Molecular Design of a Novel Ring Polyimide with Nanoscale Cavity Using DFT Calculations

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The molecular design of a novel ring polyimide derived from 2,2-bis(3,4-carboxylphenyl) hexafluoropropane dianhydride (6FDA) with *m*-phenylenediamine (MDA) has been performed. First, the optimized structures of the 6FDA-MDA model compounds were investigated using the density functional theory (DFT) at the B3LYP/6-311G(d,p) level. Using the optimized structures of the model compounds, the probable combinations to form a flat ring polyimide are considered by taking the total inner angles between the aromatic groups into consideration. Consequently, we selected several combinations with different conformations and the number of monomer units. Among them, the detailed structure of the smallest ring polyimide constructed from two units of 6FDA-MDA was investigated. We showed the flat structure of this isolated molecule and also the supposed stacked structure of two molecules using the DFT calculations. The expected structure of this small ring polyimide contains a circular hole of sub-nanometer size.
Key words: Molecular design, Ring polyimide, Internal rotation barrier, Nanoscale cavity

1. INTRODUCTION

Aromatic polyimides are known as high-performance materials and have been extensively used in the microelectronics industry as in interdielectric layers and optical devices due to their excellent physico-chemical properties [1]. In previous reports, we presented a new ring polyimide based on the monomer unit of poly(*m*-phenylene)pyromellitimide (PMDA-MDA) and determined its energy minimized geometries using the density functional theory (DFT) and *ab initio* calculations [2,3]. Six monomer units of PMDA-MDA are linked together resulting in a stable ring molecule with a plate-like structure. This ring polyimide molecule contains a circular hole of nanometer size, and it will possibly lead to a new polyimide with a lower density and a lower dielectric constant. Besides, a molecular dynamics (MD) simulation suggested that the corn-shaped conformer, one of the stable conformers of this ring polyimide, is stacked to form a long cylindrical cavity [4,5]. Analogous to the ring PMDA-MDA, we also employed the biphenyl-type polyimide derived from 3,4,3',4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) or 2,3,3',4'-biphenyltetracarboxylic dianhydride (*a*-BPDA) both with *m*-phenylenediamine (MDA). Several combinations of the *s*-BPDA-MDA unit or *a*-BPDA-MDA unit with different conformations resulted in the formation of the flat ring polyimide [6].

In this study, we show the possibility that the aromatic polyimide based on the combination of 2,2-bis(3,4-carboxylphenyl)hexafluoropropane dianhydride (6FDA) with MDA can form other ring polyimides as well as the PMDA-MDA-based and BPDA-MDA-based ring polyimides. In order to obtain information on the

molecular conformation of 6FDA, the DFT method is employed. We first focused on the dihedral angle between the phthalimide moiety and hexafluoropropane and also on their internal rotation barrier. The internal rotation barrier provides valuable information on the stability of the ring polyimide molecule. Our principal objective in this study is to find a new ring polyimide which has the possibility of stacking and forming a stable nano-scale cylindrical cavity, which will be useful in designing highly effective membrane materials used in the separation of small molecules.

2. COMPUTATIONAL METHODS

The chemical structures of the 6FDA-MDA model compounds are shown below.
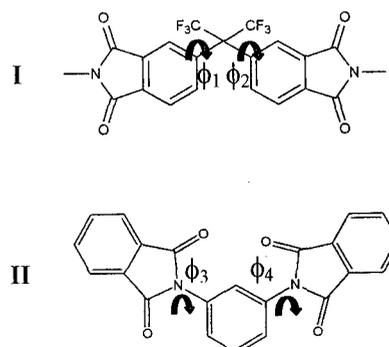
Fig.1. Chemical structures of the 6FDA-MDA model compounds.

The molecular geometry of the two compounds were completely optimized using a hybrid density functional method, Becke3LYP (B3LYP) with a 6-311G(d,p) basis set. Optimization of the ring structure constructed from several monomer units of 6FDA-MDA was also performed using the B3LYP/6-31G(d) level.

In order to obtain the rotational energy profiles around the C—C(CF$_3$)$_2$ bond, the potential energy has been calculated at 10° intervals of the dihedral angle for each model compound shown in Fig. 1. In this case, when performing the geometry optimization, two dihedral angles between the plane of the imide ring and the hexafluoropropane (C6–C1–C(CF$_3$)$_2$–C1' and C6'-C1'–C(CF$_3$)$_2$–C1) were set at constant values while all the other parameters were allowed to optimize. All the calculations were carried out on a cluster machine using 16 Pentium 4 processors with a GAUSSIAN 98, Rev.11 and the Linda program package [7].

3. RESULTS AND DISCUSSION

3.1 *Optimized geometry of 6FDA-model compound*

Figure 2 shows the three kinds of optimized structures of the 6FDA model compound with different combinations of ϕ_1 and ϕ_2. There was no significant difference in the bond lengths and bond angles among the three geometries, therefore, the individual values of the bond lengths and bond angles are not shown here.
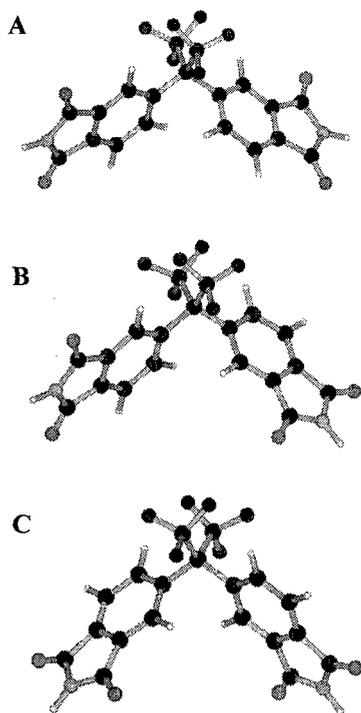
Fig. 2. Optimized geometries of 6FDA model compound with different conformation.

In Table I, the dihedral angles ϕ_1 and ϕ_2, the energy difference between the optimized structures, and also the calculated dipole moment are summarized. The geometry C having $\phi_1 = \phi_2 = -138.8°$ (or $\phi_1 = \phi_2 = 138.8°$) showed an energy minimum. However, the energy difference between the geometry C and the other

optimized structures, A or B, is fairly small at less than 0.1 kcal/mol. There was no significant difference in the dipole moment, which reflects the geometry as shown in Fig. 2. In a previous study, we obtained the two optimized geometries for model compound II [3]. One optimized geometry of compound II has $\phi_3 = 42.4°$, $\phi_4 = -42.4°$ and another one has $\phi_3 = \phi_4 = 40.9°$ using the B3LYP/6-311G(d,p) level. The latter geometry showed an energy minimum with the relative energy of 1.08 kcal/mol lower than the former [3].

Table I. Comparison of some molecular properties of the optimized structures of model compound I using B3LYP/6-311G(d,p) level.

	Geometry of model compound I		
	A	B	C
ϕ_1 (°)	−44.9	−44.3	−138.8
ϕ_2 (°)	−45.0	139.4	−138.8
Relative energy (kcal/mol)	0.02	0.08	0.0[a]
Dipole moment (D)	1.394	1.929	1.324
Θ (°)	133.7	107.8	89.6

a) SCF energy for geometry C is −1738.82516243 (Hartree).
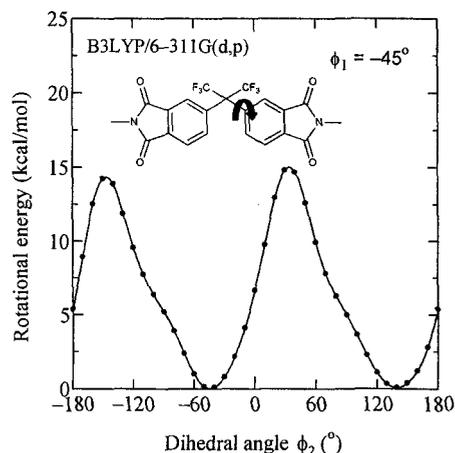
Fig. 3. Potential energy profiles for the rotation of the dihedral angle ϕ_2 when ϕ_1 is fixed at -45° in compound I.

3.2 *Internal rotation barrier in 6FDA-model compound*

Figure 3 shows the rotational energy profiles around the C—C(CF$_3$)$_2$ bond for model compound I, when the dihedral angle ϕ_1 is fixed at one of the energy-minimized value of -45°. Due to the asymmetric geometry of compound I, the rotational energy profile was also asymmetric with respect to one torsion. Two energy minimum points corresponds to the geometry A and B in Fig.2. The internal rotation barrier attained 15 kcal/mol, which is remarkably higher than that obtained for the torsion around the N-C$_{phenyl}$ bond between the phthalimide ring and phenylene ring [2]. The free rotation of the 6FDA around the C—C(CF$_3$)$_2$ bond is not feasible based on the energy barrier. Thus, the 6FDA moiety has a rigid nature [8].

3.3 Formation of 6FDA-MDA based ring polyimide

Using the information on the dihedral angles obtained in the optimized structures of the two model compounds I and II, we propose the suggested structure of the ring polyimides. First, the spatial angle between the two phthalimide rings, Θ, in the 6FDA moiety is evaluated as follows: the molecular axes of the respective phthalimide ring are drawn so that a line goes through the imide nitrogen atom, and the two axes intersect at the center carbon atom of hexafluoropropane moiety as shown in Fig. 4. The estimated spatial angles for the three kinds of optimized geometries are also included in Table I.

Table II summarizes the combination of the various 6FDA-MDA units and the possibility of formation of the 6FDA-MDA ring. When we take the group of one phthalimide linked with the m-phenylene as a unit side in the polyangular structure, we can estimate the summation of the interior angles as the ideal flat shape (SA_{poly}). As discussed above, the summation of the calculated interior angle in the ring polyimide can also be estimated from the Θ value and the *meta*-linked phenylene assuming that the geometry of the molecule becomes as flat as possible (SA_{ring}). The difference in the total interior angles, ΔSA, between the ideal flat polyangular and the corresponding ring polyimide are then estimated.
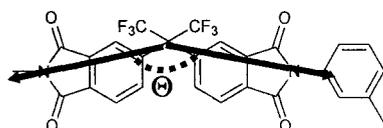
Fig. 4. Definition of the inner spatial angle Θ in the 6FDA moiety.

Table II. Various combinations of the 6FDA with MDA unit to form the ring imide molecules.

N_{unit}[1]	N_{poly}[2]	N_{DA}[3]	SA_{poly}[4]	SA_{ring}[5]	ΔSA[6]
6FDA (A) - MDA					
2	4	8	360	508	-148
3*	6	12	720	762	-42
4*	8	16	1080	1016	64
5	10	20	1440	1270	170
6	12	24	1800	1524	276
6FDA (B) – MDA					
2*	4	6	360	56	-96
3*	6	9	720	684	36
4	8	12	1080	912	168
5	10	15	1440	1140	300
6FDA (C) - MDA					
2*	4	8	360	420	-60
3	6	12	720	630	90
4	8	16	1080	840	240

[1]N_{unit}: Number of 6FDA-DA units
[2]N_{poly}: Apparent number of polyangular
[3]N_{DA}: Number of dihedral angles included in the ring imide
[4]SA_{poly}: Sum of the interior angles as the flat polyangular
[5]SA_{ring}: Sum of the interior angles of ring imide assuming the flat structure, $SA_{ring} = N_{unit}(\Theta+120)$
[6]ΔSA: $\Delta SA = (SA_{poly} - SA_{ring})$

The probable combinations are listed in Table II when ΔSA is less than $300°$. Practically, when ΔSA becomes greater than $100°$, the structure of the ring molecule is remarkably distorted and far from a flat structure such as the 6FDA-MDA ring constructed from 6 units, although the geometry is not shown. When ΔSA is smaller than $-100°$, the ring formation is also impossible. Therefore, the ΔSA value is indicative of the ring formation of polyimides as previously shown [6].

Finally, we have succeeded in obtaining five kinds of optimized geometries of 6FDA-MDA ring using the B3LYP/6-31G(d) level. They are indicated by the asterisks in Table II. The three geometries are shown in Fig.5 among the five kinds of the molecules. Each of them has a flat structure.
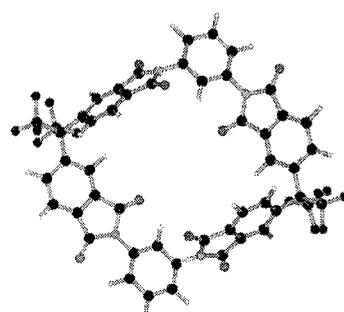
6FDA(B)-MDA (2 units)
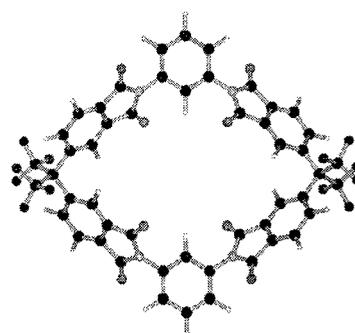
6FDA(C)-MDA (2 units)
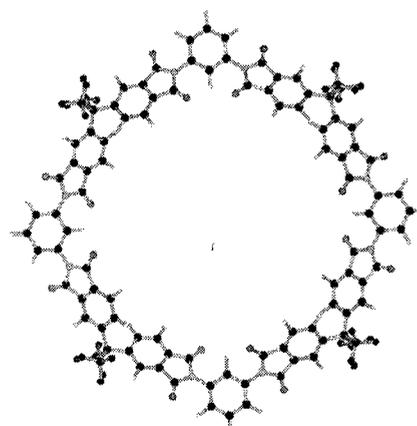
6FDA(A)-MDA (4 units)

Fig. 5. Optimized geometries for three kinds of flat ring polyimides from various units of 6FDA-MDA obtained using the B3LYP/6-31G(d) level.

Which geometry, A, B or C in the 6FDA moiety we may use affects much on the spatial distortion of the ring formation. The ring FDA-MDA (2 units) can be formed either by the geometry B or C. Similarly, the ring FDA-MDA (3 units) can be formed either by the geometry A or B. In contrast, the ring FDA-MDA (4 units) can be formed only by the geometry A. We failed geometry optimization for the other combinations without asterisk in Table II due to the high energy caused by the distortion of the ring. The relation between the N_{unit} and the geometry of the 6FDA moiety is therefore important to obtain a low energy ring conformation. We confined only to the homogeneous combination in the ring formation in this study. The ring 6FDA-MDA formed by mixed geometries of the 6FDA moiety will be shown in the subsequent paper together with energetically most favored geometries.

3.4 Smallest ring imide and nano-scale cavity

Among the five candidate molecules, two kinds of ring polyimides from 2 units of 6FDA-MDA, which is the smallest structure, was further investigated in detail. The eight dihedral angles and the energy difference between the two geometries for both forms are summarized in Table III. Although the respective values are somewhat different, the value was maintained around the optimized structure in the 6FDA moiety and MDA moiety. Based on the ΔSA and obtained geometries, it appears that the extent of the spatial distortion is greater in the 6FDA(B)-MDA form. The total potential energy was 6.2 kcal/mol lower in the 6FDA(C)-MDA form than the 6FDA(B)-MDA form, reflecting the somewhat distorted structure of 6FDA(B)-MDA. The distance between the oxygen at the opposite position was also included in Table III in order to estimate the size of the cavity in the 6FDA-MDA ring. The four oxygen atoms in the respective rings were sequentially numbered as O1, O2, O3 and O4. The size of the small hole was estimated from the atomic distance of oxygen and the van der Waals radius of oxygen (1.4 Å). The hole is an ellipse rather than a circle with the size of 3.0 Å x 5.2 Å for 6FDA(B)-MDA. In contrast, the hole is completely circular with the size of 4.0 Å x 4.0 Å for 6FDA(C)-MDA.

Finally, the possibility of the stacking of the flat 6FDA(C)-MDA (2 units) was briefly stated. Due to the strong interaction between the imide rings, the stacking of the flat ring polyimide is highly proposed for the PMDA-MDA and a-BPDA-PDA based ring polyimide [3,6]. In the case of the 6FDA–based polyimide, however, the optimization of the two molecules of 6FDA(C)-MDA (2 units) has failed due to the bulky hexafluoropropane groups by the DFT calculation. The stacking of the ring 6FDA-MDA by the self-assembly seems to be difficult to occur.

Recently, Sanui's group succeeded in the chemical synthesis of the ring 6FDA-MDA [9]. The ring PMDA-MDA and ring BPDA-MDA proposed earlier were failed to be synthesized due to the very low solubility in the solvents. In the present stage, the detailed analysis has not been performed for the practical products, but the DFT calculation will play important role in determining the molecular structure.

Table III. Comparison of dihedral angles, relative energies and O-O distances of the optimized structure of the smallest ring 6FDA-MDA using the B3LYP/6-31G(d) level.

| | Optimized geometry | |
	6FDA(B)-MDA (2 units)	6FDA(C)-MDA (2 units)
ϕ_1 (°)	−54.3	−142.1
ϕ_2	141.4	−142.1
ϕ_3	46.6	−45.7
ϕ_4	37.7	−45.7
$\phi_{1'}$	−54.3	−142.1
$\phi_{2'}$	141.4	−142.1
$\phi_{3'}$	46.4	−45.7
$\phi_{4'}$	37.6	−45.7
ℓ(O1-O3) (Å)	5.78	6.81
ℓ(O2-O4) (Å)	8.03	6.81
ΔE (kcal/mol)	6.2	0.0[a]

a) SCF energy for 6FDA(C)-MDA (2 units) is -3936.40565653 (Hartree).

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