less than 10^{-5} of those of the wildtype, respectively. Yet the mutant effects the first half reaction. Thus, the formation of the acetyl-S-enzyme mutant intermediate is evidenced from the incorporation of 0.82 equiv of ^{14}C from $^{14}CH_3COSCoA$ into the mutant. The acetyl incorporation, however, proceeds slowly, requiring 1 h incubation with $^{14}CH_3COSCoA$ for the mutant, as compared with less than 1 min for the wildtype. This is reflected in the rate of exchange of ^{32}P-CoASH with AcCoA by the acetyl-*S*-mutant enzyme. The observed *V*(exchange), 0.01 μM/(min·mg) (50 μM AcCoA, 50 μM CoASH), is compared with the *V*(exchange), 42 μM/(min·mg), under the same conditions for the exchange reaction with the wildtype.[13] These results are consistent with the view that the Cys-378 residue is involved in the proton abstraction and the reduced exchange rate observed is due at least in part to the decreased ionization of the Cys-89-SH to Cys-S^- in the mutant. It was unexpected that the sulfuryl group might be responsible for the deprotonation.

Acknowledgment. We thank Dr. Edmond Differding for the synthesis of 3-pentynoyl-SPP and Dr. Friedrich Mayerl for the measurement of V_{max}(exchange) of the thiolase (wildtype) and preparation of [^{32}P]CoASH. This work was supported by a grant from the National Science Foundation (DMB-87-06273). S.F.W. is a SERC/NATO Postdoctoral Fellow.

Supplementary Material Available: Experimental procedures (including materials and methods) (5 pages). Ordering information is given on any current masthead page.

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Azophenolic Acerands: Amine-Selective Coloration and Crystal Structure of a Piperidinium Saltex†

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Studies on saltexation[1k] involving the Coulombic attractive force between oppositely charged hosts and guests will be expected to draw a new trend in molecular recognition, since this additional binding force will affect the stability and selectivity of the major

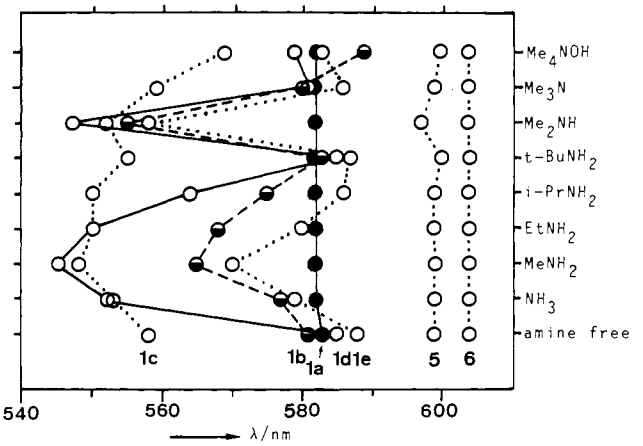
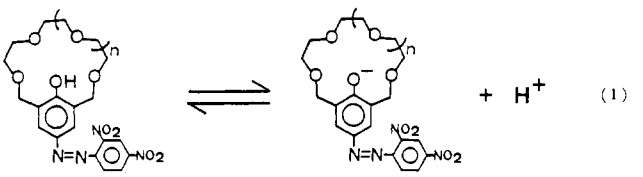
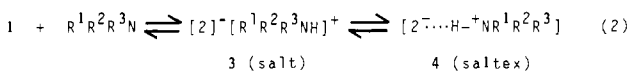


Figure 1. Absorption maxima of the colored salts of azophenols with amines.

complexes whose components, uncharged hosts and charged guests, are bound by ion-dipole interaction and/or hydrogen bonding. Indeed, such charge–charge interaction in saltexes[1] has been found to be favorable for lithium[2] and diamine[1k] selectivity of mono- and dibasic acerands, respectively. Azophenolic acerands **1**[2c,d] provide a good model to examine amine-selective saltexation because of their chromogenic property. Blue anionic ligands $\mathbf{2}^-$ can be generated by dissociation (eq 1) or neutralization (eq 2) of yellow **1**. We report here the first systematic investigation of amine-selective coloration based on saltexation of **1**, a prototypical chromoacerand.[3]





For screening experiments, cycles **1** and open chain analogues **5** and **6**[4] were treated with ammonia and 11 simple alkylamines

† Dedicated to Professor Donald J. Cram, UCLA, on the occasion of his 70th birthday.

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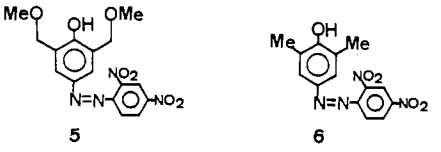
in ethanol, and the visible spectra of the resulting 84-colored salts were determined.[5] The data relating to methylated methylamines were extracted to Figure 1. The constant transition energies observed with these amines and cavityless **1a**, **5**, and **6** indicate



5 6

that there is no appreciable interaction between the anions and the counter cations in their salts; simple salts, for example, **3**(n = 0), are formed. The variable absorption maxima, however, were observed with the salts of **1** having a cavity: 555–589 for **1b**, 548–569 (**1c**), 545–585 (**1d**), and 558–587 nm (**1e**). Dimethylamine caused remarkable blue-shifts of the absorption bands compared with bulky amines such as trimethylamine, and $MeNH_2$–, $EtNH_2$–, and NH_3–**1d** combinations also gave a specifically blue-shifted λ_{max}. When several secondary amines were checked, pyrrolidine– and piperidine–**1b** and *N*-methylbutylamine–**1d** combinations also showed remarkably blue-shifted bands at 561, 559, and 557 nm, respectively, compared with **1**–2,2,6,6-tetramethylpiperidine (TMP) systems of 579–588 nm. Piperidinium salts of **1d** (λ_{max} = 580 nm) and **1e** (586 nm) with a larger cavity were no longer hypsochromic.

In chloroform, bulky secondary and tertiary amines generally gave poor yields of salts **3** in contrast with the excellent yields in ethanol. Thus the **1b**–piperidine 1:1 saltex could be isolated selectively from a 1:40:40 mixture of the **1b**–piperidine–TMP system in this solvent.

In order to confirm the mode in saltexation of **1** and to compare with that of dibasic acerand,[1k] the X-ray structure analysis of **1b**–piperidine saltex has been carried out.[6] The molecular structure of the saltex in Figure 2 shows quite a unique mode of saltexation as expected from the spectroscopic data and examination of CPK molecular models. The chromophore in the host is planar within 0.1 Å, to which the cyclic polyether chain extends perpendicularly. All the oxygen atoms point toward the nitrogen atom of piperidinium cation in chair form. The very short N^+–H···O^- type hydrogen bond of 2.654 (7) Å is found between the phenolic oxygen in the host [O(21)] and the nitrogen in the guest [N(5)], which is shorter than the corresponding bond in dibasic acerand, 2.694 (9) Å.[1k] The nitrogen of the guest also interacts with three ether oxygens [N···O from 2.946 (7) to 3.187 (7) Å] without participation of a hydrogen atom. Thus, the interaction between the piperidinium cation and azophenolate anion is mainly attributed to the strong N^+–H···O^+ type hydrogen bond and is partly supported through the N^+···O ion-dipole interactions resulting in a stable one-point binding saltex.

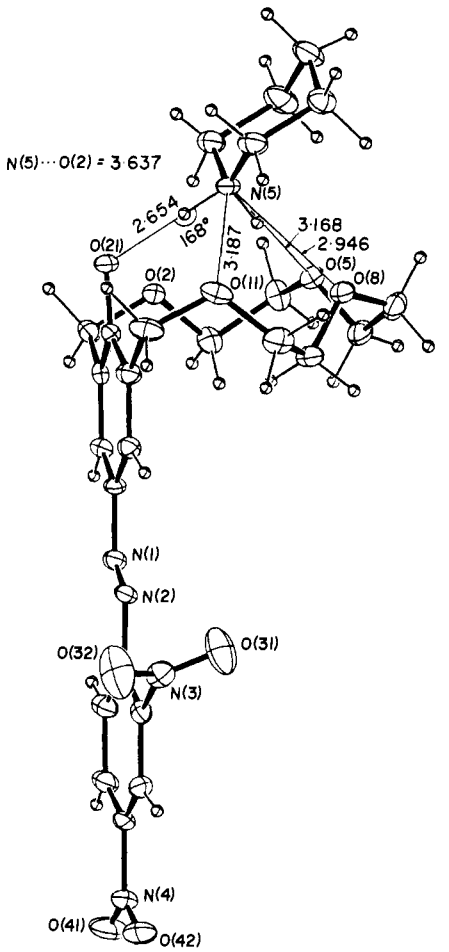


Figure 2. Molecular structure of **1b**–piperidine saltex with selected interatomic bond distances. Thermal ellipsoids for non-hydrogen atoms are drawn at 30% probability level. The hydrogen atoms are shown as the spheres with arbitrary temperature factor of 1.0 Å^2. The esd's for bond distances are in the range of 0.007–0.008 Å.

It is of interest to note that the magnitude of the observed blue-shifts does not correlate with either the acidity[9] of **1** or the basicity of the amines. As reported previously,[1k] the shifts may be interpreted with the N^+–H···O^- hydrogen bonding between the host and guest of saltexes **4**. Such hydrogen bonding has been found in the crystal structures of dibasic acerand–piperazine[1k] and **1b**–piperidine saltexes described above. The association constant for the **1b**–piperidine saltex, log K_a = 3.26 M^{-1} in $CHCl_3$, has been found to be larger than that for **1b**–*tert*-butylamine salt, 2.53 M^{-1}.[10] This finding seems to support a parallel relationship between the blue-shift in ethanol and the K_a in chloroform and indicates a result reverse to the K_a's for 18-crown-6-protonated amine complexes[12] which decrease in the order $RNH_3^+ > R_2NH_2^+$.

Enantiomeric amine-selective coloration with chiral azophenolic acerands will be published.[13]

(5) The visible spectra were measured by a similar method to that described in ref 1k.

(6) Crystal data of **1b**–piperidine saltex: $[C_{20}H_{22}O_9N_4 + C_5H_{11}N]\cdot CH_3CO_2C_2H_5$, FW = 635.7, triclinic, space group $P\bar{1}$, a = 15.636 (3) Å, b = 7.869 (1) Å, c = 12.938 (3) Å, α = 107.09 (2)°, β = 97.92 (1)°, γ = 92.28 (2)°, U = 1501.7 (5) Å^3, D_x = 1.405 g cm^{-3}, Z = 2, $F(000)$ = 676, μ(Mo Kα) = 1.2 cm^{-1}. X-ray diffraction data were measured on a Rigaku four-circle diffractometer using graphite monochromatized Mo Kα radiation. A total of 5288 independent reflections were collected up to 2θ = 50° by the θ–2θ scan technique. The intensity data were corrected for the usual Lorentz and polarization effects, but an absorption correction was not applied. The structure was solved by the direct methods (SHELXS-86)[7] and refined by the full-matrix least-squares (XRAY-76)[8] by using the 2779 observed reflections [$|F_o| > 3\sigma(F_o)$]. After the anisotropic refinement of nonhydrogen atoms in the saltex, the R index was 0.164, and any more improvement was obtained through the further refinements. The difference Fourier maps at this stage of refinement showed the significant residual electron density around the center of symmetry at (0, 0.5, 0.5). The single crystal of this saltex was obtained from the mixed solution of dichloromethane and ethyl acetate. Thus, the possibility for crystalline solvent was examined for these solvents, and ethyl acetate was found to pack around the center of symmetry in the disordered mode. The successive refinements including the disordered solvent atoms improved the R index markedly. The final R and R_w indices were 0.091 and 0.118, respectively, including hydrogen atoms with isotopic temperature factors, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and the weighting scheme used was $w = [\sigma^2(F_o) + 0.003(F_o)^2]^{-1}$.

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Supplementary Material Available: Full listings of fractional atomic coordinates and interatomic bond distances and angles of the **1b**–piperidine saltex (5 pages). Ordering information is given on any current masthead page.

Photoinduced Enzyme-Catalyzed Reduction of Nitrate (NO_3^-) and Nitrite (NO_2^-) to Ammonia (NH_3)

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The reduction of nitrate is of broad interest as a means of mimicking reduction processes of oxido-nitrogen substrates in nature and of developing novel nitrogen fixation systems.[1] Reduction of nitrate to nitrite (eq 1) is catalyzed in nature by the

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \quad (1)$$

$$NO_2^- + 6e^- + 8H^+ \rightarrow NH_4^+ + 2H_2O \quad (2)$$

$$NO_3^- + 8e^- + 10H^+ \rightarrow NH_4^+ + 3H_2O \quad (3)$$

enzyme nitrate reductase.[2] Reduction of nitrite to ammonia (as ammonium ions) (eq 2) is catalyzed in nature by the enzyme nitrite reductase.[2,3] Substantial efforts are directed toward the reduction of NO_3^- by electrochemical and photochemical means. Electrochemical reduction of NO_3^- has been accomplished by using catalytic material electrodes,[4] modified electrodes,[5] or in the presence of homogeneous catalysts[6,7] such as Co(III) or Ni(II) cyclams, Ru(II) bipyridine or Fe(III) porphyrin. Photosensitized reduction of NO_3^- to NO_2^- has been reported by using *N*-methylphenothiazine or *N,N'*-tetramethylbenzidine,[8] and reduction to ammonia was reported to occur at Pd-TiO_2 illuminated suspensions.[9] We have recently applied enzymes as biocatalysts for the photosensitized regeneration of NAD(P)H cofactors[10,11] and performed various biotransformations through photochemical means.[12] Here we wish to report on the photoinduced reduction of NO_3^- to ammonia using the two enzymes nitrate reductase and nitrite reductase as catalysts and photogenerated *N,N'*-dimethyl-4,4'-bipyridinium radical cation, viologen radical, $MV^{\bullet+}$, that act as an electron carrier and is recognized by the biocatalysts.[13]

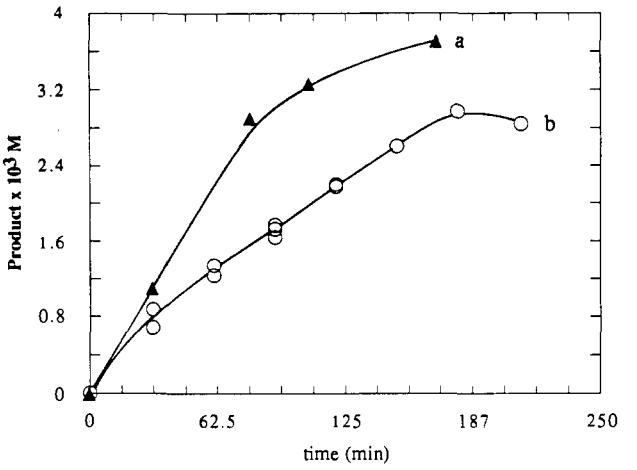

Figure 1. Rates of products formation as a function of illumination time. In all systems $[Ru(bpy)_3^{2+}] = 7.4 \times 10^{-5}$ M, $[Na_2EDTA] = 0.02$ M. (a) (▲) NO_2^- formation, pH 7.0, Tris buffer 0.1 M, $[MV^{2+}] = 3.2 \times 10^{-4}$ M, $[NO_3^-] = 9.9 \times 10^{-3}$ M, nitrate reductase 0.2 U. (b) (○) NH_4^+ formation, pH 8.0, Tris buffer 0.1 M, $[MV^{2+}] = 4.2 \times 10^{-4}$ M, $[NO_2^-] = 0.01$ M, nitrite reductase 0.06 U.

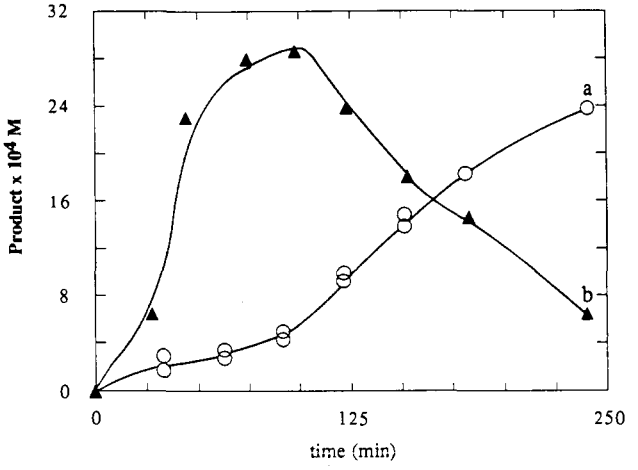

Figure 2. NO_2^- and NH_4^+ concentrations in the combined system, as a function of illumination time. (a) (○) NH_4^+. (b) (▲) NO_2^-. pH = 8.0, Tris buffer 0.1 M, $[Ru(bpy)_3^{2+}] = 7.4 \times 10^{-5}$ M, $[Na_2EDTA] = 0.02$ M, $[MV^{2+}] = 4.2 \times 10^{-4}$ M, $[NO_3^-] = 0.01$ M, nitrate reductase 1.0 U, nitrite reductase 0.35 U.

Illumination ($\lambda > 420$ nm) of an aqueous 0.05 M phosphate buffer solution, pH = 7.0, that includes Ru(II) tris-bipyridine, $Ru(bpy)_3^{2+}$, as photosensitizer, 7.4×10^{-5} M, *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+}, 3.2×10^{-4} M, as electron relay, EDTA, 0.02 M, as sacrificial electron donor, NO_3^-, 9.9×10^{-3} M, and the enzyme nitrate reductase (E.C. 1.9.6.1 from Escherichia coli), 0.2 units, results in the reduction of NO_3^- to nitrite (eq 1). The rate of NO_2^- formation[14] at time intervals of illumination is shown in Figure 1a. The quantum yield of NO_2^- formation corresponds to $\phi = 0.08$. After 310 min of illumination, ca. 60% of the original NO_3^- was converted to nitrite. The initial rate of NO_2^- formation is 0.07 μmol·min^{-1}. Illumination ($\lambda > 420$ nm) of an aqueous buffer solution, pH = 8.0, that includes $Ru(bpy)_3^{2+}$, 7.4×10^{-5} M, MV^{2+}, 4.2×10^{-4} M, as electron carrier, EDTA, 0.02 M, as

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