coated Cu grid, and wicking away the excess. TEM was performed on a Hitachi H-8100 microscope operating at 100 kV.

Mineralized gels in EHMA were prepared by placing the DRC (10 mg) and EHMA (1 g, in some cases containing 1 mg mL^{-1} of divinylbenzene) in a sealed vial and heating to about 75 °C to dissolve the DRC. A 0.2 M solution (20 mg) $Cd(NO_3)_2 \cdot 4H_2O$ in THF was then added to the solution, and the vial was capped and allowed to cool to room temperature and gel. We note that some of cadmium nitrate precipitated and settled to the bottom of the vial prior to gelation, thus reducing the actual concentration of available cadmium ions. This precipitate was avoided when working up the gels after exposure to H_2S(g). Gels were aged for approximately one week prior to exposure to H_2S(g) for 30 min, after which time the gas had diffused through most of the gel, as evidenced by a change to a yellow color. After aging the samples again (typically one week). TEM samples were prepared by removing excess organic material by dissolution of the gel in THF (the DRC is soluble in THF) and isolation of the inorganic product by centrifugation. The CdS was resuspended in THF, cast onto a TEM grid, and imaged at 200 kV.

DRC ribbons from EMA gels were mineralized from a suspension of a 3 or 5 wt.% gel (about 100 mg) in EMA (2 g). A 0.2 M solution (20 mg) of $Cd(NO_3)_2 \cdot 4H_2O$ in THF was added to this suspension, and after one hour the sample was exposed to H_2S(g) for 15 min. TEM samples were prepared 5 min after exposure by depositing a drop of the suspension onto a holey carbon grid and wicking away the excess.

Received: December 21, 2001 [Z18427]

[1] S. Iijima, *Nature* **1991**, *354*, 56.
[2] R. Tenne, L. Margulis, M. Genut, G. Hodes, *Nature* **1992**, *360*, 444.
[3] J. T. Hu, O. Y. Min, P. D. Yang, C. M. Lieber, *Nature* **1999**, *399*, 48.
[4] A. P. Alivisatos, *Science* **1996**, *271*, 933.
[5] A. D. Yoffe, *Adv. Phys.* **2001**, *50*, 1.
[6] P. V. Braun, S. I. Stupp, *Mater. Res. Bull.* **1999**, *34*, 463.
[7] J. Huang, Y. Xie, B. Li, Y. Liu, Y. Qian, S. Zhang, *Adv. Mater.* **2000**, *12*, 808.
[8] D. Routkevitch, T. Bigioni, M. Moskovits, J. M. Xu, *J. Phys. Chem.* **1996**, *100*, 14037.
[9] Y. Li, J. H. Wan, Z. N. Gu, *Acta Phys. Chim. Sin.* **1999**, *15*, 1.
[10] C.-C. Chen, J.-J. Lin, *Adv. Mater.* **2001**, *13*, 136.
[11] J. H. Adair, E. Suvaci, *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 160.
[12] N. Pinna, K. Weiss, J. Urban, M.-P. Pileni, *Adv. Mater.* **2001**, *13*, 261.
[13] L. Manna, E. C. Scher, A. P. Alivisatos, *J. Am. Chem. Soc.* **2000**, *122*, 12700.
[14] J. H. Jung, Y. Ono, K. Hanabusa, S. Shinkai, *J. Am. Chem. Soc.* **2000**, *122*, 5008.
[15] R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **2001**, *294*, 1901.
[16] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.
[17] S. Mann, G. A. Ozin, *Nature* **1996**, *382*, 313.
[18] H. Yang, N. Coombs, G. A. Ozin, *Nature* **1997**, *386*, 692.
[19] P. D. Yang, D. Y. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Nature* **1998**, *396*, 152.
[20] M. E. Raimondi, J. M. Seddon, *Liq. Cryst.* **1999**, *26*, 305.
[21] C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **1995**, *270*, 1335.
[22] P. V. Braun, P. Osenar, S. I. Stupp, *Nature* **1996**, *380*, 325.
[23] P. V. Braun, P. Osenar, V. Tohver, S. B. Kennedy, S. I. Stupp, *J. Am. Chem. Soc.* **1999**, *121*, 7302.
[24] C. M. Lieber, *Solid State Commun.* **1998**, *107*, 607.
[25] O. Savadogo, *Sol. Energy Mater. Sol. Cells* **1998**, *52*, 361.
[26] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312.
[27] J.-M. Lehn, *Supramolecular Chemistry*, VCH, New York, **1995**.
[28] S. I. Stupp, Y. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384.
[29] E. R. Zubarev, M. U. Pralle, L. Li, S. I. Stupp, *Science* **1999**, *283*, 523.
[30] J. S. Moore (Ed.), *MRS Bull.* **2000**, *25*, special issue.
[31] G. N. Tew, M. U. Pralle, S. I. Stupp, *J. Am. Chem. Soc.* **1999**, *121*, 9852.
[32] E. R. Zubarev, M. U. Pralle, E. D. Sone, S. I. Stupp, *J. Am. Chem. Soc.* **2001**, *123*, 4105.
[33] E. R. Zubarev, M. U. Pralle, E. D. Sòne, S. I. Stupp, *Adv. Mater.* **2002**, *14*, 198.

Assignment of Stereochemistry of Facially Protected Bis-porphyrins by Use of a "Molecular Ruler"**

Maxwell J. Crossley* and Pall Thordarson

Herein we introduce a "molecular ruler" concept that can be used to unambiguously assign two stereoisomers of dizinc(II) bis(C_2-capped porphyrins) that could not otherwise be assigned by conventional techniques such as ^{1}H NMR spectroscopy. In essence the molecular ruler concept involves measurement of the distance between binding sites in a ditopic host molecule by determination of the binding of bidentate guest molecules in which the recognition groups are separated by spacers of different length. In a relatively rigid host molecule, the bidentate guest molecule that best fits the host should be most tightly bound. If the bidentate guest molecule is too short to span the binding sites, an energy penalty will have to be paid to distort either the host or the guest to achieve binding at both sites. The energy penalty will appear as a lower association constant. Similarly, when a host is too long it will have to distort itself to bind at both ends. Again this is at an energy cost.

In the present case we use a rigid dizinc(II) bis-porphyrin system and measure the distance between the zinc atoms by examining the molecular recognition of α,ω-diaminoalkanes. The molecular ruler concept is used here to discriminate between two structural isomers of a facially protected bis-porphyrin. Discrimination is possible because although the zinc(II)$\cdots$zinc(II) distance is the same in each case, the distances between the sites of complexation are very different. In the *syn* isomer **4** the capping superstructure of both porphyrin units lie on the same face of the conjugated bis-porphyrin skeleton (C_{2v} symmetry) and hence the sites of complexation of the bidentate ligand both lie on the other unprotected face. In the *anti* isomer **5** (C_{2h} symmetry), the capping superstructures lie on opposite faces of the conjugated bis-porphyrin skeleton, and, therefore, so do the diagonally opposed binding sites.

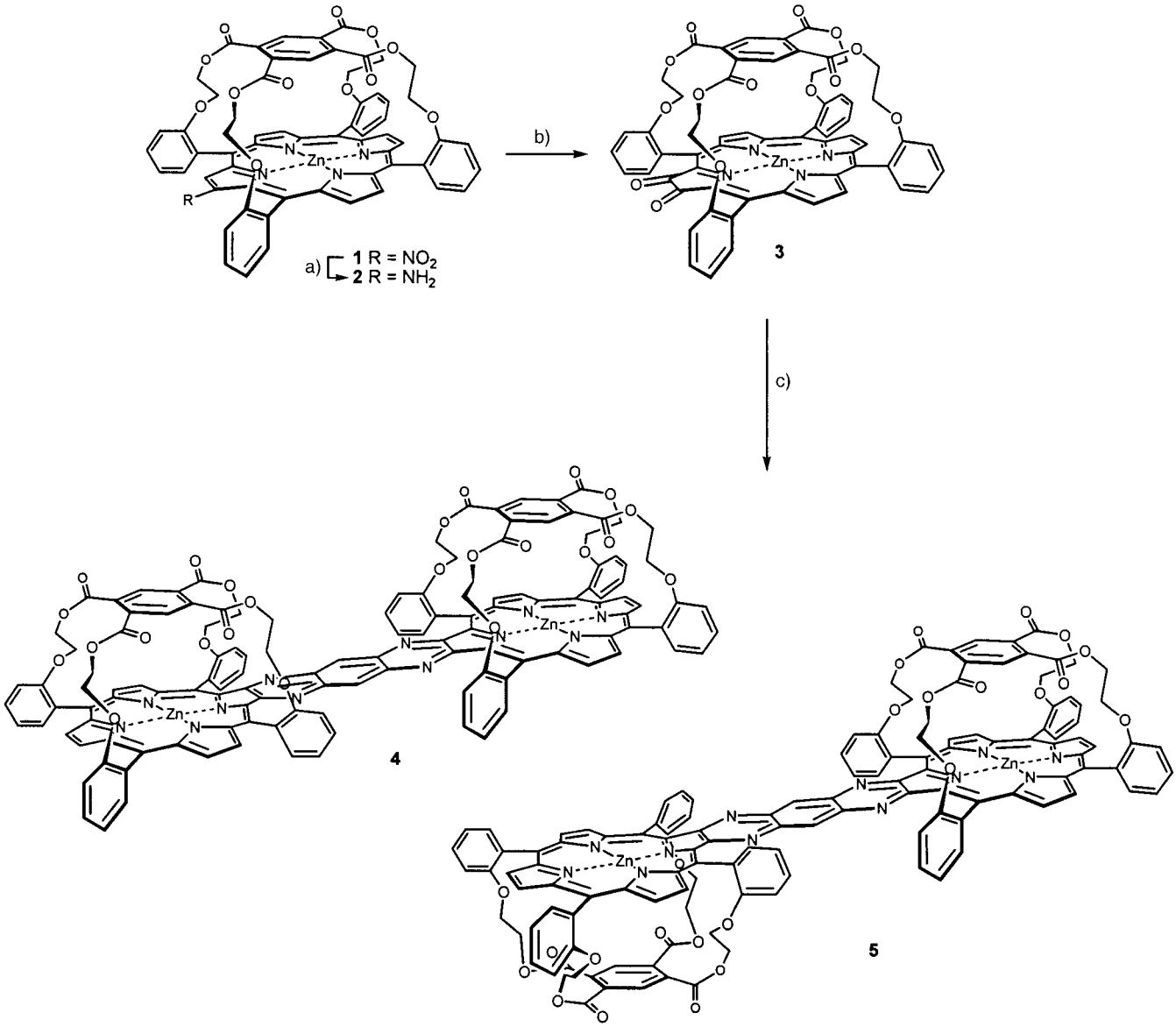
We sought the dizinc(II) *syn*- and *anti*-bis(7,8-C_2-capped porphyrins), **4** and **5**, respectively, for our studies towards self-replication of **4**. These stereoisomers were prepared by the sequence outlined in Scheme 1. The zinc(II) 7-nitro-C_2-capped porphyrin[1, 2] **1** prepared by Baldwin et al. was readily available from the unsubstituted C_2-capped porphyrin[3, 4] by our modified method for porphyrin synthesis.[5] Hydrogenation using sodium borohydride and palladium on active carbon[1, 2] gave the unstable zinc(II) 7-amino-C_2-capped porphyrin **2** that was immediately photooxidized following our methodology[6] to give the zinc(II) 7,8-C_2-capped porphy-

[*] Prof. Dr. M. J. Crossley, Dr. P. Thordarson
School of Chemistry
The University of Sydney
NSW 2006 (Australia)
Fax: (+61) 2-9351-3329
E-mail: m.crossley@chem.usyd.edu.au

[**] We thank the Australian Research Council for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

  1433-7851/02/4110-1709 $ 20.00+.50/0



Scheme 1. Conditions: a) $NaBH_4$, Pd/C/CH_2Cl_2 and MeOH; not isolated; b) *hν*, O_2/CH_2Cl_2; 36% yield from **1**; c) 1,2,4,5-benzenetetramine tetrahydrochloride/refluxing pyridine, preparative HPLC; 21% and 19% yield, respectively, for **4** and **5** from **3**.

rindione **3** in 36% yield from **1**. Following the method of Crossley and Burn,[7] condensation of two equivalents of **3** and one equivalent of 1,2,4,5-benzenetetramine in refluxing pyridine for two days, gave a 1:1 mixture of **4** and **5** in 42% yield. The two isomers where separated efficiently by preparative HPLC into the more polar compound **4** and the less polar compound **5** (Scheme 1).

All spectroscopic data for **4** and **5** were fully consistent with the expected structures of these compounds but unambiguous assignment of the stereochemistry (*syn* or *anti*) of the two fractions could not be made because the two compounds displayed very similar spectra. The largest difference in the chemical shifts between corresponding signals from the two compounds is only 0.09 ppm.

Molecular modeling (HyperChem,[8] MM+ force field modified for porphyrins[9–11]) of **4** and **5** indicated that the zinc(II)···zinc(II) distance for both compounds was essentially the same, 15.3 Å. Therefore, a ligand which is just long enough to span the two zinc(II) binding sites (15.3 Å) will form a strong intramolecular complex with the *syn* isomer **4** only (Figure 1). Clearly the same ligand would be too short to wind

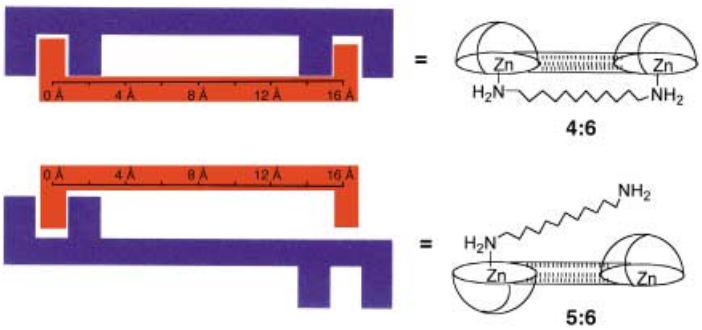
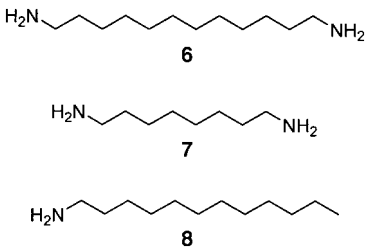


Figure 1. Schematic representation of the expected complexation between *syn* and *anti* isomers of dizinc(II) bis(C_2-capped porphyrins) and a *α*,*ω*-diaminoalkane ligand (for example, **6**) acting as a molecular ruler.

  1433-7851/02/4110-1710 $ 20.00+.50/0

itself around the *anti* isomer **5** and form such a intramolecular complex involving both faces. Binding to the second zinc(II) center by threading the ligand through the superstructure of the cap requires substantial steric interactions and distortions, and has not been observed with 7,8-capped porphyrins.

The bidentate ligands 1,12-diaminododecane (**6**) and 1,8-diaminooctane (**7**) and the monodentate ligand, 1-aminododecane (**8**), were used. Ligand **6** (span 16.4 Å[8]) can easily bind between the two binding sites of the *syn* isomer **4** whereas **7** can only span 11.3 Å[8], which is too short to bind between the binding sites of **4**.



UV/Vis and ^{1}H NMR binding studies (see Supporting Information) confirmed this. Drastic differences were seen in the binding isotherms (by UV/Vis titration) of the two fractions obtained from preparative HPLC with **6** (Figure 2). On the basis of this result, the more polar fraction was

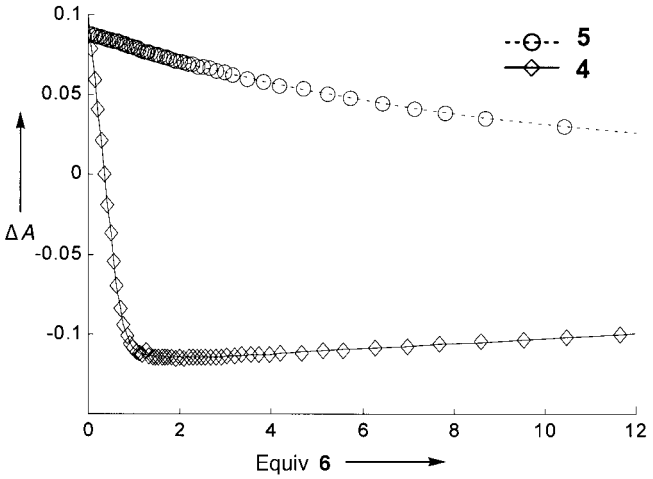


Figure 2. UV/Vis (from the Soret region, in toluene at 25 °C) binding isotherms showing the effect of titration of dizinc(II) s*yn*- and *anti*-bis(7,8-C_2-capped porphyrins), **4** and **5**, respectively, with **6**. The lines drawn between the experimental points are the calculated isotherms for the 1:1 binding model.

assigned as the *syn* isomer **4** and the less polar fraction as the *anti* isomer **5**. The 1:1 (empirical) binding constants for the complexation of the ligands **6**, **7**, and **8** to hosts **4** and **5** further highlight these differences (Table 1). Ligand **6** binds to isomer **4** approximately 2100 times more strongly than it does to isomer **5**. This is in contrast with the binding of **4** and **5** to the monotopic ligand, **8**, the binding constants of which are very similar in magnitude. The approximately fourfold stronger binding of **7** to host **4** compared to its binding to host **5** can be explained by the apparent formation of a 1:2:1 "sandwich"

Table 1. Calculated 1:1 (empirical) binding constants for the complexation of hosts **4** and **5** and the ligands **6**–**8** as measured by UV/Vis titration in $CH_3C_6H_5$ at 298 K.

Host	**6** K [M^{-1}]	**7** K [M^{-1}]	**8** K [M^{-1}]
4	$7.2 \times 10^7 \pm 18\,\%$	$1.7 \times 10^5 \pm 6\,\%$	$4.1 \times 10^4 \pm 6\,\%$ [a]
5	$3.4 \times 10^4 \pm 9\,\%$	$3.8 \times 10^4 \pm 7\,\%$	$3.3 \times 10^4 \pm 33\,\%$ [b]

[a] ^{1}H NMR titration in $CDCl_3$ at 300 K gave $K = 1.7 \times 10^4$ M^{-1}. [b] ^{1}H NMR titration in $CDCl_3$ at 300 K gave $K = 2.5 \times 10^4$ M^{-1}.

complex between **4** and **7**, similar to those reported by Anderson and Taylor,[12, 13] which, because of geometric restraints, isomer **5** cannot form.

^{1}H NMR titrations of hosts **4** and **5** with **6** further highlighted the difference between these two hosts. The formation of the complex **4**:**6** is accompanied by large upfield shifts (up to 6.2 ppm) for the ligand signals. In the much weaker **5**:**6** complex, the ligand signals were in fast exchange between the bound and unbound species and the maximum observed upfield shifts for the ligand were therefore much smaller (2.4 ppm). The much slower exchange in the complex

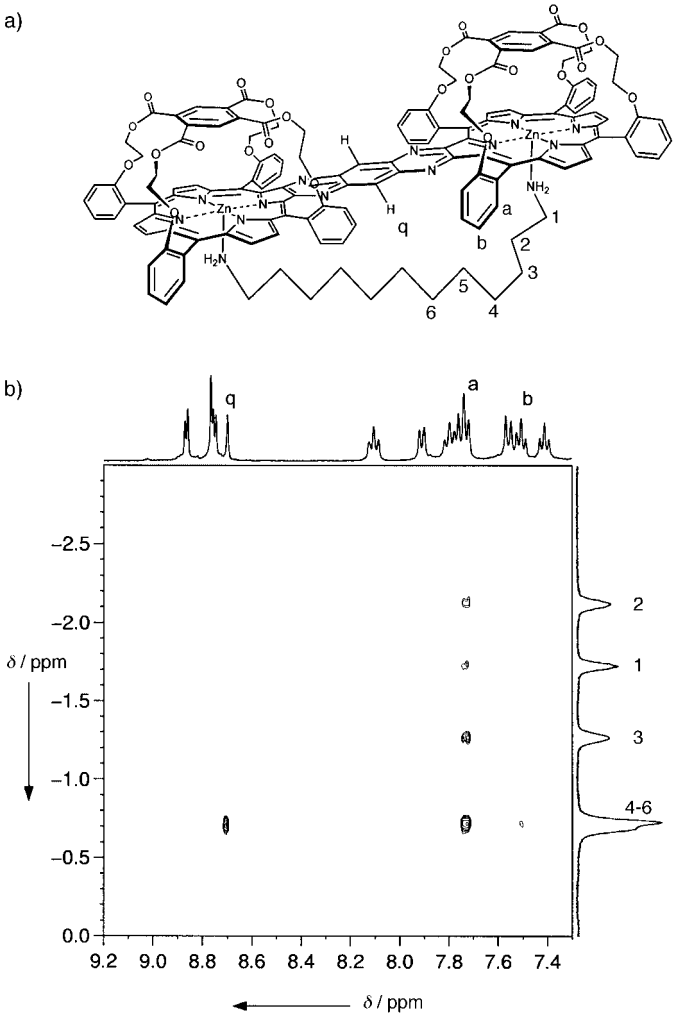


Figure 3. a) Schematic representation, with labels, of the complex formed between **4** and **6**. b) The two-dimensional ROESY ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the **4**:**6** (1:1) complex mixture. Only the peaks corresponding to the NOE cross peaks are labeled.

  1433-7851/02/4110-1711 $ 20.00+.50/0

4:**6** allowed two-dimensional COSY and ROESY ^{1}H NMR spectroscopy to be carried out at 260 K (uncorrected temperature) and the spectra obtained were fully consistent with the expected structure and symmetry of the complex. Most importantly, the ROESY spectra (see Figure 3b) showed clear NOE cross peaks between the ligand and the host. In particular, the bridging protons (q in Figure 3a) showed NOE peaks to the central portion of the ligand (CH_2 nos. 4–6, Figure 3b). Moreover, the calculated interproton distances (see Supporting Information) obtained from integration of the cross peaks in the ROESY spectra are only consistent with the structure **4**:**6**.

In conclusion, a combination of UV/Vis and ^{1}H NMR binding studies using a simple bidenate ligand as a molecular ruler have unambiguously demonstrated the structural difference between the hosts **4** and **5**: only one (*syn* isomer **4**) could form strong intramolecular complexes with **6**. In other words, molecular recognition studies were used for the structural determination of **4** and **5**, something that could not be achieved with conventional spectroscopic techniques on the compounds themselves. In other work,[14] we have shown that the molecular ruler concept can be used also for determination of the cavity size in ditopic chiral porphyrin-appended Tröger's bases.[15]

Received: November 2, 2001
Revised: March 7, 2002 [Z18142]

[1] J. E. Baldwin, J. F. DeBernardis, *J. Org. Chem.* **1977**, *42*, 3986.
[2] J. E. Baldwin, M. J. Crossley, J. DeBernardis, *Tetrahedron* **1982**, *38*, 685.
[3] J. Almog, J. E. Baldwin, R. L. Pyer, M. Peters, *J. Am. Chem. Soc.* **1975**, *97*, 226.
[4] J. Almog, J. E. Baldwin, M. J. Crossley, J. F. DeBernardis, R. L. Dyer, J. R. Huff, M. K. Peters, *Tetrahedron* **1981**, *37*, 3589.
[5] M. J. Crossley, P. Thordarson, J. P. Bannerman, P. J. Maynard, *J. Porphyrins Phthalocyanines* **1998**, *2*, 511.
[6] M. J. Crossley, L. G. King, *J. Chem. Soc. Chem. Commun.* **1984**, 920.
[7] M. J. Crossley, P. L. Burn, *J. Chem. Soc. Chem. Commun.* **1987**, 39.
[8] Calculated by molecular modeling studies using Hyperchem (PM3): *Hyperchem 6.01*, Hypercube Inc., Gainesville, FL, **2000**.
[9] O. Q. Munro, J. C. Bradley, R. D. Hancock, H. M. Marques, F. Marsicano, P. W. Wade, *J. Am. Chem. Soc.* **1992**, *114*, 7218.
[10] O. Q. Munro, H. M. Marques, P. G. Debrunner, K. Mohanrao, W. R. Scheidt, *J. Am. Chem. Soc.* **1995**, *117*, 935.
[11] H. M. Marques, O. Q. Munro, N. E. Grimmer, D. C. Levendis, F. Marsicano, G. Pattrick, T. Markoulides, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1741.
[12] H. L. Anderson, *Inorg. Chem.* **1994**, *33*, 972.
[13] P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **1999**, *121*, 11538.
[14] M. J. Crossley, L. G. Mackay, J. N. H. Reek, A. C. Try, R. A.-S. Wu, unpublished results.
[15] M. J. Crossley, T. W. Hambley, L. G. Mackay, A. C. Try, R. Walton, *J. Chem. Soc. Chem. Commun.* **1995**, 1077.

A Four-Step Alternating Reductive Dimerization/Bond Cleavage of Indenocorannulene**

Ivan Aprahamian, Roy E. Hoffman, Tuvia Sheradsky, Dorin V. Preda, Mihail Bancu, Lawrence T. Scott, and Mordecai Rabinovitz*

The reduction of polycyclic aromatic hydrocarbons (PAHs) with alkali metals yields negatively charged π-conjugated molecules,[1] which may undergo structural changes, from structural distortions[2] and aggregation,[3] to the formation of new chemical bonds.[4] An anionic dimer is produced when a new σ bond forms between two identical units.[5] Such a reductive dimerization process, that is, radical anion coupling, was observed in the reduction of azulene[6] and in the reductions of certain benzofulvene derivatives.[7] In the former case, further reduction dissociates the newly formed σ bond to afford the azulene dianion and, to our knowledge, this sequence was the first reductive dimerization/bond-cleavage process ever observed.[6] The formation of aggregates upon reduction of PAHs has been observed with the lithium salt of the corannulene tetraanion,[3a] which is the smallest curved subunit of a fullerene. However, aggregation was not observed in the reductions of corannulene derivatives with extended π frameworks, towards fullerenes.[8] Here we report that a curved polycycle, indenocorannulene (**1**), undergoes an unprecedented, alternating, four-step dimerization/bond-cleavage process upon reduction with potassium.

Reduction of **1** with potassium, by successive one-electron transfers, produces four diamagnetic reduction states. Each reduction stage was visually apparent from the change in color and this was monitored by NMR spectroscopy. The first and third stages of reduction give ions **2** (dianion, dark brown) and **4** (hexaanion, green), respectively (Scheme 1), which exhibit doubling of all the NMR resonance signals (Figure 1). The second and fourth stages of reduction give ions **3** (dianion, purple) and **5** (tetraanion, violet), respectively, which have the same simple resonance pattern as the neutral **1** (Figure 1), and their ^{13}C NMR spectra (Table 1) indicate the presence of only sp^2-hybridized carbon atoms. The ^{1}H NMR spectra of **2** and **4** did not show the presence of any dynamic processes over a wide range of temperatures; their ^{13}C NMR spectra (Table 1) each show an extremely upfield signal at $\delta = 56.5$ and 47.6 ppm, respectively (assigned to C3′, see Scheme 1). The

[*] Prof. M. Rabinovitz, I. Aprahamian, Dr. R. E. Hoffman, Prof. T. Sheradsky
Department of Organic Chemistry and
The Lise Meitner-Minerva Center for Computational Quantum Chemistry
The Hebrew University of Jerusalem, Jerusalem 91904 (Israel)
Fax: (+972) 2-652-7547
E-mail: mordecai@vms.huji.ac.il
Dr. D. V. Preda, M. Bancu, Prof. L. T. Scott
Merkert Chemistry Center, Boston College
Chestnut Hill, Massachusetts, 02467-3860 (USA)

[**] We would like to thank Prof. K. Müllen for fruitful discussions. This research was supported by the Israel Science Foundation (Grant No. 147100; M.R. and L.T.S.) and the U.S. Department of Energy (L.T.S.).

  1433-7851/02/4110-1712 $ 20.00+.50/0