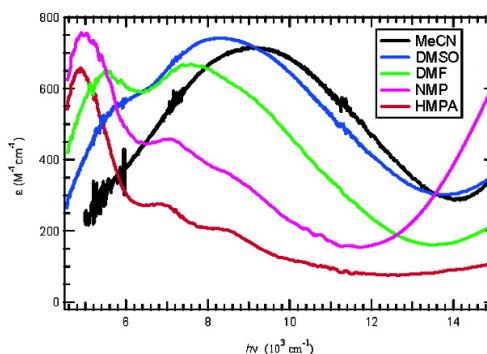
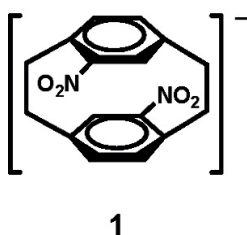


## Pseudo-para-dinitro[2.2]paracyclophane Radical Anion, a Mixed-Valence System Poised on the Class II/Class III Borderline

Stephen F. Nelsen, Asgeir E. Konradsson, and Joo P. Telo

*J. Am. Chem. Soc.*, **2005**, 127 (3), 920-925 • DOI: 10.1021/ja0441920 • Publication Date (Web): 30 December 2004

Downloaded from <http://pubs.acs.org> on March 24, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 11 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## Pseudo-para-dinitro[2.2]paracyclophane Radical Anion, a Mixed-Valence System Poised on the Class II/Class III Borderline

Stephen F. Nelsen,<sup>\*,†</sup> Asgeir E. Konradsson,<sup>†</sup> and João P. Telo<sup>\*,‡</sup>

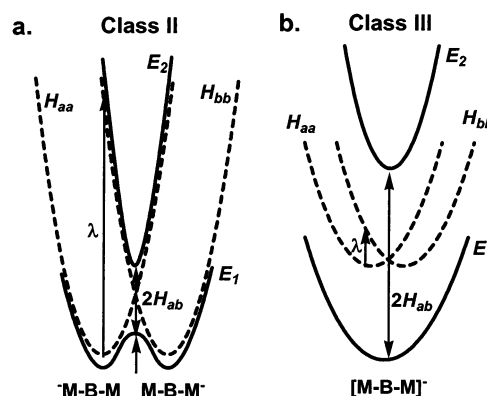
Contribution from the Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396, and Instituto Superior Técnico, Química Orgânica, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Received September 24, 2004; E-mail: nelsen@chem.wisc.edu; jptelo@ist.utl.pt

**Abstract:** Analysis of optical spectra of a pseudo-para-dinitro[2.2]paracyclophane radical anion using Marcus–Hush theory reveals that its off diagonal coupling element,  $H_{ab}$ , is large enough, relative to its reorganization energy, to change it from a localized class II compound to a delocalized class III compound by changing solvents. The optical spectra, along with frontier orbital analysis, show that the assumption that  $E_{op} = 2H_{ab}$  for class III compounds is not true in this case.

### Introduction

Symmetrical mixed-valence compounds may be formulated as  $[M-B-M]^n$  systems, where **M** is a charge-bearing unit, **B** is a bridge to which the **M** groups are symmetrically attached, and the overall charge  $n$  allows the charges on **M** to differ by one unit. When the **M** groups actually do have different charges, they are called Robin–Day Class II compounds,<sup>1</sup> which are the simplest electron-transfer (ET) systems ever devised.<sup>2</sup> As shown in the Marcus–Hush diagram of Figure 1a, intervalence compounds may be modeled as having parabolic diabatic energy wells, the dashed lines in Figure 1, corresponding to the odd electron being on the left (shown as  $H_{aa}$ ) or the right ( $H_{bb}$ ) **M** unit. They are written displaced from each other (at 0 and 1 on the horizontal, electron-transfer axis). The relative sizes of the vertical displacement between the parabolas at their energy minima, called the reorganization energy,  $\lambda$ , and the electronic interaction energy between the diabatic energy surfaces,  $H_{ab}$ , determine the shape of the ground-state adiabatic energy surface (the solid line,  $E_1$ ). When  $H_{ab}$  is smaller than  $1/2\lambda$ , the compound is localized (Class II) and  $E_1$  has a double potential minimum and a transition state between the minima at 0.5 on the horizontal axis. Class II mixed-valence compounds have a lowest energy absorption band (often called the intervalence band) that is nearly Gaussian-shaped, much broader than most optical absorption bands,<sup>3</sup> and typically lies in the near-IR region. The vertical energy gap between the adiabatic as well as the diabatic



**Figure 1.** Marcus–Hush diagrams for localized (Class II, a) and delocalized (Class III, b) intervalence compounds.

surfaces is  $\lambda$ , and energy absorption excites the system to a steeply sloping region of the excited-state adiabatic surface,  $E_2$ , which as Heller explained using time-dependent concepts, causes the broad shape of the band.<sup>4</sup> The electron-transfer mechanism assumed using two-state theory is called superexchange,<sup>5</sup> in which electrons hop simultaneously to and from the bridge, so that the overall transition is equivalent to an electron moving from one **M** unit to the other, and charge never builds up on the bridge. Hush developed a remarkably simple Gaussian approximation analysis of the optical spectrum of Class II compounds. The vertical reorganization energy ( $\lambda$ ) is the transition energy of the band maximum ( $E_{op} = \lambda$ ), and the electronic coupling  $H_{ab}$  is obtained from the bandwidth at half-height ( $\Delta\nu_{1/2}$ ), band maximum extinction coefficient ( $\epsilon_{max}$ ), and  $E_{op}$ .  $H_{ab}(\text{cm}^{-1}) = [0.0206/d_{ab}] (\Delta\nu_{1/2}\epsilon_{max}E_{op})^{1/2}$ , where  $d_{ab}$  is the ET distance on the diabatic surfaces in Å, usually

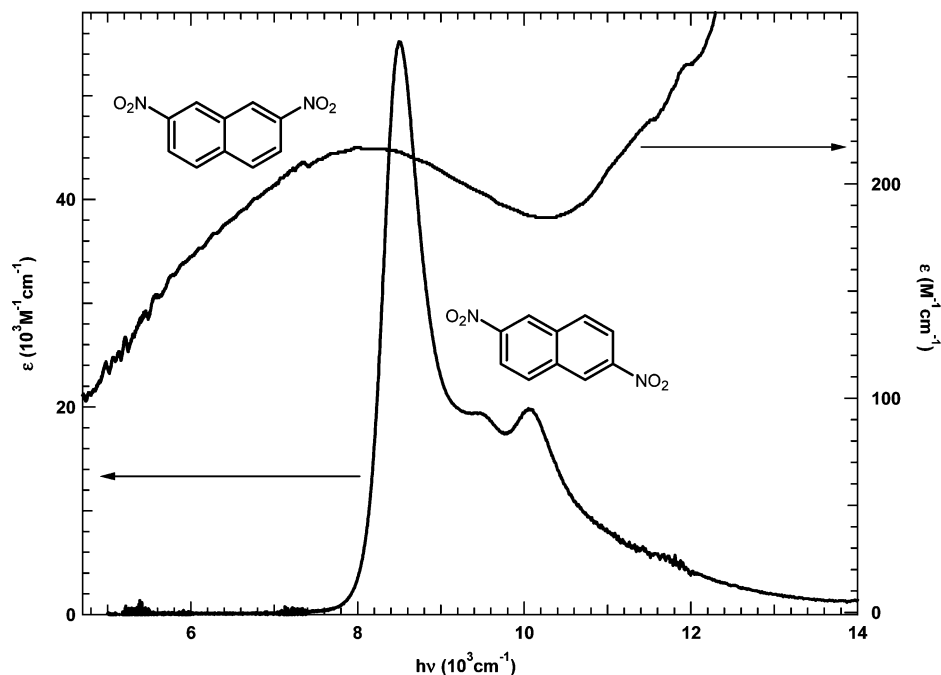
<sup>†</sup> University of Wisconsin.

<sup>‡</sup> Instituto Superior Técnico.

- (1) Robin, M.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247–422.
- (2) For reviews of electron transfer, see (a) Bixon, M.; Jorner, J. *Adv. Chem. Phys.* **1999**, *106*, 35–202. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.
- (3) (a) Bandwidth at half-height larger than  $(16 \ln(2)k_B T E_{op})^{1/2}$  (see ref 3b, which is 3400–4800  $\text{cm}^{-1}$  in the 5000–10000  $\text{cm}^{-1}$   $E_{op}$  range of the compounds discussed here). (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–444.

(4) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368–375.

(5) (a) Kosloff, R.; Ratner, M. A. *Isr. J. Chem.* **1990**, *30*, 45–58. (b) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148–13168.



**Figure 2.** Comparison of the optical spectra in DMF for the Class III 2,6- and the Class II 2,7-dinitronaphthalene radical anions.

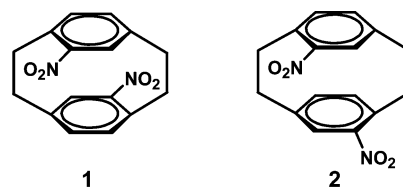
assumed from the structure. The optical method of determining the ET barrier using classical two-state theory, especially with a slight modification to allow fitting the absorption spectrum instead of assuming that the diabatic surfaces are perfect parabolas, has been shown to be remarkably successful by measuring the ET rate constant for several unusually large  $\lambda$  Class II dinitrogen-centered radical cations that have small enough ET rate constants to allow their measurement by electron spin resonance.<sup>6</sup>

Another possibility is that an intervalence compound would be charge-delocalized, having fractional charges at each **M** group that are instantaneously the same. Such systems are called Robin–Day Class III compounds.<sup>7</sup> As can be seen in Figure 1b, when  $2H_{ab}$  is large compared to  $\lambda$ , the ground-state surface only has a single minimum, at 0.5 on the ET coordinate, so the optical transition would be from one minimum to another if the two-state model is employed, providing the possibility for narrower optical absorption bands. The current great interest in exceptionally fast ET systems that lie near the Class II, Class III borderline has resulted in three reviews on the subject since 2000.<sup>8–10</sup> Our present paper concerns a radical anionic system having **M** = NO<sub>2</sub> that is so finely balanced at the borderline that changing solvent tips it between Class II and Class III, resulting in a large change in the optical spectrum, which one of us had predicted not to occur upon passing the borderline.<sup>10</sup> Delocalized dinitroaromatic radical anions exhibit rather narrow intervalence bands that typically show partially resolved vibrational fine structure,<sup>11</sup> such as that illustrated in Figure 2 for a

2,6-dinitronaphthalene radical anion in DMF. In contrast, when the substitution pattern is changed from one causing large coupling between the charge-bearing units (a “Kekule” substitution pattern),<sup>12</sup> to a “non-Kekule” one that causes small coupling, charge localization occurs.<sup>13</sup> The intervalence band then takes the familiar much broader and nearly Gaussian shape shown in Figure 1 for a 2,7-dinitronaphthalene radical anion.

## Results

We report here the optical spectra of the radical anions from two dinitro[2.2]para-cyclophanes, the pseudo-para (**1**) and pseudo-ortho (**2**) isomers, which were first correctly identified by Reich and Cram.<sup>14</sup> Harriman and Maki demonstrated in



pioneering ESR studies of electron-transfer that linking nitrobenzenes by a dimethylene (CH<sub>2</sub>CH<sub>2</sub>) bridge caused slow ET on the ESR time scale,<sup>15</sup> but the [2.2]paracyclophane system has significant through-space and through-bond interactions that enhance electronic interactions between the aromatic rings.<sup>16</sup> The spectra of **1**<sup>−</sup> in five solvents are compared in

(6) (a) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. A., II. *Science* **1997**, *278*, 846–849. (b) Nelsen, S. F.; Ismagilov, R. F.; Gentile, K. E.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 7108–7114.  
 (7) Class I was reserved for systems in which the bridge prevented any communication between the charge-bearing units.<sup>1</sup>  
 (8) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168–184.  
 (9) Demadis, K. D.; Hartshorn, C. M. Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655–2685.  
 (10) Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581–588.

(11) Nelsen, S. F.; Telo, J. P.; Konradsson, A. E.; Weaver, M. N. *J. Am. Chem. Soc.* **2003**, *125*, 12493–12501.  
 (12) Rajca, A. *Chem. Rev.* **1994**, *94*, 871–893.  
 (13) Among many others, see: (a) Gutch, J. W.; Waters, W. A.; Symons, M. C. R. *J. Chem. Soc. B* **1970**, 1261–1267. (b) Grampp, G.; Shohoji, M. C. B. L.; Herold, B. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 580–585. (c) Hosoi, H.; Mori, Y.; Masuda, Y. *Chem. Lett.* **1998**, 177–178. (d) Nelsen, S. F.; Weaver, M. N.; Konradsson, A. E.; Telo, J. P.; Clark, T. *J. Am. Chem. Soc.* **2004**, *126*, 15431–15438.  
 (14) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1968**, *91*, 3527–3533.  
 (15) Harriman, J. E.; Maki, A. H. *J. Chem. Phys.* **1963**, *39*, 778–786.

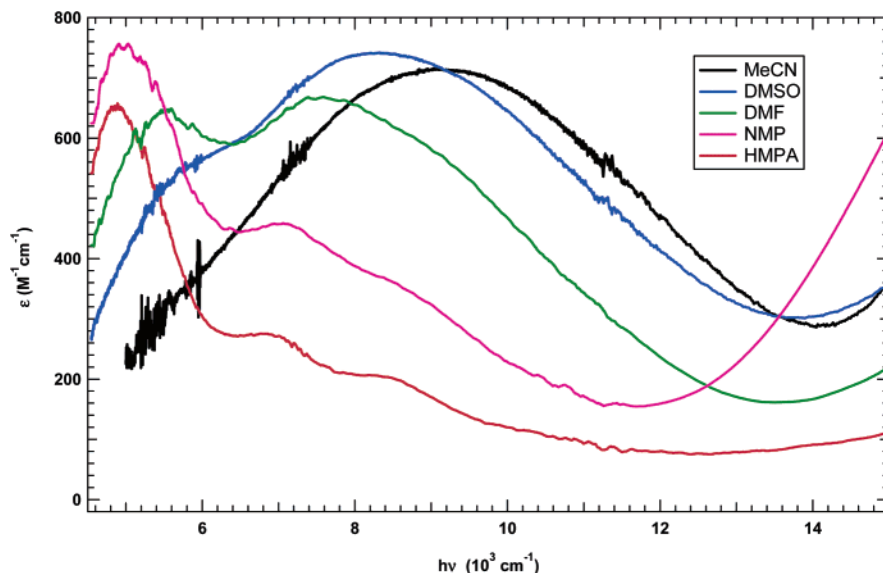


Figure 3. Spectra of  $1^-$  in five solvents.

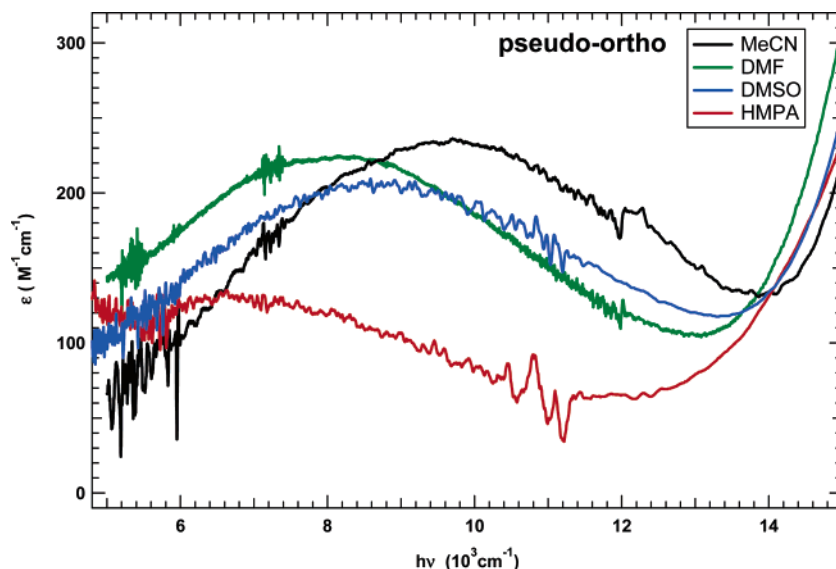
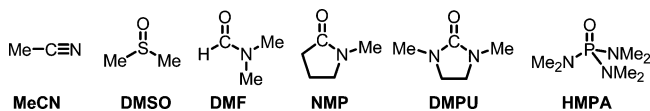


Figure 4. Spectra of  $2^-$  in acetonitrile, dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoramide.

Figure 3. The abbreviations used here for solvents are shown below.



The single nearly Gaussian band of  $1^-$  in acetonitrile moves to lower energy and develops a lower energy component in DMSO and DMF, and in NMP, DMPU, and HMPA, the low energy component is completely dominant and appears to show partially resolved vibrational fine structure resembling that of the 2,6-dinitronaphthalene radical anion. The MeCN spectrum thus appears to be that of a localized system, but the NMP, DMPU, and HMPA spectra appear to be those of a delocalized species, and the spectra in DMSO and DMF have intermediate character.<sup>17</sup>

The spectra of the pseudo-ortho isomer,  $2^-$ , in four solvents appear in Figure 4. In contrast to  $1^-$ , the spectrum of  $2^-$  in DMSO, DMF, and HMPA as well as in MeCN is that of a localized species, and no low energy band develops in low  $\lambda_s$  solvents. The band maxima become lower in DMSO and DMF (see Table 1), and the band maximum in HMPA is about  $3000\text{ cm}^{-1}$  lower than that in MeCN.

## Discussion

**Solvent Effects.** We postulate that, despite the aryl rings of [2.2]paracyclophane being formally unconjugated, there is enough electronic interaction between them in  $1^-$  to cause  $H_{ab}$  to be large enough to allow delocalization in HMPA, NMP, and DMPU, that is, that  $H_{ab} > \lambda/2$  in these solvents. The total vertical reorganization energy,  $E_{op} = \lambda$ , is the sum of its internal vibrational ( $\lambda_v$ ) and solvent ( $\lambda_s$ ) components. Although  $\lambda_s$  is often

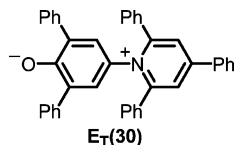
(16) (a) Heilbronner and Yang estimate the through-space  $\pi$ -system interaction parameter for [2.2]paracyclophane from photoelectron spectroscopic spectra of a series with different bridge sizes at  $7600\text{ cm}^{-1}$ .<sup>16b</sup> (b) Heilbronner, E.; Yang, Z. *Top. Curr. Chem.* **1983**, *115*, 1–55.

(17) The spectrum in *N,N'*-dimethyltrimethyleneurea, DMPU, is not shown. It is noisy and rather weak, presumably from radical anion decomposition, but resembles that in HMPA. JPT was unable to obtain spectra in acetone or propylene carbonate.

**Table 1.** Solvent "Polarity" Parameters and Observed Band Maxima

solvent	$g$	$E_T(30)$	band maxima (cm <sup>-1</sup> )	
			1 <sup>-</sup>	2 <sup>-</sup>
MeCN	0.528	45.6	9160	9660
DMSO	0.437	45.1	~8200; sh ~5760	~8500
DMF	0.463	43.8	~7580; ~5550	~8200
DMPU	0.449	42.1	~5000	
NMP	0.433	42.2	~4950	
HMPA	0.437	40.9	4850	~6600

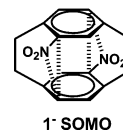
assumed to be directly proportional to the Pekar factor  $\gamma = 1/n^2 + 1/\epsilon_s$ , where  $n$  is the solvent refractive index and  $\epsilon_s$  is its static dielectric constant, the spectra for 1<sup>-</sup> indicate that its  $\lambda_s$  does not track  $\gamma$ . The spectrum in DMSO is clearly closer to that in the high  $\gamma$  MeCN, while the spectrum in DMF is closer to that of the lower  $\gamma$  solvents. Plots of band maximum versus  $\gamma$  for dinitrogen-centered Class II radical cations are also not linear with  $\gamma$ ,<sup>18</sup> but they show a significant increase in solvents of higher Gutmann solvent donicity.<sup>19</sup> For 10 bis(hydrazine)-centered ( $R_4N_2^{0/+}$ ) and bis(diazonium)-centered ( $R_4N_2^{0/+}$ ) compounds, the intervalence band transition energy maximum is 300 to 600 cm<sup>-1</sup> larger in DMF than in MeCN, despite the lower  $\gamma$  for DMF.<sup>18b</sup> Not surprisingly, the intervalence radical anions studied here show no evidence of an increase in  $\lambda_s$  as the solvent gets more donating, but instead  $\lambda_s$  for these radical anions appears to increase as the Dimroth–Reichart  $E_T(30)$  parameter<sup>20</sup> increases.  $E_T(30)$  is the transition energy for pyridinium



phenoxide  $E_T(30)$  in kcal/mol and roughly correlates with acceptor ability of the solvent, presumably because of specific solvation effects of the phenoxide oxygen,<sup>21</sup> which might be thought to reasonably correlate with specific solvation effects of the nitro oxygens in 1<sup>-</sup>.

**Calculations.** If  $\lambda_s$  has decreased enough in DMF for 1<sup>-</sup> to start showing a low energy optical component, why does the spectrum of 2<sup>-</sup> not have the same behavior? As discussed above, delocalization occurs when  $H_{ab}$  exceeds  $\lambda/2$ .  $H_{ab}$  is significantly larger for 1<sup>-</sup> than for 2<sup>-</sup>, as shown by their relative  $\epsilon_{max}$  values (see Figures 3 and 4). The ratio of transition dipole moments ( $\mu_{12}$ ) for 1<sup>-</sup>/2<sup>-</sup> obtained by integrating Gaussian fits to the MeCN absorption spectra is about 1.8. Although it is not obvious what the  $d_{ab}$  values actually are for these systems, the nitro groups are clearly further apart for 1<sup>-</sup> (the calculated N,N distances are 6.16 Å in 1<sup>-</sup> and 4.55 Å in 2<sup>-</sup>) so  $H_{ab}$  must be larger for 1<sup>-</sup>. The reason for the lower  $H_{ab}$  of 2<sup>-</sup> is clear from

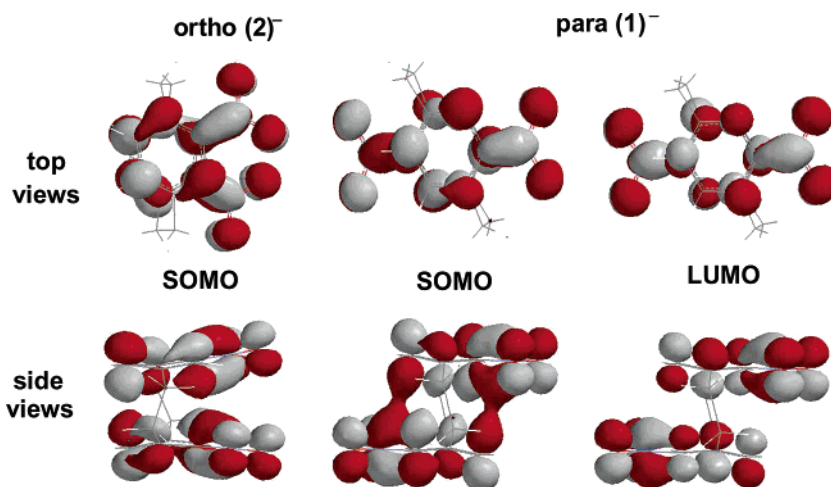
calculations on these systems. The nodal patterns for the SOMO of these two compounds differ significantly; see Figure 5.<sup>22</sup> The 1<sup>-</sup> orbitals have positive overlap between the CN bonds and the pseudo-geminal carbons on the opposite rings, as shown by the dashed lines on the 1<sup>-</sup> SOMO structure below, while the signs are opposite for 2<sup>-</sup>, causing less cross-ring interaction, as is clear in the orbital density drawings of Figure 6 (left and center).



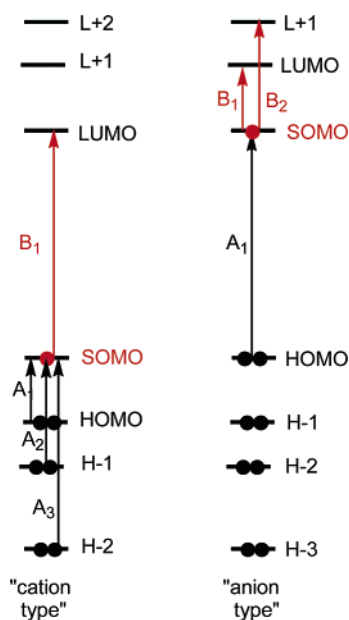
We have used simple Koopmans' theorem-based calculations to estimate the transition energies for these systems. Optical transitions in doublet systems are often discussed in terms of a restricted open shell (also called half-electron) model, where all the orbitals are doubly occupied except for one singly occupied (which we will call the SOMO or  $S$ ). This leads to orbital diagrams such as those shown in Figure 6.<sup>23</sup> Stable neutral compounds typically have a bigger gap between their highest occupied molecular orbital (HOMO or  $H$ ) and lowest unoccupied one (LUMO or  $L$ ) than between either filled or virtual orbitals. Removal of an electron then gives a cation radical with SOMO closer to the filled orbitals than the virtual ones, as shown at the left of Figure 6, and the smallest excitation energies correspond to filled orbital to  $S$  transitions, Type A, indicated as  $A_i$  in Figure 6. Addition of an electron populates the  $L$  of the neutral species, and as indicated on the right of the diagram, then the smallest excitation energies correspond to SOMO to virtual orbital transitions, type B, indicated as  $B_j$  in Figure 6. Because alternate aromatic hydrocarbons have virtual orbitals that are nearly mirror images of their filled orbitals, the absorption spectra of their radical cations and radical anions are quite similar, as already pointed by Hoijtink in 1957, discussing the spectrum from perylene in concentrated sulfuric acid as the radical cation because of its resemblance to that of the known radical anion.<sup>24</sup> Type A transitions are between Koopmans' configurations of the type  $...(H - 1)^2(H)^2(S)^1 \rightarrow ...(H - 1)^2(H)^1(S)^2$ , shown as  $A_1$  in the diagram and are also called K (for Koopmans), while the lowest energy type B transition is between non-Koopmans' configurations  $...(H - 1)^2(H)^2(S)^1 \rightarrow ...(H - 1)^2(H)^2(S)^0(L)^1$ , also called NK. However, there are no two electron orbitals in a doublet species. All of the orbitals of a radical ion are actually split by varying amounts of energy into  $\alpha$  and  $\beta$  spin sets, and electronic excitation typically does not flip spins, so the type A transitions are actually  $\beta(H) \rightarrow \beta(L)$ ,  $\beta(H - 1) \rightarrow \beta(L)$  etc., and the type B transitions are  $\alpha(H) \rightarrow \alpha(L)$ ,  $\alpha(H) \rightarrow \alpha(L + 1)$ , etc. More complex non-Koopmans' transitions also occur, such as type C,  $\alpha(H - n) \rightarrow \alpha(L + n)$  or  $\beta(H - n) \rightarrow \beta(L + n)$ , as well as multiple electron excitations such as the superexchange transition of localized intervalence radical cations, which we believe is most simply

- (18) (a) Nelsen, S. F.; Trieber, D. A., II.; Ismagilov, R. F.; Teki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 5684–5694. (b) An eleventh compound shows the opposite trend, but it is anomalous in several ways and appears likely to have an unsymmetrical solution structure.
- (19) (a) Gutmann, V. *Coord. Chem. Rev.* **1976**, *28*, 225–255. (b) Gutmann, B. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum: New York, 1980.
- (20) (a) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.
- (21) Reichardt has noted a general correlation between  $E_T(30)$  and Gutmann's acceptor number (AN),<sup>19a</sup> but the order of MeCN and DMSO is inverted between these two scales, and the observed spectral trends for 1<sup>-</sup> fit MeCN being a better acceptor than DMSO.

- (22) The calculations and drawings were carried out using Spartan'02, Wavefunction Inc., Irvine, CA.
- (23) (a) Bally, T. In *Radical Ionic Systems*; Lund, A., Shiotani, M., Eds.; Kluwer: Dordrecht, 1991; pp 3–54. (b) Čársky, P.; Zahradník, R. *Top. Curr. Chem.* **1973**, *43*, 1–55.
- (24) (a) Hoijtink, G. J.; Weijland, W. P. *Recl. Trav. Chim. Pays-Bas* **1957**, *76*, 836–838. (b) Buschow, K. J. J.; Dieleman, J.; Hoijtink, G. J. *Mol. Phys.* **1963–1964**, *7*, 1–9.



**Figure 5.** Two views of the  $\alpha$ -homo ("SOMO") orbitals of the pseudo-ortho 2<sup>-</sup> and pseudo-para 1<sup>-</sup>, compared with the LUMO (NAG lumo + 1) of 1<sup>-</sup> (right).



**Figure 6.** ROHF models of the orbital energies of a doublet radicals.

considered as a concerted double excitation  $\mathbf{B} \rightarrow \mathbf{M}^+$ ,  $\mathbf{M}^0 \rightarrow \mathbf{B}$ , but TD-DFT calculations<sup>25</sup> indicate that the lower energy transitions for many delocalized intervalence compounds, including the lower transitions of the dinitroaromatic radical anions studied here, are quite predominately either type A or B transitions.

We introduced a simple method for estimating the Hoihtink type A transition energies for radical cations using the "neutral in cation geometry" (NCG) method, in which a single point at the geometry of the radical cation is calculated with a neutral charge, so the system is closed-shell, and the orbitals involved in the transitions each have two electrons.<sup>26</sup> The equal orbital

occupancy allows Koopmans' theorem,<sup>27</sup> that ionization potentials may be equated with the negative of orbital energies,<sup>23a</sup> to work quite well. The orbital separation in an NCG radical cation calculation is a good approximation to the transition energy that would be calculated by a more sophisticated method, and even simple semiempirical calculations proved useful for understanding experimental data. We also showed previously that the calculated energies for the first transition obtained by the NCG method using AM1 semiempirical calculations give rather good correlations with experimental data for symmetrical diamino-substituted aromatic intervalence radical cations, although the calculated transition energies were high, by 2650 cm<sup>-1</sup> for a *N,N,N',N'*-tetramethyl-*p*-phenylenediamine radical cation, **TMPD**<sup>+</sup>, 3700 cm<sup>-1</sup> for the corresponding bis[9-(9-azabicyclo-[3.3.1]nonane)-protected species, and 800 cm<sup>-1</sup> for a tetramethylbenzidine radical cation.<sup>28</sup> Not surprisingly, single-point NCG calculations using UB3LYP/6-31G\* geometry (which we will call DFT for brevity) structures give answers closer to experiment than do the AM1 calculations,<sup>29</sup> and we will only use numbers obtained from DFT-optimized radical ion geometries here.

As expected, the lowest energy transitions for dinitroaromatic radical anions are not type A but type B transitions. We suggest that the correspondingly simple estimate of type B transition energies is to use orbital energy separations for the neutral at anion geometry (NAG) for the radical anions studied here. This results in no electrons in either orbital for the B transitions, so Koopmans' theorem might work as well as it does for type A transitions. In a separate study of nine dinitro radical anions bridged by planar aromatic rings, the lowest energy transitions gave an excellent correlation with NAG B3LYP B<sub>1</sub> energies, with the calculated values averaging 600 cm<sup>-1</sup> lower than the observed transition energies in DMF,<sup>30</sup> indicating that NAG calculations work rather well for dinitro radical anions. The transition energy for the intervalence band of 1<sup>-</sup> is calculated by NAG to occur at 3430 cm<sup>-1</sup>, which is 1430 cm<sup>-1</sup> lower than the observed value of 4850 cm<sup>-1</sup> in HMPA. This low

(25) (a) Burke, K.; Gross, E. K. U. A Guided Tour of Time-Dependent Density Functional Theory. In *Density Functionals: Theory and Applications*; Joubert, D., Ed.; Springer: Berlin, 1998; pp 116–146. (b) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salhub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439–4449. (c) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys. Chem.* **1998**, *109*, 8218–8224.

(26) (a) Nelsen, S. F.; Blackstock, S. C.; Yumibe, N. P.; Frigo, T. B.; Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 143–149. (b) Clark, T.; Teasley, M. F.; Nelsen, S. F.; Wynberg, H. *J. Am. Chem. Soc.* **1987**, *109*, 5719–5724.

(27) Koopmans, T. *Physica* **1934**, *1*, 104–113.

(28) Nelsen, S. F.; Tran, H. Q. *J. Am. Chem. Soc.* **1998**, *120*, 298–304.

(29) Nelsen, S. F.; Luo, Y.; Weaver, M. N.; Zink, J. I. *Beyond the Two-State model: Optical Spectra of Protected Diamine Intervalence Radical Cations Related to N,N,N',N'-Tetraalkylbenzidine*; to be published.

(30) Nelsen, S. F.; Weaver, M. N.; Zink, J. I.; Telo, J. P. To be published.

energy transition is between the orbitals shown as SOMO and LUMO in Figure 4. These orbitals differ by being the symmetric and antisymmetric “stacking” combinations of otherwise similar bonding NO<sub>2</sub>-aryl orbitals in each ring, so the transition between them measures the size of this inter-ring  $\pi,\pi$  interaction.

### Conclusion

We rationalize the much greater change in spectral shape for **1**<sup>-</sup> than **2**<sup>-</sup> as  $\lambda_s$  is decreased by lowering solvent polarity/acceptor ability to crossing the Class II/Class III borderline for **1**<sup>-</sup>. The appearance of two bands in the intermediate solvents

DMSO and DMF is unexpected, and we propose no explanation for seeing them. The optical transition in low  $\lambda_s$  solvents is clearly not caused by electron transfer between the nitro groups, and its transition energy cannot be equated with the  $2H_{ab}$  for electron transfer that is shown in Figure 1b. Instead,  $2H_{ab}$  presumably is close to the energy at which special effects appear in the optical spectrum, somewhat under  $\sim 9000\text{ cm}^{-1}$ . It would clearly be important to examine the vibrational spectra for these compounds, and we hope to be able to do so soon.

JA0441920