H, m), 2.46 (1 H, d, J = 0.97 Hz), 3.02 (1 H, br s), 3.22 (3 H, s), 7.20 (1 H, d, J = 8.43 Hz), 7.29 (1 H, d, J = 9.28 Hz), 7.51 (1 H, s), 7.65 (1 H, s), 7.72 (2 H, m). ^{31}P NMR (D_2O, 85% H_3PO_4 std, ppm): 0.99 (1 P).

Anal. Calcd for $C_{22}H_{23}Na_2PO_5 \cdot 1.5H_2O$: C, 56.06; H, 5.56; P, 6.57. Found: C, 56.11; H, 5.49; P, 6.44.

Disodium 7-(4-Methoxyspiro[1,2-dioxetane-3,2′-tricyclo-[3.3.1.1^{3,7}]decan]-4-yl)-2-naphthalenyl Phosphate (2d). A solution of disodium 7-(methoxytricyclo[3.3.1.1^{3,7}]dec-2-ylidenemethyl)-2-naphthalenyl phosphate (which was converted to the monopyridinium salt by passing the disodium phosphate as an aqueous solution through a pyridinium sulfonate Amberlite 120 plus resin followed by lyophilization [53.1 mg, 0.111 mmol]) and 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP, 20 μL of a 2% solution in $CHCl_3$ by weight) in $CHCl_3$ (10 mL) was irradiated with a 250-W, high pressure sodium lamp at 10 °C while passing a stream of oxygen through the solution. A 5-mil piece of Kapton polyimide film (DuPont) placed between the lamp and the reaction mixture filtered out unwanted UV radiation. Analytical HPLC (UV detector at 230 nm) showed complete dioxetane formation upon irradiating 5 min. After evaporation of the chloroform at 0 °C, the residue was dissolved in ice water in the presence of 15 mg of Na_2CO_3 (0.14 mmol), passed through a 0.45-μm filter, and separated by preparative HPLC on a polystyrene column with an acetonitrile/0.1% Na_2CO_3 (w/v) gradient. The fractions were frozen and lyophilized at 0 °C, yielding 85.5 mg total weight of a white fluffy powder, consisting of approximately 49.0 mg of Na_2CO_3 and 36.5 mg of dioxetane (69% yield). TLC of the product exhibited blue chemiluminescence by thermal decomposition upon heating. Enzymatic cleavage of the phosphate induced decomposition with light emission at 550 nm in 0.05 M Na_2CO_3/1 mM $MgCl_2$ solutions at pH 9.5. ^{1}H NMR (D_2O, ppm): 0.681 (1 H, d), 0.890 (1 H, d), 1.25–1.67 (10 H, m), 2.025 (1 H, br s), 2.740 (1 H, br s), 2.971 (3 H, br s), 7.15 (1 H, very br s), 7.31 (1 H, d, J = 9.28 Hz), 7.525 (1 H, br s), 7.65 (2 H, d, J = 8.6 Hz), 7.99 (1 H, very br s). ^{31}P NMR (D_2O, 85% H_3PO_4 std, ppm): 1.229 (1 P).

Acknowledgment. We thank Dr. Fritz Berthold for use of the LB95T AutoClinilumat Luminometer and Dr. Kurt Loening for assistance with nomenclature.

Registry No. **2a**, 130199-37-0; **2b**, 130199-38-1; **2c**, 130199-39-2; **2d**, 124951-97-9; **3a**, 5111-34-2; **3b**, 63469-49-8; **3c**, 5111-65-9; **3d**, 66240-21-9; **4a**, 130199-29-0; **4b**, 128542-63-2; **4c**, 124955-91-5; **4d**, 128542-60-9; **4d′**, 128542-60-9; **5a**, 130219-47-5; **5b**, 130199-30-3; **5c**, 124991-65-7; **5d**, 128557-00-6; **6a**, 130199-31-4; **6b**, 130199-32-5; **6c**, 110371-06-7; **6d**, 130199-33-6; **7a**, 130199-34-7; **7b**, 130199-35-8; **7c**, 130199-36-9; **7d**, 124951-98-0; TPP, 917-23-7; 2-adamantanecarboxaldehyde, 39750-93-1; alkaline phosphatase, 9001-78-9; 2-amino-7-methoxynaphthalene, 92287-46-2; 1-cyanoadamantane, 23074-42-2.

Supplementary Material Available: IR, ^{1}H NMR, and ^{31}P NMR (where applicable) spectral data for dioxetane phosphates **2a–c** and their corresponding synthetic intermediates (6 pages). Ordering information is given on any current masthead page.

Protonation of N,N',N''-Triphenyl-1,3,5-triaminobenzenes: Stable σ-Complexes

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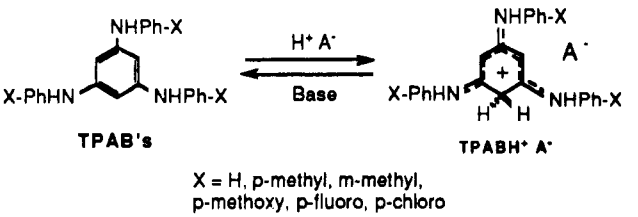
Cationic σ-complexes of aromatics are of considerable interest, most notably because of their role as intermediates in electrophilic aromatic substitution reactions.[1]

Scheme I. Protonation of TPAB's



X = H, p-methyl, m-methyl, p-methoxy, p-fluoro, p-chloro

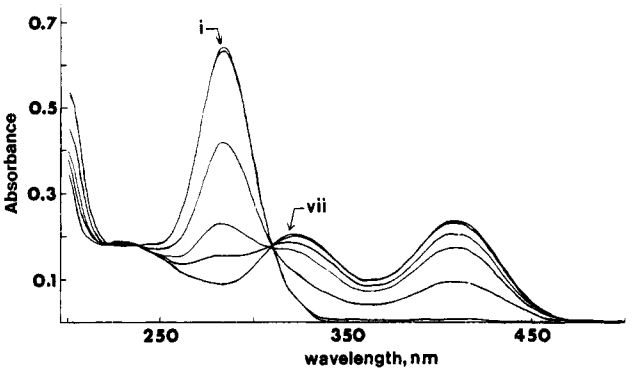


Figure 1. Spectrometric titration for nonsubstituted TPAB in 90% methanol/water at 25.0 °C, μ = 0.5 ($NaClO_4$), [TPAB] = 1.0×10^{-5} M. pH (−log [H^+]) values decrease from (i) to (vii) as follows: (i) 6.52, (ii) 4.35, (iii) 3.08, (iv) 2.38, (v) 1.76, (vi) 0.76, (vii) 0.26.

Generation of cationic σ-complexes usually takes place under severe chemical conditions and they are seldom stable enough to be isolated.[2] It has been known for some time that 1,3,5-triaminobenzene can be protonated at an aromatic carbon in solutions of intermediate pH, but instability precludes the isolation and detailed characterization of the σ-complex.[3,4] It was later shown that certain N-hexaalkylated 1,3,5-triaminobenzenes (HTAB's), the foremost of which is 1,3,5-tripyrrolidinobenzene, can form stable σ-complexes on protonation[5] and their behavior, structure, and reactions have been extensively explored.[6] Although studies of HTAB's have been fruitful, they are not very flexible with regards to introduction of functional groups that can influence the electronic structure of the molecules. It has been suggested that N-monosubstituted analogues of HTAB's will not exhibit formation of stable σ-complexes because they can easily deprotonate at nitrogen to form nonbenzenoid, tautomeric imine species.[7] However, we have recently discovered that N,N',N''-triphenyl-1,3,5-triaminobenzene[8] and its substituted analogues (TPAB's, Scheme I) undergo protonation at an aromatic ring carbon to form stable, isolable cationic σ-complexes and the pK_a's of their conjugate acids are sensitive to substituent effects.

UV–vis spectroscopy was used to investigate protonation equilibria of TPAB's in solutions of 0.5 M sodium perchlorate in 90% methanol/water.[9,10] Solutions of TPAB's

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(2) For a thorough review of the generation, characterization, and reactivity of arenium cations, see: Kopytug, V. A. *Top. in Curr. Chem.* **1984**, 122.

(3) Köhler, H.; Scheibe, A. Z. *Anorg. Allg. Chem.* **1956**, *285*, 221.

(4) Yamaoka, T.; Hosoya, H.; Nagakura, S. *Tetrahedron* **1968**, *24*, 6203.

(5) Effenberger, F.; Niess, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1067.

(6) For a recent review, see: Effenberger, F. *Acc. Chem. Res.* **1989**, *22*, 27.

(7) Effenberger, F.; Mack, K. E.; Nagel, K.; Niess, R. *Chem. Ber.* **1977**, *110*, 165.

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0022-3263/90/1955-6229$02.50/0

Table I. pK_a and UV-Visible Data for TPAB's[a]

substituent	pK_a[b]	TPAB, λ_{max} nm (log ϵ)	$TPABH^+$, λ_{max} nm (log ϵ)
p-methoxy	4.32	281 (4.7)	324 (4.3), 405 (4.3)
p-methyl	3.65	285 (4.7)	326 (4.2), 408 (4.3)
m-methyl	2.99	284 (4.8)	325 (4.2), 410 (4.3)
nonsubst	2.90	285 (4.8)	324 (4.3), 409 (4.4)
p-fluoro	2.64	281 (4.7)	321 (4.5), 406 (4.3)
p-chloro	1.14	289 (4.9)	325 (4.4),[c] 410 (4.3)[c]

[a] Values in 90% methanol/water, 25.0 °C, ionic strength = 0.50 ($NaClO_4$). [b] $K_a = [H^+][TPAB]/[TPABH^+]$, uncertainty of pK_a (±0.04). [c] Values of ϵ estimated from parameters obtained from $\epsilon = A_{TPABH}/(C_{TPABH} \times 1\ cm)$.

reversibly change from colorless to yellow and back on protonation/deprotonation. As protonation occurs, absorption bands of the neutral TPAB's at 285 ± 4 nm decrease and new bands at 325 ± 1 and 408 ± 3 nm appear as shown in Figure 1 for the nonsubstituted TPAB. Exact absorption maxima for the various TPAB's are given in Table I. Such bathochromic shifts on protonation of TPAB's are similar to those observed for HTAB's[11] and are consistent with protonation at a carbon of the central aromatic ring. For each TPAB, peak absorbances of the nonprotonated TPAB species (as shown in Figure 1) were plotted against pH and found to be consistent with a single protonation step in the pH range (ca. 1–7) investigated. Well-defined isosbestic points for each TPAB were observed between 310 and 320 nm, providing confirmation that ion, temperature, and dilution effects were minimal and indicating that only two species, TPAB and $TPABH^+$, are being observed. From pK_a values at 25 °C for the various TPAB's (Table I), it can be seen that electron-donating substituent groups favor protonation of the TPAB's while electron-withdrawing substituents make protonation more difficult. This trend suggested that a linear free energy relationship exists for the protonation of TPAB's. A plot of log $[K_{sub}/K_{nonsub}]$ for the TPAB's versus known σ values[12] results in a straight line with a correlation coefficient $R = 0.98$ as shown in Figure 2.

The values of σ and ρ for the protonation of TPAB's are consistent with the proposed reaction and offer some insight into the nature of the reaction. The σ values used are for the dissociation of substituted benzoic acids.[12] Although σ^+ values[12] might be expected to be appropriate since the organic species develops a positive charge on protonation, such values lead to a much poorer correlation ($R = 0.87$) for the parasubstituted TPAB's. This is consistent with protonation occuring on the central ring of the TPAB's since the developing charge cannot directly interact with substituents by delocalization through the outer rings using simple resonance structures. If protonation were occurring on the outer rings, σ^+ values would likely be appropriate.

The magnitude of ρ (−6.14) for protonation of TPAB's is more complex in interpretation. The value of ρ is large, especially for reaction in a highly polar protic solvent system such as methanol/water, and is consistent with the development of a full positive charge on the TPAB. However, the observations that σ rather than σ^+ values give a good correlation and that substitutents have little effect

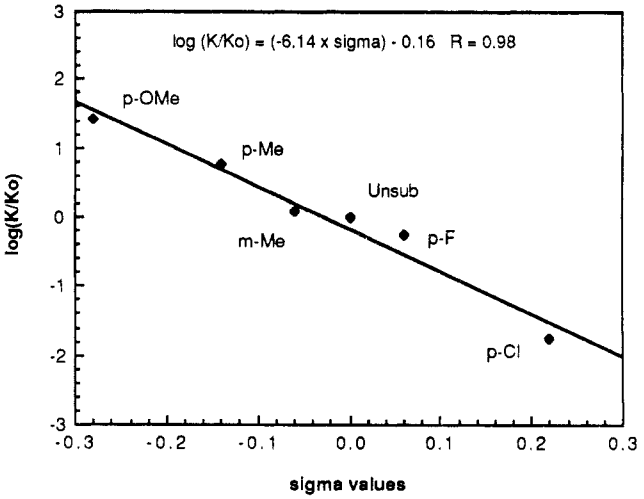

Figure 2. Hammett plot for the protonation/deprotonation equilibria of substituted TPAB's in 90% methanol/water (0.5 M $NaClO_4$); log $(K_{sub}/K_{nonsub}) = \sigma\rho$; $K = K_{sub}$, $K_0 = K_{nonsub}$.

on the comparative UV–vis spectral behavior of TPAB's before or after protonation (Table I) suggest that resonance overlap with the outer aromatic rings is small and is likely diminished further by twisting from steric interactions. These considerations suggest that the large observed ρ value is not explained adequately by simple additivity of substituent effects from the three anilino groups surrounding the central aromatic ring. It may be that TPAB systems represent a complex example of the poorly understood "positive bridge effect", exhibited in certain cases by enhanced transmission of electronic substituent effects through heteroatom-bridged diphenyl systems.[13] Duel parameter correlations[12] may lead to a better understanding of the inductive and resonance contributions of substituents to TPAB protonation equilibria.

Further confirmation that protonation is occuring at the central aromatic ring comes from initial NMR studies on the nonsubstituted TPAB. In $DCCl_3$ solution the inner ring protons (C–H) appear as a singlet at 6.34 ppm. Addition of a few drops of trifluoroacetic acid immediately causes the signal to split into two broadened singlets of two protons each at 4.90 (CH_2) and 5.67 ppm. This is similar to the behavior observed for the HTAB 1,3,5-tripyrrolidinobenzene on protonation with hydroiodic acid.[5] Broadening of the singlets in the protonated TPAB suggests that slow exchange is occuring.

The nonsubstituted TPAB was reacted with *p*-toluenesulfonic acid to give the $TPABH^+$ tosylate$^-$ **1** as a stable, highly colored, crystalline salt in order to show the stability of TPAB σ-complexes. Although non-deoxygenated solutions of **1** will darken within a few hours, the solid salt is stable indefinitely in air at room temperature. Salt **1** is soluble in polar organic solvents such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, and methanol but only sparingly soluble in chloroform, dichloromethane, and acetonitrile. Aside from the UV–vis and NMR spectral evidence for protonation of TPAB's occuring at a central ring carbon discussed above, the IR spectrum and elemental analysis of **1** are consistent with the proposed structure.

In summary, we have shown that TPAB's undergo reversible protonation at a carbon of the central aromatic ring to form stable and isolable cationic σ-complexes. pK_a values for substituted TPAB's exhibit a linear free energy

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(10) Rorabacher, D. B.; MacKellar, W. J.; Shu, F. R.; Bonavita, S. M. *Anal. Chem.* **1971**, *43*, 561.
(11) Knoche, W.; Schoeller, W. W.; Shomäcker, R.; Vogel, S. *J. Am Chem. Soc.* **1988**, *110*, 7484.
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relationship having parameters consistent with the postulated processes. Although details of the protonation reactions of TPAB's are not yet well understood, the present study provides a base for further exploration of the chemistry, structure, and physical properties of these interesting systems.

Experimental Section

TPAB's were synthesized according to literature procedures.[8] New TPAB's (*p*-methyl and *p*-fluoro) exhibited satisfactory elemental, ^{1}H NMR, and IR analyses. UV–vis spectra were recorded on a Hitachi 100-80 spectrometer equipped with a thermostated cell holder. pH measurements were made on a Corning 125 pH meter with a Metrohm 6.0216.0 combination electrode calibrated in aqueous solution using standard buffers (Fischer, Gram-Pac).

pH-Dependent UV–Visible Spectrometric Measurement. Solutions of TPAB's (ca. 1.0×10^{-5} M) were prepared by weight and sufficient $NaClO_4$ was added to attain an ionic strength of 0.50 (to minimize deviations due to ionic effects) in 90% methanol/water (100 mL of doubly distilled water to 1 L volume with distilled absolute methanol). After calibration, the pH electrode was allowed to equilibrate in 90% methanol/water for ca. 2 h prior to use. pH_{obs} values of the TPAB solutions were adjusted by using concentrated perchloric acid and/or tetraethylammonium hydroxide and UV–vis spectra were recorded at 25.0 ± 0.1 °C. pH_{obs} readings were converted to $[H^+]$ by using the relationships $[H^+] = (10^{-pH})/\gamma_{\pm}$ and $pH = pH_{obs} - \partial$, where ∂ is a correction factor for solvent effects[10,14] and the activity coefficient, $\gamma_{\pm}$, at an ionic strength of 0.5 was interpolated from the data of Akerlof.[15] Values of acid dissociation constants, K_a's, were obtained by using a nonlinear least-squares program to fit absorbance, A_j, vs $[H^+]$ data to the equation $A_j = [A_L + (A_{HL}/K_a)[H^+]]/(1 + [H^+]/K_a)$, where A_L and A_{HL} are the limiting absorbance values of the non- and monoprotonated forms of the TPAB, respectively.

Tosylate Adduct of Nonsubstituted TPAB (1). A solution of 54 mg (0.28) mmol) of *p*-toluenesulfonic acid hydrate in 5 mL of acetone was added to a solution of 100 mg (0.28 mmol of nonsubstituted TPAB in 5 mL of acetone. After swirling to mix, the solution was allowed to stand at room temperature overnight in a closed vial. The resulting solid that formed was collected by filtration, washed once with minimal cold acetone, and dried under reduced pressure to give 66 mg (45 %) of 1 as air stable, dark red crystals: mp 239–41 °C. Anal. Calcd for $C_{31}H_{29}N_3SO_3$: C, 71.10; H, 5.58; N, 8.02. Found: C, 71.05; H, 5.60; N, 7.96. IR (KBr): 3240 (NH), 1640 and 1595 (C=N) cm^{-1}.

Acknowledgment. We thank M. Craig, D. Guerrero, Y. Liang, and A. Schovanec for procedural assistance and help in the acquisition of spectral data. We are grateful to the National Science Foundation for support of D.A. through a Summer Undergraduate Research Fellowship.

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(15) Akerlof, G. *J. Am. Chem. Soc.* **1932**, *54*, 4125.

Additions and Corrections

Vol. 50, 1985

Steven H. Bertz. Tetramethyl 3,7-Dihydroxybicyclo[3.3.1]-nona-2,6-diene-2,4,6,8-tetracarboxylate: A Useful Companion to Meerwein's Ester. Topological Analysis of Bicyclo[3.3.1]nonane Synthesis.

Page 3585. The next-to-last sentence of the first paragraph in the Results section should read "The former (see Experimental Section for spectral parameters) fits (*E*)-3-methoxy-2-propenal, whereas the latter fits the symmetrically H-bonded *Z*-isomer of **2**."

Page 3591. The second and third sentences of the first procedure in the Experimental Section should be "The ^{1}H NMR spectrum of a sample extracted into $CDCl_3$ had ceased to change by this time: ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3 H), 5.65 (dd, J = 8, 13 Hz, 1 H), 7.43 (d, J = 13 Hz, 1 H), 9.45 (d, J = 8 Hz, 1 H), which is consistent with (*E*)-3-methoxy-2-propenal.[57] Approximately 20% of another compound was also present, the ^{1}H NMR spectrum of which matched that of **2**.[58,59]"

See also reference 60.

Acknowledgment. I thank Prof. H. Quast (Würzburg) for bringing to my attention the need for this correction.

(57) Maddaluno, J.; d'Angelo, J. *Tetrahedron Lett.* **1983**, *24*, 895.
(58) Bothner-By, A. A.; Harris, R. K. *J. Org. Chem.* **1965**, *30*, 254.
(59) George, W. O.; Mansell, V. G. *J. Chem. Soc. B* **1968**, 132.
(60) Bertz, S. H.; Dabbagh, G. *J. Org. Chem.* **1990**, *55*, 5162.

Vol. 54, 1989

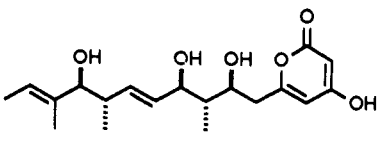
Hans P. Beutelman, Linfeng Xie, and Williams H. Saunders, Jr.*. Deuterium Isotope Effects and the Mechanism of Kinetic Enolate Formation.

Page 1704. Numbers in the last column of Table I were incorrectly transcribed and should read from top to bottom: 3.13 ± 0.29, 3.29 ± 0.31, and 6.59 ± 0.50.

Vol. 55, 1990

Hidenori Danda, Marvin M. Hansen, and Clayton H. Heathcock*. Reversal of Stereochemistry in the Aldol Reactions of a Chiral Boron Enolate.

Page 173, column 1. The structure of ACRL toxin IIIA (1) is depicted incorrectly; the correct structure is



1

Apurba Datta, Hiriyakkanavar Ila,* and Hiriyakkanavar Junjappa*. Reformatsky Reaction on α-Oxo Ketene Dithioacetals: Synthesis of Substituted and Fused Ethyl 2-Hydroxy-6-(methylthio)benzoates, 6-(Methylthio)pyran-2-ones, and 6-(Methylthio)-2(1*H*)-pyridone Derivatives.

Page 5591, Scheme V. Starting materials for entries 6 and 7 should be **10a**[a] and **10c**[b], respectively. Footnotes to Scheme V are as follows: [a] $R^1 = C_6H_5$. [b] R^1 = 4-$MeOC_6H_4$.