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To cite this Article Zheng, Hanxing , Carroll, Patrick J. and Swager, Timothy M.(1993) 'The development of polar discotic metallomesogens Vanadyl 1,3-diketonate complexes', Liquid Crystals, 14: 5, 1421 — 1429

To link to this Article: DOI: 10.1080/02678299308026454

URL: http://dx.doi.org/10.1080/02678299308026454

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LIQUID CRYSTALS, 1993, VOL. 14, NO. 5, 1421–1429

The development of polar discotic metallomesogens
Vanadyl 1,3-diketonate complexes

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The dependence of mesomorphism of 1,3-diketonate vanadium-oxo (vanadyl) complexes on the number of side chains was investigated. These complexes have a large dipole normal to the disc plane and are under investigation in an effort to generate discotic phases with polar order. Relatively complex phase behaviour is observed when the vanadyl 1,3-diketonate complexes are appended with four phenyl groups with two octyloxy or decyloxy side chains each for a total of eight side chains. These complexities are most likely related to the order/disorder associated with the polar vanadyl group. Vanadyl 1,3-diketonate complexes with four side chains were prepared by replacement of two of the phenyl groups with methyl or trifluoromethyl groups, and these complexes displayed only crystal phases. Complexes with two trialkyloxy phenyls and two dialkyloxy phenyls were synthesized and found to display a very stable D_{hd} phase. The presence of additional alkyloxy groups was found also to promote a linear chain structure, (i.e. --V=O--V=O--), in the crystal phase.

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1. Introduction

New liquid crystals with polar mesogens are of interest as a means of generating materials which can interact strongly with electric fields. Polar mesogens may also be used to produce new materials with ferroelectric behaviour, given that bulk dipolar order can be established. In the quest for new achiral ferroelectric liquid crystals, columnar phases of pyramid shaped macrocyclic organic mesogens have been investigated [1]. The pyramid shape of the mesogen in these systems promotes a head-to-tail organization and hence can create polar order within a given column. There have been a number of elegant studies on these organic pyramidal liquid crystals [1], but ferroelectric behaviour has not been demonstrated. This fact is probably due to small dipoles and large activation energies for redirecting the dipoles, since recent theoretical studies indicate that ferroelectric phases should exist [2].

As a result of these difficulties associated with prospective ferroelectric organic discotic systems, we have been focusing on inorganic vanadium-oxo (vanadyl) complexes. The vanadyl group is attractive since it often exhibits a square pyrimidal structure and has a large directional dipole associated with the V=O bond [3]. In addition, work in this laboratory has recently shown that liquid crystalline vanadyl complexes can arrange in a linear chain structure (i.e. --V=O--V=O--), thereby creating local polar order between mesogens [4]. We report herein our results on a series of discotic 1,3-diketonate vanadyl complexes for which we explore the effects of the number of side chains on the mesomorphic behaviour.

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2. Results and discussion

2.1. *Vanadyl 1,3-diketonate complexes with eight side chains*

We began our studies on complexes I in which the 1,3-diketonate groups are appended with four dialkyloxy substituted phenyl groups to give a total of eight side chains (see the structure) since the analogous copper complexes had been previously studied and found to be mesomorphic [5]. Additionally, we considered these complexes as good candidates to form linear chain structures since vanadyl acetoacetonate is known to coordinate ligands *trans* to the apical oxo [3]. The position of the V=O stretching band in the infrared spectrum is very diagnostic for the presence of linear chain structures or the coordination of axillary ligands [3, 4], and this band undergoes a characteristic shift to lower energy ($<900\,\mathrm{cm}^{-1}$) with linear chain formation. For all derivatives of I, the V=O stretching bands were determined to be at $994\,\mathrm{cm}^{-1}$. The band assignment was confirmed by synthesis of $V{=}O^{18}$ labelled complexes which gave bands at $951\,\mathrm{cm}^{-1}$, and is in agreement with the calculated value. Variable temperature infrared studies from room temperature to the isotropic phase showed the V=O band to be temperature independent. Hence, we conclude that all derivatives of I are monomeric in all of their phases.

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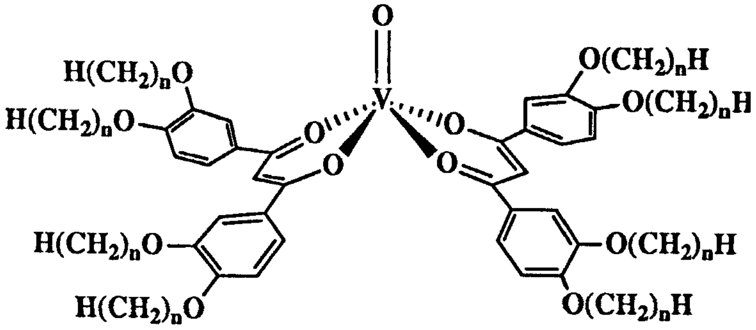
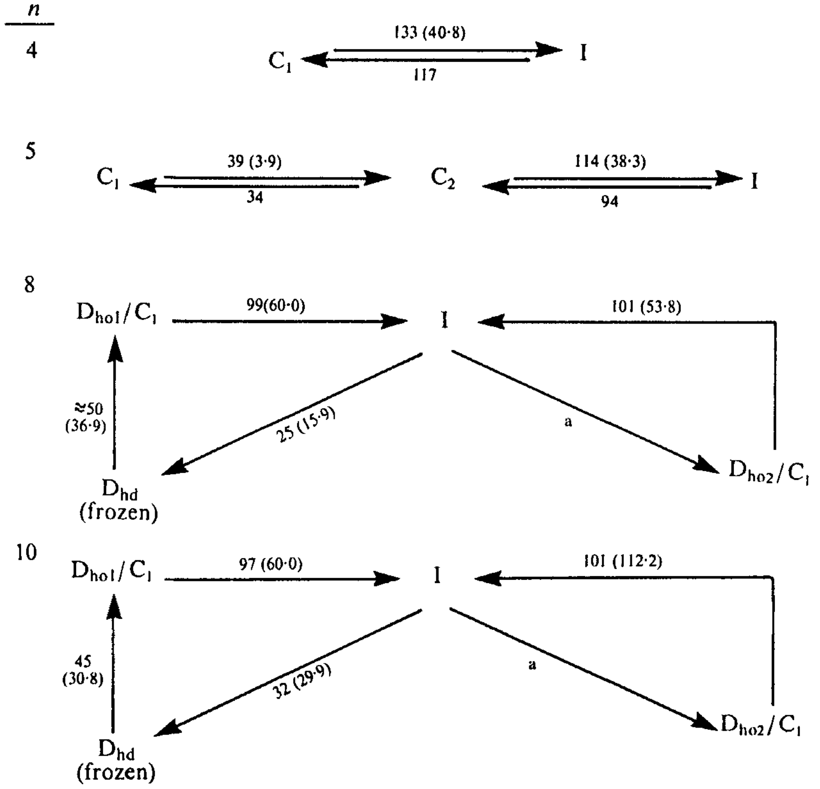


I, $n=4, 5, 8, 10$

The DSC thermograms of the first heating are different from those of subsequent heatings for all of the derivatives of I, indicating that the crystal phase produced from solution recrystallization is different from that obtained from the melt. DSC analysis indicated that all of the complexes display multiple phase transitions, and the calorimetric data as well as the phase assignments are shown in scheme 1.

Cooling I ($n=4, 5$) from the isotropic state produced crystalline (C_1) phases with sharp linear grain boundaries, and for $n=4$ the C_1 phase exhibited a biaxial interference figure under conoscopic observation. Solution recrystallized samples of $n=4$ gave single crystals satisfactory for an X-ray structure determination. Hence, in an effort to better understand the solid state organizations exhibited by these mesogens, we performed an X-ray structure determination as is shown in figure 1. This structure was refined to 7·6 per cent and further refinement was impeded by the large unit cell and the large thermal parameters of the two terminal carbons of the butyl chains. As can be seen from the structure in figure 1, the crystal phase has a tilted columnar structure with antiferroelectric order between vanadyl groups. The tendency toward an antiferroelectric organization suggests that additional geometric bias and/or linear chain formation may be necessary to produce polar order in the columns. Also shown in figure 1 is a view of a single molecule looking down the V=O axis which shows the packing of the side chains as well as their thermal ellipsoids.



a = cool to 60°C, then heat to 75°C and hold

Scheme 1. Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) in parentheses.

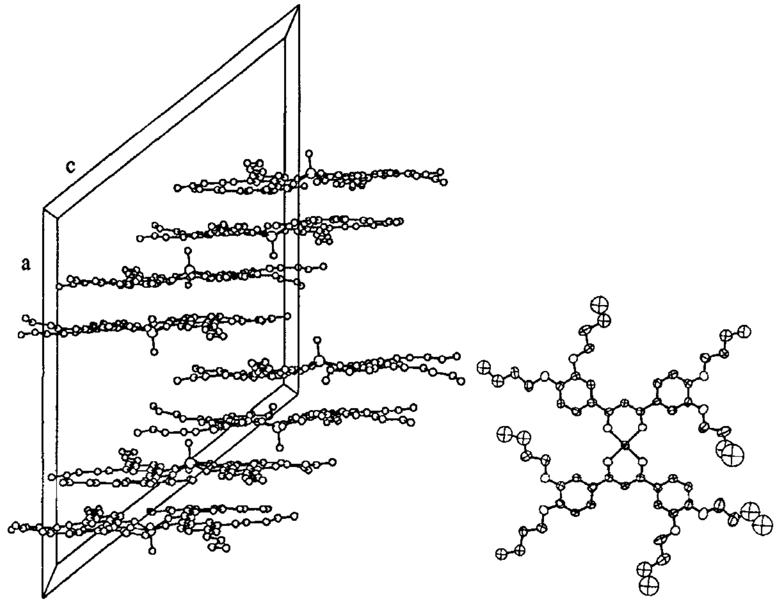


Figure 1. X-ray crystal structure of I ($n=4$). The unit cell, shown left is viewed down the *b* axis and the lattice constants are $a=29{\cdot}626(4)$ Å, $b=21{\cdot}420(3)$ Å, $c=24{\cdot}875(5)$ Å and $\beta=128{\cdot}66(1)°$. The view of a single molecule looking down the V=O bond is shown right with thermal ellipsoids drawn at 30 per cent probability.

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The complexes I ($n = 8, 10$) were found to exhibit complex polymorphism with very limited mesophase stability (see scheme 1). DSC analysis at scan rates as slow as 2°C min^{-1} shows that the transition from the isotropic phase to the monotropic phase of both complexes undergoes large supercooling (c. 40°C). Similar cooling of I ($n = 8, 10$) from the isotropic phase in an optical hot stage produced patterns which when viewed with a polarizing microscope are best described as sanded textures. Supercooling of this nature is often associated with transitions to crystal phases. However, as is shown for $n = 10$ in figure 2, X-ray diffraction shows that the resultant monotropic phase does not have crystalline order. The single low angle peak is characteristic of a hexagonal columnar lattice and is hence assigned as the (100) reflection, thus giving a intercolumnar distance of 38·6 Å. The other low angle peak at 16·4 Å is approximately where the (200) of a hexagonal lattice is expected. At 4·2 Å there is a broad diffuse peak which is characteristic of scattering from the molten side chains. These X-ray results are consistent with D_{hd} organization, however, this phase is not fluid. Hence, this phase is best described as a 'frozen D_{hd}' phase.

The frozen D_{hd} phase is stable for indefinite periods of time at room temperature, but reheating causes crystallization (see scheme 1). X-ray diffraction of I ($n = 10$), (see figure 3), reveals that there is coexistence of an unidentified crystal phase and a hexagonal ordered phase, D_{ho1}, throughout the region from 40°C to 96°C. The D_{ho1} has the same lattice constants in the low angle region as the frozen D_{hd} phase but has two additional wide angle diffraction peaks at 4·24 Å and 4·06 Å. The numerous small peaks in the X-ray diffraction from 7–20°(2Θ) are the result of a small amount of a crystal phase C_1 which is also present, with the relative amount of the crystal phase decreasing at higher temperature. The fact that the D_{ho1} phase has the same intercolumnar separation as the frozen D_{hd} phase suggests that directional disorder of the vanadyl groups may cause the unusual phase behaviour.

Experiments on I ($n = 8, 10$) with a polarizing microscope revealed that an additional phase may also be formed at higher temperatures. This phase exhibits a

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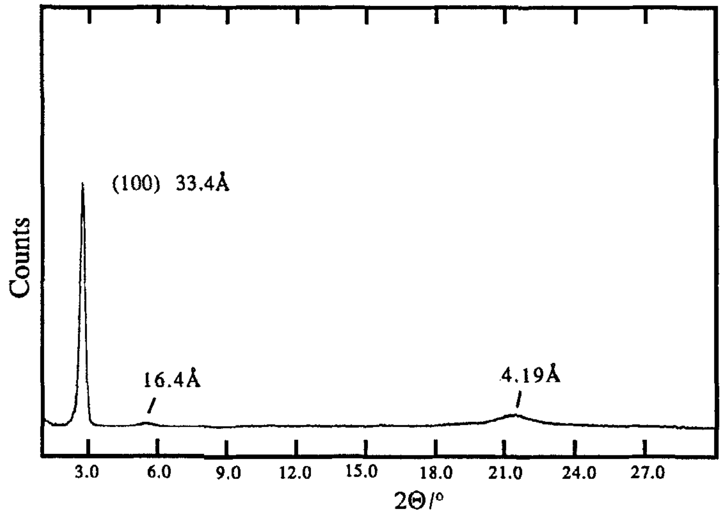

Figure 2. Monotropic frozen D_{hd} phase of I ($n = 10$) at room temperature.

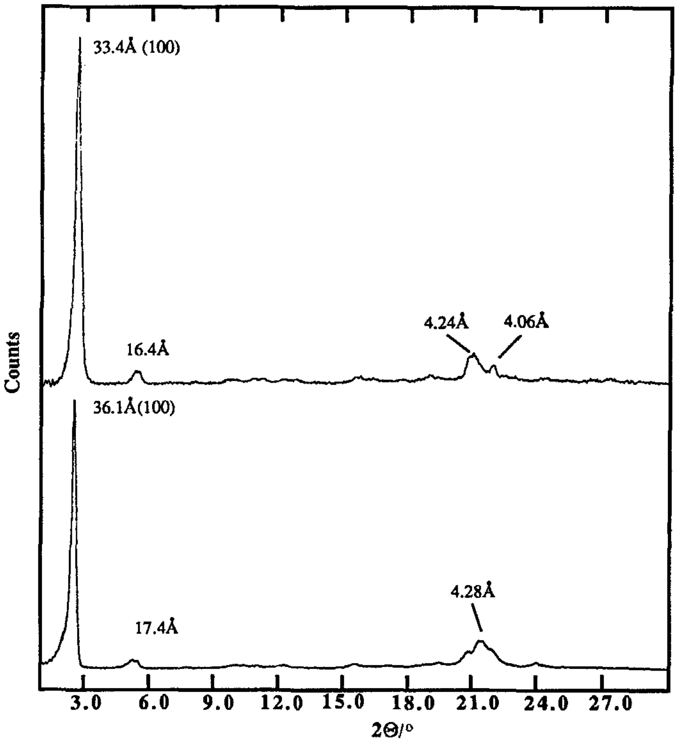

Figure 3. X-ray diffraction from the D_{ho1} phase (top) at 76°C and the D_{ho2} phase (bottom) 25°C of I ($n = 10$).

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starburst texture shown in figure 4 for I ($n = 8$). To produce this phase, the isotropic phase is cooled to 60°C then reheated to about 75°C, at which point this phase slowly develops from the isotropic phase. In the early stages of development, this texture can clearly be seen to consist of many small fibrils with a common origin. The fibrils are of variable width and are highly curved with rounded edges. As can be seen from figure 4, the starburst patterns exhibit faint extinction brushes which are approximately aligned with the polarizers. This indicates that the molecules are not tilted since it is likely that the columns are aligned with the fibril axis and the fibrils clearly extend radially outward from the origin. This phase is stable at room temperature for extended periods of time but exhibits no fluidity at this temperature. Minor fluidity is exhibited at temperatures close to the isotropic phase. X-ray diffraction (see figure 3) of this phase shows it to be an hexagonally ordered phase, D_{ho2},with a (100) peak at 36·1 Å and a (200) at 17·4 Å which corresponds to a larger intercolumnar spacing than that of D_{ho1}. A small amount of the C_1 phase is also present.

We note that the D_{ho1} and D_{ho2} phases described herein have somewhat different organization than a typical D_{ho} phase which is a result of the non-planar nature of the mesogen. The fact that there are broad multiple peaks around 4 Å suggests that the mesogens are not packing in a purely head-to-tail or head-to-head fashion but probably in a more random structure. In addition if I ($n = 8, 10$) were to pack in a highly ordered antiferroelectric structure, we would expect, based on our crystal structure, that such a crystal phase would have tilted columns, but the D_{ho2} phase does not exhibit a tilted structure.

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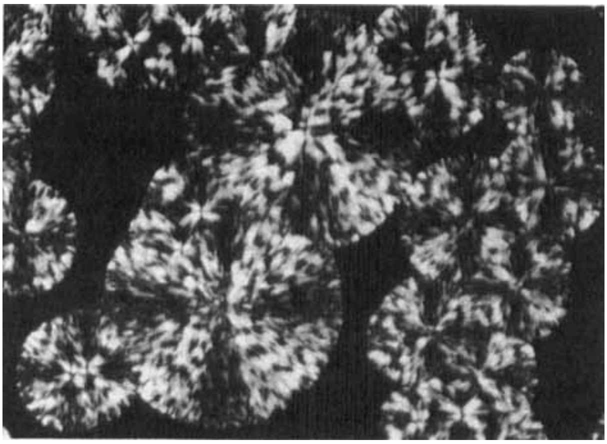
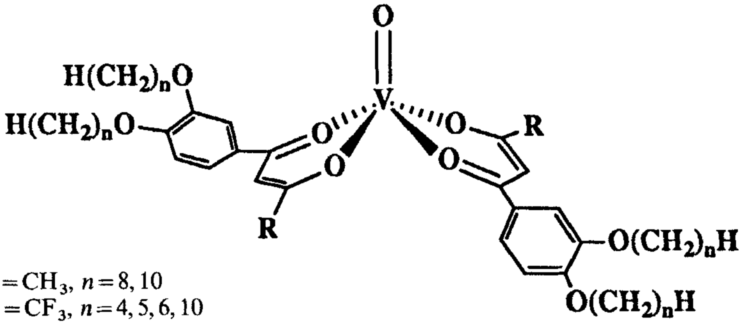


Figure 4. Starburst texture of the D_{ho2} phase of I ($n=10$) at 75°C.

2.2. *Vanadyl 1,3-diketonate complexes with four side chains*

In an effort to obtain liquid crystals which display linear chain structures and/or more ideal phase behaviour, we synthesized II and III which are substituted with four side chains (see the structure). This modification seemed likely to provide improved phase behaviour since during the course of our investigations it was reported that a related vanadyl 1,3-diketonate complex with four side chains was mesomorphic [6]. Additionally, we considered that the unusual behaviour of I ($n=8, 10$) may be in part due to the bulky nature of these complexes which could result in kinetic problems in the directional ordering of the V=O group. Hence, complexes II and III should exhibit a lower viscosity toward organization of the V=O group. The electron withdrawing trifluoromethyl group in III was also investigated as a route to increase the affinity of the vanadium centre for an additional ligand, which should promote linear chain formation.

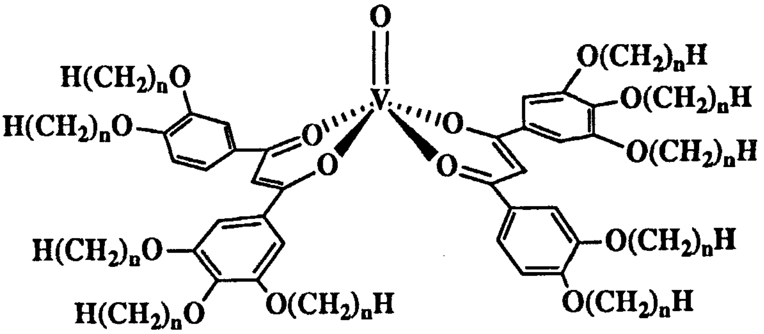


II, $R=CH_3$, $n=8, 10$
III, $R=CF_3$, $n=4, 5, 6, 10$

Unfortunately II and III are not mesomorphic and display only crystal phases. Analysis of the V=O stretching bands by infrared spectroscopy indicates a monomeric structure with V=O bands for II at 995 cm^{-1} and for III at 1003 cm^{-1} (O^{18}963 cm^{-1}).

2.3. *Vanadyl 1,3-diketonate complexes with ten side chains*

Having determined that fewer side chains did not lead to mesophase stabilization, we decided to prepare IV which has ten side chains (see the structure). This approach was prompted by other investigations in this laboratory which determined that 1,3,5-triketonate bimetallomesogens display mesomorphism with twelve side chains but not with eight [7]. Hence, given the slightly smaller nature of the 1,3-triketonate group, 10 side chains seems appropriate, and we have recently synthesized IV. The fact that additional side chains is needed is also apparent from the ORTEP (Oakridge Thermal Ellipsoid Program) of I ($n=4$) (see figure 1), which shows two voids around the mesogen which can be readily filled by the addition of two more side chains [8].



IV, $n=12$

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Upon synthesis of IV, we were surprised to find that the added alkyloxy groups promotes linear chain formation. The V=O stretching band in the crystal phase of IV was determined to be 898 cm^{-1} (O^{18}860 cm^{-1}), which is approximately 100 cm^{-1} lower than the other vanadyl 1,3-diketonate complexes discussed herein. The linear chain structure is also reflected in the colour of the complex which is green in solution and yellow in the solid state. The green colour is characteristic of the monomeric complex and the yellow indicates linear chain formation, and similar colour changes have been observed for other linear chain complexes [9].

The presence of the additional alkyloxy groups in IV was also found to stabilize the mesophase. As can be seen in scheme 2, IV displays mesomorphism over a wide temperature region without complexities such as supercooling. Cooling IV ($n=12$) from the isotropic phase produces a fluid phase with a pseudo focal conic texture shown

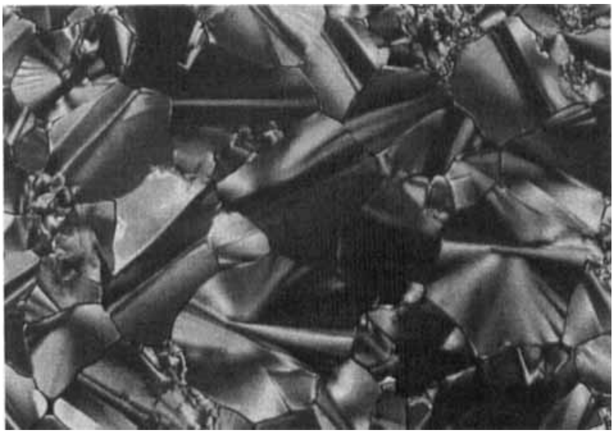

Figure 5. Pseudo focal conic texture of the D_{hd} phase of IV at 118°C.

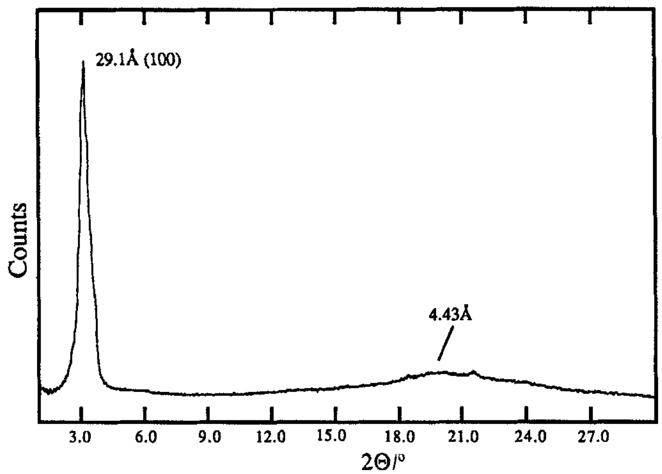

Figure 6. X-ray diffraction at 25°C of the D_{hd} phase of VI.

$$C_I \underset{14}{\overset{24\,(83\cdot3)}{\rightleftharpoons}} D_{hd} \underset{119}{\overset{122\,(8\cdot8)}{\rightleftharpoons}} I$$

Scheme 2. Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) in parentheses.

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in figure 5, indicating a D_{hd} phase. The D_{hd} assignment was confirmed by X-ray diffraction (see figure 6), which shows a strong (100) reflection at 29·1 Å corresponding to an intercolumnar distance of 33·6 Å and shows a broad diffuse diffraction at 4·43 Å which is due to scattering from the molten side chains.

Variable temperature infrared studies were performed in order to probe whether or not the linear chain phase is maintained in the mesophase. For IV ($n=12$), the V=O stretching band was found to shift to 992 cm^{-1} above 123°C when the complex is isotropic and shift to 985 cm^{-1} at 100°C when the compound is in the D_{hd} phase. Although the energy of the V=O band in the mesophase is reduced from that of the isotropic phase, the shift is much smaller than that observed in other linear chain mesophases [4, 8]. In addition, IV was observed to be green in the mesophase, suggesting a monomeric structure. Hence, if a linear chain is present in the mesophase it is very weak.

3. Conclusions

We have investigated the effect of the number of side chains on mesophase stability for a series of discotic vanadyl 1,3-diketonate complexes. Our results indicate that complexes with four side chains are not mesomorphic, complexes with eight side chains can display limited mesorphism with a non-ideal complex behaviour, and that complexes with ten side chains exhibit a D_{hd} mesophase which is stable over a wide temperature region. Additionally, we have determined that the addition of extra side chains promotes linear chain formation. The complex with ten side chains displays a linear chain structure in the crystal phase and possibly a weak linear chain structure in the D_{hd} phase. The fact that other researchers have found similar vanadyl 1,3-diketonate complexes to be mesomorphic with four side chains is surprising [6]. Our future reports will deal with additional mesophase characterization of IV and structural variations on this system, as well as polarization studies.

Elemental analysis of selected compounds†.

		Calculated (found)	
	n	C	H
I	4	68·30 (68·36)	7·95 (8·25)
	5	69·92 (69·40)	8·55 (8·61)
	8	73·35 (73·48)	9·82 (9·99)
	10	74·91 (74·57)	10·40 (10·79)
IV	12	76·50 (75·69)	11·13 (11·33)

† All compounds discussed were determined to be pure by elemental analysis.

4. Experimental

DSC investigations were carried out on a Perkin–Elmer DSC-7. Optical microscopy was carried out on a Leica polarizing microscope in combination with a Mettler FP 80HT/FP 82HT hot stage. X-ray diffraction studies were carried out on samples in capillary tubes with an INEL diffractometer with a 2 kW Cu–Kα X-ray source fitted with an INEL CPS-120 position sensitive detector and a home-built oven.

All ligands were synthesized by using literature procedures [5, 8]. The vanadyl complexes were synthesized in approximately 80 per cent yield by slow addition of aqueous solutions of $VO(SO_4)$ and K_2CO_3 to an ethanol solution of the ligand under nitrogen atmosphere. Repeated recrystallization from ethyl acetate/methylene chloride gave pure compounds as determined by elemental analysis (see the table).

We are grateful for funds provided by the National Science Foundation (DMR-9119045), the donors of The Petroleum Research Fund, administered by ACS, and The Office of Naval Research for their generous support of this work. We thank Professors J. E. Fischer and P. A. Heiney for the use of their X-ray equipment and Dr C. K. Lai for assistance.

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