ESTIMATION OF MARCUS λ FOR p-PHENYLENEDIAMINES FROM THE OPTICAL SPECTRUM OF A DIMERIC DERIVATIVE

STEPHEN F. NELSEN* AND MARIA J. R. YUNTA†

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396, U.S.A.

The radical cation of N,N'-bis-(4-dimethylaminophenyl)pyridazine ($3^{\cdot+}$) has a near-IR band with a transition energy of $29 \cdot 7 \pm 0 \cdot 5$ kcal mol^{-1} (1 kcal = $4 \cdot 184$ kJ) in acetonitrile. This band is assigned to a Hush-type charge-transfer band, and the transition energy to the Marcus λ value for electron transfer. Such a large λ is inconsistent with previous estimates of λ for intermolecular electron transfer between mono-p-phenylenediamines and their radical cations. It agrees well with estimates of λ based on AM1 semi-empirical MO calculations, which gives the enthalpy contribution to λ_{in} at about 21 kcal mol^{-1} for $3^{\cdot+}$. It is suggested that the traditional method of estimating λ_{in} by summing bond displacements weighted by force constants produces values which are significantly too low for systems such as phenylenediamines, where pyramidalization changes are important. The results suggest that λ for tetramethyl-p-phenylenediamine self-electron transfer ($1^{0/\cdot+}$) has been significantly underestimated, and that this prototype organic electron transfer reaction is not as strongly diabatic as was previously concluded.

INTRODUCTION

Derivatives of p-phenylenediamine (PD) have played a premier role in radical cation chemistry.[1a] Wurster[1b] isolated the blue N,N,N',N'-tetramethyl-PD (1) salt and other derivatives in 1879. Weitz[1c] may have been the first to recognize their true nature, designating such salts 'kationradikale' in 1928. Electron transfer (ET) between neutral 1 and its own radical cation ($1^{0/\cdot+}$ self-ET) was the first organic case for which the rate constant k_{ex} was measured, by Weissman using NMR line broadening in 1954.[2] More recently, Grampp and Jaenicke (GJ) have made PD self-ET the most thoroughly investigated organic system by carrying out detailed ESR line-broadening measurements of k_{ex} over a range of temperatures and solvents for $1^{0/\cdot+}$ and several other derivatives.[3a–d] The reported activation parameters for $1^{0/\cdot+}$ in acetonitrile[3b] give $k_{ex}(25\,°C) =$

Me$_2$N—⟨O⟩—NMe$_2$

1

$1 \cdot 6 \times 10^9$ l mol^{-1} s^{-1} [$\Delta G^{\ddagger}(25\,°C) = 4 \cdot 9$ kcal mol^{-1} (1 kcal = $4 \cdot 184$ kJ)], approximately one order of magnitude below diffusion control. GJ have analyzed the solvent dependence of k_{ex} for PD derivatives using both classical[3a,b] and more contemporary[3c,d] ET theory,[4] and their most recent conclusion is that despite the large k_{ex} value and the large π surfaces available for overlap at the transition state, PD self-ET reactions are diabatic ('non-adiabatic'), their rate constants being strongly limited by poor electronic interaction at the transition state. This conclusion is principally based on theoretical estimations of the barrier for vertical ET λ, using various levels of theory to estimate both the solvent reorganization contribution, λ_{out}, and the internal geometry organization term, λ_{in}, which are added to give λ [see equation (1)], which in combination with other estimated parameters was used to calculate k_{ex}.[3d] Fawcett and Foss[3e] carried out a slightly different analysis of GJ's data using similar ET theory to that in Refs 3c and 3d, reaching similar conclusions.

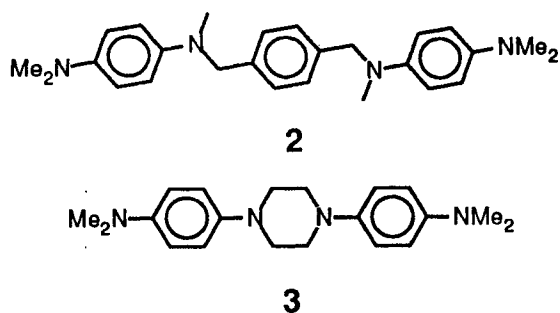$$\lambda = \lambda_{out} + \lambda_{in} \qquad (1)^{4,5}$$

A number of assumptions are involved in making theoretical estimates of λ, and it would clearly be

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* Author for correspondence.
† Present address: Universidad Comptulense de Madrid, Departamento de Quimica Organica I, Ciudad Universiteria, 28040 Madrid, Spain.

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desirable to have experimentally measured λ values for PD derivatives. In this work, we prepared and studied the bis-PD derivatives **2** and **3** in the hope of using the Hush method[5] to determine λ experimentally by observing the charge-transfer (CT) band corresponding to transferring an electron from one PD unit to the other in the radical cation form of these compounds. Hush introduced this method for intervalence transition metal complexes, which are compounds having two metal centers connected by a bridging ligand, with the metals in oxidation states which differ by one charge unit. The CT band transition energy E_{op} is equated with λ, which is widely accepted as being correct and has proven to be extremely useful in understanding ET reactions of inorganic and organometallic systems.[4,5]

RESULTS

Compound **2** was most usefully prepared by reductive bisalkylation of terephthalaldehyde (**4**) with N,N-dimethyl-p-phenylenediamine (**5**) and cyanoborohydride, followed by reductive bismethylation of the product (**6**) using formaldehyde and cyanoborohydride (Scheme 1), which produced higher yields in our hands than bisalkylating **4** with trimethyl-p-phenylenediamine (20% based on **5**, compared with 8% based on trimethyl-p-phenylenediamine, which is not commercially available).
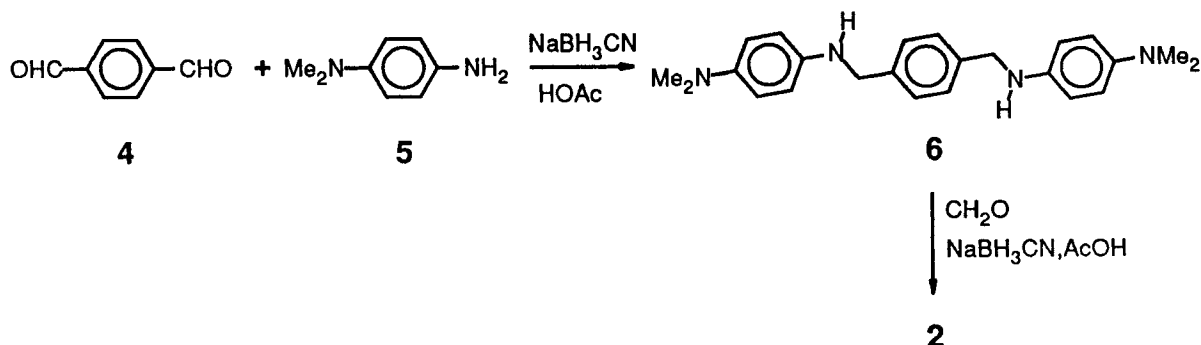
Compound **3** was prepared by refluxing a mixture of **5** with ethylene dibromide, followed by chromatography of the product mixture. Although the yield was only 5%, the simplicity of this procedure appears to us to make it more desirable than using multi-step sequences.

Cyclic voltammetric (CV) results for **1–3** in CH_3CN containing $0\cdot1$ M Bu_4NClO_4 are summarized in Table 1. The CV curves for both dimeric compounds show reversible oxidation waves at potentials near the first and second 1e oxidation waves of **1**,[6] consistent with the two PD units in **2** and **3** oxidizing nearly independently. Curves recorded in the presence of known amounts of ferrocene showed that two electrons are transferred at each wave for the dimeric compounds. If there were no interaction between the PD units, the statistical factor of two for removal of the first electron causes a $\Delta E°$ difference of $(2RT/F)\ln 2 = 35\cdot6$ mV,[7] and if the ET were completely electrochemically reversible, the CV curve would have the 59 mV peak separation of a monomeric PD derivative. The presence of the $PD^{\cdot+}$ unit in $2^{\cdot+}$ makes the removal of a second electron only slightly more difficult than the first, because the peak to peak separation is only slightly larger for **2** than for **1**. The difference in $E°$ for first and second electron removal from **3** is large enough that shoulders are observed on both oxidation waves. Simulations of CV curves for reversible and quasi-reversible

Table 1. Cyclic voltammetric data for **1–3**

	E_p^{av}(V) and ΔE_p (mV)[a]		
Compound	First waves(s)	Second waves(s)	ΔE_p^{av} (V)
1[b]	$0\cdot12$ (65) [1]	$0\cdot69$ (64) [1]	$0\cdot57$
2	$0\cdot14$ (78) {2}	$0\cdot75$ (70) [2]	$0\cdot61$
3	$0\cdot23$ (120) {2}	$0\cdot80$ (140) [2]	$0\cdot57$

[a] ΔE_p values in parentheses; the values in curly brackets are the number of electrons transferred.
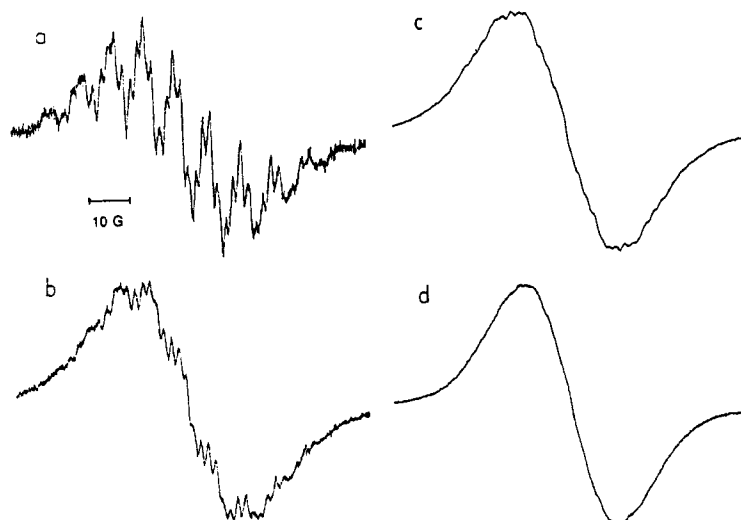[b] Data taken from Ref. 6.

Scheme 1

Figure 1. ESR spectra of $3^{\cdot+}$ generated by $NO^+PF_6^-$ oxidation in methylene chloride: (a) 200 K; (b) 220 K; (c) 240 K; (d) 280 K

systems show that the observed peak-to-peak separation for the first two oxidations of **2** (which has the closest charge-bearing nitrogens separated by seven σ bonds) correspond to about a 52 mV difference in E° or $0 \cdot 4$ kcal mol^{-1} greater than the statistically imposed difference, whereas that for **3** (having a three σ bond separation) corresponds to about 86 mV, or a $1 \cdot 2$ kcal mol^{-1} more difficult second electron removal than the first, also corrected for the statistical effect. It appears from these data that the radical cations from **2** and **3** are effectively localized in one PD unit, and that these compounds should be candidates for a Hush-type treatment if CT bands can be observed.

In contrast to $1^{\cdot+}$, neither dimeric PD derivative gives a radical cation stable enough to allow isolation. Drastic shortening of lifetimes for dimeric radical cations $M^{\cdot+}$—M^0 has been noted previously for bis-tetraalkylhydrazines.[8] Two $M^{\cdot+}$—M^0 species are nearly isoenergetic with $M^{\cdot+}$—$M^{\cdot+}$ and M^0—M^0, because ΔE° for the first two electron transfers is small, and intermolecular ET will produce these species in solution. The short lifetime for $M^{\cdot+}$—M^0 was attributed to endothermic intramolecular ET within $M^{\cdot+}$—$M^{\cdot+}$, producing M^{2+}—M^0, which undergoes rapid intramolecular proton transfer.[8] The species $3^{\cdot+}$ decomposes noticeably more rapidly than $2^{\cdot+}$ in solution, which is not surprising because the hydrazine analogue, 1,4-bisdimethylaminopyridazine, is short-lived even on the CV time scale at 1 V s^{-1} scan rates. The radical cations of **1–3** for these studies were generated by reaction of the neutral compounds with one equivalent of NO^+ PF_6^- or $(4\text{-}BrC_6H_4)_3N^{\cdot+}$ $SbCl_6^-$, and even $3^{\cdot+}$ proved sufficiently long-lived in solution to allow recording of spectra at room temperature. The ESR

spectra of both $2^{\cdot+}$ and $3^{\cdot+}$ show complex and ill-resolved hyperfine structure at low temperature, which we have not been able to analyze to extract splitting constants. In contrast to the spectrum of $2^{\cdot+}$, that of $3^{\cdot+}$ broadens greatly as the temperature is raised, blurring out the hyperfine structure (see Figure 1). This behavior is what we would expect for localization of charge on one PD unit of $3^{\cdot+}$, and ET becoming rapid enough to exhibit dynamic broadening near room temperature, but we have not quantitatively analyzed these complex spectra.

The UV–visible spectra of $1^{\cdot+}$, $2^{\cdot+}$ and $3^{\cdot+}$ are very similar, as shown in Table 2 (for the optical spectrum of 1^+ ClO_4^- in another solvent, see Ref. 9). This is consistent with the charge being instantaneously localized in one PD unit for both bis-PD compounds. No absorption was detected at longer wavelength for either $1^{\cdot+}$ or $2^{\cdot+}$. In contrast, $3^{\cdot+}$ shows absorption with a maximum in the range 945–980 nm in acetonitrile (see Figure 2). The results of three independent runs in acetonitrile at room temperature can be summarized as follows: (a) $(4\text{-}BrC_6H_4)_3N^{\cdot+}$ $SbCl_6^-$ oxidant, $\nu_{max} = 10 \cdot 46$ kK ($\lambda_{max} = 956$ nm), $\nu_{1/2} = 1 \cdot 5$ kK, ε_{min} 140 l mol^{-1} cm^{-1}; (b) NO^+ PF_6^- oxidant,

Table 2. UV–visible spectral data for $1^{\cdot+}$–$3^{\cdot+}$ in acetonitrile

Compound	λ_{max} (nm) (relative intensity, %)[a]
$1^{\cdot+}$	614 (0·61), 566 (0·61), 328 (1·00)
$2^{\cdot+}$	614 (0·63), 566 (0·62), 328 (1·00)
$3^{\cdot+}$	616 (0·33), 564 (0·30), 334 (1·00)

[a] In parentheses.
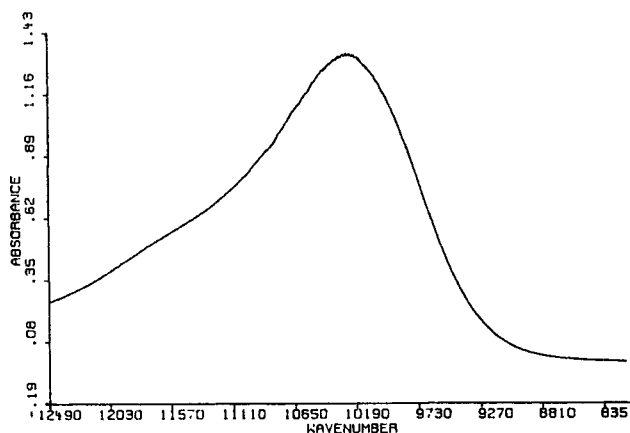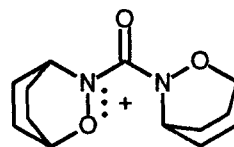
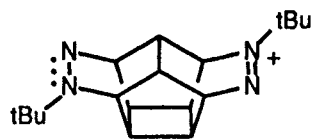Figure 2. Near-IR spectrum of $3^{\cdot+}$ obtained by $NO^+PF_6^-$ oxidation in acetonitrile with an Si detector

$\nu_{max} = 10 \cdot 21$ kK $\quad (\lambda_{max} = 980$ nm), $\quad \nu_{1/2} = 1 \cdot 6$ kK, ε_{min} 57 $1\,mol^{-1}cm^{-1}$; (c) NO^+ PF_6^- oxidant, $\nu_{max} = 10 \cdot 57$ kK $(\lambda_{max} = 946$ nm), $\nu_{1/2} = 2 \cdot 4$ kK, ε_{min} 26 $1\,mol^{-1}cm^{-1}$ ($\nu_{1/2}$ is the full band width at half-height, and ε_{min} is calculated assuming a 100% yield of $3^{\cdot+}$ based on the amount of oxidant used). Radical cation instability and hence low and decreasing intensity and non-linearity of the detector response in this region were definite problems in obtaining very reproducible data for this band. Even less stability was found for $3^{\cdot+}$ in less polar solvents, and precluded studying the solvent effect on the near-IR absorption under our conditions.
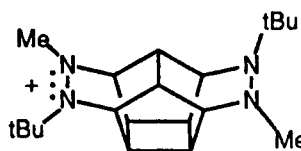
DISCUSSION

The near-IR absorption of $3^{\cdot+}$ is caused by the presence of the second, unoxidized PD unit in this molecule. We attribute the absorption maximum observed in the range 946–980 nm to a Hush-type charge-transfer band corresponding to a transition energy $E_{op} = \lambda$ of $10 \cdot 21 - 10 \cdot 57$ kK $= 29 \cdot 7 + 0 \cdot 5$ kcal mol^{-1}. In retrospect, we do not find it particularly surprising that a corresponding band was not observed for the bis(PD) compound $2^{\cdot+}$. Hush pointed out that the intensity of an intramolecular CT band is proportional to the square root of the electronic coupling matrix element (called V, H_{ab} or J in various theoretical treatments).[5] The distance between the PD units is much smaller for $3^{\cdot+}$, where the closest N atoms are separated by three σ bonds, than for $2^{\cdot+}$, where they are separated by seven σ bonds. For examples of the sharp decrease in CT band intensity as the number of linking σ bonds increases, see the work of Oevering et al.[10] on CT bands for dimethoxynaphthalene linked to 7-methylenenorbornane derivatives. Further, the piperi-

dine ring linkage of $3^{\cdot+}$ holds the nitrogen lone pairs in relatively good geometry for electronic interaction through the σ bonds, while the p-xylylene linkage of $2^{\cdot+}$ does not enforce favorable σ bond alignment, which will further decrease V, and hence the CT band intensity, of $2^{\cdot+}$.[11]

A λ for $3^{\cdot+}$ of about $29 \cdot 7$ kcal mol^{-1} is far larger than GJ's theoretical analysis produced for $1^{0/\cdot+}$ and other PD derivatives. After extensive discussion justifying their choices, they employed $\lambda \approx 19$ kcal mol^{-1} for intermolecular ET between 1 and $1^{\cdot+}$ at 333 K in acetonitrile,[3d] which would correspond to an E_{op} of 1500 nm. Obviously, both λ_{out} and λ_{in} will differ for the intermolecular $1^{0/\cdot+}$ ET and the intramolecular $3^{\cdot+}$ ET reactions, but the PD units involved are similar enough that the theoretical estimate of for λ intermolecular $1^{0/\cdot+}$ ET does not agree well with the transition energy observed for $3^{\cdot+}$. We shall argue below that GJ seriously underestimated λ_{in} for $1^{0/\cdot+}$, and that the transition energy observed for $3^{\cdot+}$ is entirely consistent with our assignment of the near-IR band as a Hush-type CT band.

Three other types of dimeric N-centered radical cations for which optical bands we have attributed to Hush-type charge transfer are now available for comparison with $3^{\cdot+}$. Charge in the bis(hydroxylamine) $7^{\cdot+}$ is instantaneously localized on one hydroxylamine unit by the criteria of CV and low-temperature ESR, and it shows a near-IR band having a transition energy which is consistent with the barrier for ET between the

Table 3. Comparison of λ values estimated from CT band maxima for dimeric
nitrogen-centered radical cations

Compound	$\lambda(CH_3CN)$ (kcal mol^{-1})	$\lambda'(AM1)$ (kcal mol^{-1})	$\nu_{1/2}$ (kK)	$\nu_{1/2}(HTL)$ (kK)
$3^{\cdot+}$	$29 \cdot 7 \pm 0 \cdot 5$	$21 \cdot 1^a$	$1 \cdot 5 - 2 \cdot 4$	$4 \cdot 9$
$7^{\cdot+}$	$22 \cdot 9$	$-^b$	$1 \cdot 8$	$4 \cdot 3$
$8^{\cdot+}$	$23 \cdot 9$	$16 \cdot 8^c$	$6 \cdot 8$	$4 \cdot 4$
$9^{\cdot+}$	$52 \cdot 2$	$45 \cdot 0^c$	$6 \cdot 5$	$8 \cdot 3$

[a] See Table 4.
[b] AM1 calculations treat amide nitrogens so poorly that we do not believe calculations of λ'
inner for $7^{\cdot+}$ have any significance.
[c] From Ref. 13.

two hydroxylamine units measured by dynamic ESR[12]
[a value of intermolecular k_{ex} is not available for the *N*-
acylhydroxylamine charge-bearing system used in this
work, and a large twist about the N—C(=O) bond in
the neutral hydroxylamine unit accompanies electron
loss in this system, making the ET process rather differ-
ent than in intervalence complexes]. The bis(hydrazyl)
radical cation $8^{\cdot+}$ shows fast ET on the ESR time-scale
even at low temperature and bis(hydrazine) radical
cation $9^{\cdot+}$ slow ET even at high temperature, and
Hush theory analysis of their optical absorption bands
has been shown to work well for both classes of com-
pounds[13] (but see earlier comment). The observed tran-
sition energies for these four radical cations [labelled
$\lambda(CH_3CN)$] are compared in Table 3.

It has been traditional to use the Marcus equation:

$$\lambda_{out} = 332 \cdot 1 \ g(r, d)\gamma \qquad (2)$$

to estimate λ_{out}. The proportionality constant given is
that which produces λ_{out} in kcal mol^{-1} when the dis-
tance in $g(r, d)$ is in Å; $g(r, d)$ is a distance parameter

for which the simplest form for dimeric compounds in
which the ET 'monomer' units of radius r are held at
a distance d is $g(r, d) = 1/r - 1/d$. The parameter γ is a
solvent polarity parameter which depends only on the
bulk solvent properties refractive index, n, and static
dielectric constant, ε; $\gamma = 1/n^2 - 1/\varepsilon = 0 \cdot 528$ for ace-
tonitrile at room temperature. The 'monomer' units
connected to give $3^{\cdot+}$, $8^{\cdot+}$ and $9^{\cdot+}$ are not very
different in size; 1 is a $C_{10}N_2$ compound, and the 2-*tert*-
butyl-2,3-diazabicyclo[2.2.2]octane hydrazyl 'mono-
meric' unit of 8 is also $C_{10}N_2$ and the methylated
hydrazine unit of 9 is $C_{11}N_2$. We would not expect sub-
stantial differences in λ_{out} for compounds in this size
range. We have discussed probable sizes of
$\lambda_{out}(CH_3CN)$ for $8^{\cdot+}$, $9^{\cdot+}$ and sesquibicyclic hydra-
zines elsewhere,[13,14] concluding that $\lambda_{out}(CH_3CN)$
values near 10 kcal mol^{-1} are reasonable (the bands for
both $8^{\cdot+}$ and $9^{\cdot+}$ are nevertheless distinctly narrower
than predicted for organic systems with reasonable ν_{in}
values employing Hush's equations[11,13]). This is not far
from the *ca* $7 \cdot 1$ kcal mol^{-1} that GJ employed for $1^{0/\cdot+}$

Table 4. AM1-calculated structures

Species	Symmetry	ΔH_f (kcal mol^{-1})^a	Rel. ΔH_f (kcal mol^{-1})	CN twist angle (°)	$\lambda'_{in}{}^a$
1	C_i	$40 \cdot 44^b$	(0)	$\pm 36 \cdot 6$	$27 \cdot 3 \ (27 \cdot 7)$
1	C_1	$40 \cdot 60$	$0 \cdot 17$	$-3, -39$	$22 \cdot 9 \ (23 \cdot 8)$
1 (n^0)	$C_{2v}(syn)$	$41 \cdot 04$	$0 \cdot 61$	$0, 0$	$18 \cdot 7 \ (19 \cdot 6)$
$1^{\cdot+}$ (c^+)	C_{2h}	$191 \cdot 65 \ (196 \cdot 04)$	(0)	$0, 0$	
3	C_1	$92 \cdot 16$	(0)	$\pm 34; \ \pm 36^c$	$27 \cdot 8^d$
3	C_1	$92 \cdot 55$	$0 \cdot 35$	$\pm 35; \ \pm 3^c$	$23 \cdot 3^d$
3 (n^0)	C_{2h}	$94 \cdot 54$	$2 \cdot 38$	$0, 0; 0, 0^c$	$21 \cdot 1^d$
$3^{\cdot+}$	C_1	$242 \cdot 07$	(0)	$-47, 1; \ \pm 0^c$	
$3^{\cdot+}$ (c^+)	C_1	$244 \cdot 51$	$2 \cdot 44$	$0, 0; 0, 0^c$	

[a] Obtained using equation (3). The first number quoted employs UHF calculations for the radical cations, and the second uses the half-electron
approximation.
[b] A C_2 structure at $\Delta H_f = 40 \cdot 49$ kcal mol^{-1} (CN twist angle $35 \cdot 2°$) and a C_s angle at $\Delta H_f = 40 \cdot 49$ kcal mol^{-1} ($34 \cdot 6°$) were also located. The relative
direction of twist at the two Ar—NMe$_2$ bonds is calculated not to be important either for Δh_f or for λ'_{in}.
[c] The first pair of angles refers to the Ar—piperazine ring twist angle, and the second to the Ar—NMe$_2$ twist angle.
[d] Calculated using the $244 \cdot 51$ kcal mol^{-1} untwisted radical cation as c^+ in equation (3). Employing the more stable $242 \cdot 07$ kcal mol^{-1} $3^{\cdot+}$ structure
(twisted at the Ar—piperidinyl N of the reduced PD unit, and the lowest energy $3^{\cdot+}$ structure we have found) produces a $1 \cdot 1$ kcal mol^{-1} higher λ'_{in}
value.

ET, and we suggest that the principal reason for the significantly different λ values for the compounds in Table 3 is not likely to be λ_{out} differences.

We shall focus this discussion on consideration of λ_{in} values, which we believe are clearly different for the systems under consideration, and are the principal cause of the different transition energies observed. As discussed previously[15] calculations of the enthalpy portion of λ_{in}, which we shall call λ'_{in} (note that the λ'_{in} quotd[3d,15] for 1 of $8\cdot2$ kcal mol^{-1} is not correct; the correct values calculated by AM1 appear here in Table 4), using the Dewar AM1 semi-empirical molecular orbital method may be carried out simply from the calculated heats of formation for geometry relaxed neutral compound and radical cation ($\mathbf{n^0}$ and $\mathbf{c^+}$ respectively), and their vertical ET species, $\mathbf{n^+}$ and $\mathbf{c^0}$ respectively, using the equation

$$\lambda'_{in} = [\Delta H_f(\mathbf{n^+}) - \Delta H_f(\mathbf{c^+})] + [\Delta H_f(\mathbf{c^0}) - \Delta H_f(\mathbf{n^0})]$$

$$= \Delta H_r(cat) + \Delta H_r(neu) \qquad (3)$$

The numbers calculated for the experimentally measured enthalpy of cation relaxations, $\Delta H_r(cat) = vIP - aIP$ for hydrazines[16] are reproduced fairly well by AM1 calculations, and the calculated changes in λ'_{in} correlate well with experimentally observed changes in activation energy for hydrazine self-ET as bicyclic ring size is changed[14] [estimates of $\Delta H_r(cat)$ from 6–31G* *ab initio* calculations are about 50% too large; AM1 calculations are unquestionably far superior for calculation of this quantity for hydrazines]. The λ'_{in} calculations also correlate well with the differences in transition energies observed for $\mathbf{8^{\cdot+}}$ and $\mathbf{9^{\cdot+}}$ (see Table 3). Qualitatively, the reason for the much higher transition energy for bis(hydrazine) radical cation $\mathbf{9^{\cdot+}}$ than for bis(hydrazyl) radical cation $\mathbf{8^{\cdot+}}$ is clearly the much larger λ_{in} term for the bis(hydrazine), which undergoes far greater internal geometry reorganization than does the bis(hydrazyl). Calculations of λ'_{in} in by the AM1 method have been experimentally demonstrated to be useful for these hydrazines and hydrazyls.

Because flattening at nitrogen for the open-shell hydrazyl system should be less difficult than for closed-shell PD derivative nitrogens, it appears qualitatively reasonable that λ_{in} would be at least as large for PD derivatives as for hydrazyls. This idea has been tested more quantitatively by AM1 calculation of λ'_{in} values for 1 and 3, which are summarized in Table 4. Calculated values of λ'_{in} depend significantly on the geometries employed for both $\mathbf{n^0}$ and $\mathbf{c^+}$, and molecules with many degrees of freedom such as PD derivatives have complex energy surfaces which are much flatter for $\mathbf{n^0}$ than for $\mathbf{c^+}$. Energy minimum conformations with nitrogen lone pair, aromatic ring carbon p-orbital twist angles in the range 34–39° are only slightly lower in energy than untwisted conformations, with this angle

near 0° (see the 'CN twist angle' column in Table 4). Calculated λ'_{in} values are significantly higher for Ar,N-twisted conformations, principally because such twisting in the quinonoid radical cation is costly in energy. We suggest that untwisted conformations, which lead to lower values of λ'_{in} when employed as $\mathbf{n^0}$ are the appropriate ones to consider despite the fact that they are not the global energy minima. It is not obvious whether it is more appropriate to use unrestricted Hartree–Fock (UHF) calculations (as we have in our hydrazine work[13,14]) or Dewar's half-electron formalism[17] for optimizing the geometry of $\mathbf{c^+}$ and obtaining the vertical cation energies ($\mathbf{n^+}$). We have examined both for 1, where use of the half-electron approximation leads to slightly (2–5%) higher calculated λ'_{in} for all three $\mathbf{n^0}$ geometries examined, and use the slightly lower λ'_{in} values obtained by using UHF calculations for the radical cations in this discussion. The lowest energy $\mathbf{3^{\cdot+}}$ conformation is significantly twisted at the reduced aryl–piperidinyl N bond, but the untwisted conformation lying $2\cdot44$ kcal mol^{-1} higher in ΔH_f gives $1\cdot1$–$1\cdot0$ kcal mol^{-1} lower λ'_{in} values for all three $\mathbf{n^0}$ geometries. We employ the lower numbers in this discussion, although using the twisted conformation higher λ'_{in} values would not change our conclusion significantly. The lowest λ'_{in} value obtained by AM1 calculations for 3 using equation (3) is $21\cdot1$ kcal mol^{-1} (Table 4). Use of this value as λ_{in} predicts E_{op} for $\mathbf{3^{\cdot+}}$ in the range $28\cdot1$–$31\cdot1$ kcal mol^{-1} for λ_{out} of 7–10 kcal mol^{-1}, so the λ'_{in} value estimated by AM1 fits the near-IR band transition energy for $\mathbf{3^{\cdot+}}$ ($29\cdot7$ kcal mol^{-1}) well if it is assumed that the band corresponds to a Hush-type ET.

The near-IR band transition energy of $\mathbf{3^{\cdot+}}$ is that expected for a Hush-type CT band, but the band observed is substantially narrower than Hush theory predicts. According to Hush theory,[5] $v_{1/2}$ should exceed $v_{1/2}(HTL) = 48\cdot06(v_{max})^{1/2}$. The bands observed for $\mathbf{8^{\cdot+}}$ and $\mathbf{9^{\cdot+}}$, where the linking groups hold the charge-bearing systems fairly rigidly and parallel to each other, are broader than $v_{1/2}(HTL)$ (but see earlier comment), whereas while those for $\mathbf{3^{\cdot+}}$ and $\mathbf{7^{\cdot+}}$, where the charge-bearing units are directed away from each other and have much more freedom to move relative to each other, are significantly narrower. We do not know why narrower bands are observed for these systems, but suspect that the effect is somehow caused by the substantial structural differences between the geometries in which in the charge-bearing units are held.

Estimation of λ for $\mathbf{1^{0/\cdot+}}$

The greater difficulty of flattening at piperidinyl than at dimethylamino nitrogen will cause a smaller inner sphere reorganization energy for 1 than for 3. The AM1 λ'_{in} for 1 which corresponds to that used for 3 above

[UHF for cations, *syn* C_{2v} untwisted $\mathbf{n}_0$ structure; that is, the lowest value predicted by AM1 calculations using equation (3)] is $18 \cdot 7$ kcal mol^{-1}. Rauhut and Clark[18] reported the same λ'_{in} values for **1** with the half-electron approximation as we obtain (Table 4). They have done a sophisticated computational investigation on self-ET for four PD derivatives including **1**, in which many issues not considered here, such as calculations on dimeric transition states for intermolecular ET, are addressed.[18] They concluded from HF/6–31G* *ab initio* calculations on the parent PD (1,4-diaminobenzene) that AM1 performs well for this particular problem. [Indeed, AM1 probably gives better answers than 6–31G* calculations for this particular problem. We have shown[18] that for geometry-constrained sesquibicyclic hydrazines, AM1 calculations are unquestionably superior to 6–31G* calculations for calculation of ΔH_f(cat) and of λ'_{in}, owing to unexpected fortunate cancellation of errors in the AM1 calculations. The 6–31G* calculations produce numbers which are significantly too high for such hydrazines, whereas AM1 gives more realistic results. The 6–31G* results are also significantly higher than the AM1 results for *p*-phenylenediamine.] Estimates made in an analogous fashion using *ab initio* calculations on the parent gave a 38% larger estimate of λ'_{in} than did AM1 (which gave $\lambda'_{in} = 22 \cdot 7$ kcal mol^{-1}) at UHF/6–31G*, but came closer to the AM1 estimate when electron correlation was included in the geometry optimization; UMP2/6–31G* calculations gave an estimate 19% higher than the AM1 value. Thus Rauhut and Clark's *ab initio* calculations on 1,4-diaminobenzene indicate that AM1 is unlikely to overestimate λ'_{in}. [Goez[19] exploited the results of AM1 calculations on $\mathbf{1}^{0/\cdot+}$ in a completely different manner, estimating λ'_{in} (which he calls λ^{∞}_{in}, following nomenclature used by GJ[3d]) at $9 \cdot 27$ kcal mol^{-1}. He used a traditional summation of bond distance changes and estimated force constant method. We do not know why his estimate of λ'_{in} is so much lower than that we and Clark obtain using equation (3), but suggest that this result reinforces our suspicion that the traditional procedure misses an important component of the vertical energy gap between $(\mathbf{n}^0 + \mathbf{c}^+)$ and $(\mathbf{n}^+ + \mathbf{c}^0)$ which λ_{in} represents. We suggest that if a summation of bond deformations and force constants which is designed to produce the vertical energy gap in fact only produces a fraction of it, there must be some unanticipated problem in properly implementing the summations.]

The substantial agreement of the λ'_{in} value calculated by AM1 with that required to fit the transition energy for $\mathbf{3}^{\cdot+}$ suggests that use of AM1 calculations with equation (3) provides a more useful way of estimating λ_{in} for organic compounds than the traditional methods, and that the $18 \cdot 7$ kcal mol^{-1} estimate of λ'_{in} we make for $\mathbf{1}^{0/\cdot+}$ is likely to be far closer to the correct value than the lower estimates of *ca*

$11 \cdot 7$ kcal mol^{-1} employed by GJ. Raising the λ value used in calculating the pre-exponential factor from the experimental rate constant significantly changes the conclusion reached by GJ that $\mathbf{1}^{0/\cdot+}$ self-ET must be strongly diabatic.[3] The number estimated for V from the observed k_{ex} value obviously will depend on exactly what theoretical expression is used for k_{ex}, including how tunnelling is handled, and on the estimates made for the barrier crossing frequency and precursor complex formation constant. Because it is not clear how to estimate these numbers accurately, uncertainty in the size of V obviously remains.

EXPERIMENTAL

1,4-Bis[(4-dimethylaminophenyl)methyl]benzene (**6**). A mixture of $1 \cdot 63$ g (12 mmol) of *N,N*-dimethyl-*p*-phenylenediamine (**4**) $0 \cdot 81$ g (6 mmol) of terephthalaldehyde (**5**) and $0 \cdot 19$ g (3 mmol) of sodium cyanoborohydride in 30 ml of acetonitrile was stirred under a nitrogen atmosphere while adding glacial acetic acid in five-drop increments over a 2 h period (25 drops total), followed by stirring at ambient temperature for 14 h. The mixture was cooled in an ice-bath while 10 ml concentrated hydrochloric acid were added dropwise, solvents were removed under reduced pressure, the residue was dissolved in 50 ml of water, basified with KOH pellets and extracted with diethyl ether. After drying with magnesium sulfate and solvent removal by rotary evaporation, $1 \cdot 98$ g (89%) of **6** were obtained as a solid, which was crystallized from aqueous ethanol, m.p. 148–150 °C. ^{1}H NMR (CDCl$_3$), δ $2 \cdot 57$ (s, 12H), $3 \cdot 20$ (br s, 2H), $4 \cdot 03$ (s, 4H), $6 \cdot 52$ (d, 4H, $J = 8 \cdot 8$ Hz, 2H), $6 \cdot 69$ (d, $J = 8 \cdot 8$ Hz, 2H), $7 \cdot 20$ (s, 2H). This material was methylated without further purification.

1,4-Bis[2-aza-2-(4-dimethylaminophenyl)propyl]benzene (**2**). A mixture of $1 \cdot 98$ g ($10 \cdot 7$ mmole) of **6** and $1 \cdot 75$ g of 40% aqueous formaldehyde solution was treated as above for the preparation of **6**, producing $0 \cdot 45$ g (23%) of **2**, which was crystallized from cyclohexane, m.p. 128–130 °C. Analysis: calculated, C $77 \cdot 75$, H $8 \cdot 51$, N $13 \cdot 92$; found, C $77 \cdot 64$, H $8 \cdot 72$, N $13 \cdot 82$%). The empirical formula $C_{26}H_{34}N_4$ was established by HR-MS. ^{1}H NMR (C$_6$D$_6$), δ $2 \cdot 59$ (s, 12H), $2 \cdot 67$ (s, 6H), $4 \cdot 19$ (s, 4H), $6 \cdot 73$ (d, $J = 9 \cdot 0$ Hz, 4H), $6 \cdot 79$ (d, $J = 9 \cdot 0$ Hz, 4H), $7 \cdot 17$ (s, 4H).

N,N'-Bis[4-dimethylaminophenyl]piperazine (**3**). A mixture of $7 \cdot 43$ g (54 mmol) of *N,N*-dimethyl-*p*-phenylenediamine (**4**) and $10 \cdot 15$ g (54 mmol) of 1,2-dibromoethane in 50 ml toluene was refluxed for 6 h under nitrogen and the solid produced was collected by filtration after cooling to room temperature. This solid was dissolved in chloroform, washed with water, dried with magnesium sulfate and chromatographed on

alumina followed by chromatography on silica gel, using chloroform as eluent. Crystallization from chloroform–pentane gave 0·516 g (5%) of **3**, m.p. 208–210 °C. The empirical formula $C_{20}H_{28}N_4$ was established by HR-MS. ^{1}H NMR (C_6D_6), δ 2·61 (s, 12H), 3·11 (s, 8H), 6·75 (d, $J = 9·0$ Hz, 4H), 6·97 (d, $J = 9·0$ Hz, 4H). ^{13}C NMR (C_6D_6), δ 41·35, 41·73, 114·26, 119·05, 144·27, 146·12.

Instrumentation. NMR spectra were recorded on Bruker WP-200 or WP-270, ESR spectra on Brucker ESP 300E, UV–visible spectra on Hewlett-Packard model 8452A diode-array and near-IR spectra on Nicolet 740 instruments. Cyclic voltammetry employed a PAR Model 273 system interfaced to an IBM PC/XT computer.

AM1 calculations. Our AM1 calculations[20] used the VAMP program (version 4.4)[21] modified for use on a Stardent 3000 computer. There is no way to ensure finding all minima using MO calculations, so enough information is included about the structures employed for the AM1 calculations to allow others to tell if significantly different structures have been obtained (see Table 4).

REFERENCES

1. (a) For a brief history of radical ion chemistry, see H. D. Roth, *Tetrahedron* **42**, 6097 (1986); (b) C. Wurster *et al.*, *Chem. Ber.* **12**, 522, 1803, 1807, 2071 (1879); (c) E. Weitz, *Z. Electrochem.* **34**, 538 (1928).
2. (a) S. I. Weissman, *J. Chem. Phys.* **22**, 1135 (1954); (b) C. R. Bruce, R. E. Norberg and S. I. Weissman, *J. Chem. Phys.* **24**, 1135 (1956).
3. (a) G. Grampp and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.* **88**, 325 (1984); (b) G. Grampp and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.* **88**, 335 (1984); $1^{0/·+}$ self-ET in CH_3CN: $\Delta H^{\ddagger} = 2·63 \pm 0·07$ kcal mol^{-1}, $\Delta S^{\ddagger} = -7·6 \pm 0·1$ cal mol^{-1}K^{-1} in the units used here; (c) G. Grampp and W. Jaenicke, *J. Chem. Soc., Faraday Trans. 2* 1035 (1985); (d) G. Grampp and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.* **95**, 904 (1991); (e) W. R. Fawcett and C. A. Foss, Jr, *J. Electroanal. Chem.* **270**, 103 (1989).
4. For recent reviews of electron transfer theory, see (a) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985); (b) N. Sutin, *Prog. Inorg. Chem.* **30**, 441 (1983).
5. (a) N. S. Hush, *Prog. Inorg. Chem.* **8**, 391 (1967); (b) for a review on applications of Hush theory to intervalence complexes, see C. Creutz, *Prog. Inorg. Chem.* **30**, 1 (1983).
6. S. F. Nelsen, C. R. Kessel and D. J. Brien, *J. Am. Chem. Soc.* **102**, 702 (1980).
7. (a) F. Ammar and J. M. Savéant, *J. Electroanal. Chem.* **47**, 115, 215; (1973); (b) J. B. Flanagen, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc.* **100**, 4248 (1978).
8. S. F. Nelsen, M. R. Willi, J. M. Mellor and N. M. Smith, *J. Org. Chem.* **51**, 2081 (1986).
9. W. C. Meyer and A. C. Albretch, *J. Phys. Chem.* **66**, 1168 (1962).
10. H. Oevering, J. W. Verhoeven, M. N. Paddon-Row and J. M. Warman, *Tetrahedron* **45**, 4751 (1989).
11. N. S. Hush, *Coord. Chem. Rev.* **64**, 135 (1985).
12. S. F. Nelsen, J. A. Thompson-Colón and M. Kaftory, *J. Am. Chem. Soc.* **111**, 2089 (1989).
13. S. F. Nelsen, H. Chang, J. J. Wolff and J. Adamus, *J. Am. Chem. Soc.* **115**, 10611 (1993).
14. S. F. Nelsen and Y. Wang, submitted for publication.
15. S. F. Nelsen, S. C. Blackstock, Y. Kim, *J. Am. Chem. Soc.* **109**, 677 (1987).
16. S. F. Nelsen, D. T. Rumack and M. Meot-Ner (Mautner), *J. Am. Chem. Soc.* **110**, 7945 (1988); (b) S. F. Nelsen, D. T. Rumack and M. Meot-Ner (Mautner), *J. Am. Chem. Soc.* **109**, 1373 (1987); (c) for a review, see S. F. Nelsen, in *Advances in Electron Transfer Chemistry*, edited by P. S. Mariano, JAI, Greenwich, CT, Vol. 3, in press.
17. M. J. S. Dewar, J. A. Hashmall and C. G. Venier, *J. Am. Chem. Soc.* **90**, 1953 (1968).
18. M. Rauhut and T. Clark, *J. Am. Chem. Soc.* **115**, 9127 (1993).
19. M. Goez, *Z. Phys. Chem., N.F.* **169**, 133 (1990).
20. M. J. S. Dewar, E. G. Zoebisch, E. F. Healey and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
21. T. Clark and G. Rauhut, unpublished.