Single-crystal X-ray Study of a Kind of Rigid Aromatic Macrocyclic [1+1] Dimer

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INTRODUCTION:

Since macrocyclic aromatic ether-ketones and ether-sulfones were first reported in the late 1980's[1], many kinds of aromatic macrocycles have been explored and studied as precursors of high-performance thermoplastics both theoretically and experimentally[2]. However, beyond the ring-chain interconversion between macrocyclic aromatic ethers and linear, high molar-mass polymers[3], little attention is paid to the rigid macrocyclic structure and the nano-scale cavity of these macrocycles.

Until these two years with the emergence of a new field of nano-technology called molecular architecture, the rigid aromatic macrocycles have began to gain more and more attention as a kind of nano-structural material because of their inherent advantages (a rigid cyclic structure, a rigid nano-scale cavity, good solubility, excellent resistibility for different chemical or physical conditions, etc). Especially compared with the other organic macrocycles such as crown ether, or, the rigid nano-scale cyclic structure is full of potential application in nano technology, such as acting as aromatic guest molecules or being ordered organized as a template for the growth of nanoparticles in a ordered way with chemical or physical methods. To approve the rigid structure and the nano-scale cavity of these aromatic macrocycles, a single-crystal X-ray study is probably the most direct way.

To be used as a kind of nano-structure material, the rigid macrocyclic aromatic oligomer must have a proper cavity size and cavity shape. According to the previous work reported about the synthesis and the single-crystal structure study of the rigid aromatic macrocycles[4], a [2+2] cyclic oligomer is always the main product having a circle-like cavity shape and a 1.4-2 nm cavity size. And a [4+4] cyclic oligomer or a larger one can also be obtained, but a smaller [1+1] cyclic oligomer is difficult to be obtained as the main product with a stable enough cyclic structure because the molecule is always highly strained for a circle-like shape.

We designed and synthesized a novel kind of rigid aromatic macrocyclic oligomer with a traditional one-step [1+1] cyclization reaction between bisphenol-A and 1,3-bis(p-fluorobenzoyl)benzene in a pseudo-high dilution condition. With a single-crystal X-ray study, the rigid cyclic structure and the nano-scale cavity of this kind of macrocyclic oligomer were well approved.

EXPERIMENTAL:

The [1+1] cyclic dimer were synthesized (showed in Scheme1) by slowly added the solution of equalmol 1, 3-bis(p-fluorobenzyol)benzene and bisphenol-A over 12 hours from a dropping funnel to a large amount of solvent containing catalyst. The single crystals of the [1+1] cyclic dimmer were grown in a dichloromethane solution at 0-5 C° for seven days with a granular shape and colorless.

For structural measurement, all single crystals were mounted in thin-walled glass capillaries. Unit cell parameters, orientation matrix, and intensity data were obtained on a Rigaku R-AXIS RAPID IP X-ray diffractometer, and the programs used to solve the structure are SHELXTL 5.01 v. The crystallographic data collected indicated that the single crystal is triclinic, P-1 with dimensions of 0.49 × 0.30 × 0.11 mm.

RESULTS AND DISCUSSION:

Figure 1 shows the molecular structure of the [1+1] cyclic dimmer. And the selected bond lengths and angles are showed in Table 1. Although the [1+1] cyclic dimmer has a relatively small size of the macroring-comprising only five aromatic units, the X-ray structure shows the molecule to be slightly strained with a free pathway through the macroring centre. And from the crystallographic data, the distance between C(1) and C(3) is about 0.96nm, and the distance between C(2) and C(3) is 0.98nm, between O(3) and O(4) is 0.84nm. Furthermore, as showed in Table 1 there were no obvious changes for the C-C, C-O bond lengths and the internal angles at carbonyl are strongly expanded, from a conventional value of 114° to ca. 120°-122°. The C(24)-O(3)-C(31) and the C(34)-C(3)-C(44) are also expanded. So the rigid macrocyclic structure of the dimmer is stable despite of its small size.

The macrocycle has crystallographic mirror symmetry about a plane passing through the 2 and 5 positions of the 1,3-substituted aromatic rings. As showed in Figure 2, the macrocycles stack along the crystallographic b direction to create continuous channels. Adjacent channels are linked by π-π stacking between the benzene-1, 3-dicarbonyl rings and a van der waals intermolecular action between the four methyl groups of two adjacent macrocycles.

Detailed discussion on the application and the single crystal structure of the [1+1] cyclic dimmer is now in progress. Financial support of this research was provided by the National Nature Science Foundation of China (No. 20104003) and the National Major Project for Fundamental Research of China (No. G2003CB615604).

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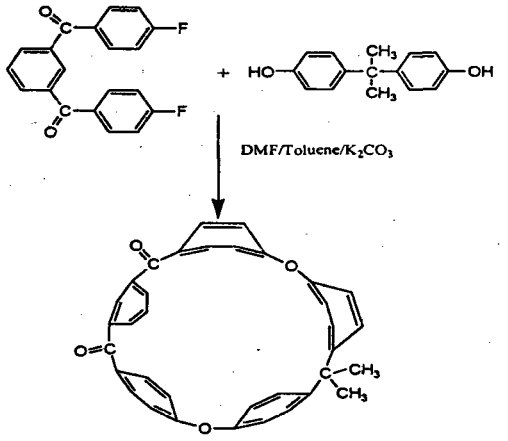


Scheme 1. Synthesis of the [1+1] cyclic dimmer

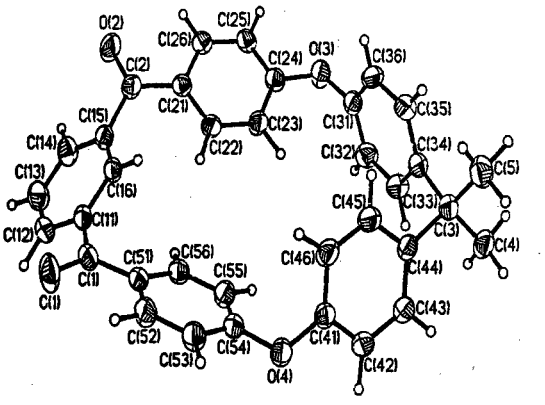
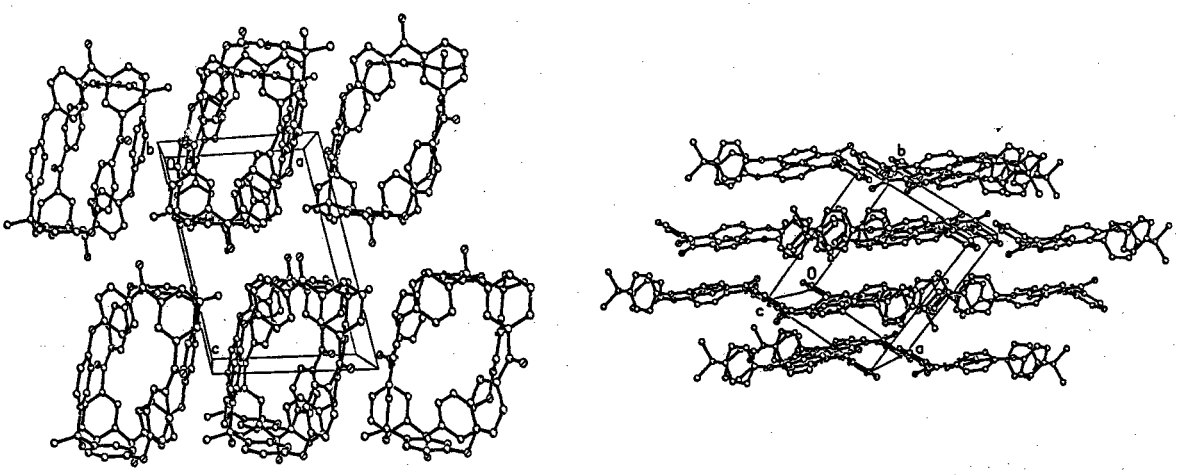


Figure 1 (a) The Perspective ORTEP drawing molecular structure of the single crystal



(a) (b)

Figure 2 Crystal Packing of the Cyclic Dimer

Bond Lengths[A]		Angles [deg]	
O(1)-C(1)	1.222(2)	C(15)-C(2)-C(21)	122.73
O(2)-C(2)	1.219(2)	C(11)-C(1)-C(51)	120.52
O(3)-C(24)	1.369(2)	C(44)-C(3)-C(34)	104.59
O(4)-C(41)	1.404(2)	C(4)-C(3)-C(5)	106.9
C(1)-C(51)	1.482(3)	C(41)-O (4)-C(54)	116,62
C(3)-C(4)	1.535(3)	C(24)-O(3)-C(31)	116.55
C(11)-C(16)	1.388(2)	C(16)-C(15)-C(14)	118.85
C(11)-C(12)	1.392(3)	C(15)-C(14)-C(13)	120.86

Table 1 the selected bond lengths and angles