COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Cyclodehydrogenation of di- and tetra(benzimidazol-2-yl)benzenes to give model heteroaromatic discotic systems

Weicheng Wu, Andrew. C. Grimsdale and Klaus Müllen*
Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany.
E-mail: muellen@mpip-mainz.mpg.de; Fax: +49 6131 379350; Tel: +49 6131 379150

Received (in Cambridge, UK) 6th February 2003, Accepted 28th February 2003
First published as an Advance Article on the web 7th April 2003

Di-and tetra(benzimidazol-2-yl)benzenes upon oxidation undergo cyclodehydrogenation with formation of N–N bonds to form planarized polycyclic compounds which are models for the cores of heteroatom-containing discotic materials, and which can be readily reduced back to the original compounds, thus demonstrating a molecular redox switch.

Cyclodehydrogenation is a well-known method for preparing polycyclic aromatic hydrocarbons from oligophenylene precursors, *e.g.* oxidation of *o*-diphenyl- and hexaphenylbenzene produces triphenylene[1] and *peri*-hexabenzocoronene (HBC),[2] respectively. Reductive cyclodehydrogenation of hexaphenylbenzene with lithium affords the dianion of diphenyltetrabenz[*a*,*c*,*h*,*j*]anthracene.[3] However, to the best of our knowledge, there is no report of similar cyclodehydrogenations being used to make bonds other than C–C bonds. The ability to make other bonds, *e.g.* C–N or N–N bonds, would enable the synthesis of discotic molecules containing heteroatoms which would have higher electron densities and perhaps higher charge carrier mobilities in columnar mesophases.[4] The change in the molecular conformation from the twisted to the flat two-dimensional structure will also improve the molecules' ability to self-assemble and thus potentially their charge carrying properties. In addition the well-known ability of N–N bonds to be reductively cleaved[5] offers the possibility to use materials containing them in a molecular redox switch. Imidazoles are promising building blocks for electron rich materials as due to their having six π-electrons delocalised over only five atoms, they have higher electron densities than six-membered rings. Further, benzimidazole derivatives can easily pick up or release protons and form networks *via* hydrogen bond bridges.[6] Therefore they are promising building units for the development of proton conducting materials. †

We report the synthesis of di- and tetra(benzimidazol-2-yl)-benzenes **1** and **2** which are the precursors to models for heteroatom-containing discotic mesogens. Such compounds are of interest as active materials in electronic devices.[7]

The compounds **1** (colorless powder) and **2** (yellow powder) were obtained in yields of 84% and 77% respectively by condensation of phthalic acid and 1,2,4,5-benzenetetracarboxylic acid respectively with *o*-diaminobenzene in a mixture of phosphorus pentoxide and methanesulfonic acid (PPMA) at 120 °C for 24 h (Scheme 1). PPMA was prepared by adding phosphorus pentoxide (30 g) to methane sulfonic acid (210 ml) in portions and stirring the mixture at 80 °C until the phosphorus pentoxide had completely dissolved. The main advantage of this method over using polyphosphoric acid (PPA) which is commonly employed for preparation of benzimidazole derivatives[8] is that PPMA is less viscous than PPA and so the reactions can proceed at lower temperatures (110–125 °C, *cf.* 220 °C).

Bis(benzimidazole)s linked *vis* C–C bonds *e.g.* **3**, or C,N–bonds, *e.g.* **4**, are readily obtained by simple procedures.[9,10] Dimers linked *via* N, N′– bonds *e.g.* **5** can only be prepared by multistep routes involving sequential closing of the imidazole rings.[11] Despite many attempts, there is to date no report of the coupling of two benzimidazole units *via* formation of a N–N bond.

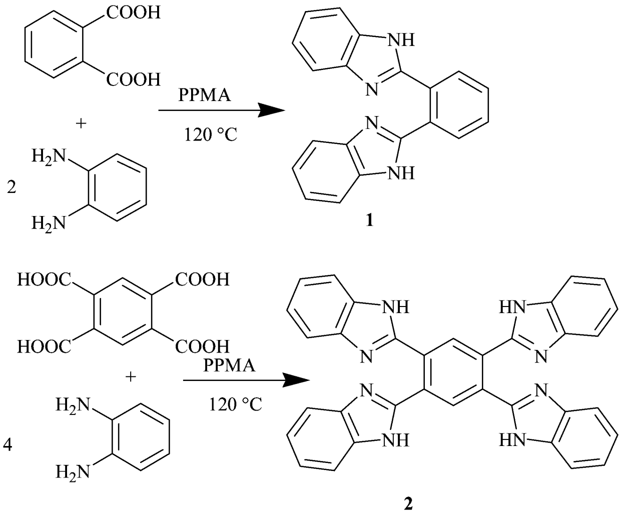
For the conversion of **1** to **6** by means of cyclodehydrogenation to create a N–N bond (Scheme 2), a number of different oxidizing agents were tested, including $FeCl_3$, I_2, PbO_2, $Pb(OAc)_4$, $NaIO_4$, $AgClO_4$ and $SbCl_5$. It was found that only $AgClO_4$, PbO_2–K_2CO_3, $SbCl_5$ and $NaIO_4$ gave an oxidation product (30–65% yield) but because of the difficulty in handling $AgClO_4$ in which traces of Ag can reduce the yield, PbO_2–K_2CO_3, $NaIO_4$ and $SbCl_5$ were preferable reagents. The best yield (65%) was obtained by stirring **6** with a large excess of lead dioxide (17 eq.) and K_2CO_3 (5.7 eq.) in a mixture of DMSO–nitrobenzene (1 : 5) at 120 °C under argon for 24 h.

The mass spectrum of the product showed the loss of 2 mass units from the structure **1** corresponding to loss of 2 hydrogens which is consistent with either **6** or **7**. While **6** has an intramolecular –N–N– linkage, **7** is an alternative possible oxidation product as oxidation of a 2, 2′-bisbenzimidazole **3** is known to produce a quinoid structure.[12]

The UV absorption spectra (Fig. 1) of the precursor **6** has a λ_{max} = 324 nm and the product a maximum at 356 nm, but the quinoid **7** should have a larger red shift than the one obtained here (32 nm). The ^{1}H NMR spectrum contains signals between 7.2 and 8.2 ppm which proved that the oxidation product was **6** not **7** whose protons should appear only in the range of 5–7 ppm.

As shown in Scheme 2, the compound **6** can be quantitatively reduced back to **1** by stirring with hydrazine in methanol at room temperature overnight. Thus **1** and **6** act as a redox molecular switch. With the linkage or cleavage of –N–N– bonds, a reversible change between three-dimensional and two-dimensional molecular conformations is obtained. This change should lead to major changes in the phase-forming and electronic properties of materials containing these cores as is seen for triphenylene and HBC.

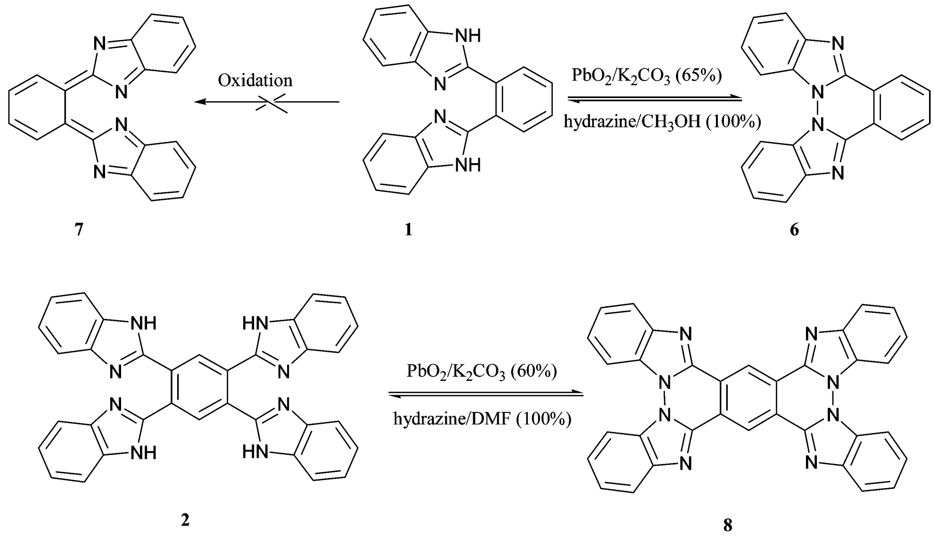
The reversible redox behaviour of the dibenzimidazolyl benzene **1** extends to tetrabenzimidazolyl benzene **2** (Scheme 2). The precursor **2** and N–N– bridged product **8** were



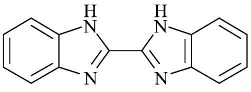
Scheme 1 Synthesis of di (**1**) and tetra(benzimidazol-2-yl)benzene (**2**).

DOI: 10.1039/b301512m

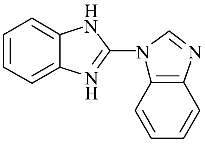
This journal is © The Royal Society of Chemistry 2003



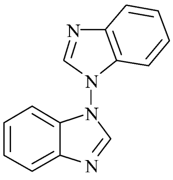
Scheme 2 Reversible ring-closure of **1** and **2**.



3



4



5

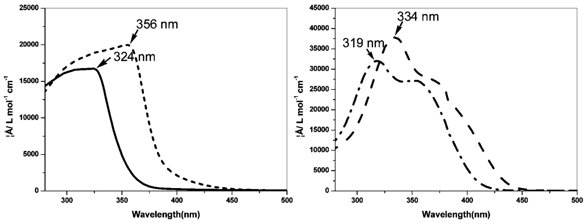


Fig. 1 UV absorption spectra of **1,2,6** and **8** in DMSO: solid line = **1**, short dashed line = **6** dashed line = **2** dash-dotted line = **8**.

characterized by ^{1}H NMR spectra. The two protons on the central benzene of **8** undergo a large shift to lower magnetic field (8.96 to 9.75 ppm) while the protons on the benzimidazole substituents show only minor changes. Because of poor solubility, compound **2** was dissolved in a different solvent (D_2SO_4+ $CDCl_3$) from **8** (DMSO-d$_6$) for ^{13}C NMR measurement.

The UV absorption spectra displayed a red shift from λ_{max} = 319 nm for molecule **7** to 334 nm for molecule **8** because of the more planar conformation of **2**. Compound **8** was readily and quantitatively reduced by hydrazine back to **2** under the same conditions as for reduction of **6** to **2**.

To conclude, di- and tetra(benzimidazol-2-yl)benzenes have been prepared in high yields. These were oxidised to produce N–N bonded polycyclic molecules, which could be readily reduced back to the starting compounds, thus demonstrating a reversible redox system. The planarized products are models for the cores of novel heteroatom-containing discotic mesogens. Derivatives of these materials functionalised with suitable substituents should show mesomorphic properties.

Research into discotic systems at Mainz is supported by the European Commission (project DISCEL) the TMR European Research Program (project SISITOMAS) and the Bundesministerium für Bildung und Forschung (Zentrum für Multifunktionelle Werkstoffe und Miniaturisierte Funktionseinheiten).

Notes and references

† Physical data for **1,2,6** and **8**. **1**: ^{1}H NMR δ(500 MHz, DMSO-d$_6$, 393 K): 8.19–8.17 (m, 2H); 7.69–7.67 (m, 2H); 7.61 (br s, 4H); 7.22–7.20 (m, 4H); ^{13}C NMR δ(125 MHz, DMSO-d$_6$, 293 K): 140.92; 128.66; 124.73; 118.55; 116.36; 115.41; 110.84; UV/Vis: λ (max) = 324 nm; MS (FD, 8kv): *m/z* (%) = 310.0 (100) [M$^+$] (calcd for $C_{20}H_{14}N_4$ = 310.36) **6**: ^{1}H NMR δ(250 MHz, DMSO-d$_6$, 293 K): 8.17–8.13 (m, 2H); 7.94–7.70 (m, 2H); 7.65–7.62 (m, 4H); 7.42–7.38 (m, 4H); ^{13}C NMR δ(125 MHz, DMSO-d$_6$, 293 K): 160.43; 143.23; 141.40; 133.31; 130.40; 128.75; 119.57; 117.93; 116.32; UV/Vis: λ (max) = 356 nm; MS (FD, 8kv): *m/z* (%) = 308.1 (100) [M$^+$] (calcd for $C_{20}H_{12}N_4$ = 308.35) **2**: ^{1}H NMR δ(250 MHz, DMSO-d$_6$, 293 K): 8.96 (s, 2H); 7.71–7.68 (m, 8H); 7.39–7.35 (m, 8H); ^{13}C NMR δ(125 MHz, D_2SO_4+ $CDCl_3$, 293 K): 140.71; 137.13; 131.12; 129.98; 127.27; 114.72; UV/Vis: λ (max) = 319 nm; MS (FD, 8kv): *m/z* (%) = 542.7 (100) [M$^+$] (calcd for $C_{34}H_{22}N_8$ = 542.61) **8**: ^{1}H NMR δ(250 MHz, DMSO-d$_6$, 293 K): 9.75 (s, 2H); 7.75–7.71 (m, 8H); 7.19–7.15 (m, 8H); ^{13}C NMR δ(125 MHz, DMSO-d$_6$, 393 K): 153.89; 140.87; 134.47; 129.32; 120.00; 114.90; UV/Vis: λ (max) = 334 nm; MS (FD, 8kv): *m/z* (%) = 538.3 (100) [M$^+$] (calcd for $C_{34}H_{18}N_8$ = 538.61)

1 A. N. Cammidge and H. Gopee, *J. Mater. Chem.*, 2001, **11**, 2773.
2 M. D. Watson, A. Fechtenkotter and K. Müllen, *Chem. Rev.*, 2001, **101**, 1267; S. P. Brown, I. Schnell, J. D. Brand, K. Müllen and H. W. Spiess, *J. Am. Chem. Soc.*, 1999, **121**, 6712; P. Herwig, C. W. Kayser, K. Müllen and H. W. Spiess, *Adv. Mater.*, 1996, **8**, 510.
3 H. Bock, Z. Havlas, K. Gharagozloo-Hubmann and M. Sievert, *Angew. Chem., Int. Ed.*, 1999, **38**, 2240–2243.
4 S. M. Draper, D. J. Gregg and R. Madathil, *J. Am. Chem. Soc.*, 2002, **124**, 3486.
5 T. Gilchrist, in Comprehensive Organic Synthesis, ed. B. M. Trost and I. Fleming, Pergamon, New York, 1991, **vol. 8**, p. 388.
6 T.-S. Chung, *Rev. Macromol. Chem. Phys.*, 1997, **C37**, 277; W. Münch, K. D. Kreuer, W. Silvestri, J. Maier and G. Seifert, *Solid State Ionics*, 2001, **145**, 437.
7 G. Kestemont, V. de Halleux, M. Lehmann, D. A. Ivanov, M. Watson and Y. H. Geerts, *Chem. Commun.*, 2001, 2074.
8 V. V. Korshak, E. S. Krongauz, A. P. Travnikova and A. L. Rusanov, *Macromolecules*, 1974, **7**, 589; S. S. Tandon, L. K. Thompson, J. N. Bridson and J. C. Dewan, *Inorg. Chem.*, 1994, **33**, 54.
9 P. N. Preston, *Chem. Rev.*, 1974, **74**, 279.
10 A. M. Simonov and S. N. Kolodyazhaya, *Khim. Geterotsik. Soedin.*, 1967, **1**, 141; *Chem. Abstr.*, 1969**, 70**, , 96704b.
11 J. de Mendoza, C. Millan and P. Rull, *J. Chem. Soc., Perkin Trans. 1*, 1981, 403; G. Speier and L. Parkanyi, *J. Org. Chem.*, 1986, **51**, 218.
12 J. H. M. Hill, *J. Org. Chem.*, 1963, **28**, 1931.