphenylenes (phase D_0) [4] and of tetrabenzocyclododecatetraene derivatives [5]. Only for chiral triphenylene esters can the pseudo focal conic textures with

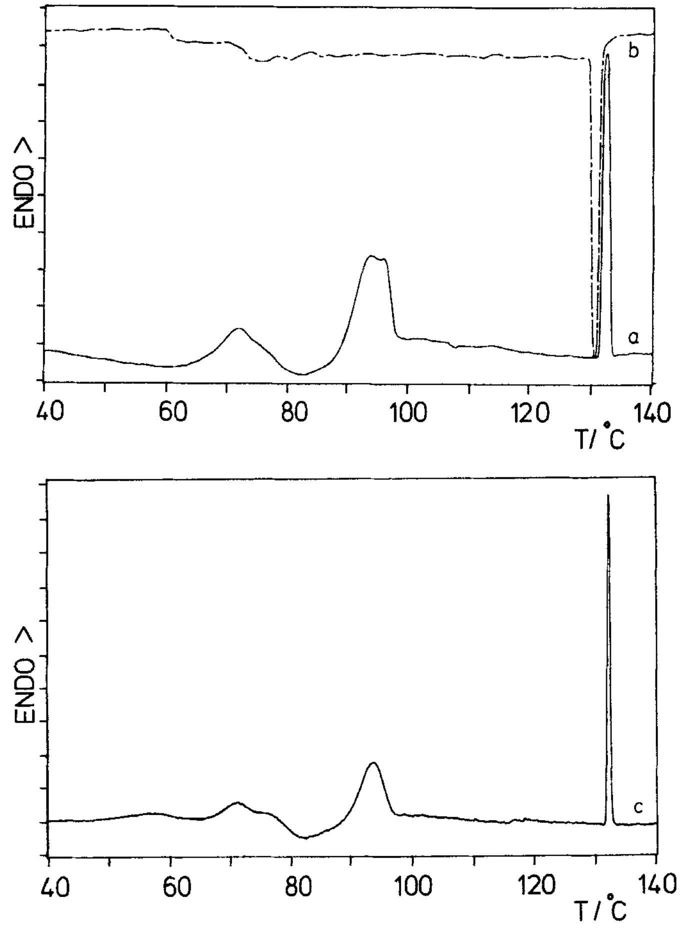
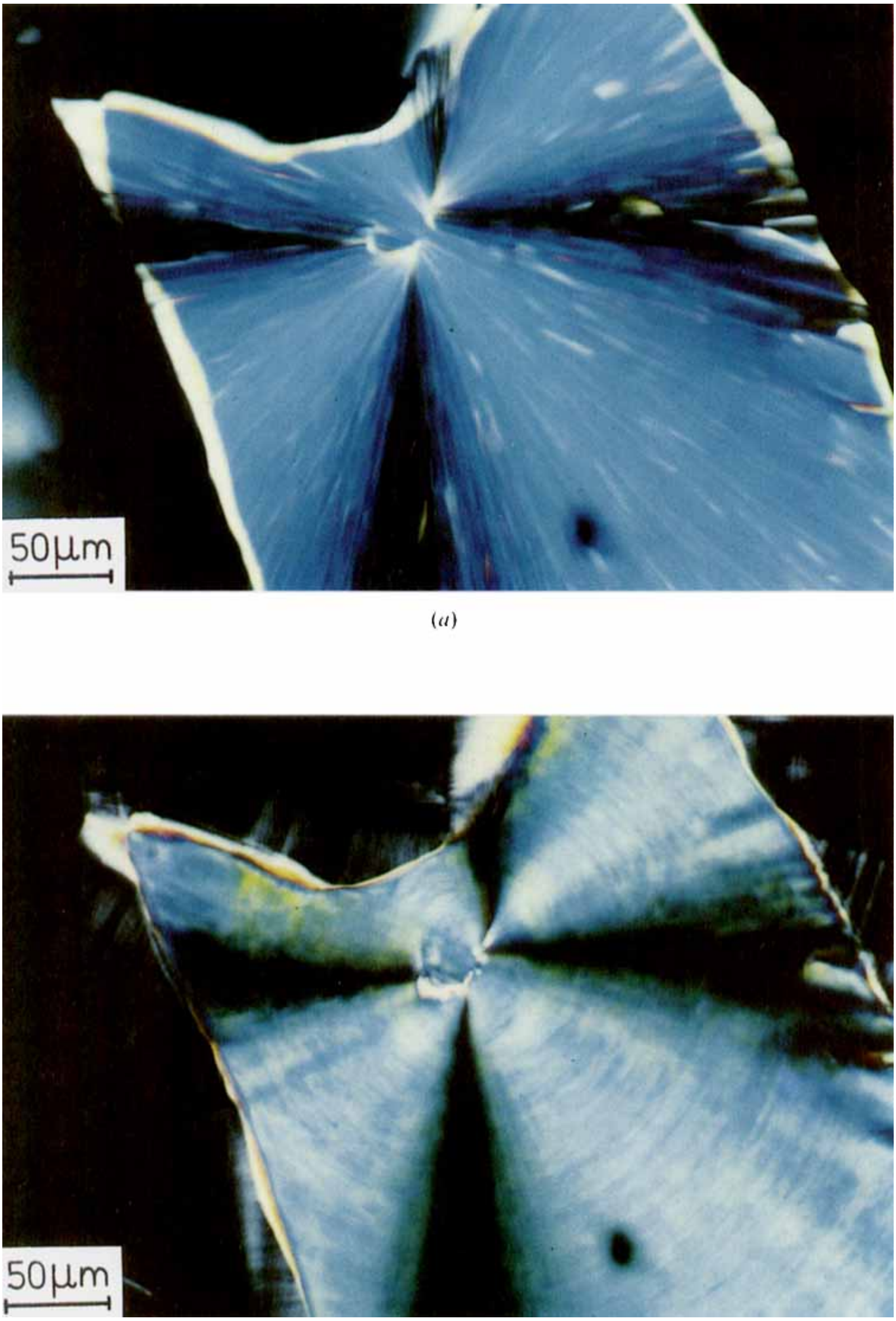


Figure 1. D.S.C. thermogram of dry **1**, (*a*, *b*) second heating and cooling (2°C/min), and (*c*) heating after several weeks (2°C/min).

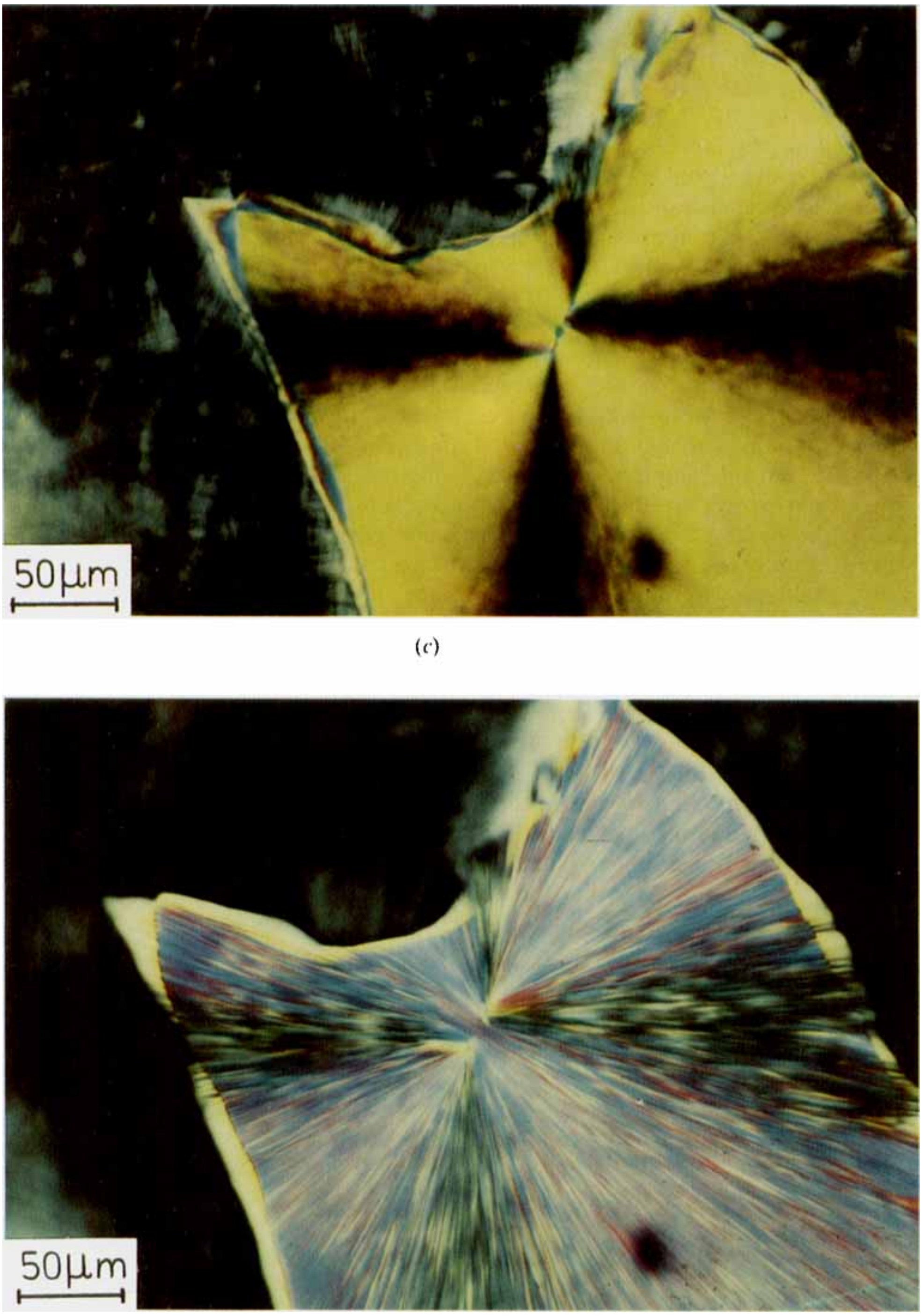
concentric arcs be related to clearly identified phases [6]. A S_E phase seems to be unlikely here because of the disc-like shape of compound **1**. Thus the question remains, whether the appearance of concentric arcs in the textures of chiral disogens is only due to a textural change within the same phase or whether it indicates the existence of a distinct mesophase or can perhaps be regarded as a transition phenomena between two phases. Only future X-ray measurements and other investigations can shed light on this situation. In this context the question arises as to whether in the region of the small and uncharacteristic low temperature phase transitions different sterical isomers, as they are thinkable in analogy to fixed structures of the unsubstituted azamacrocycle [8], play a role. The reduced flexibility of the long chain subsituted central core in solution seems to be demonstrated by broad absorptions of the core and core-neighboured protons in the ^{1}H N.M.R. spectrum.

With respect to the low temperature phases the phase behaviour is remarkably influenced and more complicated after the absorption of water, which is known to occur with the unsubstituted cyclam (R = H) [7]. Further experiments will be necessary to elucidate whether and to what extent stereo- and configurational isomers of hydrates



(a)

(b)



(c)

(d)

Figure 2. Optical texture of **1**, between crossed polarizers, (*a*) after cooling from the isotropic melt to 110°C, (*b*) after cooling to 82°C, (*c*) after cooling, at 65°C, and (*d*) on heating at 110°C.

[7] can play a specific role here. The range and the clearing point (132°C) of the highest mesophase is not affected.

The question remains as to why cyclam derivatives synthesized earlier [2] do not exhibit any mesophase. Certainly, four chain discotics [9] especially with metal complex cores [10, 11] are known. But four alkanoyl- or alkoxybenzoyl groups attached to a cyclam core do not seem to fulfil, in analogy with many other cases involving conventional cores, one of the basic conditions of discotic mesomorphism namely an optimal coverage of the peripheric area of a central core by lateral chains [12]. With respect to the bis- or tris(alkoxy) substituted benzoyl ligands the situation seems to be more complex. The 3,4,5-tris(alkoxy)benzoyl group is known to be an efficient mesogen inducing part of phasmidic [13], discotic mesogens [14] or associated discogens [15]. With cyclam as the central core, the resulting molecule possesses twelve lateral alkyl chains. The largest number of side chains described up to now for discotics is nine [12]. Not only a minimum but also a maximum number of lateral chains seems to exist for each type of central core. Beyond this the density of alkyl groups would be too high for an optimal coverage of the peripheric area, and would disturb discotic mesomorphism. Even crystallinity seems to be prevented in this way. This should explain why the tris(alkoxy)benzoyl substituted cyclam derivative (and of course the hexacyclene derivative of the same type with eighteen side chains) is described only as glassy [2]. Lowering the chain number by introducing dialkoxy substituted benzoyl groups should enhance the chance for discotic mesomorphism. Surprisingly at a first glance, the 3,5-bis(alkoxy)benzoyl derivative with the cyclam core, exhibiting now eight side chains, does not show any mesomorphism and is also described as glassy [2]. However we know that the 3,5-bis(alkoxy)benzoyl group, compared with its 3,4-isomer, seems to play a different role in the class of phasmidic and biforked mesogens [16, 17]. Furthermore the 3,4,5-tris(alkoxy)benzoate [15] and the 3,4-bis(alkoxy)benzoate of cis, cis-phloroglucitol form disc-like associates, whereas the 3,5-bis(alkoxy)benzoate derivatives do not [18]. With this knowledge this work was started in the hope of finding a liquid-crystalline cyclam derivative.

It seems to be interesting to investigate related compounds with especially smaller azacrownether units, to vary the linkage groups between core and sidegroups and to synthesize polymeric analogues. This work is in progress and the results will be published in subsequent papers.

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