

- spectra of authentic samples of the products taken in sealed tubes at 120 °C.
- (10) For an application of the qualitative rules for CIDNP to the decomposition of a closely related peroxide, see R. A. Cooper, R. G. Lawler, and H. R. Ward, *J. Am. Chem. Soc.*, **94**, 552 (1972).
 - (11) The carboxyl inversion product (**4b**) is formed in 18% yield but does not exhibit CIDNP in either the ¹H or ¹³C NMR. This supports a nonradical mechanism for formation of this product. Furthermore, **4b** is stable under the reaction conditions and is thus not a precursor of **3b** or **5-7**. The relative yields of **3b** and **5-7** are also insensitive to the concentration of **1b** (0.045-0.5 M) and to the addition of excess *m*-chlorobenzoic acid (saturated in ODCB at 0.2 M). This makes it unlikely that either induced decomposition or acid promoted ionization of **1b** contribute significantly to the reaction under these conditions.
 - (12) (a) J. W. Wilt in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, p 333; (b) E. J. Hamilton and H. Fischer, *Helv. Chim. Acta*, **56**, 795 (1973); (c) B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 1224 (1976).
 - (13) This is also supported by our inability to observe the rearranged chloroalkane, *tert*-amyl chloride, in either the CIDNP spectrum or the final product mixture after decomposition of **1b** in HCA.
 - (14) G. M. Fraser and H. M. R. Hoffman, *Chem. Commun.*, 561 (1967).
 - (15) The predominance of the less substituted olefin, **5**, suggests that the ion pairs formed from the peroxide resemble those formed in the gas phase: W. J. Marinelli and T. H. Morton, *J. Am. Chem. Soc.*, **100**, 3536 (1978); J. Bullivant, J. S. Shapiro, and E. S. Swinbourne, *ibid.*, **91**, 7703 (1969). The intermediacy of *tert*-butylcarbene, formed by hydrogen abstraction from the neopentyl radical, would be expected to yield a much higher proportion of dimethylcyclopropane than observed: W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971, p 238.
 - (16) This process has much in common with the "harpooning" mechanism for atom recombination and other well-known phenomena involving crossing of the ionic and covalent potential energy surfaces: R. K. Janev, *Adv. At. Mol. Phys.*, **12**, 1 (1976). We thank Dr. J. Bargon for suggesting this comparison.
 - (17) K. G. Taylor and M. Kaelin, Abstract of Papers, the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 20-Sept 3, 1976; P. B. Shevlin and H. J. Hansen, *J. Org. Chem.*, **42**, 3011 (1977).

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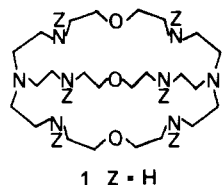
Molecular Recognition. Anion Cryptates of a Macrobicyclic Receptor Molecule for Linear Triatomic Species

Sir:

Macropolycyclic molecules provide a particularly attractive entry into the organization of space required by the design of *nonbiological molecular receptors* endowed with high recognition toward a substrate of defined geometric and electronic properties.¹

Spheroidal cavities lined with donor binding sites display spherical recognition; they form highly stable and selective inclusion complexes with spherical cations, the alkaline and alkaline-earth *cation cryptates* of macrobicyclic and macrotricyclic ligands.¹⁻³ Inversion of the properties of the nitrogen binding sites of spherical macrotricycles³ by protonation leads to highly stable and selective *anion cryptates* of the spherical halide anions.⁴⁻⁶

We now report the properties of a macrobicyclic receptor molecule **1** designed for the *recognition of linear triatomic*



species XYZ. The results obtained add a further step to an emerging new field of coordination chemistry: anion complexes or organic ligands.⁴⁻⁹

The synthesis of the bis-tren macrobicyclic **1** has been described earlier; it forms binuclear cryptates by inclusion of two

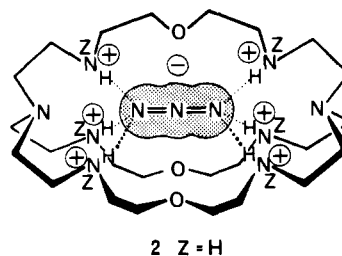
transition metal cations, each held by a tren subunit at the poles of the ellipsoidal cavity.¹⁰ Protonation of **1** in aqueous solution shows the successive fixation of six protons with the following pK's: 9.3, 9.0, 7.9, 7.4, 6.3, and 5.7 ± 0.1 (at 25 °C). The remaining two nitrogens are much more difficult to protonate (pK < 3.0); tren itself forms a triprotonated species N(CH₂CH₂NH₃⁺)₃.^{11,12} Similarly, in the hexaprotonated bis-tren molecule (**1-H₆⁶⁺**), protonation is expected to occur at the six secondary nitrogen sites in the bridges. Highly crystalline hexasalts (**1-H₆⁶⁺**)₆X⁻ (X⁻ = Cl⁻, ClO₄⁻) are obtained from methanol-water (M/W) solutions of **1** containing 6 equiv of acid.

(**1-H₆⁶⁺**) provides an ellipsoidal cavity with inverted binding sites as compared to **1** itself: three positively charged ammonium groups are located around the molecular axis at each pole of the cavity, providing sites for binding of electron-rich substrates of compatible size via ionic hydrogen bonds.

Crystalline solids are obtained from M/W solutions of the hexaperchlorate or hexanitrate of **1** containing 1 equiv of sodium azide. Analytical data indicate that they are monoazide species (**1-H₆⁶⁺**)N₃⁻·5X⁻ (X⁻ = ClO₄⁻, NO₃⁻). The infrared spectrum of the perchlorate species (in nitromethane) displays a strong band at 2085 ± 5 cm⁻¹ for the asymmetric stretching vibration of N₃⁻.¹³ It is markedly shifted from the corresponding band of unbound N₃⁻ (2052 ± 5 cm⁻¹) when excess NaN₃ is added, in the same direction as observed when N₃⁻ is bound to carbonic anhydrase (2094 cm⁻¹).¹⁴ Similarly in the presence of excess (>1 equiv) NaN₃, the Raman spectrum (aqueous solution at pH 5) shows a well-resolved doublet for the symmetrical stretching mode at 1363 ± 1 and 1343 ± 1 cm⁻¹ for complexed and free N₃⁻, respectively.¹⁵

The 250-MHz ¹H NMR spectrum of (**1-H₆⁶⁺**)₆ClO₄⁻ (in CD₃NO₂ at 24 °C) shows broadened resonances at 3.05, 3.55, and 4.00 ppm (from Me₄Si) with relative intensities of 1, 2, and 1, respectively due to CH₂N, CH₂N⁺, and CH₂O protons, confirming the hexaprotonated nature of the ligand. Addition of 1 equiv of NaN₃ gives a spectrum containing four signals of same areas at 3.0, 3.45, 3.53, and 4.03 ppm; when only 0.5 equiv of NaN₃ is added a superposition of these two spectra is obtained with additional line broadening. The azide-containing species retains the threefold symmetry of the ligand molecule: the three bridges of the macrobicyclic are equivalent; this cannot be due to exchange averaging since the **1-H₆⁶⁺** and the azide species are in slow exchange on the NMR time scale at 24 °C, as shown by the spectrum obtained at 0.5 equiv of NaN₃.

From the analytical and spectral results one may infer that the azide species is a complex of 1:1 stoichiometry and of threefold symmetry (on the NMR time scale). This agrees with its formulation as the *anion cryptate* [N₃⁻·(**1-H₆⁶⁺**)] resulting from inclusion of the azide anion into the ellipsoidal intramolecular cavity of the hexaprotonated ligand. The electronic and geometric features of the azide anion are complementary to those of the receptor molecule (**1-H₆⁶⁺**): N₃⁻ has negative charge and high electron density with cylindrical distribution at both ends;¹⁶ its size is such that it may tightly fit into the cavity and form hydrogen bonds simultaneously to the secondary ammonium sites at both poles.¹⁷ An azide cryptate structure like **2** would agree with these considerations:



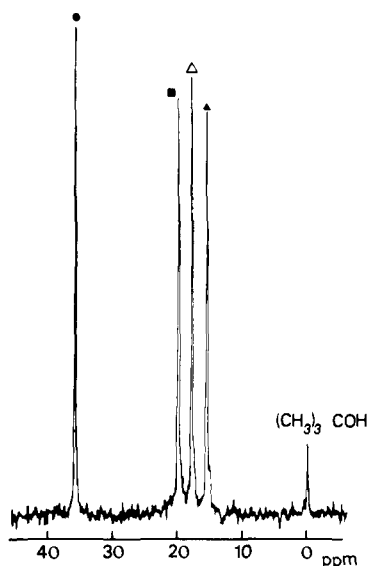


Figure 1. ^{13}C FT NMR spectrum (25 MHz) of the hexaprotonated ligand (1-H_6^{6+}) 6ClO_4^- at pH 5 in aqueous solution at 35°C ; chemical shifts are 15.8, 18.1, 20.2, and 36.5 ppm.

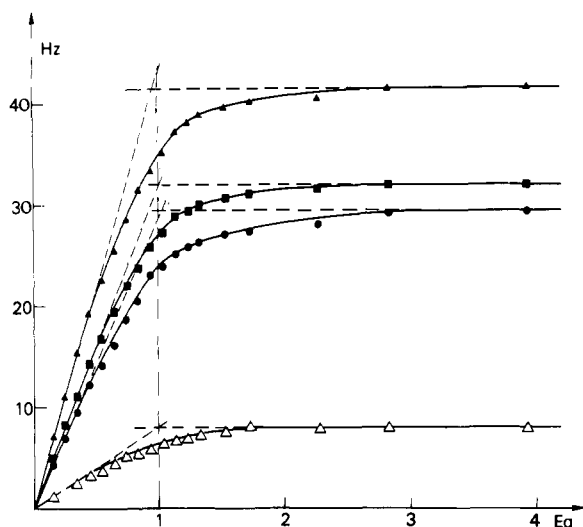


Figure 2. Progressive shifts of the ^{13}C resonances upon addition of increasing amounts (up to ~ 4 equiv) of sodium azide to the solution of Figure 1 maintained at pH 5; the limiting chemical shifts of the azide cryptate **2** are 17.5, 18.4, 21.5, and 37.7 ppm (with respect to internal *tert*-butyl alcohol).

a linear azide anion bound inside the cavity by two pyramidal arrays of three $^+\text{N}\cdots\text{H}\cdots\text{N}^-$ hydrogen bonds which hold the two terminal nitrogen sites. In the crystal structure of $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3^+)_3 \cdot 3\text{Cl}^-$, one of the chloride anions is similarly hydrogen bonded to the ammonium sites in an arrangement resembling that of each tren subunit in **2**.¹²

As in the case of spherical cryptates,¹⁻⁴ such three-dimensional binding with complete inclusion of the substrate should yield stable and selective anion cryptates. Preliminary determinations of stability constants for the binding of various anions with (1-H_6^{6+}) 6ClO_4^- have been performed using halide anion specific electrodes, shifts of the ^{13}C NMR resonances on anion addition, as well as competition experiments between different anions. The following results have been obtained.¹⁸

(1) The ^{13}C NMR spectrum of (1-H_6^{6+}) 6ClO_4^- in aqueous solution adjusted to pH 5 with perchloric acid is shown in Figure 1; addition of increasing quantities of NaN_3 shifts all four carbon resonances until a limiting shift is reached (Figure 2). Analysis of these data confirms the formation of a complex of 1:1 stoichiometry and yields a stability constant $\log K_s = 3.5 \pm 0.2$ at 35°C and 4.6 ± 0.3 at 25°C .¹⁸ NCO^- and FHF^-

also form complexes. (2) Addition of NaN_3 to a solution of $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3^+)_3 \cdot 3\text{ClO}_4^-$ in water does not give any evidence for formation of a stable complex. (3) The halide ions show $\log K_s (\pm 0.2) = 2.0$ for Br^- and < 1.0 for Cl^- and I^- in aqueous solution and 1.9 for Cl^- , 3.4 for Br^- , and 1.8 for I^- in 9/1 M/W; NO_2^- , NO_3^- , and carboxylates also form complexes with $\log K_s \sim 3.0$ for NO_3^- and 2.6 for HCO_2^- . (4) The selectivity sequence $\text{ClO}_4^- < \text{Cl}^- < \text{I}^- < \text{CH}_3\text{CO}_2^- < \text{Br}^- < \text{HCO}_2^- < \text{NO}_3^- < \text{NO}_2^- \ll \text{N}_3^-$ is neither the lyotropic series or the sequence of hydration energies, nor the anion binding sequence displayed by carbonic anhydrase.¹⁹ It indicates the operation of topological discrimination due to the receptor properties of 1-H_6^{6+} , i.e., to the shape and size of the intramolecular cavity as well as to the arrangement of the binding sites. (5) The ellipsoidal cryptand 1-H_6^{6+} is thus a *molecular receptor for linear triatomic species* of size compatible with the size of the molecular cavity.²⁰

The high stability and selectivity of the N_3^- complex with respect to anions of different shape (nonlinear, triangular, tetrahedral) are comparable with those of the spherical anion cryptates⁴ but higher than those of bovine or human carbonic anhydrase.¹⁹ These remarkable properties may again be ascribed to the cryptate nature of these complexes, i.e., to the inclusion into a closed and rigid cavity.^{1,4}

Cryptand 1-H_6^{6+} , its substituted derivatives ($\text{Z} \neq \text{H}$ in **1**), as well as ligands containing smaller or larger cavities provide an entry into a number of exciting areas of general interest: (i) receptor design for selective anion binding;⁹ (ii) structural effects on intermolecular interactions; (iii) stabilization of unstable species like F_2H^- , Cl_2H^- , F_3^- , Cl_2F^- , etc.; (iv) development of selective anion transport systems.²¹

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References and Notes

- (1) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973); *Pure Appl. Chem.*, **49**, 857 (1977); *Acc. Chem. Res.*, **11**, 49 (1978).
- (2) J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975).
- (3) E. Graf and J. M. Lehn, *J. Am. Chem. Soc.*, **97**, 5022 (1975).
- (4) E. Graf and J. M. Lehn, *J. Am. Chem. Soc.*, **98**, 6403 (1976).
- (5) B. Metz, J. M. Rosalky, and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 533 (1976).
- (6) Quaternary ammonium derivatives of spherical macrotricycles also form anion cryptates; see F. P. Schmidtchen, *Angew. Chem.*, **89**, 751 (1977).
- (7) C. H. Park and H. E. Simmons, *J. Am. Chem. Soc.*, **90**, 2431 (1968); R. A. Bell, G. G. Christoph, F. R. Fronzeck, and R. E. Marsh, *Science*, **190**, 151 (1975).
- (8) Cyclodextrins form weak inclusion complexes with some small anions: R. P. Rohrbach, L. J. Rodriguez, E. M. Eyring, and J. F. Wojcik, *J. Phys. Chem.*, **81**, 944 (1977).
- (9) Anion complexation by guanidinium ligands has been demonstrated recently: B. Dietrich, T. M. Fyles, J. M. Lehn, and L. G. Pease, unpublished results.
- (10) J. M. Lehn, S. H. Pine, E. Watanabe, and A. K. Willard, *J. Am. Chem. Soc.*, **99**, 6766 (1977).
- (11) The pK' s are 10.14, 9.43, and 8.41: S. G. Zipp, A. P. Zipp, and S. K. Madan, *Coord. Chem. Rev.*, **14**, 29 (1974); P. Paoletti and M. Ciampolini, *Rec. Sci. IIA*, **33**, 399 (1963).
- (12) The crystal structure of $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3^+)_3 \cdot 3\text{Cl}^-$ has been determined: S. E. Rasmussen and R. Grønbaek, *Acta Chem. Scand.*, **17**, 832 (1963).
- (13) D. A. Dows, E. Whittle, and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1475 (1955).
- (14) M. E. Riepe and J. H. Wang, *J. Biol. Chem.*, **243**, 2779 (1968).
- (15) We thank Dr. S. Abbott for measuring the spectra and Professor M. Leroy for the use of the Laser Raman spectrometer.
- (16) E. D. Stevens, J. Rys, and P. Coppens, *J. Am. Chem. Soc.*, **99**, 265 (1977).
- (17) The $^+\text{N}\cdots\text{N}$ distance in a $^+\text{N}\cdots\text{H}\cdots\text{N}_3^+\cdots\text{H}\cdots\text{N}^+$ arrangement with tetrahedral angles between the $^+\text{N}\cdots\text{H}$ and N_3^- axes is ~ 4.5 Å, taking an end-to-end distance of 2.32 Å for N_3^- and an $^+\text{N}\cdots\text{H}\cdots\text{N}_3^-$ hydrogen bond length of 2.94 Å as in NH_4N_3 . See U. Müller, *Struct. Bonding (Berlin)*, **14**, 141 (1973); L. K. Frevel, *Z. Kristallogr., Kristallgeom., Kristallphys.*, **94**, 197 (1936).
- (18) Since ClO_4^- also appears to complex weakly ($K_s \leq 20$), all measurements have at present been performed with respect to the six ClO_4^- anions of the ligand. Thus the present K_s values are apparent stability constants, lower than the real ones. At pH 5 the ligand **1** is mainly in the hexaprotonated form, whereas N_3^- is substantially protonated since the pK of HN_3 is 4.6. Corrections taking these pK effects into account were performed in all cases where they apply.

- (19) Y. Pocker and J. T. Stone, *Biochemistry*, **7**, 2396 (1968).
 (20) Taking into account bond lengths and van der Waals radii, one may expect that the X, Y, and Z atoms of the linear XYZ species should belong to the first row. NCS⁻ appears to be only weakly complexed by 1-H₆⁹⁺. Of course complex stability also depends on solvation effects.
 (21) Complexation of CO₂ and N₂O (whose size and shape are close to those of N₃⁻) and activation of CO₂ for hydration, reduction, and carboxylation represent another very interesting potential development. Of course, since these species are electrically neutral, the stability constants would probably be much weaker and ligand modification may be required.
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Substituent Effects on the Decomposition of 1,2-Dioxetanes

Sir:

1,2-Dioxetanes are of considerable interest as surprisingly stable strained peroxides, but especially because their thermolysis is accompanied by the emission of light. The mechanism leading to chemiluminescence is currently the subject of both theoretical¹ and experimental investigation.² We now report the observation of a substituent effect on dioxetane decomposition, which provides some insight into this mechanism.

An early suggestion by McCapra³ viewed the cleavage of dioxetanes as a concerted [$2_s + 2_s$] retrocycloaddition. Orbital symmetry conservation⁴ requires that one of the carbonyl scission products be formed in an electronically excited state. Subsequently, on the basis of thermochemical calculations, Richardson⁵ proposed an alternative mechanism involving rate-limiting O-O bond cleavage to give a biradical, which then rapidly yields carbonyl products. Such a mechanism is expected to show little if any response to electronic effects in the dioxetane. In contrast, the concerted mechanism could be sensitive to substitution, particularly if the excited state formed involved significant transfer of charge. Very recently cleavage of 1,2-dioxetanes by an intramolecular electron-transfer mechanism has been proposed,⁶ in which substituent effects should be manifested. Chemiexcitation by intermolecular electron transfer is established in electroluminescence⁷ and in a number of chemiluminescent peroxide reactions.⁸ The lack of a straightforward electronic effect on dioxetane decomposition⁹ has been taken as evidence, albeit only negative, for a biradical mechanism. By suitable substitution in the series of 1,6-diaryl-2,5,7,8-tetraoxabicyclo[4.2.0]octanes **2** we have obtained evidence suggesting that transfer of charge is important in the destabilization of dioxetanes, and in the efficient generation of singlet excited states from their decomposition.

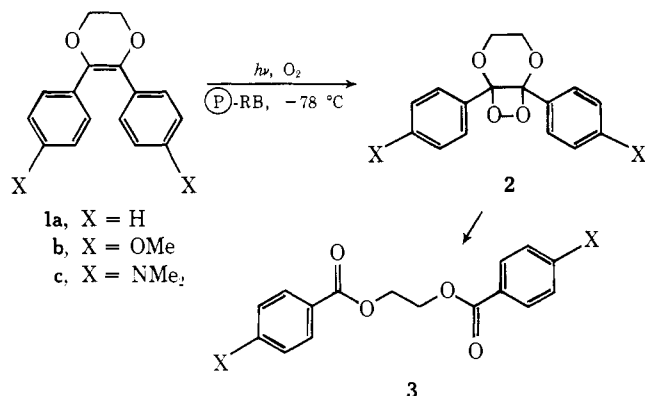


Table I. Activation Parameters and Rates of Decomposition for 1,2-Dioxetanes **2a-c**

Compd	E_a , kcal/mol	Log A	ΔH^\ddagger , kcal/mol ^a	ΔS^\ddagger , gibbs/mol ^a	Rel rate ^a
2a	24.8	12.39	24.2	-1.8	1.00 ^b
2b	24.0	12.38	23.5	-1.9	3.51
2c	19.7 ^c	11.23	19.1	-7.2	382

^a Calculated for 298.2 K. Errors ± 0.15 kcal/mol in ΔH^\ddagger and ± 0.5 gibbs/mol in ΔS^\ddagger determined by the method of Wiberg.¹⁶ ^b Corresponding to a rate constant of $1.62 \times 10^{-6} \text{ s}^{-1}$. ^c 19.7 ± 0.5 kcal/mol by the temperature drop method.¹⁷

Table II. Chemiluminescence Efficiencies of 1,2-Dioxetanes **2a-c**

Compd	$^1\phi_E$ ^a	$^3\phi_E$ ^b	$^3\phi_E/{}^1\phi_E$
2a ^c	1.9×10^{-4}	6.8×10^{-2}	350
2b ^d	2.4×10^{-4}	5.0×10^{-2}	210
2c ^e	0.22	—	<3.5 ^f

^a Chemiluminescence efficiency for the formation of singlet excited **3**. ^b Chemiluminescence efficiency for the formation of triplet excited **3**. ^c At 95.2 °C in *o*-xylene. ^d At 94.9 °C in *o*-xylene. ^e At 25.0 °C in toluene. ^f Based on a maximum value of $^3\phi_E = 1 - ^1\phi_E$.

The dioxetanes **2a-c** were prepared by low temperature photooxygenation of the corresponding olefins **1a-c**¹⁰ using polymer-bound Rose Bengal (P-RB)¹² and methods previously described.^{13,14} Yields were typically $\sim 80\%$. The dioxetanes **2a-c** were insufficiently stable for combustion analysis, but all gave a centrosymmetric AA'BB' multiplet in the ¹H NMR spectrum, as has been observed for 2,5,7,8-tetraoxabicyclo[4.2.0]octane itself.¹⁵ The ¹³C NMR spectrum of **2a** showed quaternary carbons at 109 ppm corresponding to those in the dioxetane ring. Thermolysis of **2a-c** in *o*-xylene or toluene afforded quantitatively the expected diesters **3a-c**, which were fully characterized. Rates of decomposition of **2a-c** were studied by decay of chemiluminescence and were identical with those derived by ¹H NMR.

The rate constants obtained from chemiluminescence measurements were reproducible (variation $< \pm 3\%$) and gave excellent Arrhenius plots. The relevant activation parameters and rates are summarized in Table I. Controls showed that the marked differences observed for **2c** were not due to a change of solvent from *o*-xylene to toluene. The rates of decomposition of **2c** were further independent of concentration and presence of radical inhibitor or triplet quencher. Normal decomposition rates for trimethyl-1,2-dioxetane in our sample of toluene and the identical activation energy for **2c** obtained by the temperature drop method¹⁷ in this solvent indicate that the enhanced rates observed for **2c** (Table I) are not the results of impurity catalysis. Instead, a real substituent effect is involved.

The substituent effect on rates extends also to chemiluminescence efficiencies. Esters **3a** and **3b** are not detectably fluorescent, so excited singlet and triplet yields from **2a** and **2b** were determined from Stern-Volmer plots using 9,10-diphenylanthracene (DPA) and 9,10-dibromoanthracene (DBA) as energy acceptors.^{9,17} Ester **3c** is fluorescent¹⁸ and the chemiluminescence of **2c** matches this fluorescence, allowing direct evaluation of the singlet chemiluminescence efficiency in this case. The results are presented in Table II.¹⁹ Not only is the total yield of excited states higher for **2c**, but the singlet yield is increased more than three orders of magnitude compared with **2a**.

Examination of Table I shows that, no matter what the choice of substituent constant, a linear Hammett plot is not possible using the observed activation parameters, nor can a satisfactory isokinetic relationship be obtained. These observations, taken together with the chemiluminescence efficiencies