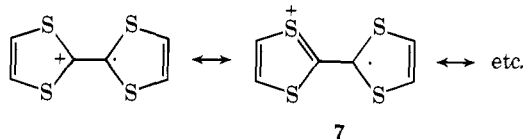
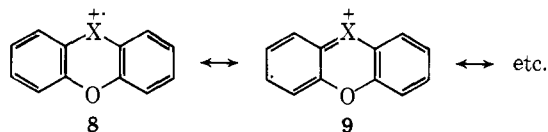


While selenium does possess a lower ionization energy than sulfur (10.4 vs. 9.8 eV),<sup>14</sup> it also forms much weaker  $\pi$ -bonds to carbon (e.g., C=S  $\pi$ -bond strength, 3.00 eV vs. C=Se, 2.15 eV).<sup>15</sup> It is the balance between these two opposing factors which may be responsible for the different trends in ionization energy observed on replacing sulfur with selenium in these heteroaromatic systems. The low ionization energy in the TTF system probably derives from its ability to distribute charge on all four sulfurs by  $\pi$ -bonding to carbon as illustrated by resonance structure 7. In



TSeF and DSeDTF radical cations, selenium should enter less effectively into such  $\pi$ -bonding, resulting in a less stable cation which raises the energy required for ionizing the neutral compound. In compounds such as 5 and 6, the ability of the heteroatom to stabilize charge is probably of greater importance than  $\pi$ -bonding to carbon, since such bonding would result in a loss of resonance stabilization (e.g., 8 contributes more than resonance forms such as 9).



Low ionization potentials have long been considered one of the key criteria in judging the ability of a donor molecule to form metallic-like charge transfer salts.<sup>8,9,16,17</sup> The present results suggest that for a given class of donors, in the absence of other mitigating factors such as steric effects, small increases in ionization energy as a function of substitution need not adversely effect the formation of highly conducting solids. More importantly, we feel that the unexpected increase of ionization energy in going from sulfur to selenium in TTF may be reflecting important differences in the character of the highest occupied molecular orbitals<sup>18</sup> for these systems. These differences could lead to changes in cation charge and spin density distribution, molecular polarizability, electron affinity, etc., which may be central to an understanding of the improved metallic-like properties of TSeF-TCNQ over TTF-TCNQ. We are currently studying these properties to further illuminate the relationship between molecular structure and solid state properties in these materials.

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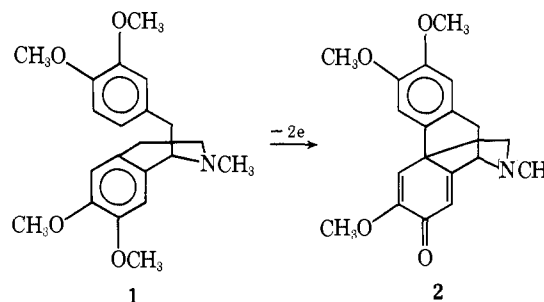
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#### Anchimeric Assistance to the Anodic Annellation of Alkaloids

Sir:

We have previously reported that laudanosine (1) and various derivatives can be cyclized<sup>1,2</sup> by oxidation at platinum in acetonitrile at potentials near 1.1 V.<sup>3</sup> A number of coupling reactions of this type have now been observed in both simple<sup>4</sup> and complex<sup>5-7</sup> methoxybiphenyls. It has been generally proposed that the mechanism involves electron transfer from an aromatic moiety and coupling of a cation radical or dication. The present study demonstrates that at low potentials (0.5 V) the amine functionality is intimately involved in the coupling reaction of 1.



Cyclic voltammetry was performed using acetonitrile solvent, 0.1 M lithium perchlorate electrolyte, and a platinum working electrode. Data are collected in Table I. The feature of interest in the voltammogram of 1 is a broad anodic peak with  $E_p = 0.55$  V. This peak is also present if a glassy carbon ( $E_p = 0.45$ ) or gold ( $E_p = 0.5$ ) electrode is employed or if tetraethylammonium fluoroborate electrolyte ( $E_p = 0.55$ ) is used. As shown in Table I, model amines<sup>8</sup> ranging from triethylamine to tetrahydroisoquinolines all have a peak in the region 0.5-0.7 V. The quaternized alkaloid (3) and the protonated alkaloid (4) do not, however, have a peak in this region. It is therefore concluded that ini-

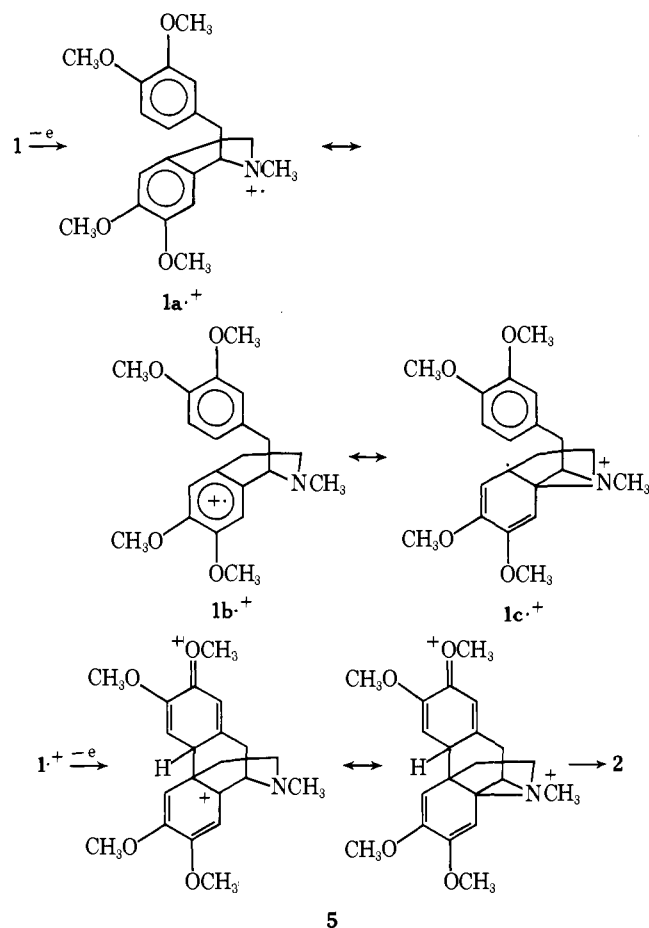
tial electron transfer from **1** at 0.5 V involves the amine moiety.

The data in Table I demonstrate further that methoxybenzyl model compounds<sup>4,5</sup> oxidize between 0.9 and 1.1 V and to a first approximation this can be assigned to loss of an electron from the HOMO of a dimethoxy alkyl aromatic moiety.

Although it seems clear from the above data that the amine function is being initially oxidized at 0.5 V, a preparative oxidation at that potential produces **2** from **1** in the same current and material yield (50–60%) as found at 1.1 V. This is also true for a number of derivatives of **1**. Quaternary salt (**3**), however, shows only background current at 0.6 V. Thus, coupling of the aromatic rings can be accomplished at potentials 400–500 mV less positive than those needed for coupling in the absence of the amine functionality. In terms of energy this amounts to 9 kcal/mol.

We propose that the amine function anchimerically assists coupling. This can be conceptualized either as an electrophilic attack on the isoquinoline aromatic ring by the aminium ion or homoconjugation between the amine and aromatic. If one considers an aminium ion (**1a<sup>+</sup>**) formed by oxidation of **1**, it is clear that homoconjugation is not only feasible but probable.<sup>9</sup> This delocalization of charge will activate the aromatic ring toward coupling.

The argument can be formalized with the following scheme.



It is of interest to note that if the amine and aromatic were to interact in a  $\sigma$  sense, this could place the pendent benzyl group in exactly the correct position for coupling to form **5**.<sup>10</sup>

There are a number of facets of the mechanism which remain unelucidated, including possible surface effects and the timing of electron transfer and chemical steps. Other intermediates involving amine–aromatic bonding are feasible

Table I. Peak Potentials from Cyclic Voltammograms<sup>a</sup>

Compound	$E_p$ (V) <sup>b</sup>
Laudanosine ( <b>1</b> )	0.55, 1.13
6'-Chlorolaudanosine	0.50, 1.25
Norlaudanosine	0.70, 1.07
<i>N</i> -Methyl-6,7-dimethoxytetrahydroisoquinoline	0.70, 1.30
<i>N</i> -Methyltetrahydroisoquinoline	0.70
Triethylamine	0.65
<i>N</i> -Methyllaudanosine perchlorate ( <b>3</b> )	1.13
Laudanosine hydroperchlorate ( <b>4</b> )	1.07
2-Methyl-4,5-dimethoxybibenzyl	0.87 <sup>d</sup>
2-Methyl-3',4,4',5-tetramethoxybibenzyl	0.90, 1.17 <sup>d</sup>
4,5-Dimethylveratrole	0.90 <sup>c,d</sup>
4,4'-Dimethoxybibenzyl	1.32 <sup>e</sup>
3,3',4,4'-Tetramethoxybibenzyl	0.93 <sup>e</sup>

<sup>a</sup>Pt anode, CH<sub>3</sub>CN, 0.1 M LiClO<sub>4</sub>, Scan rate is 0.5 V/sec. Values are obtained on first scan from 0.0 to 1.4 V. Substrate concentration is  $\sim 10^{-3}$  M. <sup>b</sup>All voltammograms showed no cathodic peak corresponding to reversible reduction of a cation radical except where noted. <sup>c</sup>Reversible. <sup>d</sup>Reference 5. <sup>e</sup>Reference 4.

and could be involved if rearrangements intercede.<sup>5</sup> The above hypothesis does, however, explain all the pertinent data and resolves several unexplained phenomena of synthetic interest in this system.<sup>1,2,11,12</sup>

The relevance of amine–aromatic interactions to biosynthetic pathways involving benzyltetrahydroisoquinolines, the chemical and electrochemical oxidations of related alkaloids,<sup>13</sup> and the anodic chemistry of benzylamines<sup>14</sup> remain to be evaluated, but should be considered.

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