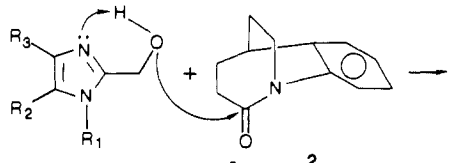
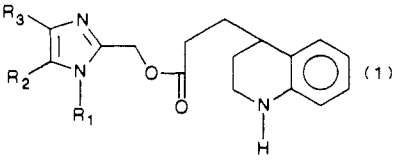


2

1a; $R_1 = R_2 = H$, $R_3 = C(CH_3)_2CO_2^-$
b; $R_1 = R_2 = H$, $R_3 = C(CH_3)_2CO_2Me$
c; $R_1 = R_2 = R_3 = H$
d; $R_1 = CH_3$, $R_2 = R_3 = H$
e; $R_1 = H$, $R_2 = R_3 = CH_3$



(1)

3a-e

lie ~8–100 fold (depending on the example[6]) below the Brønsted line indicating this group is required for maximal activity.[6] For example, if the CH_2OH unit in **1a** is replaced by CH_2OCH_3, the k_2^{max} value drops from (4.06 ± 0.05) × 10^{-2} to (5.90 ± 0.45) × 10^{-3} M^{-1} s^{-1}.

Since **1a** lies on the same Brønsted lines as defined by **1b–e**, the CO_2^- unit in this system is incapable of providing another mechanism for O-acylation[12] other than that simply dependent upon imidazole basicity. A fundamentally different or enhanced pathway such as CO_2^- acting as a general base (on N–H) in concert with the imidazole–HO interaction is expected to produce an upward deviation from the line.

Since this is not observed, at first glance one might suggest there is no positive benefit of attachment of the CO_2^- in **1a**, but we believe the situation is more subtle. The pK_a^{Im} values in Table I show the N basicity of **1a** is greater than that of comparison ester **1b**, and a corresponding increase in k_2^{max} is observed. In $EtOH/H_2O$ media of reduced polarity,[13] activity of all the imidazole alcohols is reduced as expected, and there is a noticeable drop in the pK_a^{Im} of **1b–e**. However, the electrostatic and/or H-bonding stabilization in the zwitterionic form of **1a** counteracts the general medium-induced reduction in N basicity[14] thereby enhancing the CH_2OH nucleophilicity in relation to that of **1b–e**.

In summary, the main benefit of the anionic pendant in **1a** is an electrostatic one which is manifested more prominently in media of reduced polarity. To term this system a "model" for the acylation of SPases invites comparison with the enzyme which may not be justified given the unorthodox structure of the acylating agent[6] and perhaps nonoptimal orientation of the functional groups in **1a**.[15] Rather, we prefer to view the system as a small molecule demonstration of an electrostatic role for CO_2^-–Im in direct CH_2OH acylation. Nevertheless we note that in addition to other possibilities,[1] a similar electrostatic role has been suggested for the Asp CO_2^-–His section of the triad in the SPases.[4,16]

Acknowledgment. We thank the University of Alberta and Natural Sciences and Engineering Research Council of Canada for financial support.

(12) The "trimethyl" lock engendered by the isobutyryl moiety compresses the carboxylate into a close H-bonding relationship with the imidazole as noted by Rogers and Bruice.[7d] In the latter study, a negligible effect was noted in the deacylation relative to the corresponding carboxylic ester.
(13) Åkerlöf, G. *J. Am. Chem. Soc.* **1932**, *54*, 4125.
(14) For a discussion of the effect of alcohol/H_2O mixtures on amine, acid, and amino acid pK_a's see: (a) Merle, M.; Douhéret, G.; Dondon, M.-L. *Bull. Soc. Chim. Fr.* **1966**, *Ser. 5*, 159. (b) Grunwald, E.; Berkowitz, B. J. *J. Am. Chem. Soc.* **1951**, *83*, 4939. (c) Chattopadhyay, A. K.; Lahiri, S. C. *Indian J. Chem.* **1977**, *15A*, 930.
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(16) The electrostatic role of Asp CO_2^- in enhancing the basicity of the imidazole in SPases has been discussed by the following: (a) Roberts, J. D.; Kanamori, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3095. (b) Bachovchin, W. W. *Biochemistry* **1986**, *25*, 7751. (c) Bachovchin, W. W.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 8041.

Supplementary Material Available: Tables of thermodynamic pK_a^{Im} and k_2^{max} values for **1a–e** reacting with **2** and product study data (^1H NMR, IR, mass spectral) (3 pages). Ordering information is given on any current masthead page.

Solvent-Induced Mechanism Change in Charge-Transfer Molecules. Inversion versus Rotation Paths for the *Z* → *E* Isomerization of Donor–Acceptor Substituted Azobenzenes

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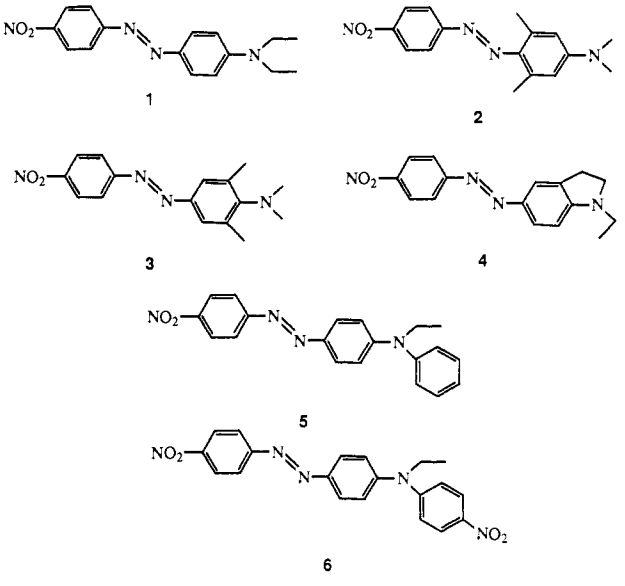
Received March 4, 1988

The mechanism for the thermal *Z* → *E* isomerization of p-donor–p′-acceptor ("push–pull") azobenzenes has generated considerable controversy.[1-9] While reaction of azobenzene is generally accepted to proceed by an inversion mechanism, in which sp^2–sp rehybridization of an azobenzene nitrogen affords isomerization via a semilinear transition state,[10-15] we and others have noted coupling of donor and acceptor substituents in compounds such as 4-(diethylamino)-4′-nitroazobenzene (DENAB) (**1**) can



1 2 3 4 5 6

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Table I. The $Z \rightarrow E$ Isomerization Rates ($\Delta G^{\ddagger}_1$, 25 °C) of *p*-Nitro-*p'*-aminoazobenzenes in Heptane and Dimethyl Sulfoxide (DMSO) and the Slopes Obtained by Least-Squares Linear Regression Analysis of $\Delta G^{\ddagger}$ versus π^* and E' versus π^* [a]

		rate ($\Delta G^{\ddagger}_1$)		$\Delta G^{\ddagger}$ vs π^*		E' versus π^*	
	solvent	s^{-1}	kcal/mol	slope[b]	(corr)	slope	(corr)
1	heptane	0.0071	(20.4)	−7.7	(0.94)	−6.8	(0.99)
	DMSO	452	(13.8)	−6.4	(0.97)[c]		
2	heptane	0.0037	(20.8)	−7.8	(0.97)	−5.7	(0.95)
	DMSO	1206	(13.2)	−7.6	(0.93)[c]		
3	heptane	0.0007	(21.7)	−7.2	(0.98)	−6.6	(0.95)
	DMSO	0.23	(18.3)				
4	heptane	0.0091	(20.2)	−8.1	(0.95)	−7.2	(0.99)
	DMSO	48300	(11.1)				
5	heptane	0.0009	(21.7)	−9.4	(0.94)	−5.4	(0.96)
	DMSO	14.0	(16.0)				
6	heptane	0.0005	(22.1)	−9.2	(0.97)	−3.1	(0.93)
	DMSO	0.011	(18.9)				

[a] $\Delta G^{\ddagger} = \Delta G^{\ddagger}_1 - (s\delta + a\alpha)$ and $E' = E_{h\nu} - (s\delta + a\alpha)$. [b] Obtained from a section of the plot with negative slope. [c] Slope obtained including heptane.

result in a lowered bond order between azo nitrogens, which favors isomerization via a rotational path.[1,6,7] Arguments favoring "rotation" center around a pronounced acceleration of thermal isomerization and striking sensitivity to solvent polarity for the p-donor-p'-acceptor azobenzenes compared to those having *only* donor or acceptor substituents.[1,2,6,7,16,17] Support for the rotational mechanism has been advanced by Asano and co-workers.[1,2] It has also been suggested, however, that these unusual rate accelerations can be accommodated by an inversion mechanism.[3-5] A strong argument favoring the inversion over the rotational mechanism is the lack of correspondingly rapid isomerization in carbon analogues of **1** such as p-amino-p'-nitrostilbene.[18] Here we present strong evidence in favor of dual mechanisms for the isomerization as a function of donor strength and solvent.

Azobenzenes **1–6** were prepared and purified as described elsewhere.[6,7,19] All show "typical" solvatochromic absorption spectra for *E* isomers with quantitative sensitivity to solvent polarity parameters such as E_T or π^*.[20-22] We have used a slight modification (eq 1) of the Taft relationship[22] to evaluate the solvatochromic behavior for the absorption maxima, corrected to E', versus π^* (Table I).

$$E' = E_{h\nu} - (s\delta + a\alpha) = s\pi^* + E_0 \qquad (1)$$

The isomerizations also show a pronounced sensitivity to solvent as has been previously found for **1**.[6,7] The isomerization is monitored following $E \rightarrow Z$ photoisomerization by flash or steady irradiation;[7] for all dyes studied the sequence is completely reversible through several cycles.[23] The reactivity order is **4 > 2 ≥ 1 > 5 > 3 > 6**, which follows decreasing ability of the *p'*-amino group to donate electrons to the azobenzene chromophore via conjugation. Rates in more polar solvents vary over up to 6 orders of magnitude (Table I). Reactivity as monitored by $\Delta G^{\ddagger}$ at 25 °C shows a good correlation with π^* when treated according to eq 2 (Figure 1) for azobenzenes **1**, **2**, and **4**; however, for azobenzenes with more weakly donating amino groups there is a clear

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_1 - (s\delta + a\alpha) = s\pi^* + \Delta G^{\ddagger}_0 \qquad (2)$$

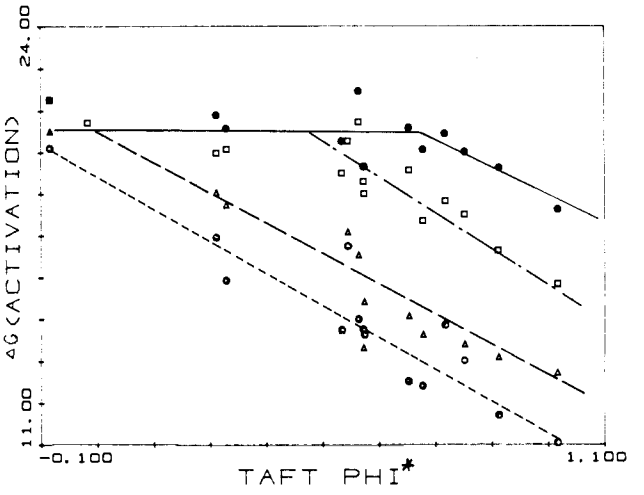
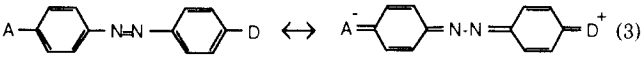


Figure 1. A plot of $\Delta G^{\ddagger}$ π^*; 2 (△), 3 (●), 4 (○), and 5 (□).

break in these plots with a nearly flat (zero slope) portion in solvents of low-to-moderate polarity and a linear decrease in $\Delta G^{\ddagger}$ with π^* for more polar solvents. The limiting $\Delta G^{\ddagger}$ value is ca. 21 kcal/mol and occurs at quite different polarities for different dyes (Figure 1, Table I).

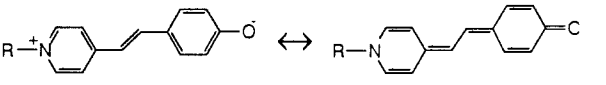
The strong and parallel decreases in $\Delta G^{\ddagger}$ and $E_{h\nu}$ with increase in solvent polarity for the azobenzenes with strong p-donor–p'-acceptor substituents are in accord with increasing importance of a charge-separated structure **7b** (eq 3). The reduction of $\Delta G^{\ddagger}$



(3)

can be plausibly accounted for by a rotational mechanism with a lower activation energy than for azobenzenes not having conjugated donor and acceptor substituents. The sharp break in the plots of $\Delta G^{\ddagger}$ versus π^* for azobenzenes **3**, **5**, and **6** (and others) suggests that two mechanisms are operative. The limiting $\Delta G^{\ddagger}$ ≈ 21 kcal/mol is very close to values measured for non-"push–pull" azobenzenes[10-12] and thus reasonable for a nearly solvent-independent inversion mechanism. These results suggest that both inversion and rotational mechanisms are available and that the extent of solvent-mediated donor–acceptor coupling (and relative importance of **7a** and **7b**) determines which path is followed.

As noted earlier, one of the major criticisms of a rotational mechanism is the lack of a corresponding low activation energy $Z \rightarrow E$ isomerization for analogous olefins.[18] However, very recent studies by Steiner and co-workers indicate merocyanines **8** and **9** show solvatochromic behavior closely related to that for azobenzenes **1**, **2**, and **4**. The solvent dependence of $E_{h\nu}$ on π^* shows a similar sensitivity but a positive slope (9.78)[24] since the ground states should be largely represented by **8**,**9a** and the excited state by the charge neutralized **8** and **9b**. These compounds, which cannot undergo isomerization via an inversion mechanism, undergo facile thermal isomerization with a solvent dependent $\Delta G^{\ddagger}$ (25 °C) = 12–23 kcal/mol in the same range as for the "push–pull" azobenzenes.[24,25] Here again linear correlations (eq 1 and 2) give slopes of the same order (6.34) as for **1** (−6.4) but of opposite sign. The remarkable parallel in reactivity between merocyanines **8** and



8,9 a **8,9 b**

8 R = CH_3 **9** R = $C_{16}H_{33}$

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9 and azobenzenes **1**, **2**, and **4** suggests that isomerization of either olefin or azobenzene chromophore by a rotational path depends strongly on a solvent and resonance assisted lowering of the bond orders to reach transition states very close to **7b** or **8**,**9b**, respectively.

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Synthesis and Crystal Structure of the First Stannacyclopropene Derivative

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Recent interest in the chemistry of the Main Group carbene analogues, R_2M: (M = Si, Ge, Sn), has centered on the reactions of these species with carbon–carbon multiple bonds.[1] Herein, we describe the reaction of a diorganostannylene (R_2Sn:), **1** [R = bis(trimethylsilyl)methyl],[2] with an acetylene **2**[3] to provide the first known example of a stannacyclopropene **3** (Scheme I). Full characterization of **3**, including the crystal structure and ^{119}Sn NMR, reveals an unique thermal equilibrium among **1**, **2**, and **3** which occurs in solution above −16 °C, with **1** and **2** being favored at higher temperatures (Scheme I).

Synthesis of **3** (Scheme I). Silylenes (R_2Si:) and germylenes (R_2Ge:) have previously been shown to react with the cyclic acetylene **2** to form the corresponding silacyclopropenes and germacyclopropenes, respectively.[1e,f] Analogously, titration of a deep red equilibrium mixture of **1** and the distannene **4** in methylcyclohexane with 1.2 equiv of **2** at room temperature results in complete decolorization of the solution. Removal of the solvent and excess acetylene under reduced pressure quantitatively provides **3** as a pale yellow crystalline material which is subsequently recrystallized twice from methylcyclohexane at −40 °C.

Compound **3** exhibits physical properties that are fully consistent with the stannacyclopropene structure.[4] A $^{13}C\{^1H\}$ NMR (75 MHz, −25 °C, methylcyclohexane-d_{14}) δ (ppm from solvent reference peak at 34.6 ppm) displays a resonance at 163.9 ppm [$^1J(^{117/119}Sn-^{13}C)$ = 9.2 Hz] which is assigned to the stannacyclopropene carbon atoms.[4] In addition, a $^{119}Sn\{^1H\}$ NMR (112 MHz, −25 °C, methylcyclohexane-d_{14}) δ (ppm from Me_4Sn, negative for upfield) shows a single resonance at −536.8 ppm which is more than 100 ppm upfield from the chemical shifts of the highly strained cyclotristannanes.[5] IR (Nujol) and Raman (solid, −60 °C) data show $\nu_{C=C}$ at 1587 cm^{-1} which first decreases in the IR and then disappears within 5 min after exposure to air.

Crystallographic Analysis of **3**.[4] As shown in Figure 1, the stannacyclopropene ring system of **3** forms an isosceles triangle with $Sn-C_{sp^2}$ bond lengths of 2.136 (5) and 2.134 (4) Å, respectively, which are comparable in length to $Sn-C_{sp^2}$ bond distances found in acyclic systems.[6] The C_1-C_2 bond length of 1.340 (6) Å is in agreement with the value found for the $C_{sp^2}-C_{sp^2}$ bond length in the analogous germacyclopropene derivative,[1e] while the exocyclic Sn–C bond lengths of 2.172 (4) Å and 2.181 (3) Å, respectively, are shorter than those found in tetrakis[bis(trimethylsilyl)methyl]distannene, **4** [2.207 (5) – 2.225 (6) Å].[2] Due to the absence of any close intermolecular distances between tin and sulfur, the difference in bond lengths between $S-C_4$ (1.849 (8) Å) and $S-C_5$ (1.776 (7) Å) may arise from crystal packing interactions.

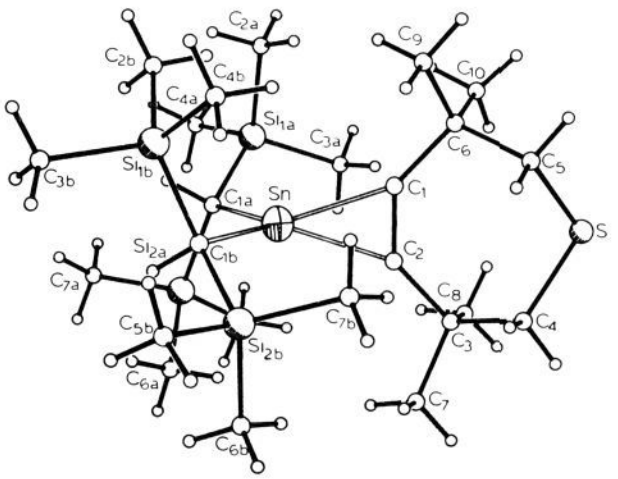
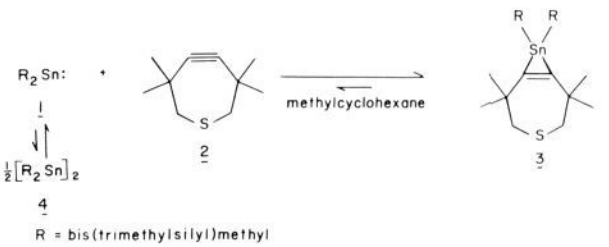


Figure 1. Crystal structure of **3**: bond lengths (Å) $Sn-C_1$ 2.136 (5), $Sn-C_2$ 2.134 (4), $Sn-C_{1a}$ 2.172 (4), $Sn-C_{1b}$ 2.181 (3), C_1-C_2 1.340 (6), C_4-S 1.849 (8), C_5-S 1.776 (7); bond angles (deg) C_1SnC_2 36.6 (2), SnC_1C_2 71.6 (3), SnC_2C_1 71.8 (3), C_1SnC_{1a} 124.0 (1), C_1SnC_{1b} 121.8 (2), C_2SnC_{1a} 121.6 (1), C_2SnC_{1b} 124.6 (1), $C_{1a}SnC_{1b}$ 110.1 (2).

Scheme I



Properties of **3**. Besides being air- and moisture-sensitive in the solid state, **3**, in solution, is in rapid equilibrium above −16 °C with **1** (and presumably, to some extent, with **4**) and the free acetylene **2**.[7] Both the $^{119}Sn\{^1H\}$ NMR and $^{13}C\{^1H\}$ NMR of **3** show temperature dependency, with no resonance for the C_{sp^2} atoms being observed at 20 °C in the latter. Upon the addition of 1.3 equiv of **2** to a solution of **3** (c = 0.069 M, methylcyclohexane), a dynamic exchange between free and complexed acetylene is observed by ^1H NMR at 20 °C (the coalescence

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(3) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189.

(4) Detailed information is supplied in the Supplementary Material.

(5) Cf. (a) δ −416.5 for hexakis(2,6-diethylphenyl)cyclotristannane [Masamune, S.; Sita, L. R.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 630] and (b) δ −378.9 for hexakis(2,4,6-triisopropylphenyl)cyclotristannane [Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390].

(6) Cf. (a) 2.15 (4) Å for triphenylvinyltin [Theobald, F.; Trimaille, B. *J. Organomet. Chem.* **1984**, *267*, 143] and (b) 2.08 (3) Å for 1,1,1-trichloroacetatotrivinyltin [Calogero, S.; Clmente, D. A.; Peruzzo, V.; Tagliavini, G. *J. Chem. Soc., Dalton Trans.* **1979**, *7*, 1172].

(7) This behavior is reminiscent of the thermal equilibrium reported between a cyclotristannane and a distannene, see ref 5b.

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