J. Chem. Research (S),
1998, 374–375
J. Chem. Research (M),
1998, 1585–1594

Synthesis and Characterization of 2,2′-Azoquinoxalines Substituted with Long Alkoxy Chains and Halogeno Groups and a Binuclear Cyclopalladated Symmetrical Azoquinoxaline Complex

Ismail Yilmaz and Özer Bekâroğlu*

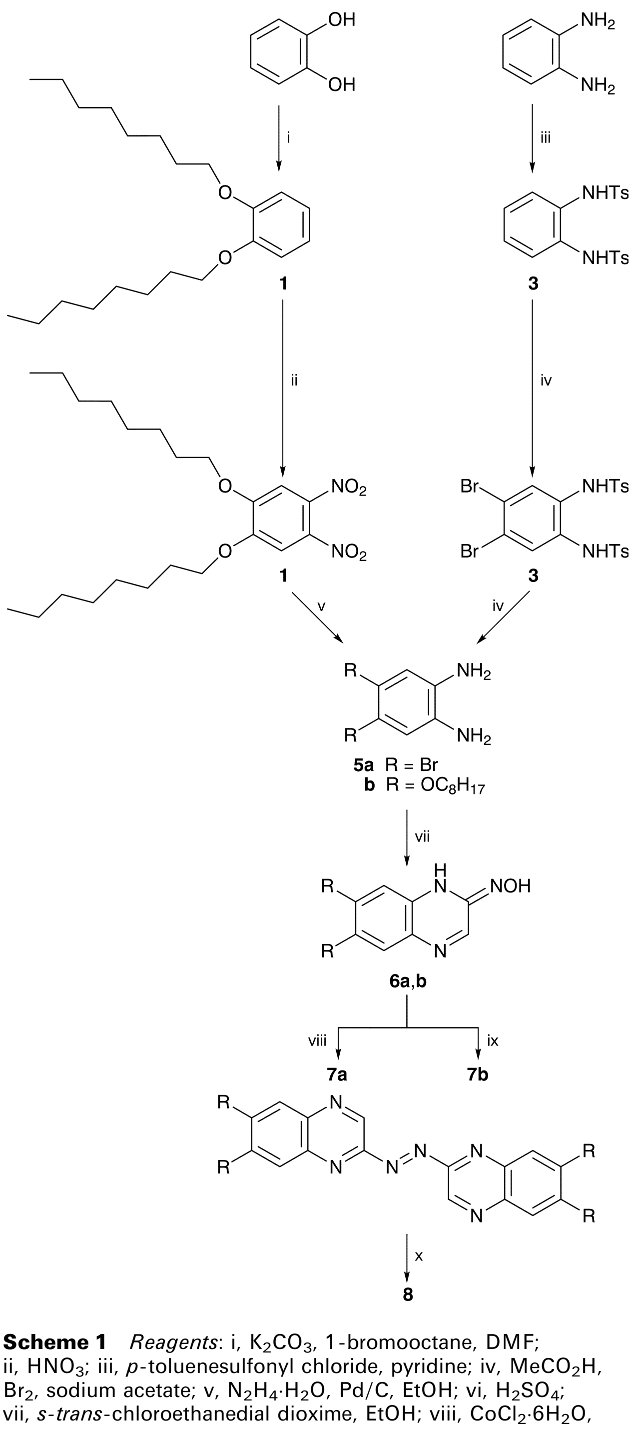
Technical University of Istanbul, Department of Chemistry, 80626, Maslak, Istanbul, Turkey

2,2′-Azobisquinoxalines substituted with bromo and octyloxy groups and symmetrical binuclear cyclopalladated azoquinoxaline are prepared from the corresponding quinoxalin-2(1*H*)-one oximes.

We have previously reported a route for the direct one-step synthesis of quinoxaline-2(1*H*)-one oximes which can be easily obtained by the reaction of aromatic orthodiamines and *s-trans*-chloroethanedial dioxime and can be converted into symmetrical 2,2′-azoquinoxalines by the template effect of cobalt(II) chloride or by treatment with potassium hydroxide.[4,5] Azobenzene-containing host systems with crown ether units have been effectively used in selective ion transport[6] as photochemically switchable molecules.

The dimeric metallomesogen, based on cyclopalladated azobenzene, exhibited nematic phases at fairly high temperatures (*ca.* 200 °C). More recently the cyclopalladated alkyl/alkoxy substituted azobenzenes[7,8] and phthalocyanines[9] having liquid crystal properties have been synthesized. Since the number of peripheral hydrocarbon chains and the possibility of hydrogen bonding are shown to have a critical influence on mesomorphism in these compounds, the chain length of the alkoxy groups in the substituted 2,2′-azoquinoxaline and symmetrical binuclear cyclopalladated azoquinoxaline was chosen to be at least six carbon atoms.

Here we describe the synthesis of new substituted 2,2′-azoquinoxalines **7a,b** and a symmetrical binuclear cyclopalladated azoquinoxaline **8** starting from catechol and benzene-1,2-diamine (Scheme 1). 4,5-Bis(octyloxy)benzene-1,2-diamine **5b** was synthesized by reduction of 1,2-dinitro-4,5-bis(octyloxy)benzene **2** which was obtained by the nitration of 1,2-bis(octyloxy)benzene **1** without following the multistep reaction sequence of published methods.[10,11] 4,5-Dibromobenzene-1,2-diamine **5a** was prepared starting from benzene-1,2-diamine in three steps with improved yields compared to reported procedures.[12,13] 5,6-Dibromoquinoxalin-2(1*H*)-one oxime **6a** and 5,6-bis(octyloxy)-quinoxalin-2(1*H*)-one oxime **6b** were obtained by the cyclization of 4,5-dibromobenzene-1,2-diamine **5a** or 4,5-bis(octyloxy)benzene-1,2-diamine **5b** with *s-trans*-chloroethanedial dioxime without the addition of any other base. To synthesise 2,2′-azobis(5,6-dibromoquinoxaline) **7a** and 2,2′-azobis[5,6-bis(octyloxy)quinoxaline] **7b**, a template reaction of $CoCl_2$ for the former and treatment of KOH for the latter were chosen in order to obtain good yields of the corresponding compounds, but the two methods could be applicable to the 15-crown-5-quinoxalinone oxime derivative to give the corresponding azo-derivative.[14] The preparation of the symmetrical binuclear cyclopalladated 2,2′-azobis-[5,6-bis(octyloxy)quinoxaline] complex **8** was accomplished by reaction of 2,2′-azobis[5,6-bis(octyloxy)quinoxaline] with $PdCl_2$ in hot DMF. In principle, the palladation of asymmetrically substituted azobenzenes[15] can take place on either of the phenyl rings, and therefore products containing isomer



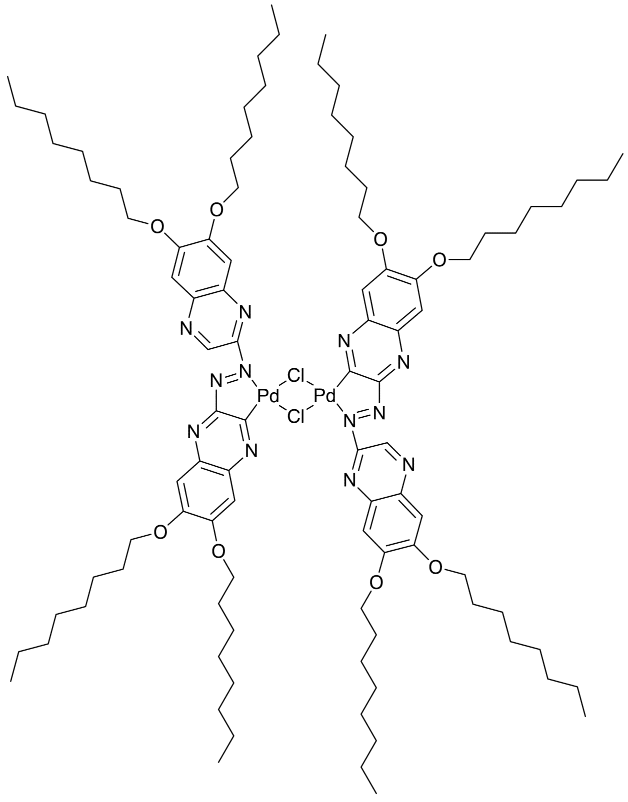
Scheme 1 *Reagents*: i, K_2CO_3, 1-bromooctane, DMF; ii, HNO_3; iii, *p*-toluenesulfonyl chloride, pyridine; iv, $MeCO_2H$, Br_2, sodium acetate; v, $N_2H_4{\cdot}H_2O$, Pd/C, EtOH; vi, H_2SO_4; vii, *s-trans*-chloroethanedial dioxime, EtOH; viii, $CoCl_2{\cdot}6H_2O$, EtOH; ix, KOH, THF; x, $PdCl_2$, DMF

---

*To receive any correspondence.

mixtures can form. However, in practice the symmetrical binuclear cyclopalladated 2,2′-azobis[5,6-bis(octyloxy)-quinoxaline] complex **8** forms as the main product and can be easily isolated without use of any further separation techniques.

The chemical shifts in the ^{1}H NMR spectra of 2,2′-azobis(5,6-dibromoquinoxaline) **7a** and 2,2′-azobis[5,6-bis-(octyloxy)quinoxaline] **7b** are in agreement with the values reported for similar compounds.[5,14] The elemental analytical result for the dark blue symmetrical binuclear cyclopalladated complex **8** reveals the presence of two palladium ions and therefore, this should have a binuclear structure bridged by two chloride ions for each metal ion, as for other asymmetrical binuclear cyclopalladated azobenzenes.



8

By comparing the solubility and melting points of these compounds, it was found that the melting point of 2,2′-azobis[5,6-bis(octyloxy)quinoxaline] **7b** (172 °C, decomp.) is lower than that of 2,2′-azobis(5,6-dibromoquinoxaline) **7a** (mp < 350 °C) which is attributed to the fact that the melting point of the compound containing the longer chain substituent decreases.[16] In contrast to the case of 2,2′-azobis[5,6(octyloxy)quinoxaline] **7b**, which is surprisingly soluble only in CF$_3$COOH and hot DMSO and can thus afford spectroscopic measurement, the binuclear cyclopalladated 2,2′-azobis[5,6-bis(octyloxy)quinoxaline] **8** is insoluble in common organic solvents, thus hindering further spectroscopic investigation even though it would be expected to be soluble to a greater extent in common organic solvents due to the long octyloxy chains of **7b** and **8**.

We thank the Research Fund of Technical University of Istanbul for Financial Support and one of us Ö.B. thanks Turkish Academy of Science (TUBA).

Techniques used: ^{1}H NMR, IR, MS, elemental analysis

References: 18

Received, 1st December 1997; Accepted, 9th April 1998
Paper E/7/08640G

References cited in this synopsis

4 A. Koçak and Ö. Bekâroğlu, *Helv. Chim. Acta*, 1984, **67**, 1503; C. Krieger, A. Koçak and Ö. Bekâroğlu, *Helv. Chim. Acta*, 1985, **68**, 581.
5 M. Ertaş, A. Gürek, A. Gül and Ö. Bekâroğlu, *J. Chem. Res.*, 1988, (*S*) 109; (*M*) 1157.
6 S. Shinkai, T. Ogawa, Y. Jusano, O. Manabe, K. Kikukawa, T. Goto and T. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 1960.
7 M. Ghedini and M. Bartolino, *Mol. Cryst. Liq. Cryst.*, 1982, **84**, 207.
8 C. C. Versace, R. Bartolino, M. Ghedini, F. Neve, S. Armentano, M. Petrov and N. Kirov, *Liq. Cryst.*, 1990, **8**, 481.
9 J. Simon and C. Sirlin, *Pure Appl. Chem.*, 1989, **61**, 11625.
10 K. Sakata and T. Annoura, *Inorg. Chim. Acta*, 1990, **176**, 123.
11 E. Lubock, A. Cygan and F. Biernat, *Tetrahedron*, 1990, **46**, 246.
12 R. C. Elderfield and V. B. Meyer, *J. Am. Chem.Soc.*, 1954, **76**, 1887.
13 G. W. H. Cheeseman, *J. Chem. Soc.*, 1962, 1170.
14 A. Gül, A. I. Okur, Ş. Can and Ö. Bekâroğlu, *Chem. Ber.*, 1986, **119**, 3870.
15 M. Ghedini, S. Armentano and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1988, 1565.
16 M. Hanack and M. Long, *Adv. Mater.*, 1994, **6**, 819.