Communications

New Porphyrin 4π-Cycloaddition Reagents and Their Use in the Preparation of Porphyrin-(Rigid Spacer)-1,10-Phenanthrolines in Which Geometric “Tuning” of the Chromophores Is a Feature

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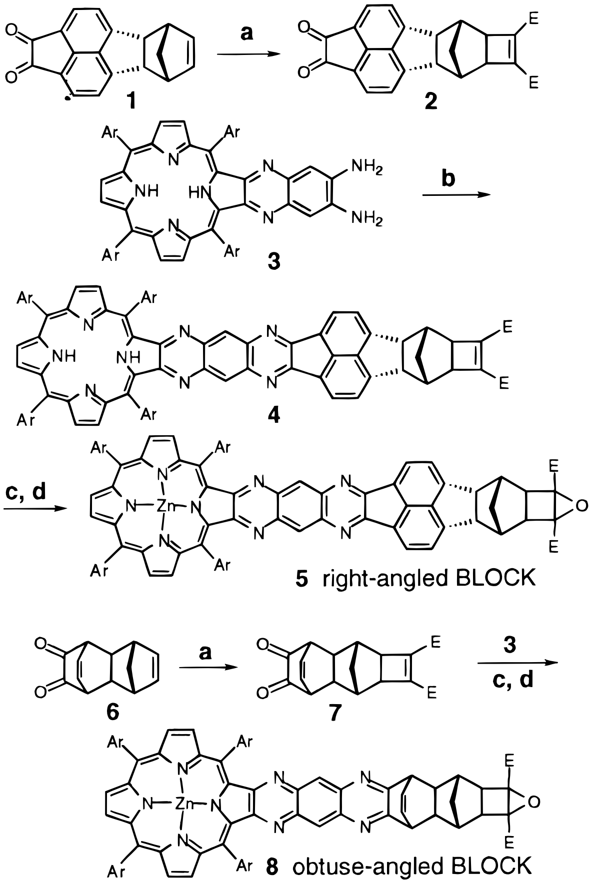
Received December 28, 1998

We report herein the first examples of porphyrin-containing reagents which act as 1,3-dipoles and illustrate their value in rigid structure formation. In the past, the synthesis of custom-designed porphyrins[1] relied on adaptations to the primary porphyrin ring synthesis in order to incorporate the required effector,[2] while others have utilized carbonyl, amine condensation reactions of preformed porphyrin diamines or porphyrin diones.[3] We have recently reported the use of dienophilic porphyrin Diels−Alder[4] reagents in synthesis,[8] and we now show that our new porphyrin reagents have far more potential for the synthesis of rigid diads. By using our ACE BLOCK assembly protocol,[9] different topologies of the chromophores can be achieved on the rigid alicyclic framework of the diad product. As both the porphyrin and the ligand BLOCKs described herein are available in right-angled and obtuse-angled BLOCK geometries, so their stereoselective fusion yields geometric variants where the interchromophoric alignment depends on BLOCK selection and an appreciation of the shape of the frame linking them (see Scheme 2).

Scheme 1



(a) DMAD, RuH $_2$CO(PPh$_3$)$_3$ C$_6$H$_6$ at reflux; (b) **2**, Pyridine, RT; (c) Zn(OAc)$_2$ DCM / MeOH; (d) ^{t}BuO$_2$H, MeLi, -78 °C, THF.

The right-angled porphyrin BLOCK **5** was prepared (Scheme 1) in three steps from the known alicyclic α-dione **1**.[10] Ruthenium-catalyzed addition[11] of dimethylacetylene dicarboxylate (DMAD) to the norbornene π-bond of **1** yielded the cyclobutene 1,2-diester **2** (20% yield, mp 276 °C) which was condensed with the “Crossley porphyrin diamine” **3**[3] to form the linked porphyrin.[4] This was metalated (90% yield, mp >350 °C), prior to epoxidation (^{t}BuO$_2$H, MeLi, −78 °C) to furnish the porphyrin cyclobutene epoxide **5** (52% yield, mp >350 °C). The obtuse-angled porphyrin epoxide **8** was produced in a similar manner, following our previously reported protocol.[8,9]

Reaction of the right-angled 1,10-phenanthroline BLOCK **9**[12] with the obtuse-angled porphyrin BLOCK **8** (which is thought to generate the active intermediate 1,3-dipole under the thermal reaction conditions) occurs on heating in THF (160 °C, sealed tube)[13] with high diastereoselectivity to produce a single adduct, **12**.[14] Similar reaction of right-angled 1,10-phenanthroline BLOCK **9** with the right-angled porphyrin BLOCK **5** afforded the ligated porphyrin **11**, while linking of the obtuse-angled 1,10-phenanthroline BLOCK **10** with the right-angled porphyrin BLOCK **5** produced the

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(1) See: Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Eds. *Comprehensive Supramolecular Chemistry*; Elsevier Science Ltd.: Oxford, 1996; Vols. 2, 4, 5, 6, 9, and 10.

(2) (a) Lash T. D. *Chem. Eur. J.* **1996**, *2,* 1197. (b) Vicente M. G. H.; Tome A. C.; Walter A.; Cavaleiro J. A. S. *Tetrahedron Lett.* **1997**, *38,* 3639.

(3) (a) Crossley, M. J.; Govenlock, L. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 2379. (b) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1569. (c) Crossley, M. J.; Hambley, T. W.; Mackay, L. G.; Try, A. C.; Walton, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1077. (d) Atkinson, E. J.; Oliver, A. M.; Paddon-Row, M. N. *Tetrahedron Lett.* **1993**, *34,* 6147.

(4) Earlier reports on the participation of porphyrins in Diels−Alder reactions include derivatives acting as the diene[5,6] or as a dienophile.[7]

(5) Liddell, P. A.; Demanche, L. J.; Li, S.; Macpherson, A. N.; Nieman, R. A.; Moore, A. L.; Moore, T. A.; Gust, G. *Tetrahedron Lett.* **1994**, *34,* 995.

(6) Zheng, G.; Kozyrev, A. N.; Dougherty, T. J.; Smith, K. M.; Pandey, R. K. *Chem. Lett.* **1996**, 1119.

(7) Tomé, A. C.; Lacerda, P. S. S.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *J. Chem. Soc., Chem. Commun.* **1997**, 1199.

(8) Warrener, R. N.; Johnston, M. R.; Gunter, M. J. *Synlett* **1998**, 593.

(9) Warrener, R. N.; Schultz, A. C.; Butler, D. N.; Wang, S.; Mahadevan, I. B.; Russell, R. A. *J. Chem. Soc., Chem. Commun.* **1997**, 1023.

(10) (a) Trost, B. M. *J. Am. Chem. Soc.* **1969**, *91,* 918. (b) Stille, J. K.; Noren, G. K.; Green, L. *J. Polymer Science* **1970**, *8,* 2215.

(11) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44,* 4492.

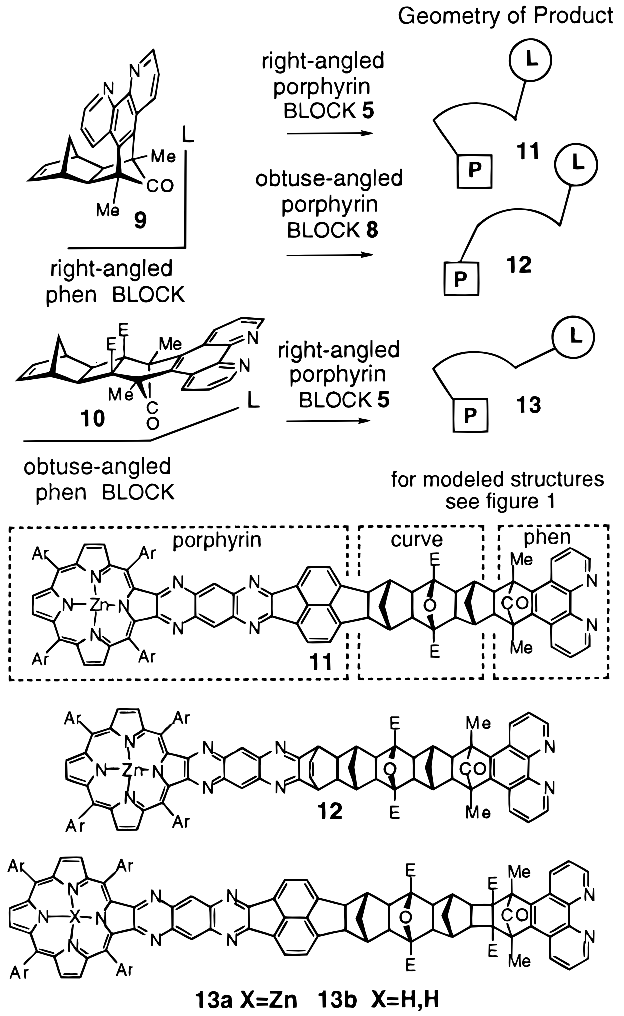
(12) Warrener, R. N.; Schultz, A. C.; Houghton, M. A.; Butler, D. N. *Tetrahedron* **1997**, *53,* 3991.

(13) Compounds **11**−**13** were contaminated with the corresponding demetalated porphyrin (e.g. 30% for **12**) when the reaction was conducted under standard conditions (dichloromethane, 140 °C, sealed tube);[9] this could be eliminated by utilizing THF as solvent.

(14) Each compound was characterised by appropriate ^{1}H NMR spectroscopy, MALDI-TOF, and/or high resolutiom electrospray mass spectrometry.

10.1021/jo982487o CCC: $18.00

Scheme 2



13a X=Zn **13b** X=H,H

coupled diad **13a**. The *exo,exo*-stereoselectivity of ACE coupling is well established with norbornene dipolarophiles,[9,15] and this allows the geometry of the chromophores in the individual BLOCKs to be carried over into the products with structural certainty. The relative orientation of the chromophores is modified by the topography of the slightly curved molecular framework separating them, and this effect can be assessed by molecular modeling (Scheme 2). The AM1 optimized structures[16,17,18] of the coupled products **11**−**13a** (Figure 1) indicate that the coupling of two right-angled BLOCKs in this curved-linker series gives a product where the orientation of the two chromophores is 33° off-parallel (cf. **11**). By way of contrast, coupling of the obtuse-angled porphyrin BLOCK **8** plus right-angled phen BLOCK **9** is a combination which has the chromophores essentially parallel (cf. **12**). The chromophores only approach an orthogonal orientation when obtuse-angled phenanthroline BLOCK **10** is coupled with the right-angled porphyrin BLOCK **5** (cf. **13**).

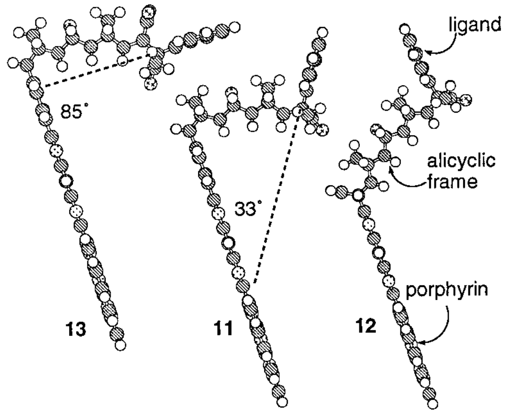


Figure 1. Geometry optimization (AM1) of structures **11**−**13**.

In summary, we have demonstrated a versatile building BLOCK route for preparing new types of porphyrins that are linked to 1,10-phenanthroline ligands. Each effector BLOCK type is available in different geometries (obtuse and right angled BLOCKs are illustrated herein), and this allows preparation of porphyrin/ligand systems where the alignment and separation of the rigidly attached chromophores can be modified over a wide range. We have recently reported the development of modified polynorbornanes with rodlike frames,[17] and currently we are applying this to develop new architectures. In addition, we have developed metalated versions of the phenanthroline BLOCKs[18] discussed above and are currently studying the coupling of these complexes with porphyrin BLOCKs to yield mixed metalated systems.

Acknowledgment. We thank the Australian Research Council (ARC grants A29532170 and A29801955) for support of this research. Ms. M. Golic is thanked for her help in the preparation of **7**.

Supporting Information Available: Experimental details for the preparation of compounds **2**, **4**, **5**, **7**, **8**, **11**, **12,** and **13**; copies of selected ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The coupling of norbornenes with cyclobutene epoxides has occurred repeatedly with *exo,exo* specificity in a whole range of examples (many unpublished) and has been established using symmetry arguments where similar chromophores are involved or by NOE measurement between appropriate protons in systems which contain different chromophores. This latter method is not possible in the present systems (**11**−**13**) owing to overlap of relevant signals.

(16) Modeling optimisations were conducted on the porphyrin free bases with bridgehead esters removed and vicinal esters replaced by anhydride groups.

(17) Margetic, D.; Johnston, M. R.; Tiekink, E. R. T.; Warrener, R. N. *Tetrahedron Lett.* **1998**, *39*, 5277.

(18) Schultz, A. C.; Johnston, M. R.; Kelso, L. S.; Warrener, R. N.; Keene, F. R. Unpublished results.