π-Acceptors in Discotic Columnar Liquid Crystals; an Octasubstituted Bis(diphenylethane-1,2-dithiol)nickel Complex

Kazuchika Ohta,* Hiroshi Hasebe, Hiroshi Ema, Tetsuya Fujimoto, and Iwao Yamamoto

Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda 386, Japan

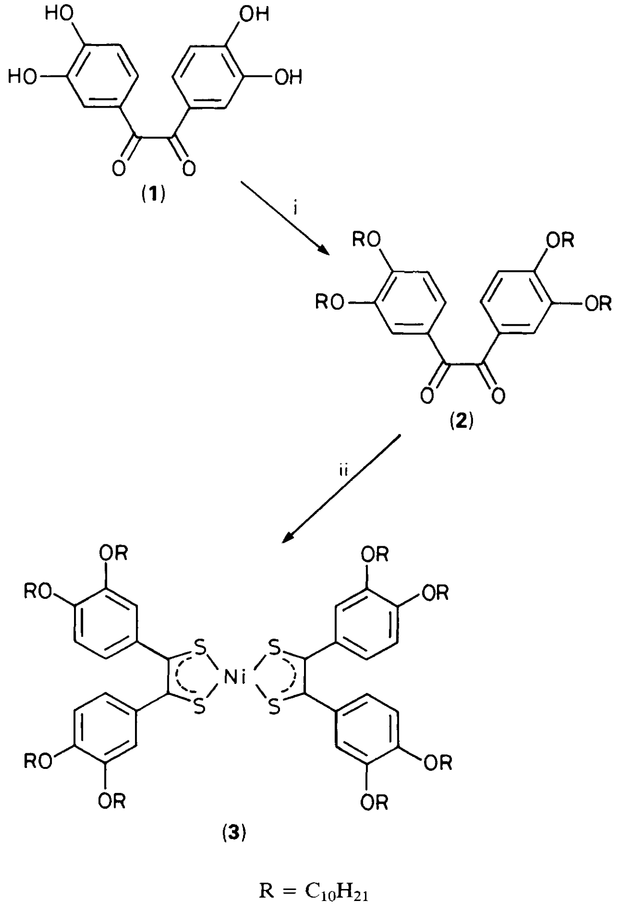
Bis[1,2-bis(3′,4′-di-n-decyloxyphenyl)ethane-1,2-dithiol]nickel, the reduction potential of which is −0.06 V (*vs.* saturated calomel electrode in CH_2Cl_2), has a hexagonal disordered columnar mesophase (D_{hd}) at 84—112 °C.

Dithiolene nickel complexes are well known to be good π-acceptors,[1] which can be applied to one-dimensional organic conductors.[2] For this application, the disc-like molecules must be stacked to form a column.[3] Discotic columnar mesogens give columnar structures for their mesophases. Mesomorphic tetrasubstituted dithiolene nickel complexes have been synthesized by two groups, Veber *et al.* and Ohta *et al.*, using different synthetic methods.[4] Veber *et al.* have recently denied the mesomorphism of these tetrasubstituted dithiolene nickel complexes.[5] Bis(β-diketonato)copper(II) complexes with four peripheral chains have been reported to have a discophase with columnar and layered structure or a discotic lamellar mesophase,[6] and bis(β-diketonato)copper(II) complexes with eight peripheral chains have been reported to have a true discotic columnar mesophase.[7] Therefore, in focusing our interest on obtaining a discotic columnar mesogen which is a π-acceptor, we have synthesized the octasubstituted dithiolene nickel complex (**3**), and found that it is a π-acceptor in discotic columnar mesogens. π-Acceptor columnar mesogens have not previously been reported. We now report the synthesis and physical properties of complex (**3**).

Complex (**3**) was synthesised as in Scheme 1, from the precursors (**1**) and (**2**) which were prepared by the method of Wenz,[8] by the method which we reported previously.[9] Complex (**3**) was purified by column chromatography [silica gel, toluene–n-hexane, 5:4 (v/v), R_f 0.56] and recrystallization from acetone–propan-2-ol to give greyish blue microcrystals, yield 41%, for which C and H elemental analyses were satisfactory. The ^1H n.m.r. and electronic spectra are consistent with the molecular structure.

The phase transformation behaviour of complex (**3**) was studied by microscopy and differential scanning calorimetry (DSC).

When the virgin microcrystals were heated from room temperature at a heating rate of 10 °C/min under the microscope, they were transformed at 84 °C into a viscous liquid



Scheme 1. Synthesis of the octasubstituted bis(dithiolene)nickel complex (**3**). *Reagents*: i, RBr, K_2CO_3; ii, P_4S_{10}, $NiCl_2{\cdot}6H_2O$.

Table 1. Transition temperatures (T_t) and enthalpy changes (ΔH_t) of complex (**3**).[a]

$$\text{Phase} \xrightarrow[\Delta H_t/\text{kcal mol}^{-1}]{T_t/^\circ\text{C}} \text{Phase}$$

$$\text{K} \xrightarrow[31.1]{84} \text{D}_{\text{hd}} \underset{2.62}{\overset{112}{\rightleftarrows}} \text{I.L.}$$

[a] Phase nomenclature: K = crystal, D_{hd} = hexagonal disordered columnar mesophase, and I.L. = isotropic liquid. 1 cal = 4.184 J.

with birefringence, a characteristic of liquid crystalline phases. On further heating, the sample cleared to form an isotropic liquid at 112 °C. When the isotropic liquid was cooled from 120 °C at a cooling rate of −10 °C/min, fan-shaped or focal conic textures appeared at 110 °C. The textures are compatible with that of the hexagonal disordered columnar mesophase (D_{hd}) reported in the literature.[10] On further cooling, these fan-shaped or focal conic textures remained even at room temperature, owing to supercooling of the mesophase without crystallization. This behaviour was also observed by DSC.

The DSC thermogram of the virgin sample at a heating rate of 10 °C/min gave two endothermic peaks at 84 °C (ΔH_t 31.1 kcal/mol) and 112 °C (ΔH_t 2.62 kcal/mol) (1 cal = 4.184 J). When the sample which had been heated above the clearing point of 112 °C was removed from the DSC apparatus and immediately placed on a stainless steel plate at room temperature, it gave only one endothermic peak at 112 °C for the second heating run (10 °C/min). Therefore, it is obvious that the supercooled liquid crystalline phase can easily be obtained at room temperature. The phase transition temperatures and their enthalpy changes are listed in Table 1.

It was confirmed by *X*-ray powder diffraction that complex (**3**) has a D_{hd} columnar mesophase. The *X*-ray pattern in the low-angle region gave three narrow reflections at *d* 28.2, 16.5, and 14.1 Å, which could be assigned to (100), (110), and (200) in a two-dimensional hexagonal lattice, respectively, lattice constant a = 32.7 Å. It gave a diffuse band at *d* 4.4 Å in the wide-angle region, which corresponds to the melt of the alkyl chains; a narrow reflection corresponding to the order of the interdisc-distance was absent in this *X*-ray region. Thus, complex (**3**) has a D_{hd} columnar mesophase. This assignment is consistent with the microscopic observations mentioned above.

The half-wave potential for the reduction of complex (**3**) determined by cyclic voltammetry is −0.06 V (*vs.* saturated calomel electrode in dichloromethane solution). This potential is somewhat less positive than that for the corresponding unsubstituted core complex, $\text{NiS}_4\text{C}_4\text{Ph}_4$ (+0.03 V).[9] Complex (**3**) is, however, thought to be a fairly good π-acceptor, comparable to haloanils (chloranil, bromanil, fluoroanil).[11] Such a π-acceptor columnar mesogen has not previously been reported.

Received, 15th February 1989; Com. 9/00722I

References

1 J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 48.

2 M. Megnamisi-Bélombé, *J. Physique*, 1983, **44**, C3-717.

3 C. Piechocki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *J. Am. Chem. Soc.*, 1982, **104**, 5245.

4 M. Veber, R. Fugnitto, and H. Strzelecka, *Mol. Cryst. Liq. Cryst.*, 1983, **96**, 221; K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, K. Matsuzaki, T. Inabe, and Y. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1986, 883; see also Corrigendum, *ibid.*, 1986, 1744.

5 M. Veber, P. Davidson, C. Jallabert, A. M. Levelut, and H. Strzelecka, *Mol. Cryst. Liq. Cryst., Lett.*, 1987, **5**, 1.

6 A. M. Giroud-Godquin and J. Billard, *Mol. Cryst. Liq. Cryst.*, 1981, **61**, 147; J. Billard, *C. R. Acad. Sci. Paris.*, 1984, **299**, 905; K. Ohta, H. Muroki, A. Takagi, K. Hatada, H. Ema, I. Yamamoto, and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 1986, **140**, 131; H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta, and I. Yamamoto, *ibid.*, 1988, **163**, 211.

7 A. M. Giroud-Godquin, G. Sigaud, M. F. Achard, and H. Hardouin, *J. Physique Lett.*, 1984, **45**, L-387.

8 G. Wenz, *Makromol. Chem., Rapid Commun.*, 1985, **6**, 577.

9 K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 1987, **147**, 15.

10 See photomicrograph in Figure 5(a) in the following paper: C. Destrade, P. Foucher, H. Gasparoux, H. T. Nguyen, A. M. Levelut, and J. Malthête, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121.

11 J. B. Torrance, *Mol. Cryst. Liq. Cryst.*, 1985, **126**, 55.