mixture of (4*R*,9*R*)-(−)- and (4*S*,9*R*)-(+)-epimers, the same enantioselective reduction takes place. Alcohol enriched in the (−)-epimers was formed in an endo/exo ratio of 8.5/1 and had an optical purity of 13.1% ee, while the recovered ketone was enriched in the (−)-epimer by 10.3% ee. Within experimental error, these results were identical with those obtained with the pure diastereoisomer.

To our knowledge, these results constitute the first experimental evidence for a free-radical chain reaction whose propagation step contains an enantioselective hydrogen atom transfer, while the enantioselective reduction of *d,l*-fenchone constitutes the first example of an enantioselective electron-transfer reaction.

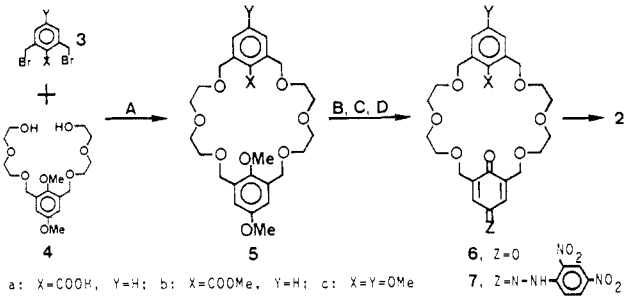

Figure 1. Synthetic scheme: (A) NaH, THF; (B) aqueous KOH, reflux; (C) $Ce(NH_4)_2(NO_3)_6$, $MeCN-H_2O$; (D) 2,4-dinitrophenylhydrazine, H_2SO_4, $EtOH-CH_2Cl_2$.

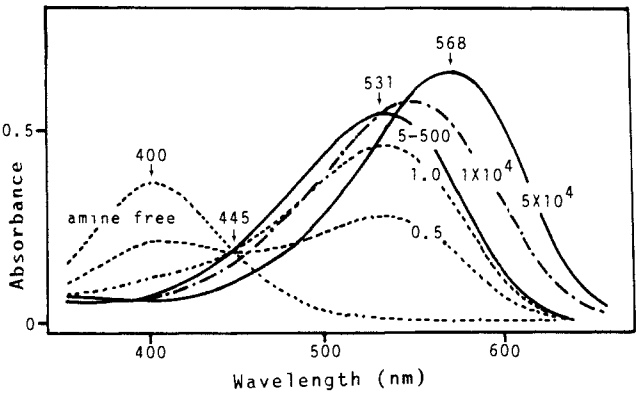

Figure 2. Visible spectra of **2a**-piperazine systems in $CHCl_3$. The numbers on the curves mean the molar ratio, piperazine:**2a**.

Synthesis, Coloration, and Crystal Structure of the "Dibasic" Chromoacerand–Piperazine 1:1 Salt Complex

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In spite of the explosive development of host–guest complexes,[1] much less attention has been focused on so-called salt complexes[2] where anionic hosts and cationic guests interact complementarily or vice versa. The *saltex*[3] is distinct from the major complexes of ligands such as crowns,[4] cryptands,[5] spherands,[6] cavitands,[7] cyclophane onium salts,[8] cyclodextrins,[9] and ionophores[10] in the following respect. Both the host and guest components in the saltexes are real ions which are held together by coulombic attraction of the opposite charges, and they are generated by neutralization or proton-transfer reactions from their ionizable precursors, acids and bases, before or during *saltexation*.[3] The unique characters of the saltexes would be advantageous to host–guest complexing in more bulky systems involving secondary and tertiary amines. Here, we propose the class name *acerands*[11] for acidic ligands as saltex precursors.

"Dibasic" chromoacerand **2a** constructed by incorporating a benzoic acid unit into "monobasic" acerands **1**[12] provides a good

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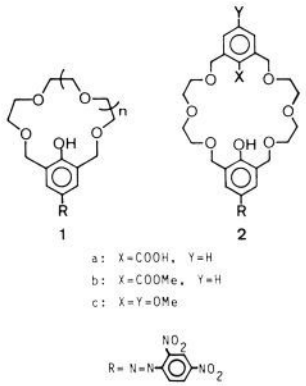

model to study saltexation with diamines, because of exact charge-matching and color developing ability of **2a**. This paper describes the synthesis of **2a–c**, their amine-selective coloration, and the crystal structure of the **2a**–piperazine 1:1 saltex.

Azophenol **2a** and **2c** were synthesized from diol **4** and dibromides **3b**[2e] and **3c**[13] via quinones **6a** and **6c**, respectively (Figure 1). Skipping the hydrolysis of ester **5b** led to **2b**.[14]

For screening experiments, a wide variety of amines[15] were treated with chromoacerands **2a–c** to yield colored ammonium phenolates whose visible spectra were determined.[16] The observed absorption maxima appeared in a wide wavelength region, 535–591 nm in chloroform. Interestingly the colored salts of bulky monoamines[17] showed the maxima being over 580 nm, whereas **2a** and diamines such as hydrazine, piperazine, *N,N'*-dimethylpiperazine, 1,4-diazabicyclo[2.2.2]octane, and *N,N,N',N'*-tetramethylethylenediamine formed the salts exhibiting the tremendously blue-shifted absorption maxima of 535–549 nm even under the same conditions. Titration experiments revealed the variable spectra in the **2a**–piperazine system[18] (Figure 2) in which the shorter wavelength band at 531 nm has been assigned to the deep violet 1:1 saltex, which was isolated from an equimolar mixture in chloroform and characterized by ^{1}H NMR spectrometry. The longer wavelength band at 568 nm is similar to those of **2b** and **2c**[18] and is probably due to the possible 1:2 salt. The association constant for the 1:1 saltex, $K_a = 2.3 \times 10^6$ M^{-1} at 25 °C in chloroform, has been found to be larger than that for the **2a**–piperidine 1:2 salt, 3.3×10^3 M^{-1},[19] by a factor of about 10^3. According to these findings, the observed blue-shifts are presumably associated with the formation of more stable saltexes at least in the present systems.

The crystal structure of the **2a**–piperazine 1:1 salt determined by an X-ray diffraction method is shown in Figure 3.[20] The figure

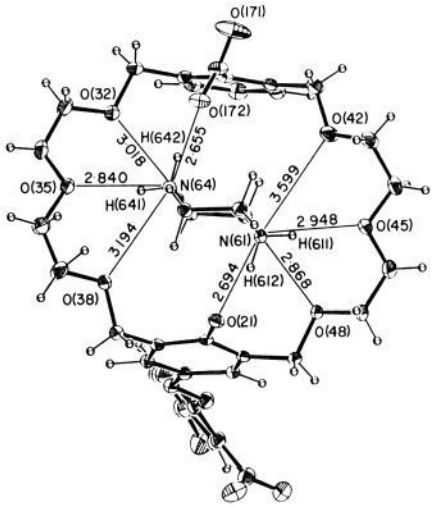

Figure 3. An ORTEP drawing of the molecular structure of the **2a**–piperazine 1:1 saltex with thermal ellipsoids at 20% probability level for non-hydrogen atoms and the spheres with 1.0 Å^2 temperature factor for hydrogen atoms. The estimated standard deviations for bond distances lie between 0.009 and 0.010 Å.

reveals that the piperazinium dication in the chair form is nicely fitted in the cavity of the dianion of **2a**. The axial NH protons of the guest make strong N$^+$–H···O$^-$ type hydrogen bonds with the phenolate and benzoate oxygens in the host judging from considerably short bond lengths, 2.694 (9) and 2.655 (9) Å, and the equatorial ones make N$^+$–H···O type hydrogen bonds with the ether oxygens O(35) and O(45) in the macroring, 2.840 (10) and 2.948 (9) Å. The great shortening of the former one from the standard N$^+$–H···O hydrogen bond, 2.83 Å,[23] stresses the importance of the O$^-$ atoms in the interaction with the guest cation.[24] It is of interest to note that all the anionic oxygens act as a binding site in crystalline saltexes from benzoic[2d] and phenolic[2i] acerands as well as **2a**. This seems to be one of the characteristics for *saltexing*,[3] which also favors lithium selectivity.[11h-k,12]

Finally, the remarkable blue-shift of the **2a**–piperazine 1:1 saltex may be interpreted with the hydrogen bonding between the phenolic O$^-$ atom and one of the axial N$^+$–H protons. The hydrogen bonding stabilizes the energy of the polar ground state more greatly than that of the less polar excited state of the chromophore. Similar blue-shifts induced by metal ions have been reported in

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(14) Carbon and hydrogen analyses (of new compounds **2a**, **2c**, **4**, and **5a–c**) were within 0.30% of theory, and ^{1}H NMR (Bruker WM 360, $CDCl_3$) and mass spectra were consistent with the structural assignments; **2a**, red plates (ethyl acetate–CH_2Cl_2), mp 136–137 °C dec; UV ($CHCl_3$) λ_{max} 400 nm (log ϵ 4.32); pK_a (10% dioxane–water) 7.04; **2b**, red glassy solid (purified by column chromatography); **2b**/**7b** = 87/13 in $CDCl_3$. **2c**, orange needles (acetone–hexane), mp 128–129 °C dec; **2c**/**7c** = 82/18 in $CDCl_3$.

(15) Primary, secondary, and tertiary alkylamines, piperidines, ethanolamines, and ethylenediamines were used.

(16) The visible spectra were measured as follows. After 10 μL of amines (3×10^{-4}–4×10^{-5} mol) was added to 2.5 mL of stock solutions (1.7×10^{-5} M) of the chromoacerands (ca. 4×10^{-8} mol) in a cell, the mixture was well shaken for a short period, and then the spectra were recorded within 5 min. Commercially available amines were used without further purification.

(17) 2,6-Dimethyl- and 2,2,6,6-tetramethylpiperidines and tributyl- and tripropylamines.

(18) In **2a**–piperidine and **2b**– and **2c**–piperazine systems, invariable bands appeared at 576, 570, and 563 nm, respectively.

(19) This value has been estimated as the formation constant for the 1:2 salt from the 1:1 salt, piperidinium carboxylate of **2a**.

(20) Crystal data of the chromoacerand **2a**–piperazine 1:1 saltex: $C_{35}H_{44}O_{13}N_6{\cdot}CH_2Cl_2{\cdot}CH_3COOC_2H_5$, M_r 929.8, monoclinic, space group $P2_1/c$, a = 20.915 (3), b = 11.499 (2), c = 18.378 (3) Å, β = 103.40 (1)°, U = 4300.2 (9) Å^3, D_x = 1.437 g cm^{-3}, Z = 4. Diffraction intensities were measured on a Rigaku four-circle diffractometer by using nickel-filtered Cu Kα radiation. A total of 6385 reflections was collected up to 2θ = 120°, among which 4898 were observed reflections [$|F_o| > 3\sigma(F_o)$]. The crystal structure was solved by the direct method (MULTAN-78)[21] and refined by the full-matrix least-squares method (X-RAY SYSTEM)[22] to the R index of 0.103, while the R_w index of 0.109 is obtained by the weighting function of $w^{-1} = \sigma^2(F_o) + 0.003(F_o)^2$. The saltex was crystallized from the mixed solution of methylene chloride and ethyl acetate, both of which were included in the unit cell. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. The carbon atom of CH_2Cl_2 could not be located because of the diffused electron density. The rather low accuracy in the positional parameters for both crystal solvents may result in the high R value for the overall crystal structure.

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(24) The corresponding N$^+$–H···O$^-$ hydrogen bonds have been reported in ammonium saltexes of phenolic[2i] (2.690 Å) and benzoic[2d] (2.676 Å) acerands. The present saltex is the first example including both of these hydrogen bonds in itself.

other chromoacerands[12] and ionophores.[25]

Supplementary Material Available: Full listings of fractional atomic coordinates and interatomic bond distances of the **2a**–piperazine 1:1 saltex (4 pages). Ordering information is given on any current masthead page.

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The Aminolysis of Methyl Formate with Aniline: Evidence for Catalysis by a Trapping Mechanism[1]

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It has been proposed that general base catalysis of ester aminolysis can involve rate-limiting diffusion-controlled proton removal from the addition intermediate $T^{\pm}$.[2,3] However, this has not been directly demonstrated for bimolecular ester aminolysis, although related reactions such as the hydrazinolysis of acetylimidazole[4] and the hydroxylaminolysis of iminium cations[5] are catalyzed by diffusion-controlled proton removal by bases. The general base-catalyzed cyclization of methyl *o*-aminophenyl propionate shows rate constants independent of base strength for three bases of pK 6–10, consistent with catalysis by diffusion-controlled proton transfer for an intramolecular ester aminolysis.[6] Buffer catalysis, with enhanced activity of bifunctional catalysts, has been observed for breakdown to amine and ester of the intermediate formed from the hydration of ethyl *N*-phenylformimidate,[7] and there is evidence that diffusion-controlled proton transfer can be product determining in the partitioning of other imidates.[2,8] We describe here direct evidence that the aminolysis of methyl formate by aniline involves enforced catalysis by strong bases that is encounter-limited. Catalysis by weaker bases involves partially rate-limiting proton transfer with $T^{\pm}$, and still weaker bases react with rate-limiting diffusional separation of the encounter complex $T^{-}\cdot BH^{+}$.[2,9] The proton-transfer step is responsible for a solvent deuterium isotope effect on general base catalysis with a maximum at $pK_{BH} \sim 5$.

The aminolysis of methyl formate by aniline shows strong catalysis by buffers at concentrations of <50 mM. Figure 1A shows the Brønsted plot for general base catalysis of aminolysis by oxygen bases of pK_{BH} from 1 to 9. Rate constants for monofunctional catalysts (solid symbols) follow a curve that approaches slopes of $\beta = 0$ and $\beta = 1.0$ for strong and weak bases, respectively. Rate constants for bifunctional catalysts (open symbols) follow a line of slope $\beta = 0$. While rate constants for bifunctional bases are similar to those for strong monofunctional catalysts, bifunctional catalysts of pK < 4.5 are more active than their monofunctional counterparts by up to 10^3-fold.

Figure 1B shows the solvent deuterium isotope effects for general base catalysis. Monofunctional catalysts (solid circles) display an isotope effect maximum of $k_B^{HOH}/k_B^{DOD} = 5$ at $pK_{BH} = 5.3$, with little or no isotope effect for catalysis by strong or very weak base catalysts. Four bifunctional catalysts show isotope effects in the range of 1.9–2.5.

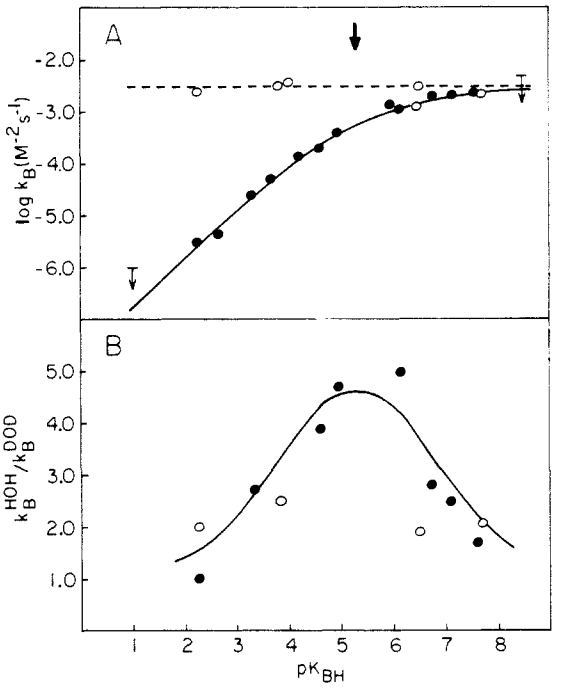
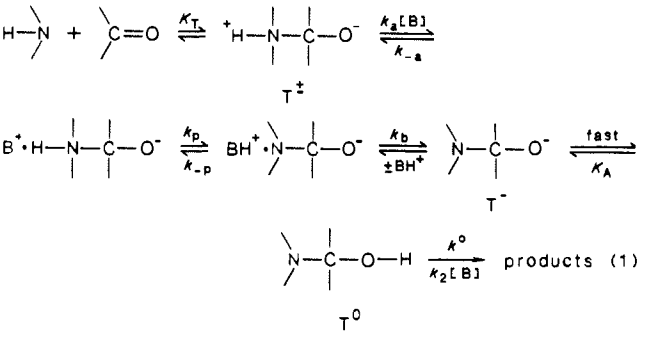


Figure 1. (A) Brønsted plot for general base catalysis of the aminolysis of methyl formate by aniline at 25 °C, ionic strength 1.0 (KCl; methylarsonate in NaCl), 0.1 M MOPS buffer. Experiments were performed between pH 7 and 8, where $T^{\pm}$ conversion to T^0 is rate-limiting.[2,17] Initial rates of formanilide formation were determined at 240 nm with aliquots of the reaction mixture quenched in 0.1 M HCl.[18] Closed symbols: monofunctional catalysts (carboxylates, cacodylate, and phosphonate dianions); open symbols: bifunctional catalysts (fluoroacetone hydrates, phosphonate, bicarbonate, methylarsonate monoanions, and phosphate dianion). The solid line was calculated for a trapping mechanism.[14] The arrow at pK = 5.3 shows the pK of $T^{\pm}$ which best fits the data.[13] (B) Solvent deuterium isotope effects for general base catalysis of the aminolysis of methyl formate by aniline. Solid symbols: monofunctional catalysts; open symbols: bifunctional catalysts. The solid line represents the isotope effect assuming a constant value of $k_H/k_D = 6.5$ for the proton-transfer step, k_p.[14]

The nonlinear Brønsted plot for monofunctional bases fits an "Eigen curve" for rate-limiting diffusion-controlled proton transfers.[10] This is consistent with the trapping mechanism shown in eq 1 in which the different regions of the Brønsted plot are



represented by three different rate-limiting steps: k_a, k_p, and k_b for strong, weak, and very weak bases, respectively. The isotope effect maximum appears in the region in which k_p is partially rate-limiting, which is typical for proton transfer between electronegative atoms.[5,11,12] The break in the Brønsted plot from slope $\beta = 1.0$ to $\beta = 0$ for monofunctional catalysts occurs at $pK_{BH} = 5.3$ (arrow, Figure 1A), which is consistent with the calculated[13]

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