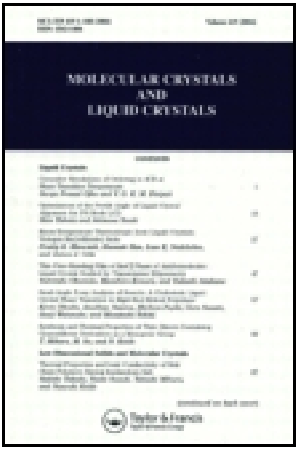


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of the First Anthraquinone Copper Complex Displaying a Columnar Phase Induced by Noncovalent π-π Interactions

Sandeep Kumar[a] & Jaishri J. Naidu[a]
[a] Centre for Liquid Crystal Research, Jalahalli, Bangalore, India

To cite this article: Sandeep Kumar & Jaishri J. Naidu (2002): Synthesis of the First Anthraquinone Copper Complex Displaying a Columnar Phase Induced by Noncovalent π-π Interactions, Molecular Crystals and Liquid Crystals, 378:1, 123-128

To link to this article: http://dx.doi.org/10.1080/713738591

Mol. Cryst. Liq. Cryst., Vol. 378, pp. 123-128
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090093

Synthesis of the First Anthraquinone Copper Complex Displaying a Columnar Phase Induced by Noncovalent π-π Interactions

SANDEEP KUMAR and JAISHRI J. NAIDU

Centre for Liquid Crystal Research, Jalahalli, Bangalore, India

The first synthesis of a novel ligand, 1-hydroxy-2,3,5,6,7-pentahexyloxy-9,10-anthraquinone, is reported. Analogous to the well-known β-diketone system, 1-hydroxy-2,3,5,6,7-pentaalkoxy-9,10-anthraquinones also form metal complexes. The first copper complex of discotic liquid crystalline 1-hydroxy-2,3,5,6,7-pentahexyloxy-9,10-anthraquinone has been prepared. The metal complex shows a columnar mesophase upon doping with trinitrofluorenone, an electron acceptor molecule. The mesomorphic behavior was studied by polarizing microscopy and differential scanning calorimetry.

Keywords: anthraquinone, rufigallol, metallomesogens, discotic liquid crystals

It has already been mentioned in hundreds of publications that the incorporation of metal into liquid crystalline compounds is of great interest because such materials are expected to have properties associated with metal atoms, such as magnetism, electron-rich nature, color, etc., in conjunction with liquid crystalline properties such as fluidity, processability, supramolecular order, etc. In recent years, a considerable amount of research has been directed towards the synthesis and characterization of new metallomesogens. The chemistry and physics of metallomesogens have recently been covered in several review articles [1–5].

Both calamitic (rodlike) and discotic (disclike) architecture are known to form metallomesogens. Like pure organic materials, metallomesogens also exhibit various mesophases such as nematic, smectic, columnar, cubic, etc.

Received 3 November 2001; accepted 23 January 2002.

We are very grateful to Professor S. Chandrasekhar for many helpful discussions. We would also like to thank Mr. Sanjay K. Varshney for the technical assistance.

Address correspondence to Sandeep Kumar, Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore, 560-013, India. E-mail: clcr@vsnl.com

β-Diketonates (Figure 1a) are amongst the most widely synthesized and studied metallomesogens [1–6]. They exhibit either calamitic or discotic mesomorphism depending on subtle differences in the molecular structure. A number of β-diketone derivatives are known to show nematic, smectic, columnar, and lamellar mesophases [1–6]. β-Diketone complexes that have both calamitic and discotic features have also been reported [7].

One of the earliest systems reported to form columnar mesophases are 1,2,3,5,6,7-hexahydroxyanthraquinone (rufigallol) derivatives. A number of alkoxy and alkanoyloxy derivatives are known to show different columnar mesophases [8]. If we compare the structure of a 1-hydroxyanthraquinone derivative (Figure 1b) with that of a β-diketone molecule (Figure 1a, keto-enol form), it can be clearly seen that there is a similarity between the two systems. Therefore, the rich chemistry that has been developed for the β-diketone system [1–7] can also be applied to the anthraquinone molecule, and thus a variety of novel metallomesogens can be prepared.

To verify our idea, we designed a monofunctionalized anthraquinone derivative **4** (Scheme 1) to prepare its metal complexes. A survey of the literature reveals that although a number of anthraquinone derivatives are known to form columnar mesophases [8], monofunctionalized anthraquinones having identical peripheral chains are not accessible. Efforts have been made to prepare monofunctionalized anthraquinone derivatives using one polar peripheral chain [8f]. However, to investigate structure-property relationship, the simplicity of a molecule having identical peripheral chains is generally preferred, and therefore a new strategy has been developed for

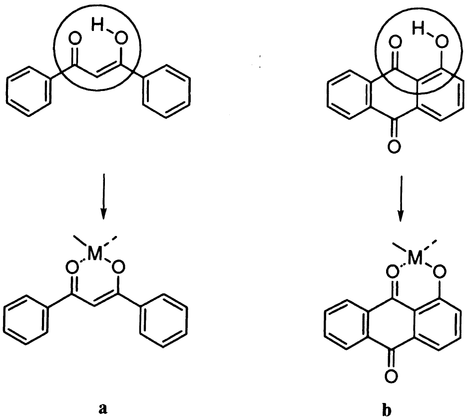
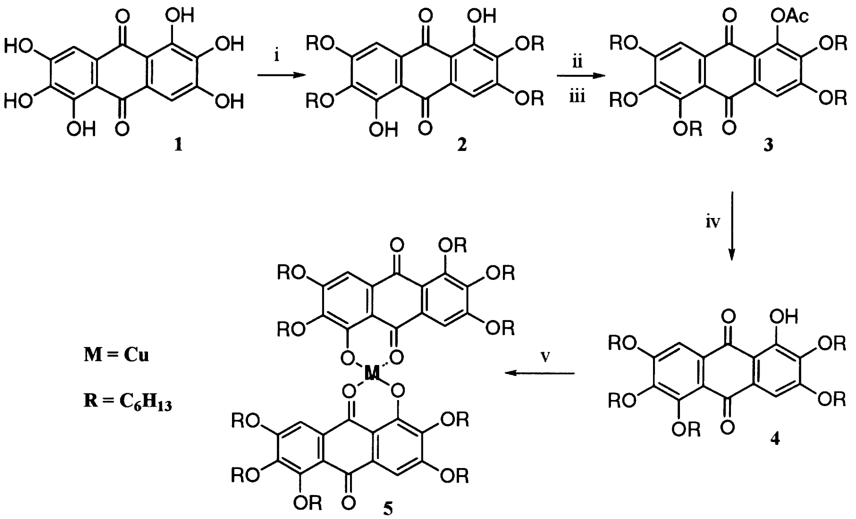


FIGURE 1 Molecular structures of (a) β-diketone and (b) anthraquinone systems.



SCHEME 1 Synthesis of 1-hydroxy-2,3,5,6,7-pentaalkoxy-9,10-anthraquinone and its copper complex. Reagents and conditions: (i) DMSO, NaOH, RBr, 50°C, 18 h, 50%; (ii) DMSO, KOH, RBr, 60C, 24 h; (iii) Ac_2O, pyridine, reflux, 40%; (iv) Aq. KOH, EtOH, reflux, 80%; (v) $Cu(OAc)_2$, EtOH, Toluene, 90%.

the preparation of monofunctionalized anthraquinone derivatives having identical peripheral chains.

The synthesis of monofunctionalized anthraquinones and their conversion to metal complexes are shown in Scheme 1. Rufigallol [9] and its tetraether were prepared following the reported procedure [8]. Further alkylation of the tetraether to prepare pentaalkoxy (monofunctionalized) derivatives results in the formation of a mixture of unreacted (tetraalkylated), pentaalkylated, and hexaalkylated products. All efforts to isolate pure monohydroxypentaalkoxyanthraquinone were futile. With the idea that the tetraalkoxy-diacetoxyanthraquinone, pentaalkoxy-monoacetoxyanthraquinone, and hexaalkoxyanthraquinone may have significantly different R_f values on a chromatographic column, the crude product was acetylated using an excess of acetic anhydride and pyridine. As expected, all the three products now can be separated readily by classical column chromatography. The pentaalkoxy-monoacetoxyanthraquinone was hydrolyzed to afford the desired monofunctionalized anthraquinone derivative. The copper complex was prepared using standard reaction conditions [6]. Charge transfer complex of the copper complex **5** was prepared by mixing equimolar amount of **5** and trinitrofluorenone in dichloromethane followed

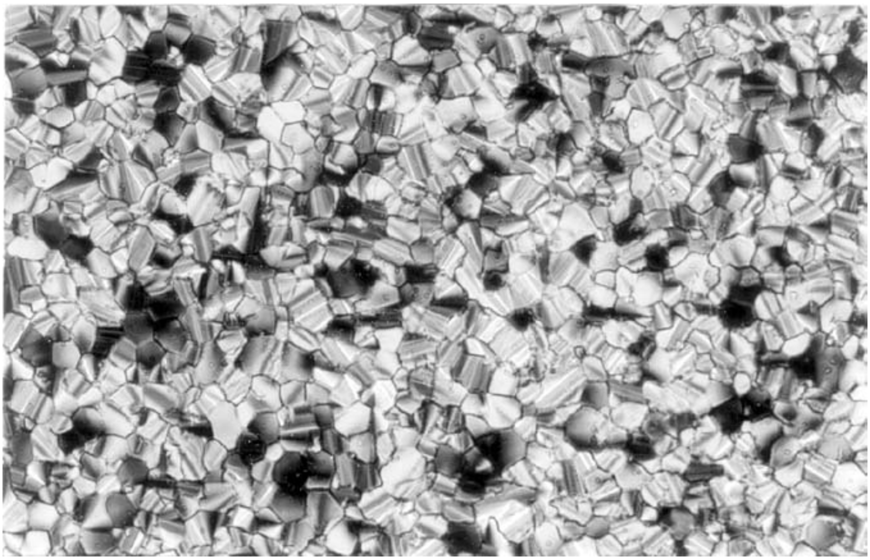


FIGURE 2 Optical texture of 1-hydroxy-2,3,5,6,7-hexyloxy-9,10-anthraquinone **4** obtained on cooling from the isotropic liquid at 25°C (crossed polarizers, magnification × 100).

by removal of solvent under high vacuum. All the compounds were fully characterized from their spectral analysis.

The thermal behavior of all the compounds was investigated by polarizing optical microscopy using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMRXP polarizing microscope and by differential scanning calorimetry (DSC7 Perkin-Elmer). The ligand, 1-hydroxy-2,3,5,6,7-pentaahexyloxy-9,10-naphthaquinone **4** was isolated as semisolid upon the addition of ethyl alcohol to the ethereal solution of pure material. It was filtered, washed with ethyl alcohol, and dried under vacuum. Upon heating, it transforms into the isotropic phase at 115.4°C (ΔH 8.5 J g^{-1}). On cooling this isotropic liquid, well-defined texture of columnar phase appears at 113.5°C (ΔH 7.7 J g^{-1}). The mesophase remains stable down to room temperature (Figure 2). Conversely, the copper complex of the compound was found to be nonmesogenic. DSC of compound **5** shows a crystal to isotropic phase transition at 171°C (ΔH 26 J g^{-1}). However, the material displays columnar phase when doped with trinitrofluorenone. The viscous 1:1 molar charge transfer complex transforms into the isotropic phase 232°C (ΔH 5.5 J g^{-1}) on heating. Upon cooling, classical textures of columnar phase appears at about 229°C and remain stable down to room temperature. Photomicrograph of the texture of a binary 1:1 mixture of compound **5** and

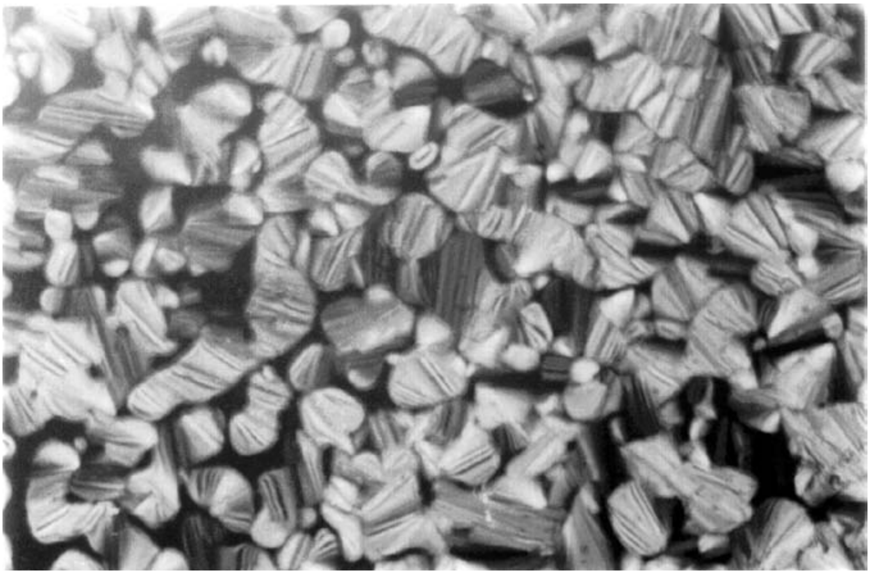


FIGURE 3 Photomicrograph of the texture of a binary 1:1 mixture of compound **5** and TNF obtained on cooling from the isotropic liquid at 200°C (crossed polarizers magnification × 200). The texture resembles well the usual texture of columnar phase.

TNF at 200°C is shown in Figure 3. Full characterization of the mesophase by X-ray diffraction studies will be reported in due course. Mesophase induction and stabilization due to charge-transfer interactions in metallomesogens as well as in classical liquid crystals is well documented [10].

The synthesis of new anthraquinone ligand opens many exciting possibilities. A variety of novel symmetrical and unsymmetrical (e.g., a combination of anthraquinone and β-diketone ligands) metallomesogens incorporating various metals such as Cu, Ni, Pd, VO, Tl, etc., can be realized. Metal bridged novel symmetrical and unsymmetrical trimers and polymers can also be prepared. Work in these directions is in progress.

REFERENCES

[1] A.-M. Giroud-Godquin and P. M. Maitlis, *Angew. Chem. Int. Ed. Engl.,* **30**, 375 (1991).
[2] S. A. Hudson and P. M. Maitlis, *Chem. Rev.,* **93**, 861 (1993).
[3] J. L. Serrano, ed., *Metallomesogens* (VCH Verlagsgesellschaft, Weinheim, 1996).
[4] B. Donnio and D. W. Bruce, *Structure and Bonding*, **95**, 193 (1999).
[5] A.-M. Giroud-Godquin, in *Hand Book of Liquid Crystals*, D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, eds. (Wiley-VCH, 1998), Vol. 2B, Chapter XIV.

[6] (a) C. K. Lai, H. B. Pan, L. F. Yang, and K. T. Liu, *Liq. Cryst.,* **28**, 97 (2001).
(b) R. Lin, C. H. Tsai, M. Q. Chao, and C. K. Lai, *J. Mater. Chem.,* **11**, 359 (2001).
(c) J. L. Serrano and T. Sierra, *Chem. Eup. J.,* **6**, 759 (2000).
(d) J. Barbera, R. Lglesias, J. L. Serrano, T. Sierra, M. R. dela Fuente, B. Palacios, M. A. Perez-Jubindo, and J. T. Vazquez, *J. Am. Chem. Soc.,* **120**, 2908 (1998).
(e) S. Tantrawong and P. Styring, *Mol. Cryst. Liq. Cryst.,* **302**, 309 (1997).
(f) T. M. Swager and H. Zheng, *Mol. Cryst. Liq. Cryst.,* **260**, 301 (1995).
(g) R. Atencio, J. Barbera, C. Cativiela, F. J. Lahoz, J. L. Serrano, and M. M. Zurbano, *J. Am. Chem. Soc.,* **116**, 115508 (1994).
(h) K. Ohto, H. Akimoto, O. Takenaka, T. Fujimoto, and I. Yamamoto, *J. Mater. Chem.,* **4**, 61 (1994). See also references given in all the above references.

[7] (a) S. Chandrasekhar, B. K. Sadashiva, and B. S. Srikanta, *Mol. Cryst. Liq. Cryst.,* **151**, 93 (1987).
(b) S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.,* **243**, 1 (1994).
(c) B. K. Sadashiva, in *Hand Book of Liquid Crystals*, D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, eds. (Wiley-VCH, 1998), Vol. 2B, Chapter XV.

[8] (a) J. Billard, J. C. Dubois, C. Vaucher, and A. M. Levelut, *Mol. Cryst. Liq. Cryst*., **66**, 115 (1981).
(b) C. Carfugna, A. Roviello, and A. Sirigu, *Mol. Cryst. Liq. Cryst.,* **122**, 151 (1985).
(c) C. Carfugna, P. Iannelli, A. Roviello, and A. Sirigu, *Liq. Cryst.,* **2**, 611 (1987).
(d) J. Billard, Z. Luz, R. Poupko, and H. Zimmermann, *Liq. Cryst.,* **16**, 333 (1994).
(e) K. S. Raja, S. Ramakrishnan, and V. A. Raghunathan, *Chem. Mater.,* **9**, 1630 (1997).
(f) K. Krishnan and V. S. K. Balagurusamy, *Liq. Cryst.,* **27**, 991 (2000).
(g) V. Prasad, K. Krishnan, and V. S. K. Balagurusamy, *Liq. Cryst.,* **27**, 1075 (2000).
(h) V. Prasad, *Liq. Cryst.,* **28**, 647 (2001).

[9] J. Grimshaw and R. D. Haworth, *J. Chem. Soc.,* 4225 (1956).

[10] (a) H. Bangs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J. H. Wendorff, and R. Wustefeld, *Adv. Mater*., **2**, 141 (1990).
(b) M. Ebert, G. Frick, C. Baehr, J. H. Wendorff, R. Wustefeld, and H. Ringsdorf, *Liq. Cryst.,* **11**, 293 (1992).
(c) K. Praefcke and D. Singer, in *Hand Book of Liquid Crystals*, D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, eds. (Wiley-VCH, 1998), Vol. 2B, Chapter XVI.
(d) D. Singer, A. Liebmann, K. Praefcke, and J. H. Wendorff, *Liq. Cryst.,* **14**, 785 (1993).