Tetrahedron Letters 49 (2008) 7149–7152

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A new type of symmetrical banana-shaped material based on *N*-methyldiphenylamine as a core moiety exhibiting an $A_d \rightarrow A_2$ transition

Krishna C. Majumdar *, Buddhadeb Chattopadhyay, Santanu Chakravorty, Nilasish Pal, Randhir Kumar Sinha

Department of Chemistry, University of Kalyani, Kalyani 741 235, West Bengal, India

ARTICLE INFO

Article history:
Received 15 August 2008
Revised 24 September 2008
Accepted 27 September 2008
Available online 17 October 2008

Keywords:
Schiff base
Bent shape
DPA
OLEDS

ABSTRACT

The synthesis and characterization of a homologous series of Schiff bases consisting of an *N*-methyldiphenylamine moiety as the central core is reported, which exhibits smectic A phase and transitions from the partial bilayer SmA_d phase to the bilayer SmA_2 phase as the temperature is lowered.

'Banana-shaped'[1–4] liquid crystals occupy one of the most exciting areas of research in both mesogenic materials and supramolecular chemistry. These materials form new smectic and two-dimensional phases, which are unlike to those obtained from normal calamitic molecules.[5,6] Such 'banana' compounds have attracted considerable interest because of their unusual electro-optical properties.[7,8] Indeed, as a result of the bent shape, a polar order within the smectic layers can be induced and some phases exhibit ferro- or antiferroelectric properties although the molecules are non-chiral.[9,10] Several compounds with bent core (BC) molecules are known to exhibit the smectic A (SmA) phase but NMR study shows that in such molecules, the angle between the two arms of the bent core is about 160 °C, which means that deviation from a rod-like structure is quite small. On the other hand, if the molecules have a highly bent core, the compounds are known to exhibit B-phases. Reddy and Sadashiva [11] also synthesized an unsymmetrical bent core molecule in which an alkoxy chain was attached to only one of the arms of the bent core, while the other arm terminates in a highly polar cyano group and observed $SmA_d \rightarrow SmA_{db}$ transitions. Low molecular weight triphenylamine (TPA) and diphenylamine (DPA) derivatives have been employed as hole-transporting materials in organic light-emitting devices (OLEDS).[12–14] Diphenylamine derivatives are also used in two-photon absorbing molecules with large non-linear molecular absorptivity to generate high-energy excited states with relative low laser energy.[15] Owing to the wide applicability of diphenylamine-based material. Herein, we report the synthesis of banana-shaped molecules with a new architecture based on the DPA core.

The synthesis of a series of banana-shaped materials **7a–e** is depicted in Scheme 1. *N*-Methyldiphenylamine **2** was formylated under Vilsmeier-Haack condition to access the core entity **3** for the synthesis of the banana-shaped molecules. 4-Nitrophenyl-4-(alkyloxy)benzoate **5** was prepared by esterification of 4-(alkyloxy)benzoic acid **4** with *p*-nitrophenol in dry DCM in the presence of triethylamine and DMAP as a catalyst. 4-Nitrophenyl-4-(alkyloxy)benzoate derivatives **5** were then reduced to 4-aminophenyl-4-(alkyloxy)benzoates **6** by catalytic hydrogenation. The diformylated derivative **3** was heated under reflux with 4-aminophenyl 4-(alkyloxy)benzoate **6** in absolute ethanol in the presence of a catalytic amount of glacial acetic acid to afford the homologous series **7a–e**. Compounds **7a–e** were characterized from their ^{1}H NMR and IR spectral data. The presence of a two-proton singlet at 8.39 ppm in the ^{1}H NMR is suggestive of the formation of a symmetrical Schiff base. The IR peak at around 1625 cm^{-1} further supports the formation of the symmetrical product.

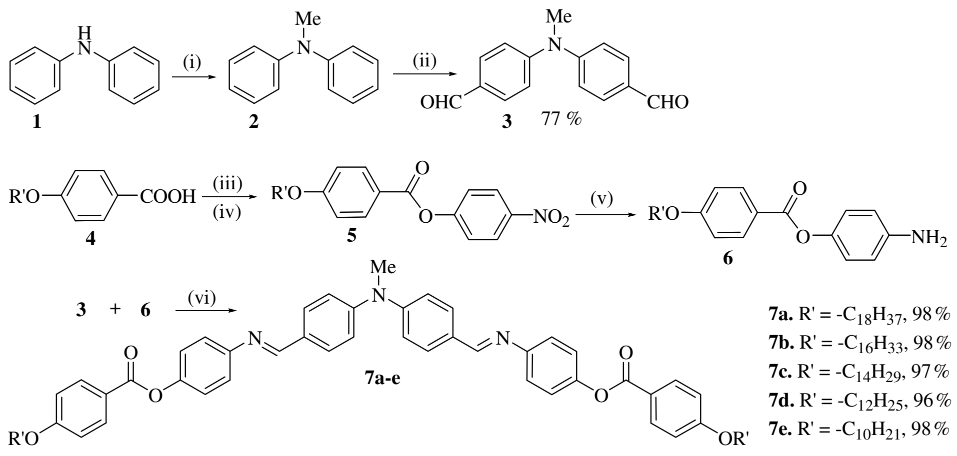
The liquid crystalline behavior of compounds **7a–e** was investigated initially with the help of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Transition temperatures and associated enthalpies obtained from DSC thermograms of compounds **7a–e** are shown in Table 1, Figure 1a and b.

The DSC thermograms of the higher homologues of the series (**7a** and **7b**) show three types of phase transition in both the heating and cooling cycles with reasonable enthalpy changes. Compound **7a**,[16] when placed in a thin cell with a cell gap of $d = 5 \pm 0.2$ μm under homogeneous planar boundary conditions, gave the textures which is shown in Figure 2a–c. A deformed

---

* Corresponding author. Tel.: +91 33 2582 7521; fax: +91 33 2582 8282.
E-mail address: kcm_ku@yahoo.co.in (K. C. Majumdar).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.09.161



Scheme 1. Reagents and conditions: (i) CH_3I, dry acetone, anhydrous K_2CO_3, NaI, reflux; (ii) $POCl_3$, DMF, reflux; (iii) $SOCl_2$, reflux; (iv) *p*-nitrophenol, CH_2Cl_2, NEt_3, DMAP (cat), rt; (v) ethyl acetate, H_2/Pd, rt; (vi) dry ethanol, AcOH, reflux.

Table 1

7a

$$\mathrm{Cr} \xrightarrow[(65.6)]{132.1} \mathrm{A_2} \xrightarrow[(14.6)]{156.6} \mathrm{A_d} \xrightarrow[(27.1)]{203.4} \mathrm{I} \xrightarrow[(25.9)]{201.6} \mathrm{A_d} \xrightarrow[(12.6)]{153.5} \mathrm{A_2} \xrightarrow[(68.6)]{120.0} \mathrm{Cr}$$

7b

$$\mathrm{Cr} \xrightarrow[(57.8)]{132.5} \mathrm{A_2} \xrightarrow[(13.9)]{159.0} \mathrm{A_d} \xrightarrow[(27.2)]{207.0} \mathrm{I} \xrightarrow[(26.5)]{205.3} \mathrm{A_d} \xrightarrow[(12.9)]{156.8} \mathrm{A_2} \xrightarrow[(60.1)]{118.8} \mathrm{Cr}$$

7c

$$\begin{tikzcd}
\mathrm{Cr} \arrow[r, "131.3", "(26.3)"'] & \textbf{Unknown Phase} \arrow[r, "133.8", "(21.1)"'] & \mathrm{A_2} \arrow[r, "162.51", "(14.0)"'] & \mathrm{A_d} \arrow[r, "209.7", "(26.6)"'] & \mathrm{I} \arrow[r, "207.9", "(26.2)"'] & \mathrm{A_d} \arrow[d, "160.41\ (12.8)"] \\
 & & & & \mathrm{Cr} & \mathrm{A_2} \arrow[l, "114.9"', "(49.6)"]
\end{tikzcd}$$

7d

$$\begin{tikzcd}
\mathrm{Cr} \arrow[r, "126.5", "(19.0)"'] & \textbf{Unknown Phase} \arrow[r, "138.8", "(21.1)"'] & \mathrm{A_2} \arrow[r, "166.6", "(14.4)"'] & \mathrm{A_d} \arrow[r, "211.4", "(26.2)"'] & \mathrm{I} \arrow[r, "209.5", "(25.8)"'] & \mathrm{A_d} \arrow[d, "164.4\ (13.6)"] \\
 & & & & \mathrm{Cr} & \mathrm{A_2} \arrow[l, "111.6"', "(32.5)"]
\end{tikzcd}$$

smectic leaf (Fig. 2a) appears from the isotropic melt in the cooling cycle with a large amount of homeotropy, which on further cooling grows slowly, and fills up the whole field of view with elliptical domains in different sites (Fig. 2b). On further cooling, the texture gradually changes at around 150 °C to a more order twisted or coiled-like structure (Fig. 2c) without any homeotropic behavior; on further cooling the sample solidified. Compound **7b** also shows a similar type of phase behavior on POM studies but the clearing temperature slightly increases in this case. Compounds **7c** and **7d** show an extra enantiotropic transition during heating cycles in DSC thermograms, but in cooling cycles they show the similar three transitions as for their higher homologues. Compound **7d,** when placed in a thin cell with a cell gap of $d = 5 \pm 0.2$ µm under homogeneous planar boundary conditions, gave the textures represented in (Fig. 2d–f) during the heating cycles. Figure 2d corresponds to an unknown phase transition, and the other two transitions were very similar to phase transitions reported for their higher homologues. On the other hand, the compound **7e** shows three similar transitions during both the heating and cooling cycles as for higher homologues.

Powder X-ray diffraction of **7a** shows a sharp peak in the low angle region implying the formation of a layered structure and a broad diffuse peak in the wide angle region centered at d-spacing of ∼4.4 Å, indicating the liquid-like arrangement of the molecules within the layers (Fig. 3). The d-spacing at two different temperatures in the low angle region is around 49 Å and 56 Å, respectively, which is sufficiently larger than the calculated molecular length ($L \sim 29$ Å) values from molecular models. The *d*-value at 140 °C is approximately double the calculated molecular length of the compound **7a**, and at 200 °C, it is approximately 1.5 times the molecular length of the compound **7a**. It is well known that when the reflection within the smectic A layer corresponds to $d \sim 2L$, the smectic A layer is called a bilayer (A_2) and when the layer-spacing is intermediate between L and $2L$ then it is called a partially bilayer (A_d) phase.[17,18] Therefore, we can designate the phase at higher temperature as A_d and at lower temperature as A_2.

Usually, for symmetric and non-polar molecules, SmA layer-spacing is approximately equal to L; however, in molecules with a strong longitudinal dipole moment near-neighbour antiparallel correlations exist that can result in subtle changes in the structure,

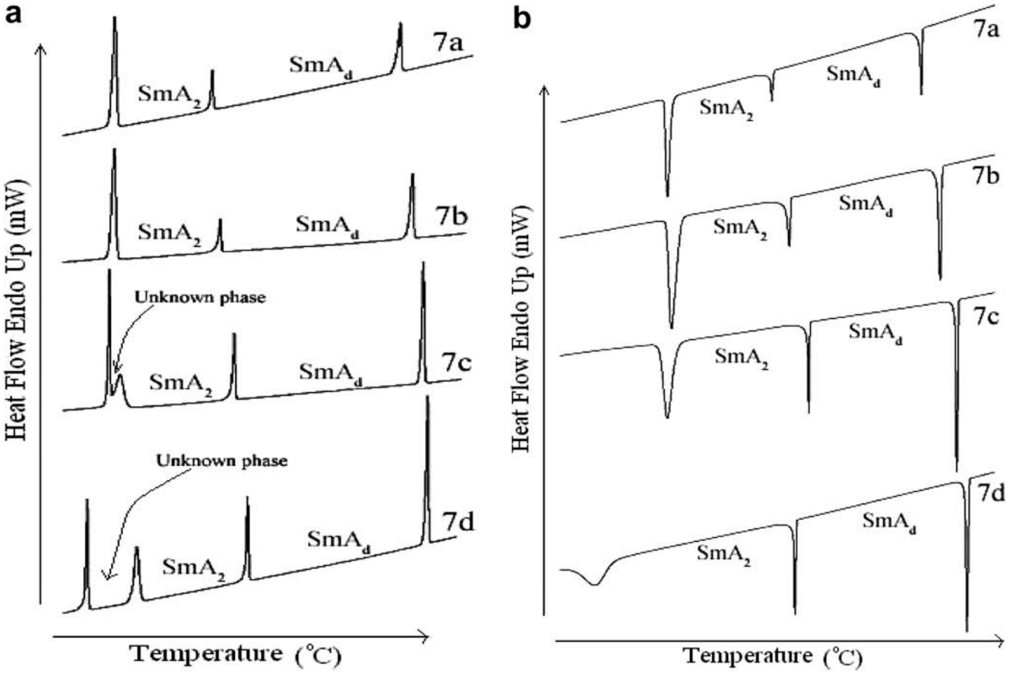


Figure 1. (a) DSC thermograms in heating cycles of **7a-d**. (b) DSC thermograms in cooling cycles of **7a–d**.

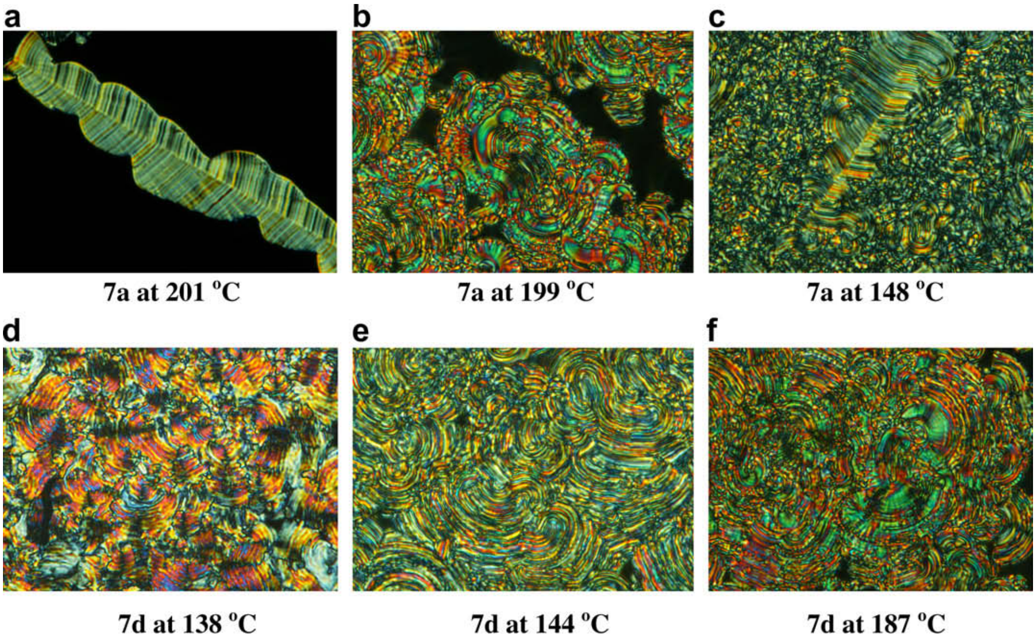


Figure 2.

which can exhibit more than one form of SmA phase. The appearance of a SmA$_d$ phase at higher temperature may be due to the overlap of two neighboring bent-shaped molecules in antiparallel orientation as in the case of highly polar rod-like molecules,[19,20] and at lower temperatures the molecules stack up in layers without overlapping with the electric dipoles concentrated at the boundary between every other layer resulting in the SmA$_2$ phase.

Conoscopic studies of **7a** were conducted by inserting Bertrand lens between the analyzer and ocular lens, observed between crossed polarizers, set at 45° to the direction of the electric field, show uniaxial interference patterns for the SmA$_d$ phase at 196 °C and SmA$_2$ phase at 140 °C (Figs. 4 and 5). In this case, the conoscopic interference pattern is not dark-like Maltese cross but is instead rather bright.

In our earlier Letter regarding a liquid crystalline material based on a TPA core, we reported[21] that trisubstitution on the TPA core with a Schiff base linkage resulted in excellent columnar mesophase behavior. On the other hand, Wang et al.[22] reported a similar type of trisubstitution with a C=C linkage, which exhibited nonmesophase behavior. This may be due to the more rigid sp^2-hybrid orbital in C=C bonds instead of a more flexible C=N bond. They also reported that disubstitution on the TPA core with a CH$_2$NH

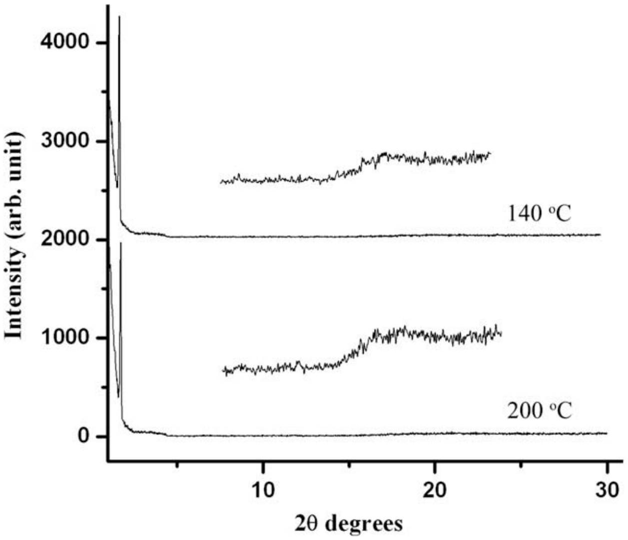


Figure 3. XRD diagram of **7a**.

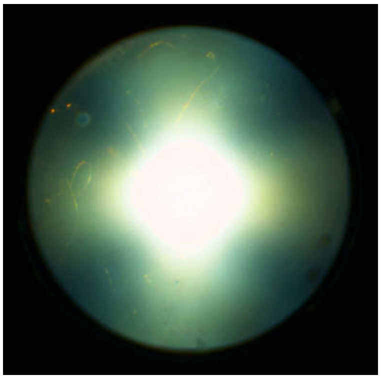


Figure 4. Conoscopic interference pattern observed for **7a** at 140 °C.

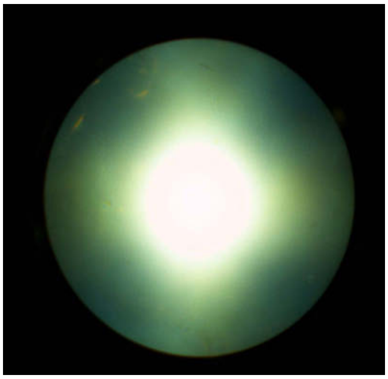


Figure 5. Conoscopic interference pattern observed for **7a** at 196 °C.

linkage resulted in similar non-mesophase behavior. At the present time, we have studied a disubstituted *N*-MeDPA core instead of the TPA core and notably, all the homologous compounds exhibit a SmA phase, which show transitions from the partial bilayer SmA$_d$ phase to the bilayer SmA$_2$ phase as the temperature is lowered.

In this DPA homologous series including both short- and long-chained members, two smectic phases are evident: smectic A$_d$ and smectic A$_2$ with temperatures of approximately 50 and 30 °C, respectively. Compounds **7c** and **7d** exhibit an unknown phase before the smectic A$_2$ phase on heating from solid or cooling from the smectic A$_2$ phase. From molecular models, it has been observed that the molecule deviates from the usual bent shape and approaches a rod-like configuration with symmetrical chains facing opposite directions. Initially, we assumed that the molecules should have a bent structure and must give banana phases; however, X-ray profiles of these compounds led to a remarkable observation in which only one small angle diffraction peak must be for the smectic fluctuation and the *d*-value larger than the molecular length indicates A$_d$ and A$_2$ phases rather than a banana phase. We conclude that this is a remarkable observation as DPA possesses numerous properties and also exhibits a smectic liquid crystalline phase.

Acknowledgments

We thank the DST (New Delhi) for financial assistance and the Material Science Department, IACS, Kolkata for HRXRD. Three of us (B.C., S.C., and R.K.S.) are grateful to the CSIR (New Delhi) for the fellowships.

References and notes

1. Niori, T.; Sekine, T.; Watanabe, J.; Furukava, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231.
2. Shen, D.; Diele, S.; Wirth, I.; Tschierske, C. *Chem. Commun.* **1998**, 2573.
3. Shen, D.; Diele, S.; Pelzl, G.; Wirth, I.; Tschierske, C. *J. Mater. Chem.* **1999**, *9*, 661.
4. Link, D. R.; Natale, G.; Shao, R.; Maclennan, J. E.; Korblova, E.; Walba, D. M. *Science* **1997**, *278*, 1924.
5. Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707.
6. Rouillon, J. C.; Marcerou, J. P.; Laguerre, M.; Nguyen, H. T.; Achard, M. F. *J. Mater. Chem.* **2001**, *11*, 2946.
7. Olson, D. A.; Veun, M.; Cady, A.; D'Agostino, M. V.; Johnson, P. M.; Nguyen, H. T.; Chien, L. C.; Huang, C. C. *Phys. Rev. E* **2001**, *63*, 41702.
8. Nadasi, H.; Weissflog, W.; Eremin, A.; Pelzl, G.; Diele, S.; Das, B.; Grande, S. *J. Mater. Chem.* **2002**, *12*, 1316.
9. Bedel, G.; Rouillon, J. C.; Maroerou, J. P.; Laguerre, M.; Nguyen, H. T.; Achard, M. F. *Liq. Cryst.* **2001**, *28*, 1285.
10. Sadashiva, B. K.; Reddy, R. A.; Pratibha, R.; Madhusudana, N. V. *J. Mater. Chem.* **2002**, *12*, 943.
11. Reddy, R. A.; Sadashiva, B. K. *J. Mater. Chem.* **2002**, *12*, 2627.
12. Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.
13. Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75.
14. Cho, J.-S.; Kimoto, A.; Higuchi, M.; Yamamoto, K. *Macromol. Chem. Phys.* **2006**, *6*, 635.
15. Koene, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235.
16. *Typical procedure for the synthesis of compound* **7a**: A mixture of compound 3 (100 mg, 0.418 mmol) and 4-aminophenyl-4-(octadecyloxy)benzoate (403 mg, 0.836 mmol) was refluxed in absolute ethanol in the presence of a catalytic amount of glacial acetic acid for 2 h. The Schiff base **7a** was precipitated out from the hot reaction mixture. It was collected, washed with hot ethanol repeatedly, and dried in vacuum.
    Compound **7a**: Yield 98%; IR (KBr): 2921, 1730, 1600, 1507 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 0.86–1.86 (m, 70H), 3.46 (s, 3H), 4.02 (t, 4H, *J* = 6.4 Hz), 6.94 (d, 4H, *J* = 8.8 Hz), 7.14 (d, 4H, *J* = 8.4 Hz), 7.19–7.23 (m, 8H), 7.82 (d, 4H, *J* = 8.4 Hz), 8.11 (d, 4H, *J* = 8.8 Hz), 8.39 (s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 14.5, 23.1, 26.4, 29.5, 29.7, 29.8, 29.9, 29.9, 30.0, 30.1, 32.3, 40.5, 68.7, 114.7, 120.7, 121.9, 122.2, 122.8, 130.3, 130.6, 132.6, 149.4, 150.2, 151.0, 159.8, 163.9, 165.4. Anal. Calcd for $C_{77}H_{103}N_3O_6$: C, 79.27; H, 8.90, N, 3.60. Found: C, 79.57; H, 8.99; N, 3.27.
17. Ostrovskii, B. I.; Pavluchenku, A. I.; Petrov, V. F.; Saidachmetov, M. A. *Liq. Cryst.* **1989**, *5*, 513.
18. de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Oxford Press, 1993.
19. Madhusudana, N. V.; Chandrasekhar, S. *Pramana Suppl.* **1975**, *1*, 57.
20. Leadbetter, A. J.; Prost, J. C.; Gsughan, J. P.; Gray, G. W.; Mosley, A. *J. Phys.* **1979**, *40*, 375.
21. Majumdar, K. C.; Pal, N.; Debnath, P.; Rao, N. V. S. *Tetrahedron Lett.* **2007**, *48*, 6330.
22. Wang, Y.-J.; Sheu, H.-S.; Lai, C. K. *Tetrahedron* **2007**, *63*, 1695.