Table I. Absorption Spectral Data[a] and Isomerization Quantum Yields[b]

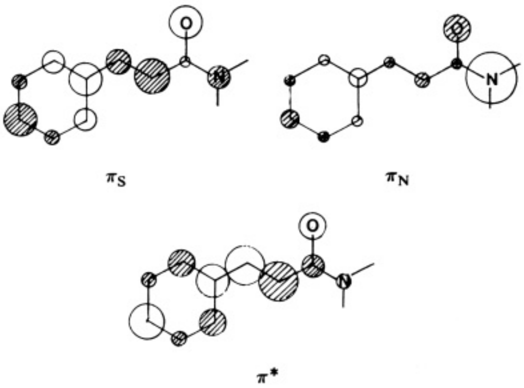
amide	X	R_1	R_2	λ_{max}	$10^{-4}\epsilon$	Φ_i
1a	H	H	H	273	1.87	0.25
1b	OCH_3	H	H	290		0.51
1c	CF_3	H	H	268	2.80	0.07
2a	H	CH_3	H	272	3.43	0.03
3a	H	CH_3	CH_3	277	2.02	0.01
3b	OCH_3	CH_3	CH_3	292	2.41	0.26
3c	CF_3	CH_3	CH_3	270	3.40	0.01

[a] Absorption spectrum in dichloromethane solution. [b] Data for 313-nm irradiation of 0.01 M amide in dichloromethane solution.

Table II. Frontier Orbital Energies (hartrees)

amide	n_0	π_N	π_S	π^*
1a	−0.3183	−0.2976	−0.2531	0.2014
2a	−0.3177	−0.2816	−0.2531	0.2013
3a	−0.3144	−0.2683	−0.2510	0.2017

Chart I. Frontier Molecular Orbitals



using protonation as a simple model for BF_3 complexation show that the π_N energy (but not π_S or π^*) is drastically lowered by protonation of the carbonyl oxygen. This should result in a reactive lowest π_S,π^* singlet for all of the amide–BF_3 complexes.

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A New Class of Chelating Agents

L. Marshall, K. Parris, and J. Rebek, Jr.*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

S. V. Luis and M. I. Burguete

Department of Chemistry, University of Valencia
Castellon de la Plana, Spain

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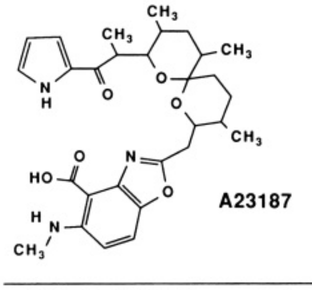
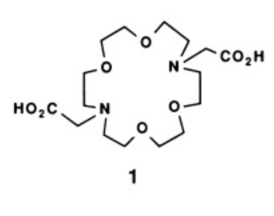
Classical chelating agents bearing carboxylate groups such as EDTA, crown ethers[1] **1**, and ionophores[2] such as A23187 share a common structural feature: only the anti lone pairs of the carboxylate achieve contact with the metal ions in the complex (eq 1). This is a constraint imposed by their molecular shapes.



A23187



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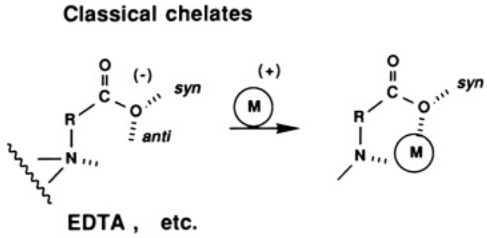
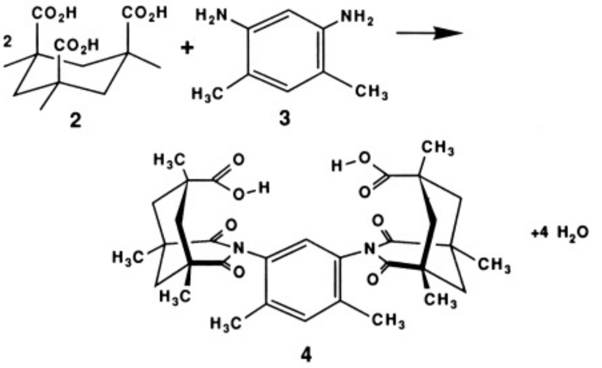


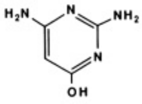
(1)

Stereoelectronic considerations,[3] however, indicate that the syn lone pairs are more basic, and this is supported by calculations,[4] structures of simple metal carboxylates in the solid state,[5] and the orientation of carboxylates at enzyme active sites.[3] Here we present structures in which the syn lone pairs are available for binding and report on their behavior as chelating agents.

The new structures are rapidly and efficiently assembled by condensation of Kemp's[6] triacid **2** with appropriate aromatic diamines such as *m*-xylidine diamine **3** (eq 2).[7] The resulting diacid **4** can be obtained by merely heating the two components in the absence of solvent. Other diamines, **5** → **8** were also converted to the corresponding diacids by this procedure.[8] When substituents ortho to the amines are present, as in **3** or **8b**[9] rotations about the C_{aryl}–N_{imide} bonds become hindered in the condensation products, and the carboxyl groups are constrained to the conformation in which the OH bonds converge.[10] This may be seen in the crystal structure of the diacid derived from **8b** (shown below in Figure 1).[11] Even without these restraining elements, intra-



(2)



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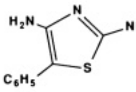

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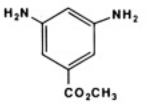

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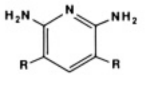

8a R=H
8b $R=CH_2C_6H_5$

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(8) All new compounds were characterized by a full complement of high resolution spectra. Compound **4** showed decomposition at >400 °C; other diacids derived from **5**; mp 225; from **6**, mp 199–202; from **7**, mp 270 dec; from **8a**, decomposition at >330 °C; from **8b**, mp 328–329. These structures are within the scope of U.S. Patent no. 4 698 425.

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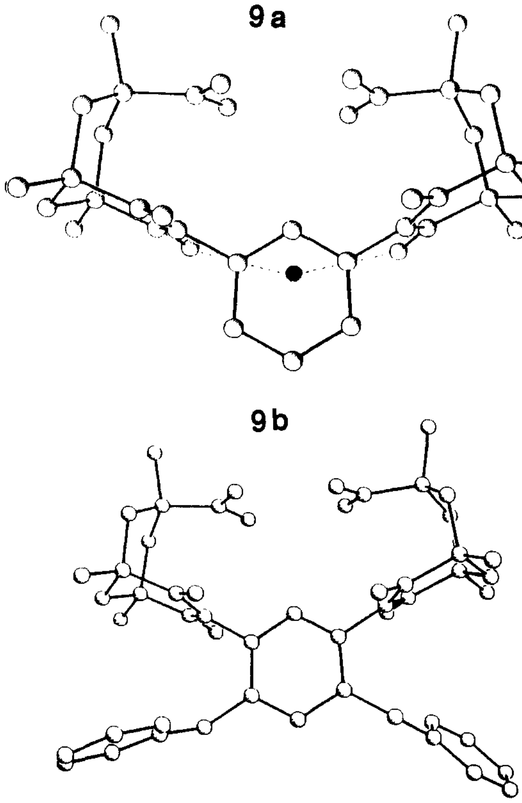

Figure 1. Crystal structures of dicarboxylic acids derived from **8a** and **8b**. In **9a**, a water molecule (●) is hydrogen bonded to two imide carbonyls and helps maintain the convergent conformation. All hydrogens have been omitted.

molecular hydrogen bonding can enforce the convergent conformation as evident in **9a** (the diacid derived from **8a**).

Several lines of evidence bear on the affinity of the new chelating agents for alkaline earth ions. First, the Δ pK_a observed[12] for the benzene derivative **4** (pK_{a1} = pK_{a2} = 11.1) suggests that dianions of the new structures provide an exquisite microenvironment for divalent ions. The diacid **9a** was sufficiently soluble in water to permit its evaluation as chelate under homogeneous conditions. With use of Ca^{2+} selective electrodes or pH titrations $K_a = 2.1 \times 10^5$ M^{-1} was measured for the diacid derivative **9a** with Ca^{2+}, assuming a 1:1 stoichiometry. This value might be compared to imidodiacetic acid,[13] for which $K_a = 7 \times 10^3$ M^{-1}.

The high lipophilicity of these systems permitted extraction of Ca^{2+} or Mg^{2+} from aqueous phases. For example, 0.1 M solutions of **4** in $CHCl_3$ were used to extract a solution of Ca^{2+} (59 ppm) and Mg^{2+} (24 ppm); >99% of the Ca^{2+} and 73% of the Mg^{2+} were removed from the aqueous phase. Parallel experiments with **9b** resulted in 97% removal of Ca^{2+} and 94% removal of Mg^{2+}.

Transport experiments using $CHCl_3$ between two aqueous solutions in a U-tube were also performed (Figure 2). The new carriers were comparable to A-23187 in their ability to transport Ca^{2+} across these model liquid membranes from a tris-buffered phase (pH = 9) to an acidic phase (pH = 1).

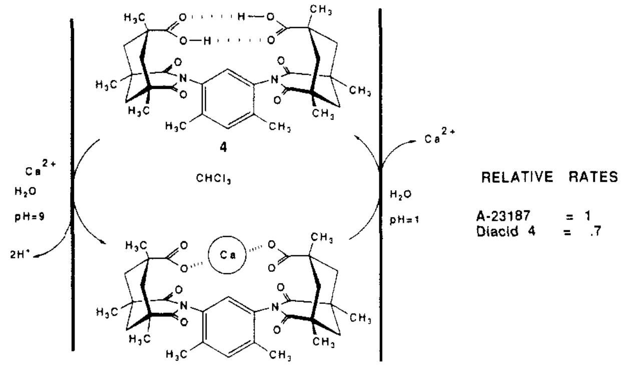

Figure 2.

Finally, an ion exchange resin was prepared and tested. The dibenzyl pyridine derivative **9b** was adsorbed on unfunctionalized 4% cross-linked polystyrene by mere rotary evaporation of its $CHCl_3$ solutions in which the resin beads were suspended. About 0.4 mmol **9b** per gram could be attached in this fashion. The resin was capable of extracting calcium and magnesium ions from brine solutions. At pH 12, with 1 equiv of Ca^{2+} in 0.1 M brine, about 20% of the sites bind Ca^{2+}, suggesting that stoichiometries other than 1:1 may be involved. Under conditions of 10-fold excess resin, the Ca^{2+} concentration in brine could be reduced from 2 ppm to <0.1 ppm. In these experiments, the polymer could be freed from metal ions by acid backwash.

In summary, a surprisingly effective, new class of chelating agents has been discovered. Their unique shapes enforce a trans relationship of the ligands in contact with the metal centers. It is likely that the catalytic behavior of metal ions bound by these new chelates will differ from ions in more conventional settings. We are exploring these possibilities and will report on them in due course.

Acknowledgment. This research was financed by Year Laboratories, Inc. The National Institutes of Health (GM 63239) supported the X-ray diffractometer used in these studies. We thank Professor Wm. Gordon for advice.

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Oxygenation of Hexafluorobenzene by Superoxide Ion

Hiroshi Sugimoto, Shigenobu Matsumoto, and
Donald T. Sawyer*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Jeffrey R. Kanofsky

Veterans Administration
Edward Hines, Jr., Hospital
Hines, Illinois 60141

A. Kasem Chowdhury and Charles L. Wilkins

Department of Chemistry, University of California
Riverside, California 92521

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The propensity of superoxide ion ($O_2^{\bullet -}$) in aprotic solvents to attack aliphatic and olefinic halocarbons via nucleophilic substitution is well documented,[1,2] and a recent report[3] establishes that this chemistry includes perchloroaromatic molecules. However, to date the C–F bond of fluorocarbons has been inert to $O_2^{\bullet -}$ (e.g., only the chlorine atoms of F_3CCCl_3 are displaced).[4] Here we report that perfluoroaromatic molecules [hexafluorobenzene

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