thanol (10 mL) was added a catalytic amount of Pd/C and the resulting solution was stirred under hydrogen gas (1 atm) for about 1 hr. The catalyst was removed by filtration and the filtrate was evaporated under reduced pressure to give **(2*R*,3*S*)-BEBA** (0.30 g, 97%) as an oil. IR ($CHCl_3$): 3028, 2925, 1706, 1490, 1449, and 1211, 883 cm^{-1}; ^1H NMR: δ 2.29 (1H, m, 2-H), 2.50 (1H, q, CH-Ph), 2.69 (1H, t, CH-Ph), 2.89-3.17 (2H, dq, 4-H),3.20 (1H, m, 3-H), 7.18-7.32 (5H, m, Ph), and 8.40 (1H, br, CO_2H); ^{13}C NMR: δ 40.0, 46.5, 50.3, 52.0, 126.8, 128.4, 128.7, 137.8 and 177.6; $[\alpha]=+9.80°$ ($c=1$, EtOH), lit[7] $[\alpha]=+9.8°$ ($c=1$, EtOH).

(2*S*,3*R*)-2-Benzyl-3,4-epoxybutanoic Acid, (2*S*,3*R*)-BEBA. This compound was prepared in a similar fashion as described above from (2*S*,3*R*)-BEBA benzyl ester in 95% yield. The spectral data (IR, ^1H NMR) were identical with those obtained for (2*R*,3*S*)-BEBA; $[\alpha]=-10.8°$ ($c=1$, EtOH).

(2*R*,3*R*)-2-Benzyl-3,4-epoxybutanoic Acid, (2*R*,3*R*)-BEBA. This compound was prepared from (2*R*,3*R*)-BEBA benzyl ester in 97% yield in a similar fashion as described for the preparation of (2*R*,3*S*)-BEBA. IR ($CHCl_3$): 3028, 2925, 1706, 1490, 1449, and 1211, 881 cm^{-1}; ^1H NMR: δ 2.55 (1H, m, 2-H), 2.71 (1H, q, CHPh), 2.84 (1H, t, CHPh), 3.10-3.13 (3H, m, 4-H_2 and 3-H), and 7.20-7.31 (5H, m, Ph). ^{13}C NMR: δ 35.5, 46.6, 50.2, 52.7, 126.7, 128.5, 128.9, 137.7, and 176.7; MS (m/z): 192 (M^+), 178, 167, 149, 121, 111, 97, 91, 85, 77, 73, 71, and 60; $[\alpha]=+1.84°$ ($c=1$, EtOH).

(2*S*,3*S*)-2-Benzyl-3,4-epoxybutanoic Acid, (2*S*,3*S*)-BEBA. This compound was prepared from (2*S*,3*S*)-BEBA benzyl ester in 95% yield following the procedure described for the preparation of (2*S*,3*R*)-BEBA. The spectral data (IR, ^1H NMR) of this compound are identical with those of (2*R*,3*R*)-BEBA. $[\alpha]=-1.72°$ ($c=1$, EtOH).

Determination of optical purity of the resolved 2-benzylvinylacetic acid. A mixture of resolved 2-benzylvinylacetic acid (49.3 mg, 0.28 mmol), L-alanine methyl ester hydrochloride (39.2 mg, 0.28 mmol), triethylamine (28.3 mg, 0.28 mmol), and DCC (20.6 mg, 0.28 mmol) in methlene chloride (10 mL) was allowed to stir at room temperature overnight. The reaction mixture was chilled in ice, then filtered to remove dicyclohexylurea. The filtrate was evaporated on a rotary evaporator under reduced pressure, and the residue was treated with ethyl acetate, whereby most of the product was dissolved in methylene chloride. The insoluble residue (dicyclohexylurea) was removed by filtration, and the filtrate was evaporated under reduced pressure. Optical purity of the resolved acid was determined from the relative NMR peak intensity of the methyl proton signals of the product at 1.34 (d) and 1.22 (d). The former signal corresponds to the methyl protons of the product formed with (*R*)-2-benzylvinylacetic acid with L-alanine methyl ester, and the latter to the methyl protons of the product formed with (*S*)-2-benzylvinylacetic acid containing as an impurity resulting from the resolution.

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Fragmentation of Tertiary Alkyl Amine Ions: Mechanism of C-C Bond Cleavage

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The multiphoton ionization of tertiary amines has been previously studied by Parker *et. al.*[1] They showed that on visible laser irradiation trimethylamine produced a parent ion, P^+ and an ion missing an H atom, $[P-H]^+$. Triethylamine formed a parent ion and an ion lacking a methyl radical, $[P-CH_3]^+$. Cyclic amines such as ABCO (quinuclidine)

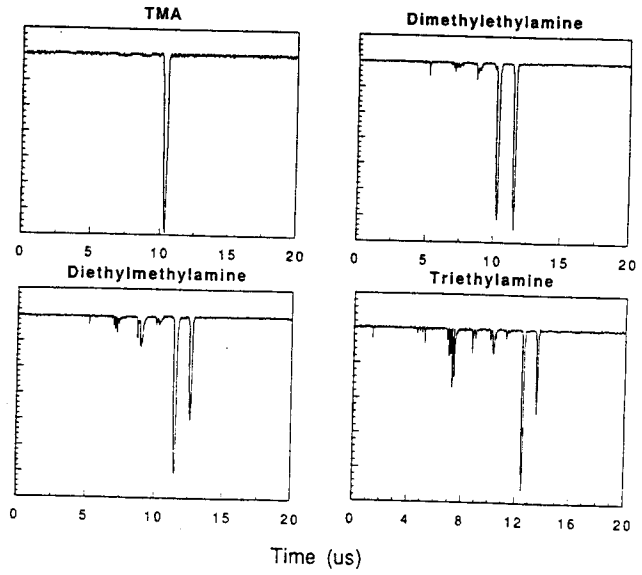


Figure 1. TOF Mass spectra of four tertiary amines irradiated by focused 614 nm light.

Table 1. Principal ions produced by irradiating tertiary amines.

Parent molecule	Ionization potential	Ion masses	
		P^+	Fragment ion
trimethylamine	7.82	59	58
dimethylethylamine	–	73	58
diethylmethylamine	–	87	72
triethylamine	7.56	101	86

and DABCO (triethylenediamine) formed a parent ion and much smaller ions.

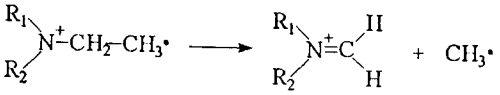
The aim of the present work was to deduce a mechanism for the above observations. A series of tertiary amines, trimethyl, dimethylethyl, diethylmethyl, and triethyl amines were irradiated with 35 mJ pulses of 614 nm light focused with a 12 cm focal length lense. The mass spectra, measured with a time-of-flight mass spectrometer (R.L. Jordan) are shown in Figure 1. Table 1 lists the principal mass peaks obtained by irradiating the four compounds. In these processes, Parker *et al.* found that the fragmentation patterns did not depend on the laser powers.[1]

Each mass spectrum is dominated by two strong peaks, the parent ion and the parent ion minus an H atom for trimethylamine and a parent ion minus a methyl radical for the other amines. At first sight it is puzzling that 1) trimethylamine does not lose a methyl group, 2) dimethylethyl and diethylmethyl amines lose a methyl group exclusively and do not lose an ethyl group, and 3) triethylamine which has no methyl group bonded to the central N atom nevertheless loses a methyl group. These observations are explained by the following mechanism.

Ionization precedes dissociation. As each 614 nm photon has an energy of 2.02 eV, the molecules can not absorb one or two red photons but will undergo a simultaneous three photon absorption to a Rydberg state, corresponding to a 3s and 3p state on the nitrogen atom. Absorption of a fourth photon produces an ion isoelectronic with a t-butyl radical or alkyl substituted t-butyl radical. Therefore, the three carbon atoms and the central nitrogen atom to which the carbon atoms have been bonded are believed to be coplanar. Since this ion has less than 0.6 eV of excess energy, dissociation requires further absorption.

The electronic absorption of t-butyl radical begins at 360 nm (3.44 eV)[2,3] and the isoelectronic NR_3^+ is therefore assumed to be able to absorb two more 614 nm photons. The resulting excited ions which is in a 3s Rydberg state has 93 kcal/mol of internal energy. This is not enough energy to break an N-C bond and therefore no attached methyl or ethyl radicals are cleaved. Instead, internal conversion occurs producing a hot radical ion.

The following unimolecular process then occurs.



The C-C bond energy of about 100 kcal/mol is compensated in part by the formation of a new π bond. The resulting double bonded structure, isoelectronic with a 1,1-dialkyl substituted ethylene has no energy level which could permit one or two 614 nm photon absorption.[4,5] For most molecules, three photon absorption is extremely weak so the above ion product should be the final product.

Trimethylamine does not liberate a methyl group on photoabsorption as do $Ga(CH_3)_3$ and $In(CH_3)_3$ but was found by Parker *et al.* to liberate an H atom. (Our resolution was not sufficient to distinguish between P^+ and $[P\text{-}H]^+$.) The release of the H atom from trimethylamine produces exactly the above ion product. The observations[1] that the tricyclic cage amines, ABCO and DABCO have very different fragmentation patterns can also be understood from the fact that a planar configuration around a nitrogen is sterically prevented.

Suppose that fragmentation were to precede ionization. After three photons are absorbed, the molecule would have enough energy (6.06 eV) to break N-C bonds almost randomly producing both ethyl and methyl radicals. In fact, photodissociation of trimethylamine at 193 nm breaks the N-C bonds producing methyl radicals.[6] However, fragmentation from the trimethylamine ions dominantly produces the parent ion minus an H atom contrary to the fragmentation from the neutral molecules. Therefore, it is believed that in the fragmentation of tertiary alkyl amines by multiphoton absorption of 614 nm photons, ionization precedes dissociation and after the parent ion absorbs two more photons, there is C-C bond breakage and a bottleneck to further absorption.

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Synthesis of a Bowl-Shaped, C_3 Symmetric Receptor with a Phosphate Functionality at the Cavity Bottom

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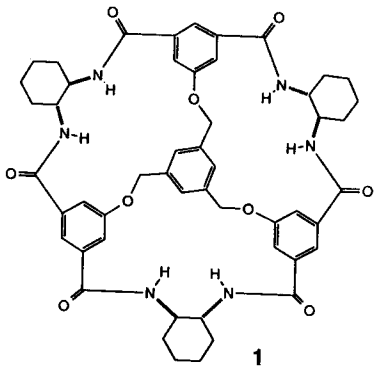
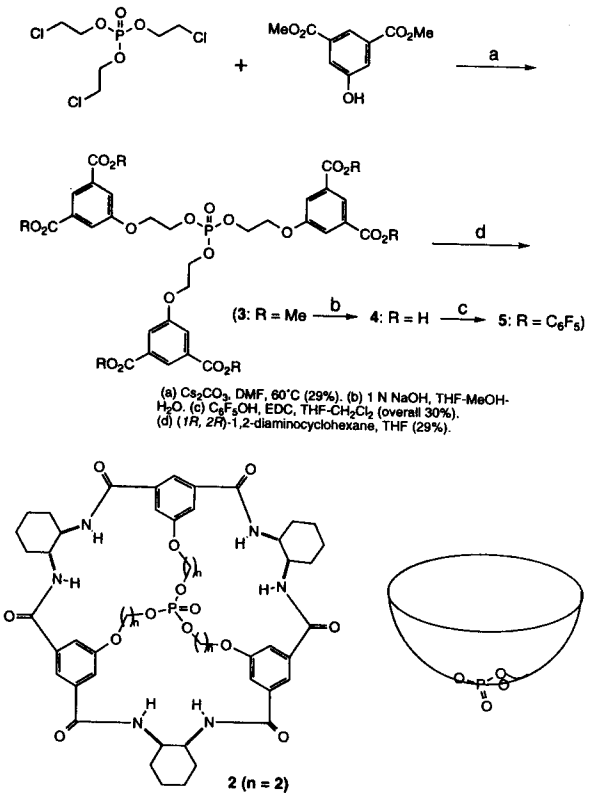
Construction of host molecules possessing a rigidly defined cavity with a concave functionality is of current interest.[1,2] Incorporation of an inwardly pointing functionality into the cavity of a bowl-shaped receptor[3] is reminiscent of the active site of enzymes. If a functional group is embedded in an appropriately sized molecular bowl with a rigid framework, the cavity will function as a reaction site or binding site with unique properties.

Previous C_3 symmetric receptor (**1**) synthesized in our group has a hydrophobic binding cavity with a preference for binding lipophilic residues.[4] We expected that introduction of a hydrogen-bonding functionality within the binding cavity would alter binding selectivity to hydrogen-bonding guests.[5]



1

In order to introduce a concave functionality into the cavity, we designed C_3 symmetric receptor (**2**) with a phosphate functionality at the bottom of the bowl (Scheme 1). CPK model of the designed receptor indicates that P=O of the phosphate is directed either inside the cavity or outside the cavity. Composed of a binding cavity with a hydrogen-bonding functionality, and hydrogen bond donor and acceptor functionalities on the periphery of the surrounding wall of the bowl-shaped host, **2** is expected to show enantio- and residue-selectivities in the binding of amino acids and small peptides.



Scheme 1. A Bowl-Shaped, C_3 Symmetric Receptor with a Phosphate Functionality at the Cavity Bottom.
(1)

The synthesis of the receptor **2** starts from the trialkylation of dimethyl 5-hydroxyisophthalate with tris(chloroethyl) phosphate as shown in Scheme 1. Ester hydrolysis and subsequent EDC coupling with pentafluorophenol furnished the cyclization precursor **5**. The final step is an intermolecular macrolactamization between a hexakis(pentafluorophenyl)ester **5** and (1*R*,2*R*)-1,2-diaminocyclohexane.[6] A solution of the active ester **5** in THF was added *via* syringe pumps over 15 h to a solution of chiral 1,2-diamine in THF (final concentration = 0.35 mM). Purification by flash chromatography furnished the macrotricycle **2** in 29% yield as a white solid.

The best evidence for the successful macrocyclization was provided by several informative differences between the ^1H NMR spectrum of **2** and that of its acyclic precursor **5**. The 500 MHz ^1H NMR in DMSO-d_6 displayed a simple spectrum as would be expected for the symmetrical structure. Three different aromatic proton peaks, two different methine proton signals in a cyclohexane part, two different amide proton signals of the ^1H NMR spectrum, and two different carbonyl carbon signals of the ^{13}C NMR spectrum presumably result from the partial asymmetric structure of overall C_3 symmetric receptor (see the Experimental section). Furthermore, mass spectrum showed an M+1 signal at m/z 958.

It is expected from the CPK models that the 3-dimensional structure of the receptor **2** is similar to that of the previously synthesized C_3 receptor **1**.[4] However, it has more rotatable bonds between meta-substituted aromatics of the cavity wall and the phosphorus atom at the cavity bottom. Therefore, **2** should be conformationally more flexible than **1**. Viewed