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Spectroelectrochemistry of Aromatic Ligands and Their Derivatives. 1. Reduction Products of 4,4′-Bipyridine, 2,2′-Bipyridine, 2,2′-Bipyrimidine, and Some Quaternized Derivatives[1]

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Cathodic reductions and reduction products of 4,4′-bipyridine (I), *N*-methyl-4,4′-bipyridinium$^+$ (monoquat; II), *N*,*N*′-dimethyl-4,4′-bipyridinium^{2+} (paraquat; III), 2,2′-bipyridine (IV), 4,4′-dimethyl-2,2′-bipyridine (V), the ethylene-bridged diquaternized derivative 6,7-dihydrodipyrido[1,2-*a*:2,1-*c*]pyrazinedium^{2+} (diquat; VI), unbridged diquaternized *N*,*N*′-dimethyl-2,2′-bipyridinium^{2+} (VII), and 2,2′-bipyrimidine (VIII) have been investigated by cyclic voltammetry and spectroelectrochemistry. As expected, quaternization and the incorporation of added nitrogens in the ring both lead to easier reductions. The radicals formed by one-electron reduction of I–IV show very similar spectra, assignable in terms of a simple Hückel molecular orbital scheme. Thus, N-methylation lowers the energy of the LUMO in I but does not alter its nature. The same scheme, after allowing for loss of symmetry, correlates with established treatments of the reduction products of IV, which we have extended to VI, VIII, and the related reduced species. In all cases studied, the reduction orbital is related to $\pi(7)$ of biphenyl, the transition $\pi(6) \rightarrow \pi(7)$ moves, where the rings can rotate, to lower energy on reduction, and bands in the near IR-visible region are observed and assigned to transitions from $\pi(7)$ to higher orbitals.

Introduction

The polarographic reduction of I has been studied extensively,[2] but we are aware of no spectroscopic studies of the electrochemically reduced species. Peaks have been tabulated for I^- reduced by, and ion paired with, alkali metals in tetrahydrofuran[3] and rather similar spectra, assigned to the N-hydrogenated neutral radical $I{\cdot}H^{\bullet}$, the conjugate acid of I^-, observed as transients by pulse radiolysis of I in water.[4] The closely related species III is an important herbicide (paraquat) and redox indicator (methylviologen), and has been used as an electron relay in photochemical electron-transfer processes;[5] the spectrum of the singly reduced species has been described in this context without assignment.[2e] The electrochemical reductions of IV and V have been described.[2] The electronic spectra of IV^- and IV^{2-}, as their lithium salts in tetrahydrofuran, have been reported and detailed assignments given,[6] using a full SCF treatment that acts as a check on the much simpler theoretical methods used here. VI is the herbicide diquat, and III and IV have been reviewed at length in this context.[2k] We show here that published spectra attributed[7] to VI^- are in fact due to VI^{2-}, thus displaying the advantages of in situ spectroelectrochemistry as a technique. While a number of complexes of VIII have been studied electrochemically,[8] we are aware of no such studies on VIII itself, and no reports of the properties of its reduction product. As part of our studies of bipyridine derivatives[9] and complexes related to N-methylated bipyridines,[1] we have compared the reductive electrochemistry and spectroelectrochemistry of all these species.

Experimental Section

I, IV, and V (Aldrich) and the perchlorate salts of III and VI (BDH) were used as supplied without further purification. VI as iodide was prepared from IV by the method of Homer and Tomlinson.[10] II as iodide was prepared from I as described in ref 2i. III and VII as iodides were obtained by the reaction of I and IV respectively with excess refluxing iodomethane for 8 h. Water (distilled) was boiled to remove oxygen and allowed to cool under a steam of argon. VIII was prepared by a typical reverse diazotization reaction, using the procedure of Bly and Mellon,[11] but using refluxing NaOH, rather than KCN, to decompose the intermediate Cu(I) complex. Spectrol grade dimethylformamide (DMF) as purchased from BDH was stored over molecular sieves. HPLC grade acetonitrile was purchased from Rathburn Chemicals and purified as described by Winfield.[12] Tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) was prepared from the aqueous acid and hydroxide, recrystallized twice from ethyl acetate/pentane, and washed repeatedly with water. Spectra were collected on a Perkin-Elmer Lambda 9 spectrophotometer. Cyclic voltammetry was performed under argon in a Metrohm cell equipped with the cross-section of a 0.1-mm diameter platinum wire as working electrode and a 5-mm length of similar platinum wire as counter electrode, using a PAR 173 potentiostat and 175 signal generator with provision (PAR 170) for IR compensation, results being recorded on a JJ X-Y recorder, Model P 151. (The same potentiostat was then used for controlled potential electrolysis in

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Table I. Reduction Potentials of Some Free and Quaternized Bipyridines[a]

compds	$E_{red}^{(0/-1)}$	$E_{red}^{(-1/-2)}$
I	−2.394 (0.069)[b]	−2.875 (irr)[c]
II	−1.248 (0.065)	−1.756 (irr)
III	−0.580 (0.065)	−0.956 (0.076)
IV	−2.563 (0.074)	−3.198 (0.116)
V	−2.786 (0.074)	
VI	−0.639 (0.064)	−1.050 (0.074)
VII	−0.900 (0.125,inc)[d,e]	
VIII	−2.422 (0.063)	−2.939 (0.073)
III	−0.342 (0.065)[f,g]	−0.722[f,g] (0.076)
	−0.272 (0.039)[d,f,h]	

[a] Data by cyclic voltammetry, potentials in volts vs ferrocene/ferrocenium$^+$ in stated solvents at 25 °C. Measurements taken vs Ag/0.01 M $AgNO_3$–0.09 M $TBABF_4$ in stated solvent except when stated otherwise, but referred to ferrocene/ferrocenium$^+$/0.1 M $TBABF_4$ in solvent/cell combination used. [b] $E_{pa}-E_{pc}$ (V). [c] Denotes (chemically) irreversible redox processes with peak potential given (scan rate 200 mV s^{-1}). [d] Two-electron reduction process (after ref 21). [e] Denotes incomplete chemical reversibility (scan rate 200 mV s^{-1}). [f] Solvent: water–KNO_3/KOH solution (0.1 M/0.005 M) V vs SCE at 25 °C. [g] Concentration 0.005 M. [h] Concentration 0.05 M.

the spectroelectrochemistry experiments.) For both types of experiment, the reference electrode was a silver wire in contact with a solution in the appropriate solvent of 0.09 M $TBABF_4$ and 0.01 M $AgNO_3$, connected through a porous Vycor frit to a solution of 0.1 M $TBABF_4$ and hence through a second frit to the solution at a point close to the working electrode. The reference electrode was protected from light and regularly inspected and tested against the ferrocene/ferrocenium$^+$ couple. All measured reduction potentials are referred to the ferrocene/ferrocenium$^+$ potential obtained under identical conditions. Solutions were typically 0.005 M for cyclic voltammetry and 0.001 M for spectroelectrochemistry, and 0.1 M $TBABF_4$ was used as supporting electrolyte, except where stated otherwise. Scan rates were varied from 20 to 200 mV s^{-1}, causing apparent peak positions to vary by at most 10 mV; effects on mean peak positions were negligible. Controlled potential reduction for spectroelectrochemistry was carried out in a special 1-mm path quartz cell with platinum gauze working electrode, as described previously.[1,9,13] (The short path length helps to ensure quantitative electrolysis of the interrogated material and to reduce gross convective mixing with material in the barrel of the cell). Applied potentials were nominally around 100 mV more negative than the mean of CV forward and return waves, thus ensuring approximately 98% conversion of all the material in the optical pathlength. Essential features of the experiment are that the working electrode covers the area sampled by the light beam, that the counterelectrode compartment is isolated by a porous Vycor frit from the main body of the solution, that satisfactory isosbestic points are obtained, and that the starting spectrum can be convincingly regenerated by reversal of the electrolysis. We have found that the lack of any one of these features, even in experiments conducted by experienced and reliable workers, can lead to spurious results. In our hands, the initial current falls away over several minutes as the material in the light path is electrolyzed, but a small residual current (less than 1% of initial value) remains due to diffusion of material from the barrel of the cell toward the working electrode. All species except VII, which showed some electrochemical irreversibility, were subjected to this procedure.

Results and Discussion

The perchlorate salt of III was insoluble in DMF and was therefore examined in water, using 0.005 M KOH (to increase the solvent window before onset of hydrogen evolution) + 0.1 M KNO_3 as supporting electrolyte. All other materials were examined in DMF. The observed potentials are collected in Table I.

Table II. Main Bands of Reduced Species in DMF–$TBABF_4$ Solution at 25 °C (λ nm (ν 1000 cm^{-1}) (ε × 10^{-3} dm^3 mol^{-1} cm^{-1}))

compd	$\pi(6) \rightarrow \pi(7)$	$\pi(7) \rightarrow \pi(10)$	$\pi(7) \rightarrow \pi(8,9)$
I^-	393 (25.5) (19.2)	595 (15.4) (5.8)	954 (10.5) (2.6)
II^-	365 (27.4) (17.8)	545 (18.4) (5.5)	780 (12.8) (1.9)
$(II)_2^{2-}$	368 (27.2) (15.0)	551 (18.2) (4.2)	800 (12.5) (2.3[a])
III^-	395 (25.3) (17.8)	601 (16.6) (5.5)	909 (11.0) (2.1)
III^{2-}		395 (25.3)[b] (18.3)	
IV^-	397 (25.2) (19.1)	582 (17.2) (6.1)	882 (11.3) (2.6)
V^-	384 (26.0) (19.3)	571 (17.5) (6.2)	863 (11.6) (2.5)
VI^-	313 (31.9) (11.7)	425 (23.5) (6.1)	815 (12.3) (2.8)
VI^{2-}	394 (25.4)[b] (17.0)		
$VIII^-$	361 (27.7) (20.5)	500 (20.0) (6.5)	800 (12.5) (1.8)
$(VIII)_2^{2-}$	357 (28.0) (19.5); 416 (24.0) (23.5)	463 (21.6) (4.5)	790 (12.7) (2.7)

[a] Very broad. [b] Not determined.

In general, the materials examined show two accessible reductions, the first being chemically and electrochemically reversible. Methyl substitution caused a shift to more cathodic potentials, as expected, and (presumably for this reason) the second reduction of V was not observed. In VII, the one-electron reduction product decomposed on a time scale of seconds; this instability is not shown by III^-, and we tentatively attribute it to a combination of steric and electronic effects, such as crowding in planar VII^- and benzylic stabilization of hydrogen loss products. The reduction of I is some 150 mV easier than that of IV, consistent with the simple theoretical treatment discussed in the following text, according to which the electron density in the reduction orbital is higher para than ortho to the ring–ring bond. Both reductions of VIII occur at less negative potential than in IV, no doubt because of the presence of additional nitrogens in place of carbon.

The electronic spectra of representative reduced species are shown in Figure 1; the others are available as supplementary material. Band energies and assignments are collected in Table II. The assignments of Table II are based on a simple Hückel treatment in which overlap is ignored and energies expressed in terms of parameter β and $\alpha(N)$, where β represents a resonance term (taken as equal for all nearest neighbor π-interactions) and $\alpha(N)$ the extra Coulomb term at nitrogen due to its higher electronegativity. Implicit in this treatment is the assumption that the rings are coplanar. This is more likely to hold good for the anions (in which $\pi(7)$ is populated) than for the parents, in which dihedral angles of up to 40° are known.[14] One major theoretical simplification arises for the singly reduced species; since they consist of a closed shell to which one electron[15] has been added, the transition energies can be treated to a good approximation as one-electron energy differences. Our assignments are related to those of König and Kremer[6] for the 2,2′-bipyridyl radical anion, with the exception that for I, III, and VIII (and to a good approximation II) our case is conceptually simpler, and the selection rules more rigid, because of the higher symmetry. The lowering in energy of $\pi(6) \rightarrow \pi(7)$ on going from the parent to the anion may be attributed in part to a reduction in dihedral angle, which would raise $\pi(6)$ and lower $\pi(7)$ simultaneously; however, this is not a complete explanation, since III and VI are planar species and a similar lowering of frequency on reduction occurs[9] in coordinated IV. In the neutral ligand, the lowest transition is $\pi(6) \rightarrow \pi(7)$, in the range 260–300 nm. This transition still occurs in the reduced species, in which $\pi(7)$ is half-full,

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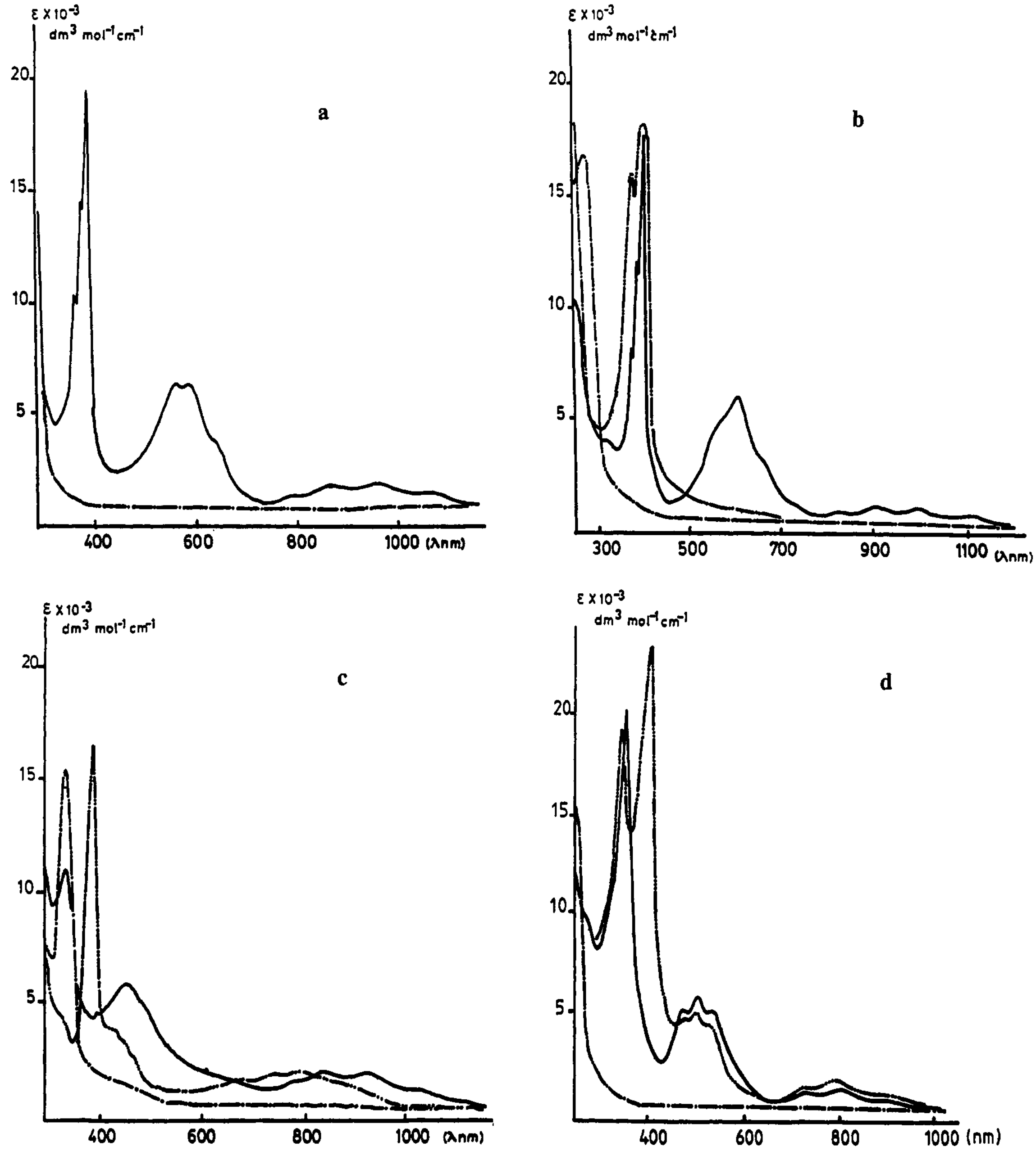

Figure 1. Electronic absorption spectra of some free and quaternized bipyridines in DMF–TBABF$_4$ at 25 °C. Key: (a) 4,4′-bipyridine (I), (b) *N,N*′-dimethyl-4,4′-bipyridinium^{2+} (monomer, III), (c) 6,7-dihydrodipyrido[1,2-*a*;2,1-*c*]pyrazinedium^{2+} (VI), (d) 2,2′-bipyrimidine (VIII); −·− parent, — singly reduced species, −··− doubly reduced species, −···− dimer.

but lower energy transitions from π(7) to π(8–11) are now possible.

4,4′-Bipyridine Derivatives. These are strong resemblances between the spectra reported by Kalyanaraman, Rao, and George for alkali metal reduction of I[3], the transient spectra found by Simic and Ebert[4] under pulse radiolysis of I in water at pH 3.7 or 7, and our spectra for singly reduced I–III. The main difference is that we observe the relatively weak π(7) → π(9), which correlates with transitions symmetry-allowed in planar biphenyl but not in benzene. As required by D_{2h} symmetry, however, π(7) → π(8) is very weak or absent. We infer that, as required by our simple theory, the relative energies of π(6), π(7), and π(10) are insensitive to the effective electronegativity of nitrogen. All these spectra can be accommodated by the same molecular orbital scheme, with N-methylation lowering the energies of the LUMO and near-LUMO orbitals without changing their nature. The spectra of the 4,4′-bipyridyl anion and its N-protonated conjugate acid should also be very similar, thus accounting for the insensitivity[4] of Simic and Ebert's pulse radiolysis results to pH.

In the singly reduced species, the absorption assigned to π(6) → π(7) shows vibrational structure, with a spacing around 1000 cm^{-1}, which we attribute to ortho C–H bending modes. The general shift of π(6) → π(7) to lower energy on reduction is consistent with the onset of coplanarity, although the use of a one-electron model for the parent is questionable. π(7) → π(10) shows a more regular progression at around 1380 cm^{-1}, consistent with a transition whose main effect is to weaken the interring bond. There is good experimental evidence[16] for the sensitivity

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of this bond to the degree of population of $\pi(7)$. Similar vibrational structure is found in $\pi(7) \rightarrow \pi(9)$. The vibrational progressions in II$^-$ are generally less well-developed than those in the other species discussed. The main structural difference between II and these other species that II has two different kinds of ring, which would perhaps account for the poorer resolution of the vibrational structure, but the reason for the decreased width of $\pi(7) \rightarrow \pi(10)$ in II$^-$ is not obvious. The spectrum of III^{2-} is less easily understood, since the species is no longer aromatic and the transition are from closed-shell to open-shell configurations, but the strong peak observed is provisionally assigned as $\pi(7) \rightarrow \pi(10)$, now shifted to higher energy by the full double bond connecting the rings in the ground state. The weakness of $\pi(7) \rightarrow \pi(9)$ in the doubly reduced species can be understood by inspection of the form of this transition. While symmetry-allowed, local transition moments almost cancel, and it seems likely that in III$^-$ intensity is in fact borrowed from $\pi(5) \rightarrow \pi(7)$, which is of the same symmetry. In the doubly reduced species, of course, this transition is no longer available. The strong resemblance in position and intensity between the band we assign as $\pi(6) \rightarrow \pi(7)$ in III$^-$, and that we assign as $\pi(7) \rightarrow \pi(10)$ in III^{2-}, is a possible source of confusion and delayed on understanding of these spectra, but the excellent agreement of our present scheme with the very thorough calculations of König and Kremer[6] (see the following text) for IV and its reduction products gives us confidence in our present assignments.

2,2′-Bipyridyl and its derivatives can be understood using the closely related molecular orbital scheme of König and Kremer,[6] in which the selection rules are relaxed by loss of symmetry relative to the 4,4′-bipyridyl series. The absence of vibrational structure, and of a shift on reduction, in $\pi(6) \rightarrow \pi(7)$ of VI$^-$ may be due to the rigidity imposed by the bridge. This structure is also absent in VIII$^-$, as required by the proposed assignment to ortho C–H. The spectrum of VI^{2-} presents similar problems to that of III^{2-}, and a similar assignment is suggested. In both VI$^-$ and VIII$^-$, $\pi(7) \rightarrow \pi(10)$ shows a short progression with spacing around 1400 cm^{-1}, as expected for a transition that reduces the order of the interring carbon–carbon bond, but does not affect bonding within the rings. The somewhat longer spacing in $\pi(7) \rightarrow \pi(9)$ can then be related to the associated changes in intraring bonding.

Dimerization. Dimerization is known to occur in the one-electron reduction products of III$^-$ in water;[17] this no doubt explains the changes in the CV curve from one-electron reduction at 0.005 M to a more facile 2-electron reduction at 0.05 M, and we infer that the dimerization is fast on the time scale (a few seconds) of the CV sweep. In agreement with previous reports,[18] we also see a new band at 355 nm at concentrations of reduced III higher than 0.05 M. This we tentatively attribute to a transition related to the $\pi(6) \rightarrow \pi(7)$ transition in the monomeric species. The other dimer transitions also appear to correlate with bands in the monomers. The nature of the dimerized material is unknown, but it would seem that the interaction between the moieties is relative weak. We found no evidence of dimer formation in DMF at concentrations up to 0.1 M, and we attribute this difference to higher charge–charge repulsion in the less polar solvent.

At concentrations of VIII$^-$ in DMF higher than 0.003 M, as shown in Figure 1, a new band appears at 24 040 cm^{-1} (416 nm), similar to that reported for the dimer of III$^-$. This we attribute to a transition, presumably related to the $\pi(6) \rightarrow \pi(7)$ transition in the monomeric species, associated with dimer formation. If we take the molar extinction coefficient in the dimer to be about twice that of the corresponding monomer band, this would imply a formation constant of around 300 M^{-1}. This dimerization is without apparent effect on the electrochemistry of VIII in dilute (0.003 M) solution. However, 0.02 M solutions that have been maintained for 1 min at −2.422 V show their cathodic wave at −2.530 V, with anodic return wave at −2.494 V, consistent with the slow formation of a species that takes part in a 2-electron redox process. The behavior of II$^-$ in DMF is very similar.

Conclusions

Our results agree well with previous reports for III$^-$ and IV$^-$. For I$^-$, we suspect that the spectrum was correctly observed in pulse radiolysis, but understandably misassigned as an example of the spectrum of IH•, which, by analogy with II$^-$, should be extremely similar. A spectrum obtained by chemical reduction of VI has been generally attributed[7a] to VI$^-$; however, it is in fact identical with our spectrum for VI^{2-}. In view of this, we further validated our assignment of the spectra to the respective species by regenerating the true spectrum of VI$^-$ as an intermediate in the reoxidation of VI^{2-} to VI. Of course, our finding in no way vitiates analyses for VI based on colorimetry of this reduced species. The spectra of III^{2-} and VI^{2-} strongly resemble that published for IV^{2-},[6] thus making it possible to treat the entire series of reduced species within a single theoretical framework.

The spectroelectrochemistry of all the species described here can be assigned using the simplest possible Hückel treatment, described by Maier and Turner[14] for biphenyls. In this, MO's are constructed from in-phase and out-of-phase combinations of benzene-like orbitals. Neglecting overlap and nonneighbor interactions and assuming all resonance integrals β equal, we can calculate orbital energies as a function of c, the cosine of the ring–ring dihedral angle, and express the effects of substitution of C by the more electronegative N in terms of a parameter $\alpha(\mathrm{N})$. This procedure gives a set of first-order electron densities and orbital energies. For the singly reduced species, in which we have a single electron in addition to the full π-levels, we can directly calculate transition energies, while the symmetries and forms of the wavefunctions lead to predictions of relative intensities. These results are collected in the supplementary material. The reduction orbital is $\pi(7)$, the lowest π^* level. Prominent features of the predicted spectrum are $\pi(6) \rightarrow \pi(7)$, predicted at $-\beta(22c/3)$, and $\pi(7) \rightarrow \pi(10)$, predicted at $-2\beta c/3$, both being independent of α. In this model, alkylation lowers the energy of the frontier and near-frontier orbitals, but does not affect their nature, while both N-alkylation and changes in the position and extent of ring nitrogen incorporation are without effect on the relative spacings of $\pi(6)$, $\pi(7)$, and $\pi(10)$.

We now consider the data of Table II in more detail. With the exception of VI$^-$, all the monomeric singly reduced species show a very narrow range of values for $\pi(6) \rightarrow \pi(7)$, from 25 200 to 27 700, as predicted by our simple theory. This is remarkable; the energy of $\pi(7)$, as measured by reduction potentials, varies by 2.2 eV over the range of species studied, but the energy of this transition varies by only 0.3 eV. There seems little clear rationale to the observed small variations, so that closer scrutiny of the data may not at this level of theory be profitable. The same is even more true for the other transitions observed, where the observed maximum is quite clearly sensitive to

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the shape of the Franck–Condon envelopes.

Elementary theory is less successful in predicting the effects of geometrical constraint. In VI$^-$, $\pi(6) \rightarrow \pi(7)$ occurs at higher energy than in IV$^-$, consistent with the existence of a geometrical constraint that limits c by preventing the rings from becoming coplanar. However, such a constraint should have the effect of lowering the energy of $\pi(7) \rightarrow \pi(10)$, so that the sum of the energies of these two transitions remains constant. This is contrary to what is found.

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Supplementary Material Available: First-order electron densities, orbital energies, and one-electron transition energies in 2,2′-bipyridine and 4,4′-bipyridine and electronic absorption spectra of some additional bipyridines (7 pages). Ordering information is given on any current masthead page.

Cross-Interaction Constants as a Measure of the Transition-State Structure. 14. Nucleophilic Substitution Reactions of 1-Phenyl-2-propyl Benzenesulfonates with Anilines in Methanol

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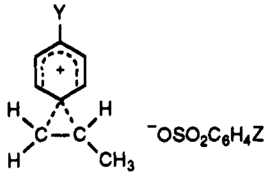
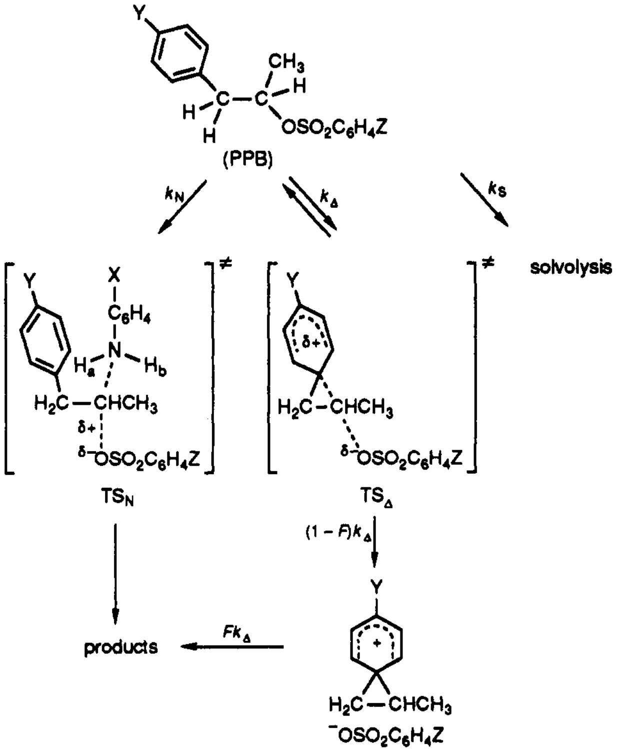
The kinetics of the reactions between 1-phenyl-2-propyl benzenesulfonates (PPB) and anilines in methanol at 65.0 °C are investigated, and the mechanism is discussed on the basis of various selectivity parameters, especially on the cross-interaction constants, ρ_{ij}. The aryl participation is significant only with the p-CH_3O-substituted substrate. ρ_{XZ} is positive, and accordingly the transition state (TS) variations with substituents are consistent with those predicted by the potential energy surface diagram. The TS is of an intermediate type between that for an associated (tight) and a dissociated (loose) S_N2 process; it is rather tight, but bond breaking is ahead of bond making with positive charge development at the reaction center in the TS. The possibility of front-side attack with a four-center TS is precluded because of strong steric hinderance in a close approach of the two bulky groups, the nucleophile and leaving group, on the same side in the front-side attack.

In a previous work,[1] we have shown that in the solvolysis of 1-phenyl-2-propyl benzenesulfonates (PPB) in methanol–acetonitrile mixtures the solvent-assisted path, k_S in Scheme I,[2,3] is more favored in the competition with the aryl-assisted path, k_Δ (for solvolysis, only these two paths are available), and the transition-state (TS) structure shifts toward that resembling the ion pair like intermediate,[4] I, as the solvent nucelophilicity decreases with the concomitant increase in the solvent polarity.[5] It was concluded that the aryl-assisted pathway prevails over the solvent-assisted path when the nucleophilicity of solvent[6] is low,



(I)

Scheme I



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