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Preliminary communication

Tetraphenylenes as novel saddle-shaped building blocks of columnar and smectic liquid crystals

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We report the synthesis and liquid crystalline properties of novel mesogenic octaalkyloxytetraphenylenes. Starting from 4-bromoveratrol, the saddle-shaped target tetraphenylenes were obtained in five steps. Compounds with shorter C7–C12 alkyl chain lengths displayed enantiotropic hexagonal columnar mesophases. For the decyloxy derivative a lattice constant $d=27.4$ Å was determined by X-ray diffraction. The compounds with longer C13–C16 alkyl chains exhibited enantiotropic mesophases, which are most probably smectic in nature. X-ray diffraction of the $R=C_{14}H_{29}$ derivative indicated a phase transition within the smectic mesophases.

Over the last decade there has been an increasing body of experimental evidence that even molecules devoid of a flat aromatic core are able to form columnar mesophases [1]. In particular, bowl-shaped or pyramidal columnar liquid crystals such as tribenzocyclononenes (cyclotriveratrylenes) [2], tetrabenzocyclododecatetraene [3], metacyclophanes [4], calix[4]arenes [5], self-assembled dendrimers [6] as well as triazacyclononanes [7] have been extensively studied by several groups. Zimmermann, Luz and co-workers have elegantly shown that tribenzocyclononenes exist in two isomeric forms, i.e. crown and saddle, which may interconvert at elevated temperatures [2*a*,*b*]. However, no other saddle-shaped columnar mesogens have been reported. Tetraphenylene may be a promising candidate for this purpose [8]. X-ray data of the parent system [9], tetrabenzo[*b*,*h*,*n*,*t*]tetraphenylene [10], octamethoxytetraphenylene [11], several host–guest complexes of tetraphenylene [8*a*], and substituted derivatives [12] clearly reveal the saddle or tub shape in the solid state. Here we report the preparation of novel mesogenic octaalkyloxytetraphenylenes and the characterization of their mesomorphic properties.

As shown in the scheme, base-promoted aryl coupling of 4-bromoveratrol (**1**) in the presence of *n*BuLi in THF at −78°C [13] and subsequent bromination gave 5,5′-dibromo-1,1′,2,2′-tetramethoxybiphenyl (**2**) in 56% overall yield. Following a procedure described by Rathore and Kochi, deprotonation of biphenyl **2** with *n*BuLi and treatment with $CuCl_2$ [11] gave tetraphenylene **3** in less than 17% yield, which could not be improved even by the use of strictly anhydrous $CuCl_2$. After considerable experimentation, product **3** could be obtained in 63% yield by employing a transmetallation with $ZnBr_2$ and $CuCl_2$ [14]. The following sequence of demethylation to octahydroxytetraphenylene **4** and subsequent alkylation proved to be especially capricious. Treatment of octamethoxytetraphenylene **3** with BBr_3 in CH_2Cl_2 at −50°C, hydrolysis with degassed MeOH and evaporation of the solvents yielded a colourless, extremely air-sensitive solid. Even traces of oxygen resulted in immediate formation of dark violet quinoid products. This lability is in contrast to related systems such as 3,3‴,4,4′,4″,4‴,5′,5″-octahydroxy-1,1′,2′,1″,2″,1‴-quaterphenyl which could be

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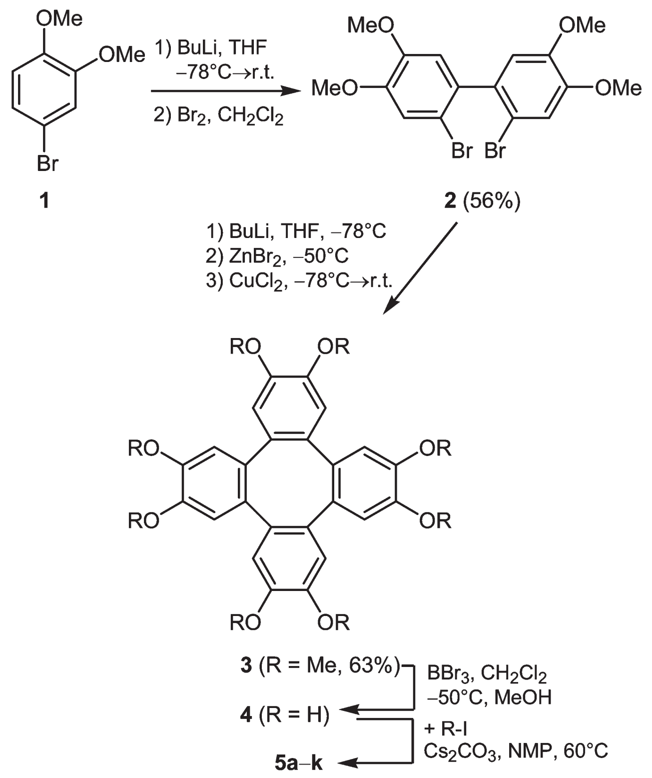

5	R =	**5**	R =
a	C_6H_{13}	**g**	$C_{12}H_{25}$
b	C_7H_{15}	**h**	$C_{13}H_{27}$
c	C_8H_{17}	**i**	$C_{14}H_{29}$
d	C_9H_{19}	**j**	$C_{15}H_{31}$
e	$C_{10}H_{21}$	**k**	$C_{16}H_{33}$
f	$C_{11}H_{23}$		

Scheme. Synthesis of octaalkyloxytetraphenylenes **5a**–**k**.

handled without special care [13]. Thus, in order to avoid oxidation, compound **4** was directly alkylated without further purification. Whereas heating of compound **4** with alkyl bromides in the presence of K_2CO_3 in DMF at 140°C gave no trace of products **5**, conversion of **3** with KOMe to the corresponding potassium alkoxide and subsequent reaction with alkyl bromides in MeCN at 70°C resulted in only 1–6% yield for **5**. A significant improvement was achieved, however, by using alkyl iodides and Cs_2CO_3 in *N*-methyl-2-pyrrolidone (NMP) at 60°C, giving the desired alkoxyphenylenes **5a**–**k** after 3–7 days reaction time in 30–40% yield.

A typical procedure is exemplified for the preparation of compound **5e**. A 1 M solution of BBr_3 in CH_2Cl_2 (1.05 mmol) was added to **3** (1 mmol) at −50°C under an inert gas atmosphere. After stirring at room temperature for 1 h, the reaction mixture was evaporated at 60°C under vacuum (10 mbar) and then hydrolysed with absolute degassed MeOH (5 ml mmol^{-1} **3**). All volatile materials were removed at 60°C under vacuum (10 mbar); intermediate **4**, iododecane (1.2 mmol referred to **3**) and anhydrous Cs_2CO_3 (5 mmol) in NMP (1.5 ml) were then reacted at 60°C (tlc control). After removal of the solvent, the residue was chromatographed on SiO_2 with hexanes/ethyl acetate (20/1) and finally purified by MPLC with hexanes/ethyl acetate (40/1) to give **5e**. ^1H NMR (500 MHz, $CDCl_3$): 6.65 s (8H, Ph–H); 4.00–3.89 m (16H, OCH_2); 1.80–1.75 m (16H, $OCH_2C\underline{H}_2$); 1.47–1.40 m (16H); 1.32–1.25 m (96H, $(CH_2)_6$); 0.88 t (24H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): 14.1 (CH_3); 22.7, 26.1, 29.4, 31.9 (CH_2); 69.4 (OCH_2); 115.0, 134.4, 147.9 (Ph). Anal: calcd for $C_{144}H_{256}O_8$ C 81.75, H 12.20; found C 81.70, H 12.28%.

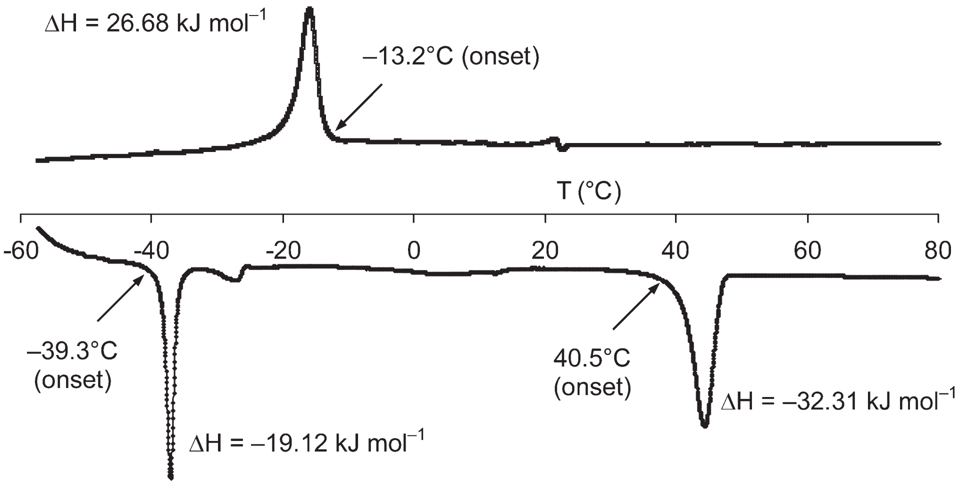

Figure 1. DSC curves (first heating and cooling cycle) of tetraphenylene **5f**. Heating rate 2 K min^{-1}.

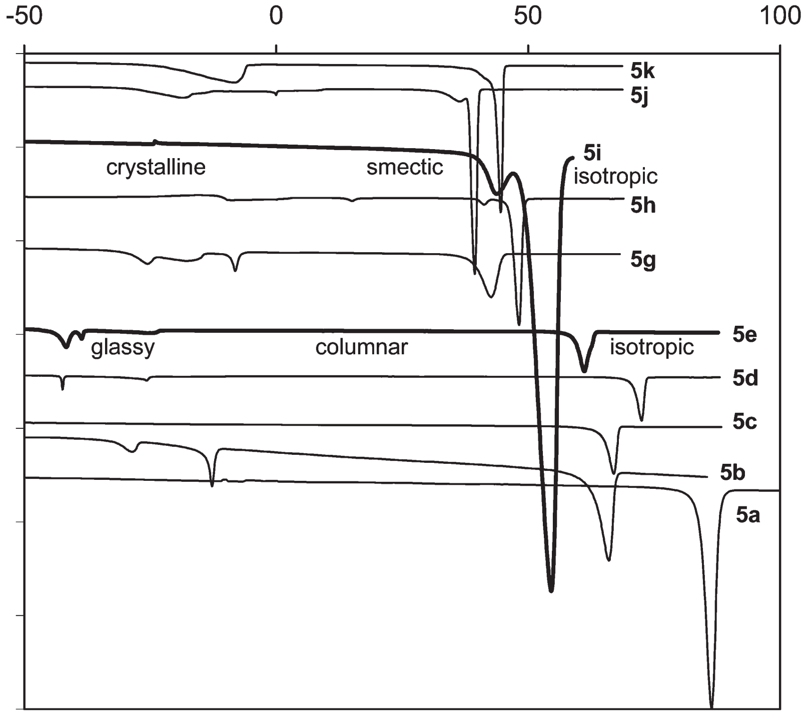

Figure 2. DSC curves (first heating) of tetraphenylenes **5a**–**e**,**g**–**k**. Heating rate 2 K min^{-1} for **5a**,**c**–**e**,**g**,**h**,**j**,**k** and 5 K min^{-1} for **5b**,**i**. The phase transitions are also present in the corresponding cooling cycle; however, supercooling was observed to varying extents.

The mesomorphic properties of products **5a**–**k** were studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Due to extensive supercooling only virgin samples, which had been stored for several days at −78°C (dry ice), gave reproducible phase transitions in the DSC. An example of this supercooling is given in figure 1 for compound **5f**, where the clearing point is observed on heating at about 39°C. By contrast, in the cooling cycle the transition from the isotropic to the columnar state is observed at about −15°C. Even at a temperature of −60°C no indication of crystallization and/or a glass transition was detected. For the remaining compounds **5a**–**e**,**g**–**k** only the heating cycles are shown in figure 2.

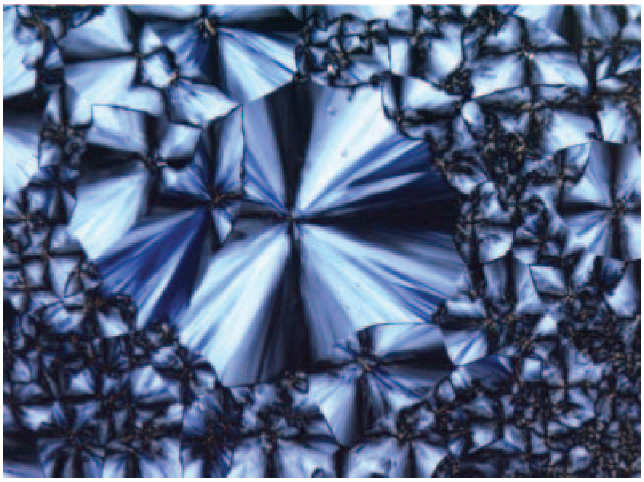

Figure 3. Mesophase texture of derivative **5e** at room temperature upon cooling from 80°C at 5 K min^{-1} (magnification 100 ×).

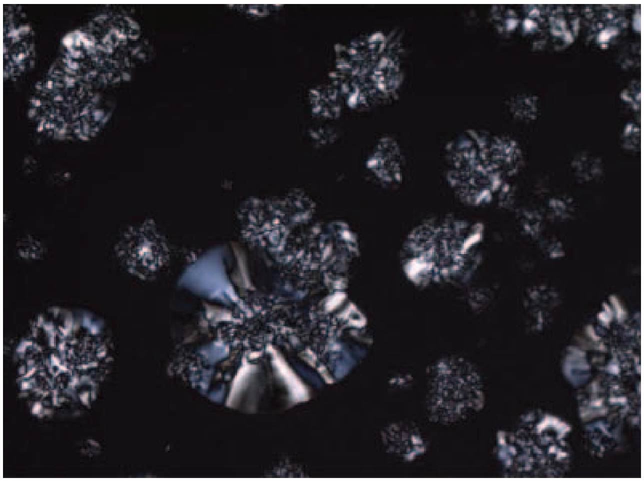

Figure 4. Mesophase texture of derivative **5h** after storage for six days at room temperature upon cooling from 46°C (magnification 200 ×).

Whereas compound **5a** is non-mesogenic, compounds

5b–k display enantiotropic mesophases. Under POM upon cooling from the isotropic phase, tetraphenylenes **5b–g** ($R = C_7H_{15}$ to $C_{12}H_{25}$) showed fan-shaped textures typical for columnar mesophases. As an example, the texture of tetraphenylene **5e** is shown in figure 3. In contrast, alkyloxyphenylenes **5h–k** ($R = C_{13}H_{27}$ to $C_{16}H_{33}$) show different phase behaviours in DSC. POM also reveals different textures as compared with the derivatives with shorter alkyl chain lengths, however, they were not characteristic of a certain mesophase type. The texture of compound **5h** is shown in figure 4.

X-ray investigations (Cu Kα radiation, $\lambda = 1.5418$ Å) of the decyloxy derivative **5e** confirm the formation of a columnar mesophase. The diffuse scattering profile observed for the isotropic melt of **5e** at 65°C (lower curve in figure 5) abruptly changes below 59°C into a sharp scattering profile with pronounced reflections in the small angle regime originating from long range intercolumnar ordering. At 55°C (upper curve in figure 5) three distinct maxima at scattering angles $\theta = 1.82°$, 3.35°, and 3.68° are observed. These maxima confirm a 2D-hexagonal columnar mesophase with lattice constant $a_0 = 27.4$ Å that leads to scattering maxima at $\theta_{(10)} = 1.86°$, $\theta_{(11)} = 3.23°$, and $\theta_{(20)} = 3.72°$ (the remaining scattering peak observed at $\theta = 2.29°$ in the upper curve of figure 5 is a satellite peak of the (1 0) reflection due to small contributions of parasitic Fe Kα radiation). In particular, the presence of the characteristic (1 1) reflection, incommensurate with the other peaks, clearly indicates the two-dimensional hexagonal lattice of the Col_h mesophase.

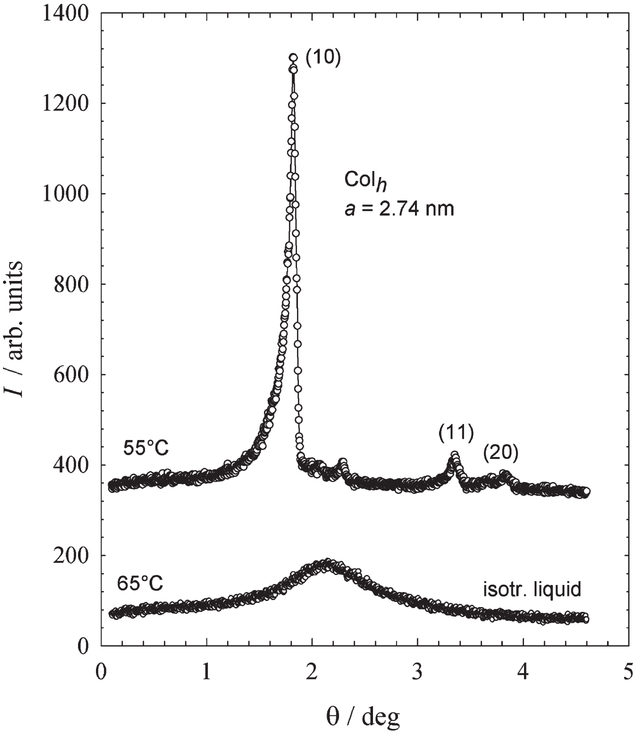

Figure 5. Small-angle X-ray scattering profiles of the isotropic (65°C, lower curve) and the liquid crystalline (55°C, upper curve) phases of compound **5e**. The latter confirms a hexagonal-columnar mesophase (Col_h) with pronounced (1 0), (1 1), and (2 0) reflections. The remaining scattering peak at $\theta \approx 2.3°$ originates from parasitic Fe Kα radiation.

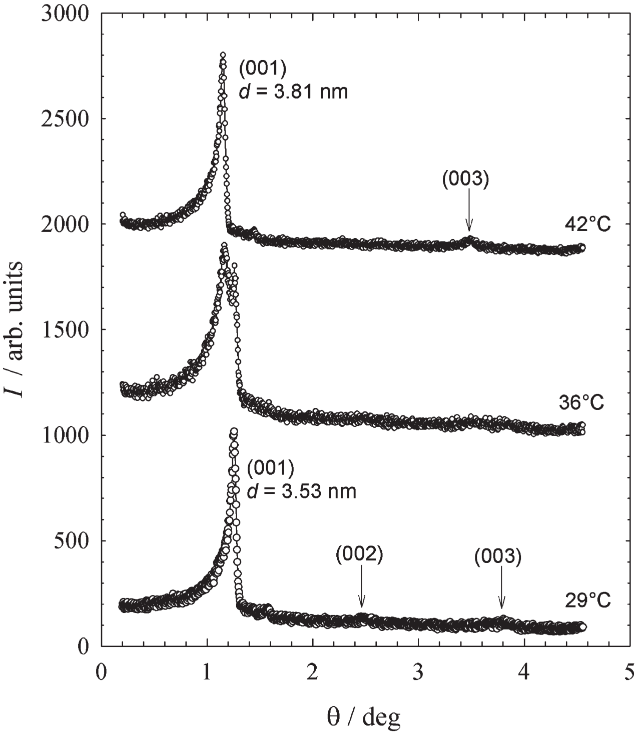

Figure 6. SAXS profiles from the mesophases of derivative **5i**. The absence of mixed reflections (specifically the (1 1) reflection in the columnar phases as shown in figure 4) at 42 and 29°C indicates smectic-like 1D-translational order in both phases. At 36°C a transition between the two smectic phases is observed.

In clear contrast to this result, the mesomorphic state(s) of the tetradecyloxy derivative **5i** seem to have smectic order. The presence of commensurate (0 0 *l*) layer reflections together with the absence of any (1 1) reflection in the small angle X-ray scattering (figure 6) indicates an only one-dimensional smectic-like translational ordering. At 42°C, first and third order layer reflections are found at scattering angles of 1.16° and 3.48°, respectively, both corresponding to a smectic layer spacing of $d = 38.1$ Å. At 36°C this smectic phase transforms into a second smectic phase with somewhat reduced layer thickness. At 29°C first (1.25°), second (2.49°), and third order (3.76°) layer reflection peaks are observed, which result in a layer spacing of about

35.3 Å. The coexistence of both phases observed at 36°C indicates a first order transition probably between an orthogonal smectic phase above 36°C and a tilted smectic phase with reduced layer thickness at lower temperatures. To date neither POM nor wide angle X-ray scattering have provided conclusive results, and thus, the exact natures of these two smectic phases have not been unambiguously.

In conclusion, novel mesogenic octaalkyloxytetraphenylenes **5b–k** have been prepared. Whereas derivatives **5b–g**, with ≤ 12 carbon atoms in the alkyl chain, display columnar mesophases, compounds **5h–k**, with ≥ 13 carbon atoms, show smectic mesophases. The additional smectic to smectic phase transition which was observed in the temperature-dependent XRD pattern of the tetradecyloxy derivative **5i** is currently under further investigation.

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References

[1] (*a*) Tschierske, C., 2001, *Annu. Rep. Prog. Chem., Sect. C*, **97**, 191; (*b*) Tschierske, C., 1998, *J. mater. Chem.*, **8**, 1485.

[2] (*a*) Luz, Z., Poupko, R., Wachtel, E. J., Zimmermann, H., and Bader, V., 2003, *Mol. Cryst. liq. Cryst.*, **397**, 367; (*b*) Zimmermann, H., Bader, V., Poupko, R., Wachtel, E. J., and Luz, Z., 2002, *J. Am. chem. Soc.*, **124**, 15286; (*c*) Jakli, A., Müller, M., and Heppke, G., 1999, *Liq. Cryst.*, **22**, 945; (*d*) Budig, H., Lunkwitz, R., Paschke, R., Tschierske, C., Nütz, U., Diele, S., and Pelzl, G., 1996, *J. mater. Chem.*, **6**, 1283.

[3] (*a*) Percec, V., Cho, C. G., and Pugh, C., 1991, *J. mater. Chem.*, **1**, 217; (*b*) Percec, V., Cho, C. G., and Pugh, C., 1991, *Macromolecules*, **24**, 3227.

[4] (*a*) Arcioni, A., Tarroni, R., Zannoni, C., Dalcanale, E., and du Vosel, A., 1995, *J. phys. Chem.*, **99**, 15981; (*b*) Dalcanale, E., du Vosel, A., Levelut, A. M., and Malthête, J., 1991, *Liq. Cryst.*, **10**, 185; (*c*) Cometti, G., Dalcanale, E., du Vosel, A., and Levelut, A.-M., 1990, *Chem. Commun.*, 163.

[5] (*a*) Xu, B., and Swager, T. M., 1993, *J. Am. chem. Soc.*, **115**, 1159; (*b*) Komori, T., and Shinkai, S., 1993, *Chem. Lett.*, 1455.

[6] Percec, V., Glodde, M., Johansson, G., Balagurusamy, V. S. K., and Heiney, P. A., 2003, *Angew. Chem., int. Ed.*, **42,** 4338.

[7] (*a*) Schmidt, S., Lattermann, G., Kleppinger, R., and Wendorff, J. H., 1994, *Liq. Cryst.*, **16**, 693; (*b*) Lehn, J.-M., Malthête, J., and Levelut, A.-M., 1985, *J. chem. Soc., chem. Commun.*, 1794.

[8] (*a*) Mak, T. C. W., and Wong, H. N. C., 1996, in *Comprehensive Supramolecular Chemistry*, Vol. 6, edited by D. D. MacNicol, F. Toda and R. Bishop (Oxford: Elsevier), pp. 351–369; (*b*) Mak, T. C. W., and Wong, H. N. C., 1987, *Top. curr. Chem.*, **140**, 141; (*c*) Wen, J.-F., Hong, W., Yuan, K., Mak, T. C. W., and Wong, H. N. C., 2003, *J. org. Chem.*, **68**, 8918.

[9] Irngartinger, H., and Reibel, W. R. K., 1981, *Acta Crystallogr.*, **B37,** 1724.

[10] Iyoda, M., Kabir, S. M. H., Vorasingha, A., Kuwatani, Y., and Yoshida, M., 1998, *Tetrahedron Lett.*, **39,** 5393.

[11] Rathore, R., le Magueres, P., Lindeman, S. V., and Kochi, J. K., 2000, *Angew. Chem., int. Ed.*, **39,** 809.

[12] (*a*) Rajca, A., Wang, H., Bolshov, P., and Rajca, S., 2001, *Tetrahedron*, **57**, 3725; (*b*) Rajca, A., Safronov, A., Rajca, S., and Wongsriratanakul, J., 2000, *J. Am. chem. Soc.*, **122**, 3351; (*c*) Rajca, A., Safronov, A., Rajca, S., and Shoemaker, R., 1997, *Angew. Chem., int. Ed. Engl.*, **36**, 488.

[13] Schulte, J. L., and Laschat, S., 1999, *Synthesis*, 475.

[14] (*a*) Kabir, S. M. H., Hasegawa, M., Kuwatani, Y., Yoshida, M., Matsuyama, H., and Iyoda, M., 2001, *J. chem. Soc., Perkin Trans. 1*, 159; (*b*) Kabir, S. M. H., and Iyoda, M., 2000, *Synthesis*, 1839.