Electronic Structures of a Macrocyclic Fulleropyrrolidine

Sungu Hwang[†], Jong Myong Lee[‡], and Il Cheol Jeon[‡]*

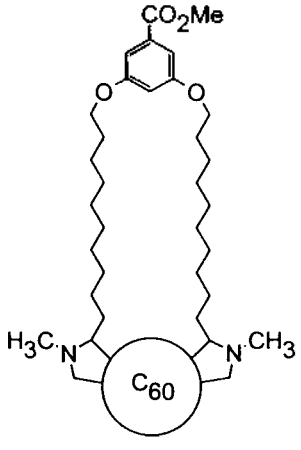
[†]*The Research Institute for Basic Sciences, Seoul National University, Seoul 151-742, Korea*
[‡]*Department of Chemistry, Jeonbuk National University, Jeonbuk 561-756, Korea*
Received June 25, 1996

The electronic structures of twenty-seven isomers of a macrocyclic fulleropyrrolidine are investigated with semi-empirical extended Hückel (EH) molecular orbital method. The geometry of each isomer is determined by the molecular mechanics and dynamics methods based on UFF (universal force field) empirical force field. The calculated geometries, such as the carbon-carbon distances of the fullerene moiety, are in good agreement with those of related fullerene derivatives. The EH calculation shows that the formation of macrocyclic pyrrolidine ring on fullerene moiety results in the reduction of the HOMO-LUMO energy gap. From the graphical analysis of the DOS (density of states), PDOS (projected DOS), and MOOP (molecular orbital overlap population) curves, we can find that this reduction is due to splitting of the HOMO of fullerene moiety, which results from the symmetry-breaking and the distortion of the buckminsterfullerene framework from its ideal icosahedral structure.

Introduction

Since the discovery of buckminsterfullerene (C_{60}),[1] the synthesis and characterization of its derivatives have been an important area of research due to their possible application to superconductor, optical devices, ferromagnetic materials, batteries, catalysts, sensors, and membranes.[2,3] Examples of well characterized fullerene derivatives include Diels-Alder adducts,[4] methano-bridged fullerenes from carbene addition reactions,[5] and five membered ring adducts synthesized by [3+2] cycloadditions of trimethylenemethanes.[6]

Recently, we have reported a novel macrocyclic fulleropyrrolidine,[7] **1**, which is prepared from the 1,3-dipolar cycloaddition of azomethine ylide to C_{60}. The molecule is synthesized in the course of looking for the intramolecular electron transfer system of fullerene-metal complexes. As the first step to understand the physicochemical properties of **1**, we investigate its electronic structure and geometry. Since geometrical structure of the macrocyclic fulleropyrrolidine has not been reported so far, we optimize the structure using molecular mechanics (MM) and molecular dynamics (MD) techniques, which are widely used in the studies of organic, inorganic, and biochemical materials.[8] The electronic structure is investigated by the use of the extended Hückel molecular orbital (EHMO) method.[9] Although the EH method is known to be a very approximate one, it has been used frequently in qualitative studies in organic, inorganic and surface chemistry due to its simple and transparent nature of calculation and analysis, and its applicability to large systems.[10] Since the EH method is not reliable in predicting the optimal geometry, the geometrical structure obtained from MM and MD calculations is used as an input geometry. As shown in Figure 1, the macrocyclic fulleropyrrolidine has twenty-seven geometrical isomers and the prevailing geometry is not yet determined experimentally. So, the calculations are performed on all the isomers and the common features are presented in this paper.



1

*To whom correspondence should be addressed.

Computational Details

The macrocyclic fulleropyrrolidine studied in this work, **1**, has twenty-seven isomers: there exist nine different addition sites (Figure 1a) and three different relative positions of alkyl chains in two five-membered pyrrolidine rings at each addition site (Figure 1b). The nomenclature of the isomer used in the Tables 3-5 is such that the first letter (*e.g.* a of a1) represents the addition site and that the second digit (*e.g.* 1 of a1) represents the relative position of alkyl chains in two five-membered pyrrolidine rings. Geometry of each isomer is optimized with UNIVERSAL force field[11] implemented in CERIUS[2] modeling software.[12] Energy of each structure is initially minimized by Fletcher-Powell algorithm,[13] and then the anneal dynamics simulation is performed. In the anneal dynamics process,[14] the temperature is altered in time increments from an initial temperature to a final temperature and back again. The temperature is changed by adjusting the kinetic energy of the structure. At the end of each temperature cycle, Fletcher-Powell minimization was performed on the lowest energy structure of that cycle to find the structure of the lowest energy and the result is saved in a trajectory file. This annealing allows the energy

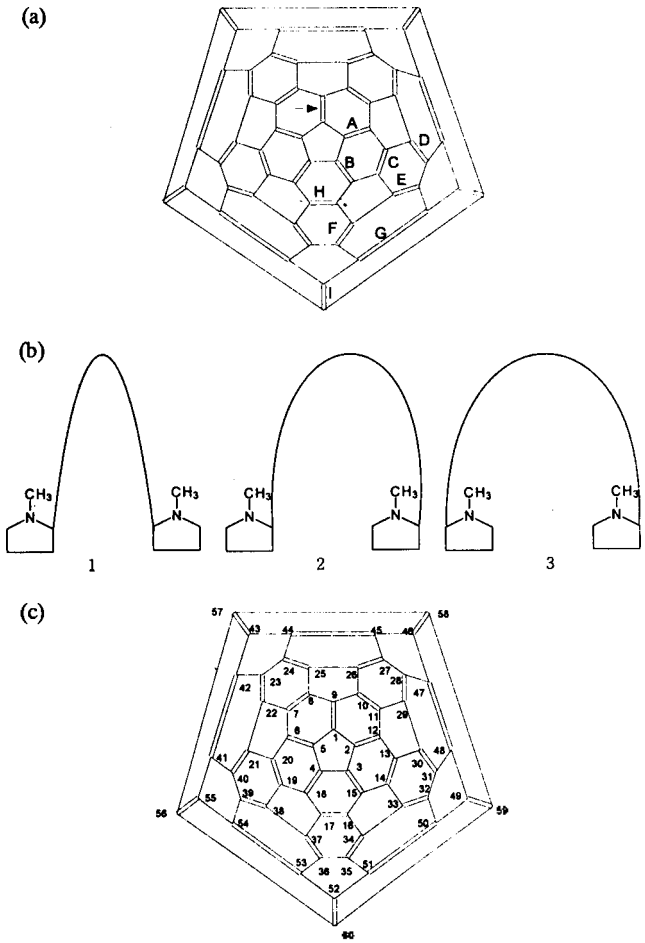


Figure 1. (a) Addition patterns for the isomers of the macrocyclic fulleropyrrolidine. The first five-membered ring is formed at the double bond marked by the arrow, and the next ring is formed at the double bonds marked by the alphabetic letters. (b) The relative position of the alkylchains in two five-membered pyrrolidine rings at each addition site. (c) Numbering system for C60 moiety of macrocyclic fulleropyrrolidine.

of the structure to be minimized gradually without trapping in a local energy minimum. The parameters for the anneal dynamics simulation used in this study are listed in Table 1. The minimum energy structure obtained from the annealing process is then further minimized by Fletcher-Powell algorithm until the RMS force on the structure is less than 0.005 kcal/(mol·Å). The atomic charge parameters are calculated by the charge equilibration method of Goddard and Rappé[15] and periodically updated after every ten steps in MM and MD process. The non-bonding interaction neighbors lists are also updated after every ten steps.

The electronic structure is calculated in the framework of EHMO method[9] for the geometries obtained in the anneal dynamics-minimization process. The EH parameters used in this work are listed in Table 2. The density of states (DOS), projected density of states (PDOS), and molecular orbital overlap population (MOOP) curves are used in the analysis of the calculation results. A detailed description of the analysis based on the DOS, PDOS and MOOP curves was given elsewhere.[10] Therefore we briefly summarize here only the essential features. The DOS curve represents the number of states in the given energy range, and the PDOS curve shows the contribution of a specific part (an atom, an orbital, or a fragment) to the DOS. The MOOP is an overlap-population-weighted density of states, and shows the contribution of orbitals in the given range to the bonding of two specific atoms or fragments. The positive regions of the MOOP curve signify bonding and negative regions represent antibonding. By comparing the peaks in the DOS, PDOS, and MOOP curves, we can assign the origin of the peaks of DOS curves, and understand the bonding nature of a molecular orbital corresponding to a specific peak appeared in a DOS curve.

Table 1. The parameters of the anneal dynamics used in this study

Parameter	Value
total number of the annealing cycle	10
initial temperature (K)	300
final temperature (K)	1000
temperature increment (K)	100
the number of time steps at each temperature	50

Table 2. The EHMO parameters used in this work

Orbital	Hii	ζ
H 1s	−13.60	1.300
C 2s	−21.40	1.625
C 2p	−11.40	1.625
N 2s	−26.00	1.950
N 2p	−13.40	1.950
O 2s	−32.30	2.275
O 2p	−11.40	2.275

Results and Discussion

The calculated energy of each fulleropyrrolidine is listed in the Table 3 and the relative energy is shown in Figure 2. The minimum energy isomer is d3, and the energy of each isomer shown in Table 3 and Figure 2 is relative to the isomer d3. The isomers b2 and f2 are within 2 kcal/mol from the energy of d3. However, the energy difference is so small that we are not able to draw a conclusion on the stability of isomers. The isomer a1 has the highest conformational energy among twenty-seven isomers. It seems likely to be due to large distortion of fullerene framework from their ideal one. This distortion is reflected as the large value of the bond stretching and the angle deformation energies of a1 compared with the other isomers (See Table 3).

Calculated geometrical parameters of fullerene moiety are listed in Table 4. The C-C bondlengths where the cycloaddition occurred are calculated to be 1.57-1.59 Å, which is in agreement with the result obtained from the semi-empirical PM3 calculation on $C_{60}H_2$[16] and with X-ray crystal structure of osmylated C_{60}.[17] The average C-C bondlength connecting to the addition site is 1.52-1.53 Å, which is also in good agreement with previous works on $C_{60}H_2$ and on osmylated

Table 3. The Relative Energies of the Isomers of the Fulleropyrrolidine (units: kcal/mol)

model[a]	bond[b]	angle[c]	torsion[d]	inversion[e]	Coulombic[f]	v.d.W.[g]	total E[h]	rel. E[i]
a1	43.552	282.235	360.495	54.241	−12.791	148.363	876.096	52.517
a2	40.789	281.362	348.596	54.294	−0.940	149.858	873.958	50.379
a3	39.470	273.321	357.793	54.199	−2.890	145.130	867.023	43.445
b1	34.914	271.859	352.230	53.669	0.776	134.770	848.219	24.640
b2	32.367	264.540	343.888	53.679	−5.815	136.244	824.903	1.324
b3	32.635	263.239	356.938	53.693	0.126	122.990	829.619	6.040
c1	32.443	259.783	351.568	53.701	−1.268	132.640	828.867	5.288
c2	31.859	263.741	353.407	53.708	−4.116	137.153	835.752	12.173
c3	33.131	268.557	345.440	53.706	0.467	139.007	840.309	16.730
d1	33.324	266.057	352.946	53.610	−7.792	141.364	839.510	15.931
d2	32.769	260.317	358.038	53.684	3.463	121.042	829.314	5.735
d3	33.849	266.058	346.765	53.595	2.094	121.217	823.579	0.000
e1	33.082	260.455	355.075	53.648	6.558	128.705	837.522	13.943
e2	31.553	261.402	364.814	53.688	4.900	119.161	835.519	11.940
e3	31.961	264.405	350.490	53.688	2.344	124.132	827.019	3.440
f1	33.790	269.288	351.824	53.644	−7.946	138.445	839.045	15.466
f2	33.566	266.174	351.128	53.656	0.697	119.751	824.973	1.394
f3	32.238	265.808	346.712	53.772	3.865	126.753	829.149	5.571
g1	33.401	269.842	345.236	53.637	−1.304	135.144	835.956	12.377
g2	32.604	265.010	351.288	53.658	8.670	121.571	832.800	9.221
g3	32.889	267.168	351.662	53.744	12.559	118.347	836.369	12.790
h1	32.038	260.368	348.499	53.609	−5.627	140.814	829.701	6.122
h2	33.738	266.637	350.734	53.635	−3.663	126.526	827.607	4.028
h3	33.210	268.240	347.093	53.645	2.532	125.649	830.369	6.790
i1	34.980	269.280	349.175	53.629	−5.746	136.273	837.590	14.012
i2	33.901	261.385	351.113	53.611	3.923	123.787	827.721	4.142
i3	33.012	265.874	349.130	53.684	3.589	128.057	833.345	10.605

[a]The nomenclature of the isomer is such that the first letter (*e.g.* a of a1) represents the addition site (See Figure 1a) and that the second digit (*e.g.* 1 of a1) represents the relative position of the alkylchains in two five-membered pyrrolidine ring at each addition site (See Figure 1b). [b]The energy of deformation of bond lengths. [c]The energy of deformation of bond angles. [d]The energy of deformation of torsion angles. [e]The energy of inversion or out-of-plane motion. [f]The nonbonding interaction energy (Coulombic representation of electrostatic interactions). [g]The nonbonding interaction energy (van der Waals interaction). [h]The total energy of the isomer. [i]The relative energy of the isomer with respect to d3 isomer.

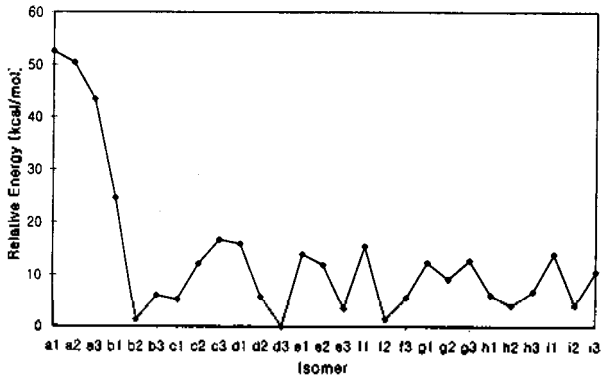


Figure 2. The relative energy of the isomers of the macrocyclic fulleropyrrolidine.

C_{60}.[16,17] The other C-C bond lengths in the fullerene moiety are also in agreement with previous works,[16-19] and we can see that the effect of cycloaddition on the C-C bond distances is limited to the region near the carbons where the cycloaddition are occurred, as calculated in other work.[14]

From now on, we concentrate on the electronic structure of the macrocyclic fulleropyrrolidine. Since the relative energies between isomers are relatively small, and thus the prevailing isomer is not able to be exactly assigned, we perform the EH calculation on each isomers, and focus on the common features of the electronic structures. The calculated HOMO-LUMO energy gap is listed in Table 5. The energy gap ranges from 1.356 eV (for c3 isomer) to 1.597 eV (for b1 isomer). The HOMO-LUMO splitting of the pristine buckminsterfullerene is calculated to be 1.877 eV, which is consistent with the experimentally determined value from photoemission studies of 1.7 eV.[20] It is reduced by the cycloaddition by 0.280-0.521 eV. The overall feature of the electronic structure of each isomer is similar with each other: The energy of the LUMO is nearly unaffected by the cycloaddition, whereas that of the HOMO is much upward shifted.

In Figure 3, we represent the DOS, PDOS, and MOOP curves of d3 isomer of the fulleropyrrolidine, which has lo-

Table 4. Selected Bond lengths of the Isomers of the Fulleropyrrolidine

model[a]	r_1[b] (Å)	r_2[c] (Å)	r_3[d] (Å)	r_4[e] (Å)
a1	1.592	1.534	1.477	1.355
a2	1.583	1.544	1.481	1.354
a3	1.584	1.537	1.480	1.354
b1	1.583	1.525	1.480	1.354
b2	1.575	1.525	1.480	1.354
b3	1.573	1.525	1.480	1.354
c1	1.570	1.528	1.479	1.354
c2	1.570	1.528	1.479	1.354
c3	1.571	1.528	1.479	1.354
d1	1.578	1.527	1.479	1.354
d2	1.574	1.527	1.479	1.354
d3	1.573	1.528	1.479	1.354
e1	1.573	1.529	1.479	1.354
e2	1.574	1.527	1.479	1.354
e3	1.573	1.527	1.479	1.354
f1	1.580	1.528	1.479	1.354
f2	1.574	1.529	1.479	1.354
f3	1.576	1.528	1.479	1.354
g1	1.580	1.528	1.479	1.354
g2	1.573	1.528	1.479	1.354
g3	1.573	1.528	1.479	1.354
h1	1.571	1.527	1.479	1.354
h2	1.573	1.528	1.479	1.354
h3	1.574	1.527	1.479	1.354
i1	1.578	1.529	1.479	1.354
i2	1.574	1.530	1.479	1.354
i3	1.575	1.527	1.479	1.354

[a]The nomenclature of the isomer is such that the first letter (*e.g.* a of a1) represents the addition site (See Figure 1a) and that the second digit (*e.g.* 1 of a1) represents the relative position of the alkylchains in two five-membered pyrrolidine ring at each addition site (See Figure 1b). [b]The average carbon-carbon bondlength at the addition sites. [c]The average carbon-carbon bondlengtth near the addition sites except for a1, a2 and a3 isomers. In a1, a2, and a3 isomers, the carbon-carbon distance connecting the addition sites (C1-C2 in Figure 1c) is longer than those at the addition sites; 1.646 Å (a1), 1.635 Å (a2), and 1.630 Å (a3). This distance is not included in the average for a1, a2, and a3 isomers. [d]The average carbon-carbon single bondlength. [e]The average carbon-carbon double bondlength.

Table 5. The Positions of HOMO and LUMO of the Isomers of the Fulleropyrrolidine

Model	LUMO (eV)	HOMO (eV)	H-L gap (eV)
a1	−9.697	−11.261	1.564
a2	−9.692	−11.271	1.579
a3	−9.688	−11.275	1.587
b1	−9.648	−11.245	1.597
b2	−9.659	−11.232	1.573
b3	−9.650	−11.230	1.580
c1	−9.640	−11.009	1.369
c2	−9.658	−11.018	1.360
c3	−9.655	−11.012	1.357
d1	−9.653	−11.229	1.575
d2	−9.640	−11.227	1.588
d3	−9.644	−11.233	1.589
e1	−9.643	−11.135	1.492
e2	−9.666	−11.122	1.456
e3	−9.664	−11.127	1.464
f1	−9.664	−11.137	1.473
f2	−9.652	−11.144	1.492
f3	−9.673	−11.147	1.473
g1	−9.705	−11.195	1.490
g2	−9.699	−11.199	1.499
g3	−9.711	−11.200	1.489
h1	−9.658	−11.231	1.573
h2	−9.663	−11.237	1.574
h3	−9.647	−11.232	1.585
i1	−9.723	−11.205	1.482
i2	−9.722	−11.201	1.479
i3	−9.719	−11.199	1.480
C_{60}	−9.676	−11.553	1.877

[a]The nomenclature of the isomer is such that the first letter (*e.g.* a of a1) represents the addition site (See Figure 1a) and that the second digit (e.g. 1 of a1) represents the relative position of the alkylchains in two five-membered pyrrolidine ring at each addition site (See Figure 1b).

west energy among the isomers, to understand the change of electronic structures upon cycloaddition. The curves for the other isomers are qualitatively equivalent to those of d3.

The total DOS curve of fulleropyrrolidine is depicted in Figure 3b) and the projections of DOS on to the pyrrolidine adduct and the fullerene are shown in 3a) and 3c). Finally the MOOP curve for the pyrrolidine-fullerene bond is shown in 3d). In the energy levels corresponding to the frontier orbitals (HOMO and LUMO, marked by arrows in the Figure 3b) of fulleropyrrolidine, the bonding or antibonding interaction between fullerene moiety and the adduct does not occur. The frontier orbitals are nonbonding ones between fullerene moiety and the adduct, which are shown in the Figure 3a) and Figure 3d). The peaks corresponding to the frontier orbitals in Figure 3a) are not seen in Figure 3d). The HOMO of fulleropyrrolidine comes from the fullerene moiety and the LUMO comes from the adduct, which is easily seen by comparison of the peaks in Figure 3a), b) and c). The states which are produced by the interaction between fullerene and the adduct lie about 1 eV below the HOMO of the fulleropyrrolidine, as you can see in Figure 3d).

The upward shift of the HOMO with respect to the pristine buckminsterfullerene and the associating reduction of the HOMO-LUMO gap upon the cycloaddition is due to the splitting of the HOMO of buckminsterfullerene which results from the reduction of symmetry and the distortion of the buckminsterfullerene framework from its ideal icosahedral structure. This is clearly seen in Figure 4. The PDOS curve upon fullerene moiety is shown in Figure 4a), and the DOS curve of fullerene moiety distorted by the cycloaddition is

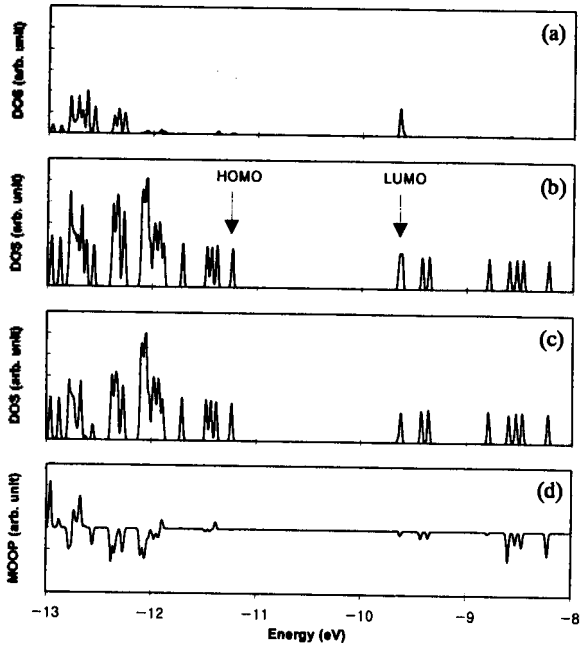


Figure 3. (a) The projected DOS curve onto the pyrrolidine adduct, (b) The DOS curve of d3 isomer of macrocyclic fulleropyrrolidine, (c) The projected DOS curve onto the fullerene moiety, and (d) The molecular orbital overlap population (MOOP) curve of adduct-fullerene bonding.

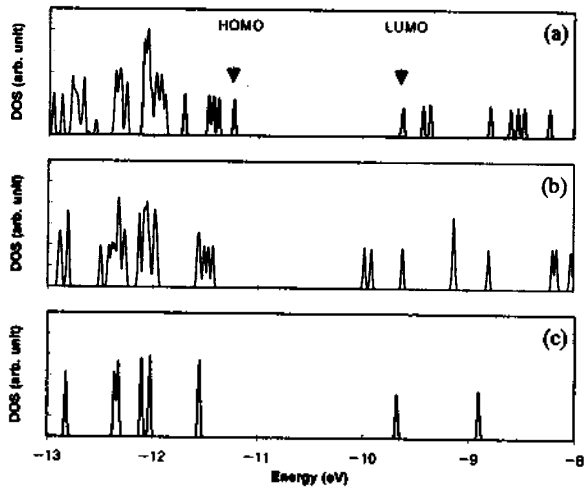


Figure 4. (a) The projected DOS curve of macrocyclic fulleropyrrolidine onto fullerene moiety, (b) the DOS curve of fullerene moiety of macrocyclic fulleropyrrolidine, and (c) the DOS curve of pristine buckminsterfullerene.

presented in Figure 4b). For the comparison, the DOS curve of ideal buckminsterfullerene is given in Figure 4c). The HOMO of buckminsterfullerene is splitted into several part due to the symmetry reduction and the distortion from the ideal framework (Figure 4c)→Figure 4b)), and then further splitted by the first order perturbation exerted by the cycloadduct (Figure 4b)→Figure 4a)). Besides these features, new peaks can be found especially near −12.7 eV, and the shift of the orbital is also found near the LUMO. The new peaks appeared near −12.7 eV are contributed from the interaction with adduct. They are related to the interaction between occupied orbitals, and thus have little effect on the stability of the fulleropyrrolidine. The shift of orbital near the LUMO does not affect severely on the stability, since the LUMO of fulleropyrroline comes from the adduct.

Summary

We carry out the MM, MD, and EHMO calculations on the twenty seven isomers of a macrocyclic fulleropyrroline. Through MD and MM study, we calculate the relative energies of the various isomers and optimize the geometrical structure of isomers. The d3 isomer has the minimum conformation energy. However, the relative energies between the isomers are so small that we are not able to assign the prevailing isomers. We performed the EHMO calculations on the minimized structure to investigate electronic structures of macrocyclic fulleropyrrolidine. The HOMO-LUMO splitting is reduced by the addition reaction and the energy of the HOMO is upward-shifted. However, the HOMO is not involved in the bonding between buckminsterfullerene and adduct. Thus, the upward shift of the HOMO is due to the reduction of the symmetry, the distortion of fullerene moiety from its ideal structure, and the first order perturbation by the adduct.

Acknowledgment. This work is supported by a Grant (No. BSRI-96-3430) from the Basic Research Science Program, Ministry of Education, and in part by KOSEF (93-0500-07-01-3). One of the authors (S. Hwang) thanks Dr. Yun Hee Jang for helpful discussions.

References

1. Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
2. Hirsch, A. *The Chemistry of the Fullerenes*; Georg Thieme Verlag Stuttgat: New York, 1994.
3. Kroto, H. W.; Fisher, J. E.; Cox, D. E. *The Fullerenes*; 1st ed., Pergamon Press: Oxford, 1993.
4. Tsuda, M.; Ishida, T.; Nogami, T.; Kuronr, S.; Ohasi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 11296.
5. Vasella, A.; Uhlmann, P., Waldraff, C. A. A.; Diederich, F.; Thilgen, C. *Angew. Chem.* **1992**, *104*, 1383.
6. Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594.
7. Bang, G. S.; Chang, W.; Moon, J.-M.; Kim, S. H.; Jeon, I. C. *Bull. Kor. Chem. Soc.* **1996**, *17*, 107.
8. Some general reviews: (a) Lipkowitz, K. B.; Boyd, D. B. Eds., *Reviews in Computational Chemistry*; VCH Publishers Inc.: New York, 1990. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington D. C., 1982.
9. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
10. Jang, Y. H.; Hwang, S.; Kim, H. *Surface Sci.* **1995**, *340*, 245.
11. Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard III, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*,

10024.
12. The results of molecular mechanics and molecular dynamics studies in this work are generated using the program Cerius^{2} ™, which was developed by Molecular Simulations Incorporated.
13. Press, W. H.; Flannery, B.P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes, The Art of Scientific Computing*; Cambridge University Press: New York, 1986; Chapter 10.
14. *Cerius2 Simulation Tools User's Reference*; Molecular Simulations Incorporated, 1994.
15. Rappé, A. K.; Goddard, W. A. *J. Phys. Chem.* **1991**, *95*, 3358.
16. Matsuzawa, N.; Dixon, D. A.; Fukunaga, T. *J. Phys. Chem.* **1992**, *96*, 7594.
17. Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312.
18. Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160.
19. Keshavarz-K, M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371.
20. Fann, Y. C.; Singh, D.; Jansen, S. A. *J. Phys. Chem.* **1992**, *96*, 5817.

Liquid Chromatographic Resolution of Both π-Acidic and π-Basic Analytes on a Chiral Stationary Phase Derived from (S)-Tyrosine

Myung Ho Hyun and Chung-Sik Min

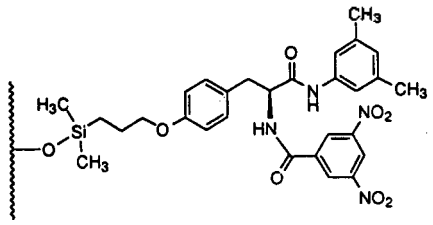
Department of Chemistry, Pusan National University, Pusan 609-735, Korea
Received July 26, 1996

Chiral recognition models for resolving π-basic N-acyl-α-(1-naphthyl)alkylamines and π-acidic N-(3,5-dinitrobenzoyl)-α-amino alkyl esters on a (S)-tyrosine-derived chiral stationary phase (CSP) containing both π-basic and π-acidic interaction site have been proposed. In the models, the CSP was supposed to interact with the analytes through the π-π interaction between the 3,5-dinitrophenyl or the 3,5-dimethylphenyl group of the CSP and the 1-naphthyl or the 3,5-dinitrophenyl group of the analyte, and through the hydrogen bonding interaction between the appropriate N-H hydrogen of the CSP and the appropriate carbonyl oxygen of the analyte. In this instance, the alkyl substituent of the pertinent enantiomer of the analyte was found to intercalate between the adjacent strands of the bonded phase and consequently control the trends of the separation factors.

Introduction

Liquid chromatographic resolution of enantiomers on CSPs has been known to be one of the most accurate and convenient means in determining the enantiomeric composition of chiral compounds.[1] Therefore, there have been significant efforts for developing efficient CSPs for the liquid chromatographic resolution of enantiomers and various CSPs derived from optically active natural or synthetic chiral compounds are now available.[2] Among various CSPs, Pirkle-type CSPs have been known to separate two enantiomers by forming energetically different two transient diastereomeric π-π complexes with two enantiomers. For example, CSPs containing π-acidic aryl functional group have been applied for resolving π-basic racemates.[3] Similarly, CSPs containing π-basic aryl functional group have been used for resolving π-acidic racemates.[4] In this context, CSPs containing both π-acidic and π-basic aryl functional groups are very interesting in that they can resolve either π-basic or π-acidic racemates. However, up to now, only a few CSPs containing both π-acidic and π-basic aryl functional groups have been reported.[5]

Recently, we reported in a short communication that CSP **1** prepared by grafting simple achiral 3,5-dimethylaniline to (S)-N-(3,5-dinitrobenzoyl)tyrosine unit can be successfully used in resolving either π-basic or π-acidic racemates or in



CSP **1**

separating simultaneously π-basic and π-acidic racemates.[6] However, the detailed synthetic procedure for CSP **1** and the chiral recognition mechanism have not been reported. In this study, we wish to report the detailed synthetic procedure for CSP **1**. In addition, we wish to propose chiral recognition models which can be applied for rationalizing the resolution behaviors of representative π-acidic and π-basic racemates on CSP **1**.

Experimental