Tetrahedron 65 (2009) 3664–3667

Contents lists available at ScienceDirect

Tetrahedron

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

Conformational isomerism in 1,2-di-*o*-tolylnaphthalenes: selective rotation of the 2-aryl ring

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ARTICLE INFO

Article history:
Received 22 November 2008
Received in revised form 6 February 2009
Accepted 26 February 2009
Available online 5 March 2009

Keywords:
1,2-Diarylnaphthalenes
Conformational behavior
Selective rotation
Dynamic NMR

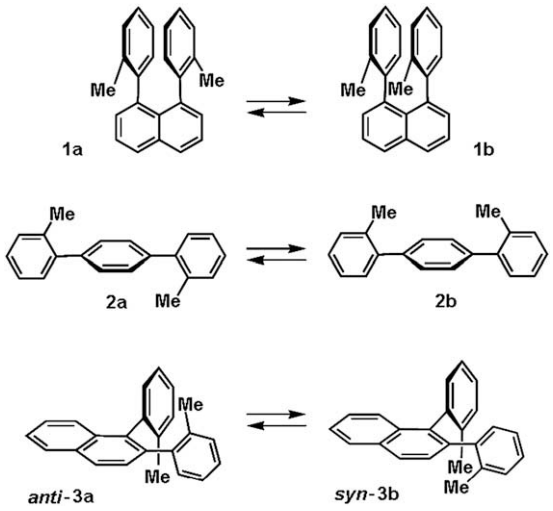
ABSTRACT

Two derivatives (X=Cl, CN) of 1,2-ditolylnaphthalene were prepared as models to investigate their conformational behavior that could involve rotation of either of the tolyl rings. The existence of *anti* and *syn* atropisomers was evident from their ^{1}H NMR spectra at room temperature indicating two pairs of well-resolved singlets for the methyl protons. Dynamic ^{1}H NMR studies estimated the rotation barrier to be about 76–82 kJ mol^{-1}, a value consistent with selective rotation of the 2-tolyl ring in the conformation inter-conversion.

1. Introduction

Restricted rotation (atropisomerism) of sterically hindered groups in a large number of molecules has been studied experimentally.[1] There has been continued interest in the conformational analysis of oligophenyls by various spectroscopic, analytical, and computational studies.[2] The dependence on their conformational behavior in crystal growth,[3] organic/metal interface,[4] and polymer properties[5] have been reported. Earlier efforts were directed toward the observation and/or isolation of the *syn* and *anti* conformational isomers of *ortho*-disubstituted benzene derivatives or polyarylbenzenes.[6] Clough and Roberts[7] successfully separated the *anti*-**1a** and *syn*-**1b** isomers of 1,8-di-*o*-tolylnaphthalene **1**, which had an observed rotational barrier of 101 kJ mol^{-1}, although the half-life with respect to inter-conversion in solution was about one day. Unique spectral and laser characteristics of 1,4-di-*o*-tolylbenzene **2** have been observed[8] but experimental identification of its atropisomers *anti*-**2a** and *anti*-**2b** was only recently reported in an NMR study at −150 °C.[9]

In this work we report the conformational study of two derivatives of 1,2-di-*o*-tolylnaphthalene **3**. In principle an inter-conversion between the two atropisomers of **1** or **2** could be achieved by rotation of either of the two tolyl rings. In **3**, there is a unique possibility that atropisomerization engages selective rotation of only one of the tolyl rings that involves a relatively lower conformational barrier (Scheme 1).



Scheme 1. Atropisomerism in selected teraryls.

2. Results and discussion

A synthetic route to 1,2-diphenylnaphthalenes using 1-benzamido-2-naphthol **5**[10] was reported by Mustafa and Kamel.[11]

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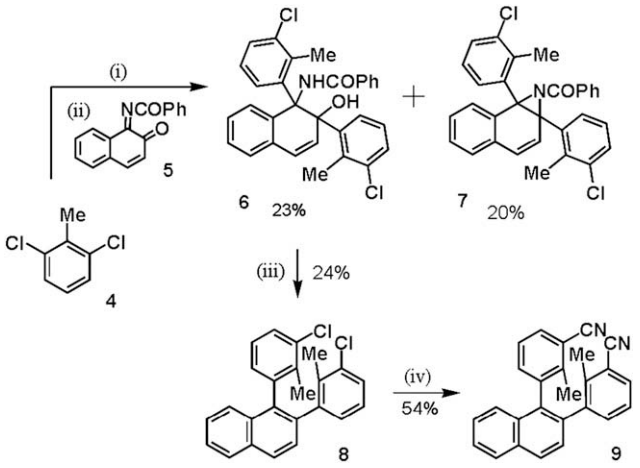
0040-4020/$ – see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.tet.2009.02.068

A summary of our synthetic approach to 1,2-diarylnaphthalenes **8** and **9** is illustrated in Scheme 2. Introduction of the 3,3′-substituents should not affect their conformational behavior with reference to that of the parent molecule **3**. The spherical Cl and cylindrical CN groups are, however, expected to exert appreciable buttressing effects[12] in raising their rotational barrier to be readily estimated by dynamic ^{1}H NMR spectroscopy. In addition the polarized *ortho*-Cl and CN functions should indirectly induce more significant chemical shift difference in the methyl proton signals between the *anti* and *syn* isomers.



Scheme 2. Synthesis of 1,2-diarylnapthalenes **8** and **9**. Reagents and conditions: (i) Mg/$BrCH_2CH_2Br$ (cat.), THF, reflux, 3 h; (ii) **5**, benzene, reflux, 3 h; rt, 8 h; (iii) Zn, AcOH, 2% aq $[H_3O]^+_2[PtCl_6]^{2-}$ (cat.), concd HCl, reflux, 16 h; (iv) CuCN, *N*-methyl-2-pyrrolidinone, reflux, 32 h.

Addition of the Grignard reagent of 2,6-dichlorotoluene (**4**) to 1,2-napthoquinone-1-benzimide (**5**) unexpectedly led to the isolation of two products obtained in similar yields of about 20% after chromatography. The desired product **6** was the one eluted second from column chromatography. A rather broad melting point in the range of 248–254 °C was observed for this product even after repeated recrystallizations (methanol/chloroform). In its ^{1}H NMR spectrum (25 °C) broad and unresolved signals were observed at δ 1.4–2.9 (methyl protons) and δ 7.2–7.7 (aromatic protons). Overlapping AB quartets of the vinyl protons appeared at δ 6.3–7.0, with a major AB quartet (J 9.6 Hz) observed at δ 6.45 and 6.85. At −20 °C, up to six singlets were observed for the methyl protons but the region for vinyl protons became more complicated. Most of these signals coalesced at ca. 70 °C. At 120 °C two broad singlets at δ 2.06 and 2.11 were observed for the methyl protons and a major AB quartet (J 9.8 Hz) appeared at δ 6.54 and 6.90. Consecutive *anti* and/or *syn* addition of Grignard reagent of **4** to **5** would be expected to afford a mixture of up to four stereoisomers of **6**. Restricted rotation of the aryl rings would further result in different conformers. Steric consideration would expect preferred *anti* addition of Grignard reagents of **4** to **5** to give mainly *trans*-**6**. The presence of rotational isomers was believed to be responsible for the broad melting point and ^{1}H NMR signals observed. At the higher temperature limit, rapid rotation of the aryl rings within the NMR time scale would result in simpler averaged signals, e.g., two singlets for the methyl protons in *trans*-**6**.

The component eluted first from column chromatography showed a molecular ion at m/z 495 with a correct isotope pattern for two chlorine atoms. The base peak was observed at m/z 105 corresponding to the C_6H_5CO fragment. Its IR spectrum indicated the absence of O–H group but the C=O absorption was clearly observed at 1635 cm^{-1}. The above spectral data are consistent with

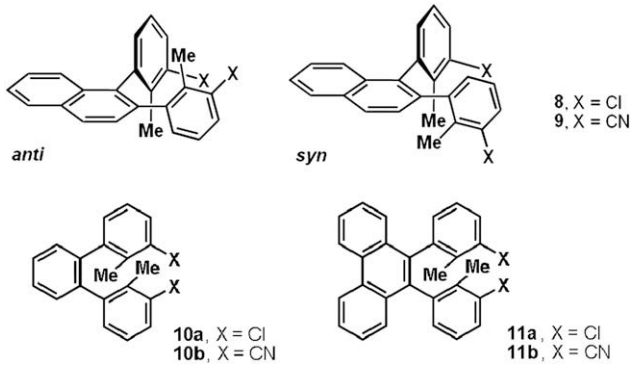


Figure 1. *Anti* and *syn* conformers of teraryls **8**, **9**, **10**, and **11**.

the structure of aziridine **7**. Two major singlets (likely due to a mixture of rotational isomers) at δ 2.03 and 2.32 were observed for the methyl protons in its ^{1}H NMR spectrum. Results from the elemental analysis supported the structure of **7**. Formation of aziridine **7** should have derived from an intramolecular elimination (dehydration) of **6**, although no similar product was reported in the preparation of 1,2-diphenylnaphthalene.[11] On the other hand, similar elimination reactions to form aziridines were observed in *trans*-α-phenylselenonylbenzamide[13] and *trans*-α-bromoacetamide,[14] albeit under basic conditions. In going from **6** to **7**, both S_N1 and $S_2$2 mechanisms were conceivable. The former was more likely in acidic medium in the work-up and chromatography, and particularly under the acidic conditions employed in the subsequent intended conversion of **6** to **8**.

Conversion of **6** to diarylnaphthalene **8** was carried out with zinc dust in acetic and hydrochloric acids in the presence of a catalytic amount of chloroplatinic acid.[11] The aziridine **7** was obtained as a side product. In the ^{1}H NMR spectrum of **8**, four singlets were observed for the methyl protons at δ 1.87, 2.07, 2.15, and 2.21 in a ratio of 3:5:3:5. That was consistent with a mixture of rotational isomers *anti*-**8** and *syn*-**8** (Fig. 1), with the expected two methyl signals from each isomer. Treatment of **8** with CuCN in refluxing *N*-methyl-2-pyrrolidinone (von Braun reaction)[15] gave the dinitrile **9**. In its ^{1}H NMR spectrum, the methyl protons also appeared as two pairs (3:2) of singlets at δ 2.44, 2.29 and 2.39, 2.08 respectively, indicating the existence of *anti*-**9a** and *syn*-**9b** (Fig. 1).

The existence of *anti* and *syn* isomers of 1,2-diarylbenzenes **10**[12a] was evident from ^{1}H NMR studies with barriers to rotation of 62–75 kJ mol^{-1}. Rotational barriers in 9,10-diarylphenanthrenes **11**,[16] however, were found to involve much larger barriers in the range of 115–158 kJ mol^{-1}. Their conformational behavior in **11** could not be studied[16a] by dynamic ^{1}H NMR spectroscopy and experimental data were estimated by a gas chromatographic method.[16b,c] Dynamic ^{1}H NMR (300 MHz) studies of **8** and **9** at high temperatures were attempted using deuterated nitrobenzene as the solvent. A solvent shift of the methyl signals was observed accompanied by relatively poorer resolution (compared to that in $CDCl_3$) of these signals. The observed spectra, however, still showed four well-resolved methyl signals appropriate for conformational studies based on the coalescence temperature method[17] to estimate the free energy of activation ($\Delta G_c^{\ddagger}=4.57T_c[9.97+\log_{10}(T_c/\Delta\nu)]$).[18] An advantage of studying the diarylnaphthalenes **8** and **9**, compared with the highly symmetrical **10** and **11**, is that coalescences of two pairs of methyl signals could be used to give a more accurate estimate of the energy barrier.

Another interesting feature in the rotational isomerism of 1,2-diarylnaphthalenes is the four possible transition states **Ia–Id** (Fig. 2) versus the respective sets of two in the 1,2-diarylbenzenes (**IIa** and **IIb**) and 9,10-diarylphenanthrenes (**IIIa** and **IIIb**). In any of

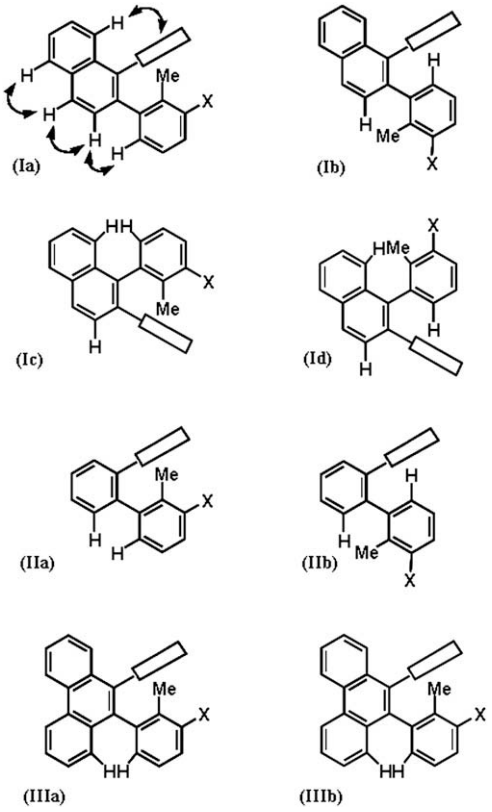


Figure 2. Transition states in the rotational isomerism in *ortho*-diarylbenzenoids.

these transition states, one aryl ring is expected to be near perpendicular and another near planar to the reference central benzenoid moiety. The rotational barriers for the aryl rings in **10** and **11** are <75[16] and >110[17] kJ mol^{-1}, respectively. Such a large difference in conformational barrier is clearly explained when the 'bay region' steric interactions are considered as in **IIa** versus **IIIa** or **IIb** versus **IIIb**. These are qualitatively consistent with an expected increase in the relative measures of steric effects observed going from triphenylene to dibenzochrysene. Among the possible transition states **Ia**–**Id** (Fig. 1), the pair of **Ia** and **Ib** would then be expected to be relatively more stable than **Ic** and **Id** on the basis of steric considerations. The rotational barriers of the aryl rings in **8** and **9** should then be similar to those observed for **10a** and **10b** but much lower than those for **11a** and **11b**.

In the ^{1}H NMR spectrum (300 MHz; $C_6D_5NO_2$) of a mixture of *anti*-**8** and *syn*-**8**, two pairs of methyl signals were observed at δ 2.44, 2.29 and 2.39, 2.08, respectively, in a ratio of ca. 1.4:1.0. All four methyl signals broadened as the temperature was raised and the two singlets at δ 2.44 and 2.39 ($\Delta\nu$=15.2 Hz) first collapsed at 78 °C followed by those at δ 2.29 and 2.08 ($\Delta\nu$=62.4 Hz) at 98 °C. At 120 °C, two singlets were observed at the averaged chemical shifts of δ 2.42 and 2.19, respectively. This phenomenon is typical of a dynamic uncoupled AB system. When the sample was cooled, the original spectrum at room temperature was again observed. This is consistent with a true conformational inter-conversion between the rotational isomers *anti*-**8** and *syn*-**8**. In the ^{1}H NMR spectrum (300 MHz; $C_6D_5NO_2$) of a mixture of *anti*-**9** and *syn*-**9**, two pairs of methyl signals were observed at δ 2.21, 2.07 ($\Delta\nu$=17.9 Hz) and 2.15, 1.87 ($\Delta\nu$=60.1 Hz), respectively, also in a ratio of ca. 1.4:1.0. The relatively more deshielded methyl signals in **9** are likely due to the anisotropic effect of the cyano group. As a sample of *anti*-**9** and *syn*-**9** was warmed, a similar coalescence phenomenon of the methyl signals was observed with T_c values at 110 °C and 122 °C, respectively.

Table 1
Comparison of dynamic ^{1}H NMR data for the barrier to rotation in 1,2-diarylbenzenes and 1,2-diarylnaphthalenes

Cpd	$\Delta\nu$/Hz	k_c/Hz	T_c/°C	$\Delta G_c^{\ddagger}$/kJ mol^{-1}
8[a]	17.9	39.8	110	82.2
	60.1	133.5	122	81.0
9[a]	15.2	33.8	78	75.6
	62.4	138.6	98	75.7
10a[b]	7.0	15.6	58	74.0
10b[b]	5.6	12.5	42	70.9

[a] Our work; ^{1}H NMR spectra determined on a 300 MHz spectrometer.
[b] Reference 16; ^{1}H NMR spectra determined on a 90 MHz spectrometer.

The relevant data from the dynamic NMR studies of **8** and **9** are summarized in Table 1. For **8** or **9**, values of the transition state free energy at coalescence, $\Delta G_c^{\ddagger}$, calculated from coalescences of the two pairs of methyl signals agree very well to give a good estimate of the rotational barrier for the aryl rings. In going from the dinitrile **9** ($\Delta G_c^{\ddagger}$=ca. 75.7 kJ mol^{-1}) to dichloride **8** ($\Delta G_c^{\ddagger}$=ca. 81.6 kJ mol^{-1}) an increase in energy barrier was observed. This is consistent with an increase in steric demand[19] going from the cylindrical cyano group to the spherical chlorine atom. A greater steric demand (buttressing effect) of the substituent 3′-X would thrust the 2′-methyl group closer to the π-cloud of the opposite aryl ring in **Ia** or H3 in **Ib**, thus increasing the energy barrier for isomerization.

The conformational energy barriers observed for **8** and **9** are similar to those reported for **10a** and **10b** (Table 1) but much lower than those for **11** ($>$110 kJ mol^{-1}). This is clearly consistent with the qualitative prediction discussed earlier that rotational isomerization in **8** and **9** would likely involve the transition states **Ia** and/or **Ib**, which are similar to **IIa** and **IIb**, respectively (Fig. 2). In addition to the buttressing effect of the substituent 3′-X, **Ia** would also experience a tunneling buttressing effect involving the H5→H4→H3→H6′ interaction while an H5→H4→H3→2′-Me interaction would exist in **Ib** (Fig. 2). These steric interactions are believed to account for the relatively higher rotational energy barriers in **8** and **9** compared to those for **10a** and **10b**, respectively (Table 1).

3. Conclusion

The dynamic ^{1}H NMR studies of **8** and **9** provided good evidence that they behave differently from the conformational isomerization in 1,8-di-*o*-tolylnaphthalene **1**, 1,4-di-*o*-tolylbenzene **2**, and 1,2-di-*o*-tolylbenzenes **10** in that **8** and **9** could involve rotation of either of their tolyl rings. In conclusion, the conformational isomerization of *anti* and *syn* atropisomers of 1,2-di-*o*-tolylnaphthalene **3** is thus expected to proceed selectively via rotation of only the 2-tolyl ring.

4. Experimental section

4.1. Benzamide 6 and aziridine 7

A solution of 2,6-dichlorotoluene (9.24 g, 57.4 mmol) in dry THF (50 mL) was added dropwise to a mixture of magnesium turnings (1.40 g, 57.4 mmol) and catalystic amount of 1,2-dibromoethane under nitrogen atmosphere. The mixture was refluxed gently for about 3 h until all magnesium dissolved. The Grignard reagent formed was cooled and dry benzene (50 mL) was added. 1,2-Naphthoquinone-1-benzimide (**5**) (1.5 g, 5.74 mmol) was then added and the mixture was further refluxed for another 3 h. After additional stirring for another 8 h at room temperature, the reaction mixture was cooled in an ice-bath and an aqueous solution of ammonium chloride was added slowly with stirring. The organic layer was separated and the aqueous layer was extracted three times with dichloromethane. The combined organic extracts were washed, dried and evaporated to yield the crude product, which

was chromatographed on silica gel using a mixture of dichloromethane and hexane (3:1) as the eluant. Eluted first was the aziridine derivative **7** (0.56 g, 20%), mp 130–136 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.0–8.0 (m, 16H, ArH and CH=CH), 6.70 (br d, *J* 8 Hz, 1H, CH=CH), 2.32, 2.03 (s, total 6H, CH_3); IR (KBr) 3235 (br), 1640, 1505, 1470, 1425, 1372, 1295 (br), 1270 (br), 1000, 780, 748, 708 cm^{-1}; MS *m*/*z* 495 ($M^{\bullet+}$, 65), 105 (100), 77 (60). Anal. Calcd for $C_{31}H_{23}ONCl_2$: C, 75.00; H, 4.67; N, 2.82%. Found: C, 74.27; H, 4.46; N, 3.26%. M_r calcd for $C_{31}H_{23}ONCl_2$: 495.1156; found (MS): 495.1156. Eluted next was the desired product **6**, 0.68 g (23%). Recrystallization of a sample from chloroform/benzene gave colorless crystals of **6**, mp 248–254 °C. ^{1}H NMR (300 MHz, DMSO-d_6/$CDCl_3$), refer to discussion in the text; IR (KBr) 3450, 3400, 3140 (br), 2920, 2840, 1700, 1500, 1480, 1420, 1300, 1285, 1100, 1050, 1020, 1000, 800, 760, 730, 710, 625 cm^{-1}; MS *m*/*z* 513 ($M^{\bullet+}$, 1), 496 (1), 408 (52), 345 (28), 254 (10), 153 (38), 105 (100), 77 (60), 28 (69). Anal. Calcd for $C_{31}H_{25}O_2NCl_2$: C, 72.38; H, 4.90; N, 2.72%. Found: C, 72.37; H, 4.74; N, 2.78%.

4.2. 1,2-(3-Chloro-2-methylphenyl)naphthalene 8

To a solution of **6** (4.00 g, 7.78 mmol) in glacial acetic acid (200 mL) was added finely powdered zinc dust (15.27 g, 233 mmol) in three equal batches at intervals followed by catalytic amount of a 2% aqueous solution of chloroplatinic acid was added. Concentrated hydrochloric acid (60 mL) was then added slowly. The reaction mixture was refluxed for 16 h and thereafter, it was poured into water and extracted with dichloromethane. The organic extract was washed with water, aqueous sodium bicarbonate solution, dried, and evaporated. The crude product was chromatographed on silica gel using dichloromethane/hexane (1:1) as the eluant. The first major component collected was the desired product **8**, 0.74 g (24%). It was recrystallized from cyclohexane to give colorless crystals of **8**, mp 108–110 °C. ^{1}H NMR δ 6.8–8.2 (m, 12H, ArH), 2.21, 2.07 (s, total 2H, CH_3), 2.15, 1.87 (s, total 6H, CH_3); IR (KBr) 3082, 2960, 2925, 2860, 1590, 1560, 1500, 1430, 1375, 1330, 1260, 1210, 1190, 1145, 1112, 1070, 1020, 918, 870, 825, 728, 750, 718, 690, 648 cm^{-1}; MS *m*/*z* 376 ($M^{\bullet+}$, 100), 342 (25), 326 (10), 289 (22), 215 (33), 144 (15), 85 (14), 57 (34), 43 (27). Anal. Calcd for $C_{24}H_{18}Cl_2$: C, 76.59; H, 4.79%. Found: C, 76.24; H, 4.67%. Eluted next was the aziridine **7** (0.69 g; 25%) identical to the sample obtained earlier.

4.3. 1,2-(3-Cyano-2-methylphenyl)naphthalene 9

Copper(I) cyanide (11.68 g, 130.4 mmol) was added to a solution of **8** (4.92 g, 13.04 mmol) in *N*-methyl-2-pyrrolidinone (150 mL). The reaction mixture was heated under reflux for 16 h. It was cooled to about 60 °C and another batch of copper(I) cyanide (11.68 g, 130.4 mmol) was added. The reaction mixture was further refluxed for another 16 h. It was cooled to about 100 °C and poured into concentrated NH_3/ice (1:1; 300 mL). After mixing thoroughly for 15 min, the mixture was filtered. The residue was successively extracted with dichloromethane and filtered. The organic fractions were combined and evaporated to give a brown residue. The residue was redissolved in ether and repeatedly washed with dil. HCl (1 M). The ether extract was dried and evaporated to give the crude product. After column chromatography on silica gel with hexane/dichloromethane (1:1) as the eluant, the fractions found to contain the product were combined and evaporated to give **9**, 2.55 g (54%). A sample recrystallized from cyclohexane/benzene afforded colorless crystals of **9**, mp 170–172 °C. ^{1}H NMR δ 7.1–8.2 (m, 12H, ArH), 2.44, 2.29 (s, total 2H, CH_3), 2.39, 2.08 (s, total 2H, CH_3); IR (KBr) 2210, 1430, 1375, 1260, 1230, 820, 800, 740, 720 cm^{-1}; MS *m*/*z* 358 ($M^{\bullet+}$, 100), 343 (30), 240 (22). Anal. Calcd for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82%. Found: C, 87.07; H, 5.10; N, 7.82%.

Acknowledgements

This work was supported by the Singapore Ministry of Education AcRF Tier 1 Grant R-143-000-248-112. The authors thank the staff at the Chemical, Molecular and Materials Analysis Center, Department of Chemistry, National University of Singapore, for their technical assistance.

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