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Comparison of *V* Values for Some Nitrogen- and Metal-Centered π-Bridged Mixed-Valence Compounds

Stephen F. Nelsen,* Hieu Q. Tran, and Mark A. Nagy

Contribution from the Department of Chemistry, University of Wisconsin,
1101 University Avenue, Madison, Wisconsin 53706-1396

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Abstract: Delocalized radical cations having two nitrogen-centered charge bearing units bridged by π systems may be considered Class III intervalence compounds. The transition energy of the longest wavelength band may therefore be equated with the E_{op} of Hush theory, which is twice the electronic interaction matrix element *V*. The optically estimated value of *V* ($V_{op} = E_{op}/2$) drops significantly (6.0 kcal/mol) when the methyl groups of tetramethyl-*p*-phenylenediamine radical cation (1^+, V_{op} = 23.3 kcal/mol) are replaced by phenyl groups in the tetraphenyl compound (3^+) and detectably (0.6 kcal/mol) when they are replaced by bicyclic alkyl groups in bis(9-azabicyclo[3.3.1]non-9-yl)-*p*-phenylenediamine (4^+). The V_{op} values observed for *n* bonds connecting the nitrogens follow the relationship $V = V_0 \exp(-\beta_n(n-1)/2)$ rather well for dinitrogen (n = 3), *p*-phenylene (n = 5), and biphenylene (n = 9) bridges with $\beta_n \sim 0.3$. AM1-NCG calculations are fairly successful at predicting changes in E_{op} for these compounds and 1,5-dimethyl-1,5-dihydrophenazine radical cation (8^+) but fail totally for methylviologen radical cation (10^+). AM1 calculations predict $[Me_2N(CH=CH)_yNMe_2]^+$ to localize at y = 6 and $[Me_2N(C≡C)_yNMe_2]^+$ at y = 5, and in both cases calculated *V* drops below calculated $\lambda/2$, as expected. *V* values for nitrogen-centered and transition metal-centered intervalence compounds are compared. Significantly larger *V* values for the nitrogen-centered examples cause charge delocalization to occur for larger π systems than for transition metal-centered examples.

Introduction

Delocalization and Localization in PD Derivatives. The first organic radical cations ever isolated were *p*-phenylenediamine (**PD**) derivatives,[1] of which the *N,N,N′,N′*-tetramethyl compound (**TMPD**$^+$), 1^+, is the most studied example. A formal possibility for its instantaneous charge distribution is that **TMPD**$^+$ would exist with one dimethylamino group oxidized to the +1 state and the other reduced, as indicated below in structures 1^+**A** and 1^+**B**, and then an intramolecular electron transfer, ET, which might be extremely rapid, would interchange
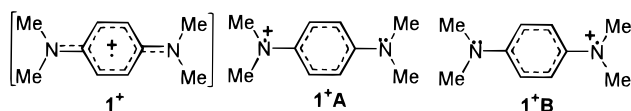

the roles of the nitrogens (1^+**A**⇌1^+**B**). It is well-known, however, that 1^+ has its charge and spin delocalized over the eight p-orbital π system, that is, 1^+ exists as 1^+**A**↔1^+**B**, with equivalent, partially oxidized dimethylamino groups. Instantaneous localization of charge in a **PD** derivative is more than a formal possibility, because the bis-hydrazine radical cation, 2^+, does have one oxidized and one reduced hydrazine unit, although the ET interconverting the **A**- and **B**-type structures
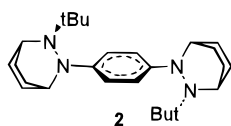
is rapid on the ESR time scale at −78 °C in methylene chloride.[2] In the nomenclature introduced by Robin and Day for compounds having transition metals as the charge-bearing units,[3] the charge-localized **A**⇌**B** systems are Class II intervalence (*IV*) compounds, while the delocalized **A**↔**B** systems belong to Class III. *IV*-Compounds have two charge-bearing units connected by a bridge and an overall oxidation state formally putting these units in different oxidation states.

Hünig developed the analogy between symmetrical radical cations which may be generally characterized as having 2n+3 π electrons on 2n+2 sp²-hybridized atoms (and were assumed to be delocalized), with diamagnetic cations having 2n+4 π electrons on 2n+3 sp²-hybridized atoms, calling them violenes and cyanines respectively.[4] They are written schematically below for diamino-terminated systems of the type we will discuss. This paper focuses on estimations of the electronic
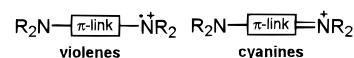
interaction between nitrogen-centered charge-bearing units of π-bridged Class III *IV-CT* systems (violenes) and compares them with cyanines and π-bridged transition-metal centered systems.

Hush Theory Analysis of Electronic Interaction between Charge Bearing Units. Hush developed simple theory for understanding *IV*-compounds and interpreting their optical spectra.[5] A two state model is used, with *A* and *B* initial and

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.
(1) For the early history of radical ion studies, see: Roth, H. D. *Tetrahedron* **1986**, *42*, 5097.

(2) Nelsen, S. F.; Ismagilov, R. F. *J. Am. Chem. Soc.* **1996**, *118*, 6313.
(3) Robin, M.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247.
(4) (a) Hünig, S.; Berenth, H. *Topics Curr. Chem.* **1980**, *92*, 1. (b) The violene name refers to the color of tetraphenylhydrazine radical cation.
(5) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.

final states (wave functions ψ_A and ψ_B respectively). The initial state $H_{AA} = \langle \psi_A|H|\psi_A \rangle$ and final state $H_{BB} = \langle \psi_B|H|\psi_B \rangle$ are assumed to be equivalent harmonic oscillators so the energy surfaces are parabolas which lie at 0 and 1 on an ET coordinate X. For the symmetrical compounds we consider, these diabatic parabolas have the same shape and minima at the same potential energy: $H_{AA} = \lambda X^2$, $H_{BB} = \lambda(1-X)^2$. The parabolas cross when $X = 0.5$, at potential energy $\lambda/4$. When the initial and final states undergo electronic mixing, measured by the electronic coupling matrix element $\langle \psi_A|H|\psi_B \rangle$, which we will call V, the secular equation is a simple 2×2 determinant with V as the off-diagonal elements and produces the adiabatic curves shown in eq 1,[6] which has been shown to hold for all values of V.[6b]

$$E_{1,2} = 0.5[\lambda(2X^2 - 2X + 1)] \mp 0.5[\{\lambda(2X - 1)\}^2 + 4V^2]^{1/2} \quad (1)$$

Electronic mixing leads to an avoided crossing: $E_2 - E_1$ (at $X = 0.5$) = $2V$. ET becomes slow as V approaches zero, the extinction coefficient, ϵ, for the IV charge transfer (CT) absorption band approaches zero, and the compound becomes Robin-Day Class I. Using the parabolic diabatic energy surfaces, the transition energy of the IV-CT band at its maximum extinction coefficient, E_{op}, is equal to the vertical reorganization energy of Marcus theory, λ.[7–9] The barrier between the two minima for a Class II compound decreases as V increases and completely disappears when V reaches $\lambda/2$, causing the system to change from a Class II to a Class III IV-compound. As emphasized by Creutz,[10] E_{op} changes from being a measure of λ (Class II) to being a measure of $V = E_{op}/2$ (Class III). There is, however, an important point that we have not seen made in the literature. Despite the vertical minimum-to-minimum appearance of the intervalence band in a plot of energy versus X, the ET coordinate for a Class III compound is not really significant, and the IV-CT band can vary from being a nearly vertical excitation to being very nonvertical. For example, hydrazine radical cations ($\mathbf{y} = 0$ violenes)[4b] are clearly delocalized (Class III) systems having a very large V. Their $\pi \rightarrow \pi^*$ transition involves a very large geometry change. The relaxed excited state has two antibonding π^* and only one bonding π electron and is twisted 90°. A 90° twist leads to charge localization in ground state hydrazine radical cations, so the ET coordinate X is obviously inappropriate for use with these compounds. The large geometry change causes the largest Franck–Condon factors for the transition to be to highly vibrationally excited states and E_{op} to be significantly higher than $2V$. The $\mathbf{y} = 0$ violenes are clearly a separate class from π-bridged violenes as far as their optical absorption spectra are concerned, and we discuss hydrazine radical cation absorption spectra separately.[11]

(6) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A.: Chem.* **1994**, *82*, 47.

(7) When vibronic coupling theory[8] is employed, λ is greater than E_{op} by as much as a few kcal/mol, the exact amount depending upon the vibrational reorganization energy, λ_v, the solvent reorganization energy, λ_s, and the energy of the vibronic coupling frequency, $h\nu_v$. λ is also not exactly equal to E_{op} if the diabatic energy surfaces are not parabolas.

(8) (a) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (b) Jortner, J.; Bixon, M. *J. Chem. Phys.* **1988**, *88*, 167.

(9) Expressions containing direct overlap of the charge-bearing centers are also available,[6] but direct overlap should be negligible for the cases considered here.

(10) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(11) (a) Nelsen, S. F.; Blackstock, S. C.; Yumibe, N. P.; Frigo, T. B.; Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 143. (b) Nelsen, S. F.; Tran, H. Q.; Ismagilov, R. F.; Chen, L.-J.; Powell, D. R. Submitted for publication.

It is important to know how V and λ change with structure to predict whether a given IV-compound will be localized or delocalized. We refer to $E_{op}/2$ values for Class III π-bridged IV-diamines, where the IV transition is nearly vertical and should be an excellent approximation to the V of ET theory, as V_{op} to distinguish them from V values estimated by other methods. V_{op} for Class III IV-compounds can be much more accurately determined than V can be estimated for any Class II IV-compounds. Estimation of V for the latter requires knowing the concentration and band width at half-height in addition to E_{op}, which must be determined for a band that is far broader, and also requires estimation of the electron transfer distance (d).[5] We will refer to values of V for Class II IV-compounds estimated using Hush theory as V_H. We report energies in kcal/mol (1 kcal/mol = 349.8 cm^{-1} = 0.0434 eV).

Estimation of E_{op} Using Semiempirical Calculations. To help interpret E_{op} data, we shall examine calculations of the 0,0 band enthalpy difference between the ground and first optically allowed excited state of the cation, E_{calc}, using the simple "neutral in cation geometry" (NCG) algorithm,[12] on AM1-UHF optimized radical cation structures. Optical transition energies are difficult to calculate because they involve transitions between orbitals of different electron occupancy, and orbital energies are very sensitive to electron occupancy. Even when states are well described by single configurations (which is not always the case), the difference in energy between states is very different from the difference in energy between the orbitals involved in a transition. Extensive configuration interaction is typically required to calculate any state energy differences. For the special case of radical cations, calculation of the neutral compound in the geometry of the radical cation places the same number of electrons in the orbitals involved for Koopmans' states, which are those which involve transitions between filled orbitals and the singly occupied orbital of the radical cation.[13] It is also necessary to calculate oscillator strengths, because some of the orbital energy gaps obtained by this NCG method do not correspond to allowed transitions and do not contribute to the optical spectrum.[12] Despite not using configuration interaction, it has been shown with *ab initio* calculations that E_{calc} using NCG gives a good estimation of the 0,0 band energy gap for cases in which non-Koopmans states are not involved.[11a] Whether the semiempirical calculations we employ here are good enough to give the experimental value for a given compound and whether the observed transition corresponds to formation of a Koopmans' state are obvious separate questions. We shall consider $V_{calc} = E_{calc}/2$ values using the NCG method in comparing V_{op} values for different compounds.

***p*-Phenylene-Linked Diamine Radical Cations.** There is only a small geometry change between the ground and first excited states for $\mathbf{PD}^+$ derivatives, making their IV bands narrow, with resolved vibrational structure. The lowest energy component for $\mathbf{1}^+$, the 0,0 band, is slightly higher in intensity than the 0,1 band, which lies 4.00 kcal/mol (1400 cm^{-1}) higher in energy in acetonitrile. Only a small range of E_{op} for $\mathbf{1}^+$ in solution has been reported, although the range observed increases to 2.3 kcal/mol when matrix experiments are included.[14] Replacing the methyls of $\mathbf{1}^+$ by phenyl groups in $\mathbf{3}^+$ ($\mathbf{TPPD}^+$) causes a large decrease in E_{op} (corresponding to a decrease in V_{op} of 6 kcal/mol), see Table 1.[14e] Brouwer and co-workers found a similar change for replacing methyl groups by aryl ones

(12) Clark, T.; Teasley, M. F.; Nelsen, S. F.; Wynberg, H. *J. Am. Chem. Soc.* **1987**, *109*, 5719.

(13) Bally, T. *Radical Ionic Systems*; Lund, A., Shiotani, M., Eds.; Kluwer: Dordrecht, 1991; p 3.

3: TPPD
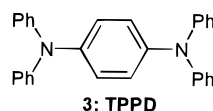
in a σ-bridged *IV*-diamine, piperazine radical cation, and pointed out that it occurs because *V* is sensitive to the spin density at the atoms coupling with the bridging units.[15] This effect can even be detected when the dimethylamino groups of 1^+ are replaced with larger saturated alkyl groups in the 9-azabicyclo-[3.3.1]nonyl-substituted compound 4^+ (**33N)$_2$PD$^+$**), causing a 1.1 kcal/mol decrease in E_{op}.

4: 33N)$_2$PD   **5: k33N)$_2$PD**
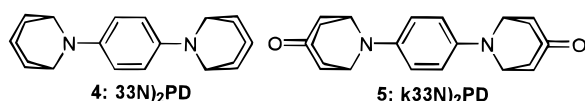
Slightly more effective delocalization of the partially oxidized nitrogen p lone pairs onto the bicyclic alkyl groups of 4^+ than onto the methyl groups of 1^+ should occur. In keeping with this hypothesis, bis-γ-keto substitution of the bicyclononyl rings in 5^+, which hardly affects the geometry about the nitrogens but decreases the ability of the bicyclononyl rings to stabilize the positive charge, causes E_{op} to increase to nearly the same value as for 1^+. The X-ray crystal structure of 5^+ has demonstrated that like 1^+, the nitrogens are planar, and the N-Ar bonds untwisted.[16] Table 1 also shows E_{calc} values obtained using NCG calculations on AM1-UHF structures. The E_{calc} values are somewhat larger than E_{op}, but the large effect of replacing methyl by phenyl substituents is handled rather well. It will be noted that NCG calculations incorrectly get E_{calc} to be larger for 4^+ than for 1^+, but do get the size of the effect of keto substitution in 5^+ relative to 4^+ about right. The entries shown for 4^+ and 5^+ are for geometries constrained to be untwisted at the N-aryl bonds. AM1-UHF optimizes 4^+ as 12° twisted, but this twist is only calculated to stabilize the system by 0.15 kcal/mol, and such calculations are known to also improperly twist other systems containing bicyclo[3.3.1]non-9-yl groups, including the hydrazine and alkene radical cations.

Dependence of *V* on the Number of Bonds in the Bridge and on Twisting. It has been common to discuss the drop-off in electronic coupling as the size of the link increases in terms of an exponential dependence on either distance or on the number of connecting bonds, n.[17] The distances for the *IV* oxidation level systems actually studied are not usually known experimentally, and it is not really the distance between the groups but the electronic coupling transmitted through the connecting link that determines *V*. For the intramolecular cases

(14) Data recorded in matrices give lower E_{op}. (a) $\lambda_{max} = 637$ nm ($E_{op} = 44.9$ kcal/mol) in *sec*-BuCl at 77 K: Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988. (b) $\lambda_{max} = 632$ nm ($E_{op} = 45.2$ kcal/mol) in 3-methylpentane at 77 K; $\lambda_{max} = 626$ nm ($E_{op} = 45.7$ kcal/mol) in 1:1 Cl$_3$CF:(CF$_2$Br)$_2$ at 77 K: Meyer, W. C.; Albrecht, A. C. *J. Phys. Chem.* **1962**, *66*, 1168. (c) $\lambda_{max} = 615$ nm ($E_{op} = 46.5$ kcal/mol) in CHCl$_3$ at room temperature (RT): Cauquis, G.; Serve, D. *Anal. Chem.* **1972**, *44*, 2222. (d) $\lambda_{max} = 614$ nm ($E_{op} = 46.6$ kcal/mol) in MeCN at RT: Nelsen, S. F.; Yunta, M. J. R. *J. Phys. Org. Chem.* **1994**, *7*, 55. (e) $\lambda_{max} = 606$ nm ($E_{op} = 47.2$ kcal/mol) in MeCN at RT (not correct, from 13d and Table 1): Cauquis, G.; Delhomme, H.; Jene, D. *Tetrahedron Lett.* **1972**, 1965.

(15) Brouwer, A. M.; Wiering, P. G.; Zwier, J. M.; Langkilde, F. W.; Wilbrandt, R. *Acta Chem. Scand.* **1997**, *51*, 217.

(16) Nelsen, S. F.; Ramm, M. T.; Ismagilov, R. F.; Nagy, M. A.; Trieber, D. A., II; Chen, X.; Gengler, J. J.; Qu, Q.; Brandt, J. L.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1997**, *119*, 5600.

(17) (a) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (b) The factor of 2 in eq 2 is present because the rate constant for ET is proportional to V^2 when *V* is small. We shall retain this factor of 2 to enable easier comparison with literature values.

Table 1. Comparison of Optical Data at Room Temperature and E_{calc} for Violenes

compd	n	solvent	λ_{max}, nm	$E_{op} = 2V_{op}$, kcal/mol	E_{calc}, kcal/mol	$E_{calc} - E_{op}$, kcal/mol
1^+(**TMPD$^+$**)	5	CH$_3$CN	614[a]	46.6	54.1	7.6
3^+(**TPPD$^+$**)	5	CH$_3$CN	825[b]	34.7	40.0	5.3
4^+(**33N)$_2$PD$^+$**)	5	CH$_3$CN	628	45.5	56.1	10.6
5^+(**k33N)$_2$PD$^+$**)	5	CH$_3$CN	616	46.4	56.9	10.6
6^+(**33NN=)$_2^+$**)	3	CH$_3$CN	458	62.4	68.2	5.7
7^+(**TMB$^+$**)	9	CH$_3$CN	1018[c]	28.1	30.4	2.3
8^+ (**DMDP$^+$**)	3	CH$_3$CN	726[d]	39.4	44.5	5.1
10^+ (**MV$^+$**)	7	DMF	1120[e]	25.5	71.9(!)	+46.4

[a] See ref 14 for literature data. [b] From ref 14e. In CHCl$_3$ $\lambda_{max} = 853$ nm ($E_{op} = 33.5$ kcal/mol).[14c] [c] The 0,0 band is the most intense, and a vibrational splitting of $\sim$1280 cm^{-1} is seen to the 0,1 band. $\lambda_{max} = 1075$ was observed in a *sec*-butyl chloride matrix at 77 K.[14a] [d] For the 0,0 band, which is slightly lower in intensity than the 0,1 band at 660 nm. Brandish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42*, 561, report $\lambda_{max} = 719$ under these conditions. [e] From ref 21.
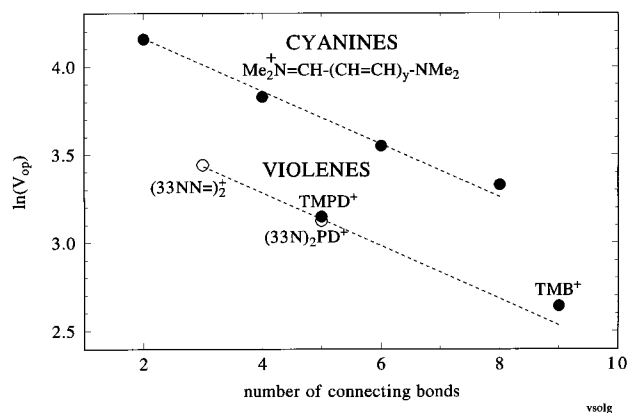

Figure 1. Violenes: plot of $\ln(V_{op})$ versus n for 6^+ (**33NN=)$_2^+$**), 1^+ (**TMPD$^+$**), 4^+ (**33N)$_2$PD$^+$**), and 7^+ (**TMB$^+$**). The broken line shows $V_{op} = 41.8 \exp(-0.15n)$. Cyanines: plot of $\ln(V'_{op})$ vs n for dimethylaminocyanines.[22] The broken line shows $V'_{op} = 74.4 \exp(-0.15n)$.

we consider, the coupling depends upon bond overlaps, and the bond alignment is often not the all *anti* arrangement which leads to the largest distance for a given n. We shall use the formulation in eq 2 (which is eq 14 of ref 17) for analyzing experimental data. The factor of two in the denominator of

$$V = V^0 \exp(-\beta_n(n-1)/2) \qquad (2)$$

the exponential term is sometimes absorbed into the scaling constant, which of course halves the β value obtained.[17b] The β_n values for *anti*-aligned σ-bridges are typically about 1.0.[6b] A smaller β_n certainly occurs for well-aligned π systems. The **PD** derivatives of Table 1 have $n = 5$, and V_{op} is rather insensitive to whether the charge-bearing unit is a dimethylamino or a 9-azabicylo[3.3.1]nonyl group. *IV-CT* band data for the $n = 3$ bicyclononyl-protected 2-tetrazene radical cation 6^+ and the $n = 9$ p,p'-biphenylene-bridged bisdimethylamino radical cation 7^+ (tetramethyl-*p*-benzidine, **TMB**) also appear in Table 1.

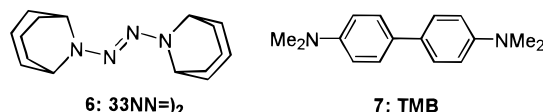**6: 33NN=)$_2$**   **7: TMB**

Figure 1 shows a plot of $\ln(V_{op})$ vs n for these two compounds and their **PD** analogues, along with a line corresponding to $V_{op} = 41.8 \exp(-0.3(n-1)/2)$. Despite the obvious difference
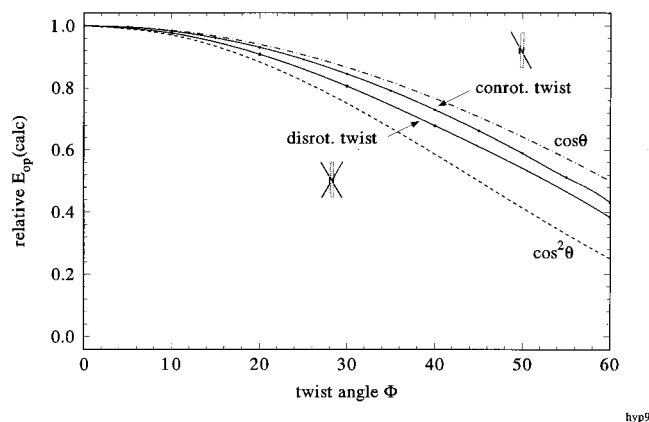
Figure 2. Plot of relative values of AM1-NCG calculated E_{op}(calc) versus twist angle ϕ for 1^+ with the nitrogens constrained to be planar.

between $-N=N-$ and the structurally similar $-C_6H_4-$ and $-C_6H_4-C_6H_4-$ as π-bridges, the eq 2 relationship works rather well (at least partially by accident; see below). Considering pairs with the same *N*-alkyl groups, the 4^+ ($(33N)_2PD^+$), 6^+ ($(33N-N=)_2$) comparison gives $\beta_n = 0.31_6$, and the 1^+ ($TMPD^+$), 7^+ (TMB^+) comparison, $\beta_n = 0.25_3$. Reimers and Hush pointed out that effects of twisting need to be included when considering an exponential relationship of V with n because V should be proportional to $\cos\phi$ at any bonds in the bridge.[18] 5^+ has been shown to be untwisted by X-ray crystallography,[16] implying that both 4^+ (calculated $\phi = 12°$ minimum only 0.15 kcal/mol more stable than the $\phi = 0$ D_{2h} structure) and the sterically less hindered 6^+ (calculated $\phi = 0°$) should not be twisted either. Although 7^+ might be twisted at its central bond, the calculated twist is only 14°, and AM1 overestimates the twist in biphenyl itself (obtaining 40.9°, compared with the experimental value of 32°). A 14° twist in 7^+ only would increase E_{op} by a factor of 1.03 for an untwisted conformation, which lowers the β_n estimate to 0.24.

The $E_{calc} - E_{op}$ values for 6^+ and 7^+ are smaller than those for the alkylated **PD** derivatives, but AM1-NCG calculations predict the changes in E_{op} for these $n = 3-9$ compounds rather well. A principal reason for considering E_{calc} values is to be able to better estimate the effects of twisting in the bridge, which cannot be directly studied experimentally. Although E_{calc} for twisting 7^+ (TMB^+) about its central single bond is proportional to $\cos\phi$ as is calculated by extended Hückel methods for similar twists[18] and has always been assumed in the literature, twisting about both N−Ar bonds of 1^+ ($TMPD^+$) (fixing the nitrogens planar) does not lead to quite such a simple result. E_{calc} for 1^+ deviates detectably from a $\cos^2\phi$ relationship and is also slightly sensitive to the relative direction of twists. As shown in Figure 2, disrotatory twists, which make the angle between the nitrogen p orbital axes 2ϕ, give a slightly smaller E_{calc} than do conrotatory twists, which keep the nitrogen p orbital axes parallel, and both lie between a $\cos\phi$ and $\cos^2\phi$ relationship. Thus AM1-NCG calculations of E_{op} for 1^+ with imposed N−Ar twists indicate that the nitrogens interact detectably with each other through the *p*-phenylene bridge. Such interaction does not occur detectably for neutral **2**, because its conrotatory and disrotatory twisted diastereomers have the same free energy (shown by ^{13}C NMR experiments).[2]

Dependence of V_{op} on Bridge Structure. Changes in bridge structure clearly will change E_{op}, because they will change the spin distribution significantly. The doubly $n = 3$ bridged *N,N′*-dimethyl-1,5-dihydrophenazine cation, 8^+ (**DMDP$^+$**), provides

an excellent example of this. E_{op} is only 0.63 times as large as for the singly-bridged $n = 3$ example, 6^+, and 0.85 times that


8: DMDP
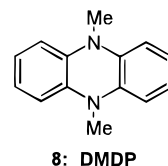
for the $n = 5$ 1^+. Nevertheless, AM1-NCG calculations, which get the nitrogens of 8^+ planar but a 13.5° CCNC angle in the central ring, get about the same $E_{op} - E_{calc}$ value as for the singly bridged examples, so they handle this example rather nicely.

It is well-known that in contrast to *p*-phenylene compounds, *m*-phenylene ones have poor interaction between two spin-bearing centers because of the nodal properies of the orbitals involved, and the *m*-phenylene bridge is commonly used to encourage formation of high spin ground states for bi- and polyradicals.[19] These nodal properties lead to low V values for *m*-phenylene *IV*-compounds. Bonvoisin and co-workers have carried out interesting studies on meta-linked bis- and tristri-arylamines, which have Class II (localized) intervalence oxidation states.[20] Extraction of V requires establishing the concentration of oxidized species (and the difference in $E°$ values is small enough that corrections must be made for coexistence of more than one oxidation state in the solution) and assigning an electron transfer distance which is rather ill-defined (estimated N,N distances were employed). Their most interesting compound for the present purpose is 9^+, for which V_H of 0.66 kcal/mol was obtained for the $n = 12$, and $V_H = 1.11$ for the $n = 8$
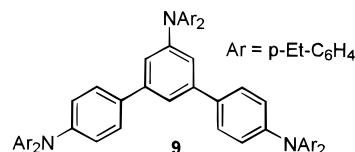
IV bands, respectively. These values are much smaller than for the para-bridged Class III and are certainly influenced by the large (and unknown) twist angles expected for these hindered systems. Nevertheless, the β_n calculated from the estimated V_H values is 0.26, which is within experimental error of that obtained from E_{op} for $n = 5$ and $n = 9$ para-substituted compounds. We expect the same values because the twists and meta substitution effects for the two pathways in 9^+ should be the same, so the β_n comparison only represents the effects of adding more aligned bonds. We suggest that obtaining the same β_n values for Class II and Class III compounds provides valuable verification that the V_{op} values for these Class III compounds really do measure the V of ET theory and that the Hush method for extracting V from Class II compounds is internally consistent with values observed for Class III compounds.

The radical cation from methylvioligen (10^{2+}, also called paraquat) shows three absorptions having vibrational structure,

10: MV^{2+}
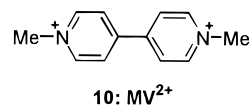
and the longest wavelength peak resolved for the longest wavelength band is at lower energy than that of any of the other compounds considered.[21] The E_{op} of 25.5 kcal/mol for this n

(18) Reimers, J. R.; Hush, N. S. *Inorg. Chem.* **1990**, *29*, 3686.

(19) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

= 7 system is smaller than that for the n = 9 7^+. The band assignments based on Hückel calculations and upon comparison with 4,4-dipyridine radical anion seem reasonable.[21] AM1-NCG calculations totally fail for 10^+, the lowest energy E_{calc} being over 46 kcal/mol higher than E_{op}. We presume that the observed band corresponds to transition to a non-Koopmans' state,[13] which the NCG calculations do not treat at all.

Comparison with Cyanines and Calculated Values. There has been considerable study of the optical spectra of cyanines $11(y)^+$, which are also called polymethine dyes.[22] There is obviously a relationship between the optical absorptions of cyanines and violenes, which we have not seen discussed in relation to electronic interactions.
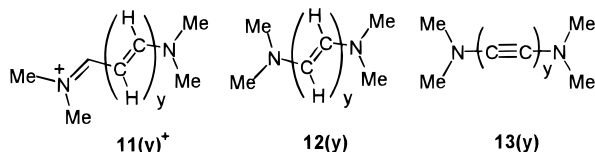
Figure 1 includes optical data for $11(y)^+$, using $V'_{op} = E_{op}/2$, as we did for the violene radical cations. The dashed lines drawn have slope −0.15 and show that similar dependence on distance is observed for these two classes of compounds. These lines correspond to eq 2 V^0 = 41.8 kcal/mol for the violenes, and V'^0 = 74.4 kcal/mol for $11(y)^+$ (in ethanol).[23] The smaller V^0 for the violenes presumably largely reflects poorer electronic coupling caused by the larger energy gap between singly and doubly occupied orbitals than for the fully occupied orbitals of the cyanines.

Somewhat surprisingly, no experimental optical spectral data are available for $12(y)^+$. We did AM1-UHF calculations on all *trans* $12(y)^+$ for y = 1−6 to find out how large y has to be to cause charge localization. All of these radical cations are calculated to be essentially planar at the heavy atoms. The (CH=CH)-bridged $12(1)^+$ has V_{calc} = 36.72 kcal/mol, which is 2.50 kcal/mol higher than its (N=N)-bridged analogue, tetramethyl-2-tetrazene radical cation. This result makes it likely that the β_n values for 6^+ vs 4^+ and 1^+ vs 7^+ being so similar is partially an accident caused by an (N=N) π bond causing less effective coupling than a (CH=CH) π bond. A plot of $\ln(V_{calc})$ vs n for $12(y)^+$ is nearly linear for the n = 3−7 members, with eq 2 parameters V^0_{calc} = 51.82 kcal/mol, $\beta_{n,calc}$ = 0.23, but the plot curves to detectably smaller β_n at higher y values. Charge localization is calculated for $12(6)^+$ (n = 13). The C_1 symmetry energy minimum structure of $12(6)^+$ is 1.83 kcal/mol more stable than the C_2-constrained structure and has a 0.036 Å N−CH bond length difference and 0.111 charge difference at the nitrogens, and the more negatively-charged nitrogen has an average bond angle at N, α_{av}, of 118.7°.[24]

According to Hush theory, localization occurs when $\lambda/2$ is greater than V, so we have also examined vertical reorganization enthalpies, λ'_{calc}, values using the published method[25] λ'_{calc} = $[\Delta H_f(n^+) − \Delta H_f(c^+)] + [\Delta H_f(c^0) − \Delta H_f(n^0)]$, where n and c
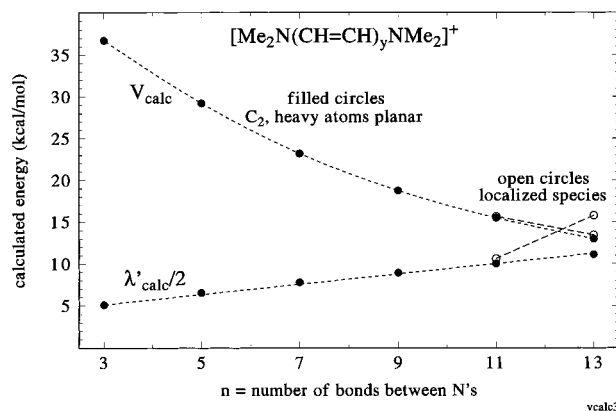

Figure 3. Filled circles: V_{calc} versus $\lambda'_{calc}/2$ plot for all *trans* $12(y)$ constrained to C_2 geometry, and to planarity of the heavy atom system for neutral y = 1 and 6 (see text). Open circles: similar data for localized y = 6 and the anomalous[24] localized y = 5 species.

refer to the geometries of the relaxed neutral and cation, and the superscript is the charge present. The geometries calculated for $12(y)^0$ (C_2 symmetry) as y is changed show complex behavior. $12(1)^0$ is calculated to be significantly nonplanar, α_{av} = 114.9°, N lone pair, π twist angle ϕ = 20.7°, and twist at the double bond ψ = 7.2°. Restricting the heavy atoms to planarity raises ΔH_f by 4.79 kcal/mol. The AM1 structure agrees well with *ab initio* optimized structures: for [RHF/6-31G*] and RMP2/6-31G* structures α_{av} = [114.5°]113.5°, ϕ = [22.2°]-20.1°, ψ = [4.4°]5.7°.[26] Presumably the nitrogens have such strong interaction through a single π bond that the lone pair interactions which make hydrazine twist 90° are still felt significantly. In contrast to NH$_2$-substituted analogues,[27] $12(2)^0$ to $12(5)^0$ are calculated by AM1 to be essentially planar at the heavy atoms. Surprisingly to us, AM1 calculations on $12(6)^0$ give a nonplanar structure, α_{av} = 116.7° and ψ = 3.60° at the terminal double bonds. Restricting the heavy atom framework to planarity increases ΔH_f 1.53 kcal/mol, and restricting one nitrogen to planarity increases it 0.75 kcal/mol, but optimization with the constraints removed gives a nearly C_2 structure of similar energy to the C_2 optimized one. Neutral $12(y)$ changing structure significantly at the y value for which the cation localizes may have some significance, but we are unable to say why it occurs in these calculations. Figure 3 addresses why localization occurs for $12(6)^+$ in AM1 calculations. The filled circles show V_{calc} and $\lambda'_{calc}/2$ as a function of n for $12(y)$ (restricted to having planar heavy atoms for n = 3 and 13, so the series is structurally uniform). λ'_{calc} depends strongly upon neutral species geometry. The nonplanar AM1

(20) (a) Bonvoisin, J.; Launay, J.-P.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1994**, *98*, 5052 (correction: **1996**, *100*, 18006). (b) Bonvoisin, J.; Launay, J.-P.; Verbouwe, W.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1996**, *100*, 17079.

(21) Braterman, P. S.; Song, J.-I. *J. Org. Chem.* **1991**, *56*, 4678.

(22) (a) Dähne, S. *J. Am. Chem. Soc.* **1995**, *117*, 12855. (b) Dähne, L.; Reck, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 690.

(23) Scheibe, G.; Grosse, D.; Heiss, J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 374.

(24) Interestingly, although the C_2 structure for the $12(5)^+$ is an energy minimum, starting from the C_1 structure of $12(6)^+$ with two CH groups omitted, a minimum 0.21 kcal/mol more stable than the C_2 structure was found. It has a 0.020 Å difference in N−CH bond lengths and a 0.085 difference in charges at N, but both nitrogens are planar. This structure appears intermediate between the significantly localized $12(6)^+$ and the delocalized $12(1)^+$ to $12(5)^+$. It is not clear why even a "poorly localized" minimum was found, because as shown in Figure 3, V_{calc} exceeds $\lambda'_{calc}/2$. The localized and delocalized $12(5)^+$ minima are similar enough in enthalpy that it is not clear which would really be most stable at higher levels of calculation. A C_1 minimum was not located for $12(4)^+$.

(25) Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677.

(26) We thank Timothy Clark for providing this calculation.

(27) (a) AM1 calculations get the NH$_2$-substituted y = 3 analogue of $12(3)$ to have pyramidalized nitrogens, in agreement with both X-ray structures on derivatives and 6-31+G* calculations.[27b] AM1 thus treats NH$_2$-substituted y = 3 comparably to 6-31G* *ab initio* calculations (and far better than 3-21G calculations, which get the nitrogens planar). (b) Erker, G.; Pfaff, R.; Kowalski, D.; Würthwein, E.-U.; Krüger, C.; Goddard, R. *J. Org. Chem.* **1993**, *58*, 6771.

energy minimum for **12(1)** produces a λ'_{calc} which is 19 kcal/mol higher than the planar one. $\lambda'_{calc}/2$ increases nearly linear with n, while V_{calc} drops somewhat less than exponentially. V_{calc} is higher than $\lambda'_{calc}/2$ for the artificially constrained planar **12-(6)**, $n = 13$ (filled symbols), so if **12(6)**$^+$ were planar and delocalized like the lower members of the series, V is predicted to be greater than $\lambda/2$. However, allowing relaxation to the charge localized species, which has lower enthalpy, substantially increases λ'_{calc} without increasing V_{calc} very much, and these calculations fulfill the Hush criterion that localization occurs when $\lambda/2$ becomes greater than V. Localization might well occur at smaller **y** in solution, because solvation always favors charge localization, and these calculations do not include solvent reorganization, so the real λ will be larger than that calculated.

We also calculated the acetylene-bridged series, **13(y)**$^+$. Symmetry was only restricted to C_2, but the **y** = 1−4 cations are optimized with nearly planar heavy atoms and linear NC$_{2y}$N units, and the **y** = 5 and 6 members were also calculated in this geometry, to give an isostructural series. In constrast to **12(y)**$^+$, where $\beta_{n,calc}$ decreases noticeably with increasing **y**, the $\ln(V_{calc})$ vs n plot for delocalized **13(y)**$^+$ is linear from **y** = 1−6, and $V°_{calc} = 50.05$, $\beta_{n,calc} = -0.256$. These calculations get C≡C units to be slightly less efficient couplers than CH=CH units, both in terms of $V°_{calc}$ and faster fall-off in V_{calc} as more units are added. Localization occurs for **13(5)**$^+$ (localized structure 1.02 kcal/mol more stable than the delocalized one), and the localized structure is 9.42 kcal/mol more stable than **13(6)**$^+$ having enforced C_2 symmetry. In both cases the delocalized structure appears to be a second energy minimum. Although especially the lower members of the neutral **13(y)** series are complex geometrically because of low barriers and slightly bent minima at several bonds, making finding a consistent geometry series for obtaining λ'_{calc} difficult, both localized **13(5)**$^+$ and **13(6)**$^+$ clearly have V_{calc} less than $\lambda'_{calc}/2$, as expected.

Comparison of N-Centered with Transition Metal-Centered Intervalence Complexes. It is interesting to compare the above results for intervalence compounds with amine charge-bearing units with those for the intensively studied ruthenium(pentammine) systems.[3] Reimers and Hush have recently discussed the dipyridylethylene-bridged (NC$_5$H$_5$-(CH=CH)$_y$H$_5$C$_5$N) bisruthenium(pentammine) intervalence oxidation state (+5) complexes, which we will call **14(y)**.[18]

14(y)
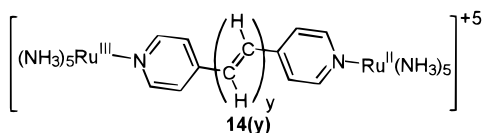
They are Class II, localized compounds, for which V was estimated using Hush theory. We will only consider the **y** = 0 and 1 examples that, for technical reasons, gave much better estimates of V_H. For **14(0)**, the 4,4′-bipyridyl complex, $V_H = 1.12(4)$ kcal/mol and for **14(1)**, $V_H = 0.86(4)$ kcal/mol.[18] Calculations indicate that V is proportional to the twist angle ϕ between the aryl rings or the aryl ring and the double bond, assumed to average to 32° for the **y** = 0 complex and 17° (two such twists) for the **y** = 1 complex from data for biphenyl and styrene, which gives V^0_H for hypothetically untwisted complexes of 1.32 and 0.94 kcal/mol. Comparing these V^0_H values for

14(0) and **14(1)** produces $\beta_n = 0.34$,[28] fairly close to but slightly higher than the β_n obtained above using E_{op} for nitrogen-centered Class III compounds. It should be noted that V_{op} for **7**$^+$ is an order of magnitude larger than V_H for its $n = 9$ organometallic analogue **14(0)**, presumably principally a result of far larger N$_p$,C$_p$ than Ru,N$_p$ overlap. The large difference in V values rationalizes the former being a Class III compound and the latter Class II, although the larger λ_v expected for an amine charge-bearing unit also contributes.

The ruthenium-ammine analogue of **1**$^+$ is the Creutz−Taube complex (the first transition metal-centered intervalence compound prepared), bis(pentaammineruthenium)pyrazine^{5+}, **14(pz)**. Whether it is Class II or Class III generated an enormous amount of discussion,[29] but **14(pz)** is now generally recognized to be

14(pz)
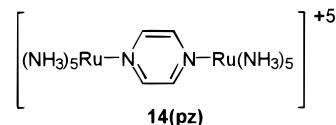
Class III (delocalized) based on optical, electrochromic, ESR, and other experimental data, combined with their successful modeling.[30] It seems to us unfortunate that the ∼1600 nm near IR band is still referred to as an intervalence transition,[31] because assignment of this band as the Hush-type intervalence band for which $E_{op} = 2V$ seems be the source of all the confusion. If the near-IR band were Hush's intervalence band, **14(pz)** could not be a Class III intervalence complex, because V_{op} would have to be ∼9 kcal/mol, clearly too large, so early assignments for **14(pz)** were to Class II. As now assigned, this band is not related to the intervalence transition of Hush theory. Instead, the near IR band is the third optical transition of this Class III system. The lowest energy band was only observed with considerable difficulty, because it is only about 5% the intensity of the near IR band. It occurs in the IR, at about 2000 cm^{-1} (which was pointed out to be close to an 1837 cm^{-1} theoretical estimate), and is so broad that seeing it requires substantial effort to be put into solvent baseline corrections, using both normal and deuterated solvent.[30e] Piepho has given detailed consideration to complex vibronic coupling models of the absorption bands for **14(Pz)**.[30f] We note that Hush's assignment of E_{op} for lowest energy band of a Class III complex as being equal to $2V$ does not address the orbital structure of the band. Using the β_n of 0.17 obtained from the Class II **14(0)** and **14(1)** predicts a V_H of 2.6 kcal/mol for **14(pz)**, and half the transition energy for the longest wavelength band using the 1837 cm^{-1} theoretical value is 2.6 kcal/mol, which is also within experimental error of that reported experimentally. The simple Hush theory

(28) (a) Many other values for these intensively studied compounds exist in the literature. For example, using slightly different experimental V_H values and ignoring twisting effects, Woitellier and co-workers[28b] obtain $\beta_n = 0.09$ for **9(0)**:**9(1)** and also calculate 0.09 using extended Hückel calculations for **n** = 0−4 and 8.[28c] (b) Joachim, C.; Launay, J. P.; Woitellier, S. *Chem. Phys.* **1990**, *147*, 131. (c) Note that the values quoted in 28b are β (Å^{-1}); we converted them to the β_n used here.

(29) Fürholz, U.; Bürgi, H.-B.; Wagner, F. E.; Stabler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121.

(30) (a) Hush, N. S.; Edgar, A.; Beattie, J. K. *Chem. Phys. Lett.* **1980**, *69*, 128−33. (b) Dubicki, L.; Ferguson, J.; Krausz, E. R. *J. Am. Chem. Soc.* **1985**, *107*, 179. (c) Dubicki, L.; Ferguson, J.; Krausz, E. R.; Lay, P. A.; Maeder, M.; Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1985**, *107*, 2167. (d) Ondrechen, M. J.; Ko, J.; Zhang, L.-T. *J. Am. Chem. Soc.* **1987**, *109*, 1672. (e) Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Joss, S. *J. Am. Chem. Soc.* **1989**, *111*, 548. (f) Piepho, S. B. *J. Am. Chem. Soc.* **1990**, *112*, 4197.

(31) (a) Lu, H.; Petrov, V.; Hupp, J. T. *Chem. Phys. Lett.* **1995**, *235*, 521. (b) Dong, Y.; Hupp, J. T.; Yoon, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 4379.

analysis works well for **14(pz)** and also indicates that Hush analyses for both Class II and Class III compounds are internally consistent.

Lapinte and co-workers have established that the acetylene-bridged iron systems **15(2)** and **15(4)** are both Class III compounds,[32] as Gladysz and co-workers have established for **16(2)**.[33] The intervalence band optical data for Lapinte's

15(y)   **16(y)**
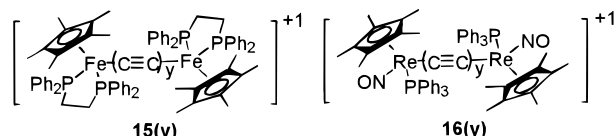
cylindrically symmetrical linear carbon chain bridged compounds, 1302 nm in CH_2Cl_2 for the $n = 5$ **15(2)**,[32a] and 1958 nm in CH_2Cl_2 for the $n = 9$ **15(4)**,[32b] produce a β value of 0.20, smaller than that obtained for the anisotropic pyridine-based ligands in ruthenium compounds. Lapinte and co-workers have also studied the 1,4-diethynylbenzene-bridged compound, which is also $n = 9$, with the middle two C≡C units of **14(4)** replaced by a benzene ring. They obtain $\lambda_{max} = 2016$ nm, so V_{op} is 97% as large as for the linear C_8 bridge.[32c] The $n = 5$ systems **15(2)**[32] and **16(2)**[33bf] have $E_{op}/2$ values of 11.0 and 11.9 kcal/mol respectively, larger by factors of 4.2 and 4.6 than that of **14(pz)** (using the 2.6 kcal/mol estimate) but smaller than that for the $n = 5$ diamine **1$^+$** by about a factor of two.

Conclusions

The β_n value in eq 2 derived from E_{op} of Class III N-centered *IV*-compounds having p-phenylene and dinitrogen bridges with $n = 3-9$ (∼0.3) is only slightly smaller than that derived by Hush's analysis of Class II metal-centered *IV*-compounds with bipyridine and bipyridyl-ethylene bridges having $n = 9-11$ (0.34), and the latter value is consistent with E_{op} of the $n = 5$ pyrazine-bridged Class III Creutz−Taube complex. Thus

equation of $E_{op}/2$ for Class III compounds with the *V* of ET theory leads to values which are consistent with *V* values estimated using Hush theory for Class II compounds. V_{op} depends strongly upon the orbital structure of the bridge and also upon that of the charge-bearing units, a factor which has sometimes been ignored in comparing experimental results with theory. π-Linked amine-centered intervalence compounds show a much stronger tendency to be delocalized than their transition metal-centered counterparts, despite dialkylamino groups having larger λ values than transition metal-centered charge-bearing units, beause *V* values for the amine-centered charge-bearing units is significantly larger. AM1 E_{calc} values correlate fairly well with E_{op} values for π-linked diamines, including the doubly-linked **8$^+$**. The E_{calc} value for **10$^+$** (**MV$^+$**) is nowhere near E_{op}, presumably indicating that **10$^+$** has a non-Koopmans' excited state. It is clear that omitting configuration interaction by using NCG calculations ignores many possible effects. We find it surprising that NCG calculations perform as well as they do in estimating E_{op} values for most of the compounds studied. Comparison of AM1 V_{calc} with $\lambda'_{calc}/2$ values for violenes **12-(y)$^+$** and **13(y)$^+$** are consistent with the localization at **y = 6** and 5, respectively, calculated for the geometry-optimized structures. This indicates that the V_{calc} and λ'_{calc} values obtained by the simple methods used here are internally consistent with the calculated structures. A major factor that is ignored in these calculations is solvent reorganization energy, which will certainly increase the real λ for the charge-localized structures.

Experimental Section

4,[34a] **5**,[15,34a] **6**,[34b] and **7**[35] were prepared as previously described. **7$^+$** decomposes upon attempted isolation, and spectra were obtained by *in situ* oxidation with less than 1 equiv of NOBF$_4$. Optical spectra were recorded on Hewlett-Packard 8452A diode array (cutoff 820 nm) or Perkin Elmer Lambda 20 (cutoff 1100 nm) instruments. Calculations used Clark's VAMP package.[36]

(32) (a) Le Narvor, N.; Toupet, L.; Lapinte, N. *J. Am. Chem. Soc.* **1995**, *117*, 7129. (b) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477. (c) Private communication from Prof. Lapinte.

(33) (a) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509. (b) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775. (c) The larger **y** value compounds are unstable in their intervalence oxidation state and have not been studied.[25d,e] (d) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655. (e) Bartik, T.; Bartik, B.; Brady, M.; Dembninski, R.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414. (f) Although Gladysz uses the more intense, shorter wavelength near IR bands in estimating *V* for **10(2)**, we suggest that only the longest wavelength band should be employed, as indicated by the behavior of **8-(pyz)**, where employing excitation to higher levels clearly does not allow estimation of *V*. If the three bands observed for **10(2)** represent vibrational coupling, the 0,0 band is that needed for estimation of *V*.

(34) (a) Nelsen, S. F.; Kessel, C. R.; Grezzo, L. A.; Steffeck, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5482. (b) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

(35) Giumanini, A. G.; Chiavari, G.; Musiani, M. M.; Rossi, P. *Synthesis* **1980**, 743.

(36) Most VAMP calculations used version 5.6 (on an IBM RS-6000). See: Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T. *VAMP 5.0*; Oxford Molecular: Oxford, 1994.