PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Journal Name

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Influence of bridge-reduced state levels on the electron transfer within 2,7-dinitroanthracene radical anion

J. P. Telo*[a] and Á. Moneo[a]

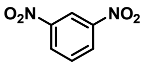
Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

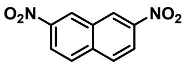
www.rsc.org/

Optical and EPR spectroscopy show that the 2,7-dinitroanthracene radical anion has an (apparent) electronic coupling much higher than its N,N distance and non-kekule substitution would suggest. The results can only be explained if a low-lying bridge redox state is influencing the electron transfer.

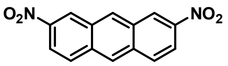
1,3-Dinitrobenzene (**1**) radical anion was one of the first species where intramolecular electron transfer was studied by EPR spectroscopy in the early 60s.[1]



1



2



3

Radical anions like **1**$^-$ are mixed-valence organic compounds,[2] although the concept of mixed-valence came up later and applied initially to bi-metallic coordination compounds.[3,4] The near-infrared spectra of radicals **1**$^-$ and **2**$^-$ in MeCN are shown in Fig. 1.[5,6]

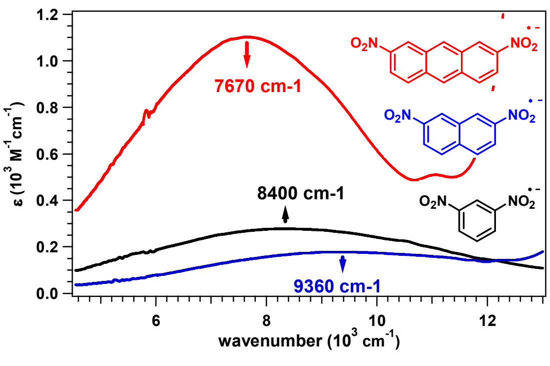


Fig. 1 Near-Infrared optical spectra of 1$^-$-3$^-$in MeCN.

Both show the wide and Gaussian-shaped intervalence band characteristic of localized (Class II)[2] mixed-valence compounds, for which the energy maximum corresponds to the reorganization energy λ, according to the Marcus-Hush two-state model.[4,7]

Theory predicts that λ should increase with the distance between the charge-bearing units (CBU, the nitro groups in this case) through its solvent component λ_S, because this energy depends on the change of the dipole moment upon electron transfer. Also, according to the Hush formula for the shape of the intervalence band, ε_{max} is proportional to the electronic coupling between CBU (H_{ab}), and this should decrease exponentially with distance between nitro groups. In fact, the band maximum increases by 960 cm^{-1} from **1**$^-$ to **2**$^-$ and ε_{max} decreases, as predicted by theory.[2]

This papers concerns the longer 2,7-dinitroanthracene radical anion (**3**$^-$), which we expected to show an intervalence band weaker than **2**$^-$ and shifted to even higher energies, for the reasons explained above. Surprisingly, the band of **3**$^-$ in MeCN (Fig. 1) is much more intense and shifted toward lower energies as compared to the band of its shorter analogue **1**$^-$ in the same solvent. Applying the Hush equation to the parameters of the bands in MeCN (Fig. 1) yields H_{ab}=540 cm^{-1} for **1**$^-$ and H_{ab}=310 cm^{-1} for **2**$^-$.[5,6] However, for the band of **3**$^-$ a value of H_{ab}=470 cm^{-1} is obtained, even though the distance between nitro groups is higher. Apparently **3**$^-$ seems to have a smaller reorganization energy than **2**$^-$, and a larger electronic coupling between nitro groups, which does not conform to common electron transfer theory.

The EPR spectra show also the same unusual behaviour. There is no evidence of dynamic effects at room temperature and the spectra can be well simulated with averaged nitrogen coupling constants, showing that the rate of intramolecular electron transfer between the nitro groups is fast in the hyperfine timescale. Broadening effects can only be detected at low temperatures in MeCN and PhCN. Computer simulation of the experimental EPR spectrum of **3**$^-$ in MeCN at 230 K (Fig. 2) affords a rate constant for intramolecular electron transfer of k=4.0×10^9 s^{-1}. The EPR rate constants of **1**$^-$ and **2**$^-$ for the same solvent and temperature are 3.1×10^9 s^{-1} and 3.2×10^8 s^{-1}, respectively.[5,6] Although the EPR results confirms **3**$^-$ as a Class II mixed-valence radical in MeCN, the rate constant should be smaller than that of either **1**$^-$ or **2**$^-$, because the rate of electron transfer decreases with the increase of the distance between the donor and the acceptor.

Fig. 3 shows how the intervalence band of **3**$^-$ changes in solvents that induce smaller reorganization energies than MeCN

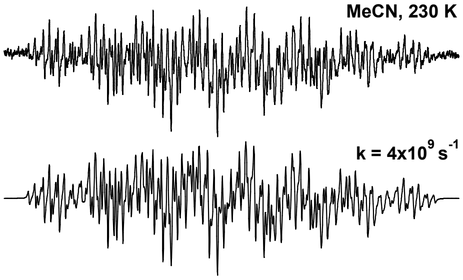


Fig. 2 Experimental EPR spectra of **3**$^-$ in MeCN at 230 K (up) and computer simulation (low) with the following hyperfine coupling constants (Gauss): a_{N1}=6.43, a_{N2}=0 (average a_{2N}=3.215), a_{H1}=6.10, a_{H2}=1.90 (average a_{2H} = 4.00), a_{2H} = 1.02, a_{2H} = 0.44, a_{H} = 3.77, a_{H} = 0.62

does. The band shifts toward lower energies as predicted, becoming flat and more asymmetric in PhCN. We used Infrasil quartz cells to extend the spectra to the short-wavelength infrared region. The spectra in HMPA and THF show a more intense and narrower band centred at 4200 cm^{-1} with an ill-defined shoulder at 5700 cm^{-1} consistent with an unresolved vibrational progression, which is typical of a Class III (delocalized) mixed-valence radical.

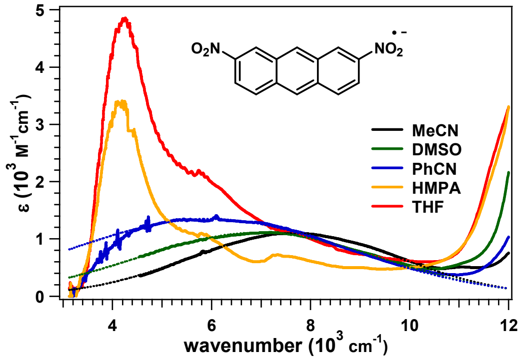


Fig. 3 Near-Infrared optical spectra of **3**$^-$ in several solvents (full lines) and Gaussian fits of the Class II bands (dotted lines).

This solvent-dependent transition from Class II to Class III is rare, but was found before for other dinitroaromatic radical anions,[8] although this is the first time the same effect is found in a radical with a non-kekule substitution pattern. In this kind of substitution the nitro groups (or any other CBU) cannot be π-bonded in classical resonance structures and show normally low electronic couplings. Charge-delocalization occurs when $\lambda < 2H_{ab}$, and since dinitroarene radical anions have reasonably high reorganizations energies, delocalization of charge (Class III) was found only for systems with high H_{ab}, which is the case of most kekule-substituted dinitroarenes.[9] Fig. 3 also shows Gaussian fits (dotted lines) for the Class II intervalence bands. The calculated Gaussian curves fit well the bands in MeCN and DMSO, but the experimental band in PhCN shows a substantial "cutoff" effect in the low-energy side, as Nelsen suggested should occur near the Class II/III borderline.[10] According to the classical Hush model, the cutoff occurs when the energy equals $2H_{ab}$, and it is interesting that the cutoff in the PhCN band starts exactly at the maximum of the HMPA and THF Class III bands, which, according to the two-state model, equals $2H_{ab}$.

Fig. 4 shows the full-spectra of **3**$^-$ in the two "extreme" solvents, MeCN and THF, together with the TD-DFT calculated vertical excitations and the corresponding main assignments of the transitions using Hoijtink restricted open-shell nomenclature, which designates filled orbital to singly occupied orbital (somo) transitions as type A, and somo to virtual orbital transitions as type B. Any other transition not involving somo is type C.[11] DFT calculations are known to overestimate delocalisation and to yield charge-delocalised structures in compounds known to be localised. Structure optimization of **3**$^-$ in THF yields a charge-delocalised structure with equal bond-lengths in both nitro groups, even starting from an asymmetric initial structure. Surprisingly, the same calculations using MeCN as a solvent yield an asymmetric structure 0.76 kcal/mol more stable than the optimized symmetrical one. However, the structural difference between the two nitro groups is not enough to reproduce the experimental change in the energy of the intervalence transition with solvent. The energies of the other electronic transitions are well predicted by the TD-DFT calculations. The intervalence transition is B1 (somo to lumo), as is usual in mixed valence radical anions,[8,9] and the second band at 13000 cm^{-1} is mainly B2 (somo to lumo+1).

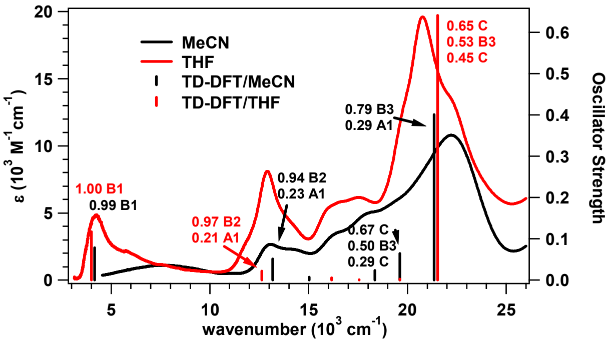


Fig. 4 Full spectra of **3**$^-$ in MeCN and THF. Sticks show TD-DFT calculated transition energies (UB3LYP/6-31+G (2d,p), CPCM solvent model).

The results shown above for **3**$^-$ cannot be explained by the usual Marcus–Hush two-state model. We suggest that in this case a low-lying bridge redox state is influencing the electron transfer. Bridge oxidation effects were found before in organic mixed-valence radical cations. Nelsen and co-workers found evidence of a bridge-oxidation state in the spectra of a 9,10-bis(hydrazine)anthracene radical cation,[12] and Lambert published several examples of bis(triarylamine) radical cations (including one anthranyl-bridged) where the bridge-levels have to be included in the electronic description of the systems.[13] More recently, a diruthenium radical cation with a diethynylanthracene bridging ligand was found to exist mainly as a bridge-oxidized state, with the metal-centred mixed-valence state lying above in energy.[14] Clearly the presence of one anthracene unit on the bridge seems to be important for the stabilization of the bridge-oxidized electronic state in radical cations due to the lower oxidation potential of this molecule, but the present work is the first evidence of a similar effect in an anthracene-bridged radical anion. In fact, the reduction potential of anthracene is 0.58 V less negative than that of naphthalene,[15] which results in a smaller energy gap between the one-electron reduced state of the bridge and that of the nitro groups in **3**$^-$, as compared to **2**$^-$. According to superexchange theory, electron tunneling through the bridge is facilitated by low-energy gaps between the bridge and the CBU.[16] In this case, the two-state model is no longer valid because bridge-centred electronic surfaces have to be taken into account in a 3-state model. We retained the H_a and H_b designation for the two parabolic energy surfaces with the electron located on each of the nitro groups and add a third diabatic energy surface, H_c, corresponding to the negative charge located in the bridge. H_c is symmetrically centred at the reaction coordinate x=0.5, and Δ is the vertical energy displacement of its energy minimum compared to the H_a and H_b minima. As in the two-state model, H_{ab} corresponds to the direct electronic coupling between CBU, but now a second electronic coupling $H_{ac} = H_{bc}$ (which we will simply call H_{ic}, with $i = a,b$) will express the interaction between the CBUs and the bridge. The system is described by the 3×3 secular determinant shown on Eq. 1, where E is the energy of the system. Eq. 1 corresponds to a 3rd-degree polynomial on E, whose solutions are the three adiabatic energy states of the system (X_1, X_2 and X_3, see ESI for calculation details).

$$\begin{vmatrix} H_a - E & H_{ic} & H_{ab} \\ H_{ic} & H_c - E & H_{ic} \\ H_{ab} & H_{ic} & H_b - E \end{vmatrix} = 0 \qquad (1)$$

For delocalized ground states (Class III) the intervalence transition will be the energy difference between the adiabatic states X_1 and X_2 at x=0.5, and for this point the equation has analytic solutions. In this case the energy of the transition is independent of the reorganization energy of the nitro-to-bridge electron transfer, λ_{bridge}, which is the curvature of the H_c parabola. This corresponds to the energy necessary to transfer an electron from the reduced nitro group to the bridge without structural changes on the molecule or in the solvation shell. The negatively-charged nitro groups should be much more strongly solvated than the bridge-reduce state, where the charge lays on carbon atoms, so we suggest that the bridge reorganization energy should be within the limits $\lambda<\lambda_{\text{bridge}}<\lambda/2$. The direct coupling between nitro groups should be smaller than the 310 cm^{-1} value for **2**$^-$, and we will use H_{ab}=0 for simplicity in the subsequent calculations.† The values of λ, H_{ic} and Δ were estimated by fitting the three-stage model to the first two bands of **3**$^-$ (see ESI for details). Using the energies of the bands in THF, a delocalized ground-state is obtained for H_{ic}=4275 cm^{-1} and $\lambda <$ 6000 cm^{-1}, yielding Δ=6000 cm^{-1} for $\lambda =$ 6000 cm^{-1} (Fig. 5, left-hand side). Changing the solvent to MeCN should increase λ significantly, but we couldn't fit the energies of the two bands in this solvent without decreasing H_{ic}. The best fit was achieved with λ=10200 cm^{-1}, Δ=7000 cm^{-1} and H_{ic}=2800 cm^{-1} (Fig. 5, right-hand side).

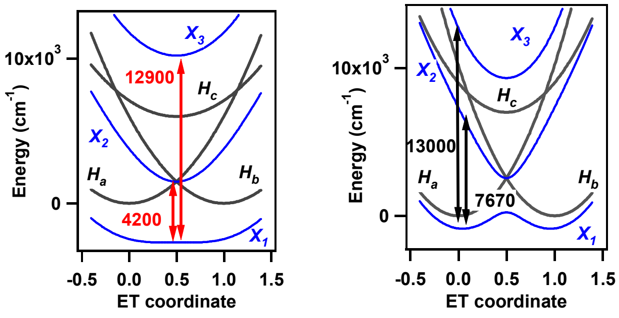


Fig. 5 Marcus-Hush 3-state model diagrams built to fit the transitions of **3**$^-$ in THF (Class III, left-hand side) and in MeCN (Class II, right-hand side).

Contrary to the delocalized case, the energy of the electronic transitions of the Class II intervalence band does depend on the reorganization energy of the bridge, and we used λ_{bridge}=8000 cm^{-1}. However, changing λ_{bridge} in the range 5000-10000 cm^{-1} has only a marginal effect on the energy of the transitions.

In conclusion, the 2,7-dinitroanthracene radical anion (**3**$^-$) spectra shows a gradual replacement of the Class II wide and featureless intervalence band in MeCN by the narrow Class III band in solvents that induce smaller reorganization energies. This would mean that this radical should have a smaller reorganisation energy than its shorter analogue **2**$^-$ and/or a higher electronic coupling between nitro groups, which cannot be explained by the simple two-state model. However, the reorganization energy for **3**$^-$ in MeCN estimated by applying a 3-stage model that includes an extra bridge-reduced state is higher than the one for **2**$^-$ in the same solvent, which now conforms to the common theory of superexchange electron transfer.[16] The 3-state model also explains the apparent higher electronic coupling found in **3**$^-$.

Notes and references

[a] Centro Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. jptelo@tecnico.ulisboa.pt

† Using 0<H_{ab}<250 cm^{-1} doesn't affect the energy profiles significantly.

Acknowledgements:We thank the Fundação Para a Ciência e Tecnologia through its Centro de Química Estrutural and Projects PEst-OE/QUI/ UI0100/2013

Electronic Supplementary Information (ESI) available: Experimental Techniques, Theoretical Calculations, Three-Stage Model calculations and Optimized Geometry Coordinates. See DOI: 10.1039/c000000x/

1 J. H. Freed, P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 1881; J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, 1963, **39**, 778; J. H. Freed, G. K. Fraenkel, *J. Chem. Phys.*, 1964, **41**, 699.
2 J. Hankache and O. S. Wenger, *Chem. Rev.*, 2011, **111**, 5138; A. Heckmann and C. Lambert, *Angew. Chem. Int. Ed.*, 2012, **51**, 326.
3 M. Robin and P. Day, *Adv. Inorg. Radiochem.*, 1967, **10**, 247; C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1969, **91**, 3988.
4 N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391; N. S. Hush, *Electrochim. Acta*, 1968, **13**, 1005.
5 J. P. Telo, A. S. Jalilov and S. F. Nelsen, *J. Phys. Chem. A* 2011, **115**, 3016; A. Moneo and J. P. Telo, *J. Phys. Org. Chem.*, 2012**, 25**, 1139.
6 J. P. Telo, M. C. B. L. Shohoji, B. J. Herold and G. Grampp, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 47; S. F. Nelsen, M. N. Weaver, A. E. Konradsson, J. P. Telo and T. J. Clark, *J. Am. Chem. Soc.*, 2004, **126**, 15431; J. P. Telo, S. F. Nelsen and Y. Zhao, *J. Phys. Chem. A* , 2009, **113**, 7730.
7 R. A. Marcus, *J. Chem. Phys.* 1956, **24**, 966; R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.
8 S. F. Nelsen, A. E. Konradsson and J. P. Telo, *J. Am. Chem. Soc.*, 2005, **127**, 920; S. F. Nelsen, N. M. Weaver and J. P. Telo, *J. Am. Chem. Soc.*, 2007, **129**, 7036; S. F. Nelsen, K. P. Schultz and J. P. Telo, *J. Phys. Chem. A*, 2008, **112**, 12622; R. M. Hoekstra, J. P. Telo, Q. Wu, R. M. Stephenson and S. F. Nelsen and J. I. Zink, *J. Am. Chem. Soc.*, 2010, **132**, 8825.
9 S. F. Nelsen, A. E. Konradsson, N. M. Weaver and J. P. Telo, *J. Am. Chem. Soc.*, 2003, **125**, 12493; S. F. Nelsen, M. N. Weaver, J. I. Zink and J. P. Telo, *J. Am. Chem. Soc.*, 2005, **127**, 10611.
10 S. F. Nelsen, *Chem.-Eur. J.*, 2000, **6**, 581.
11 G. J. Hoijtink and W. P. Weijland, *Recl. Trav. Chim. Pays-Bas*, 1957, **76**, 836; K. H. J. Buschow, J. Dieleman, G. Hoijtink, *J. Mol. Phys.*, 1963, **7**, 1.
12 S. F. Nelsen, R. F. Ismagilov and D. R. Powell, *J. Am. Chem. Soc.*, 1998, **120**, 1924.

13 C. Lambert, G. Noll and J. Schelter, *J. Nat. Mater.*, 2002, **1**, 69; C. Lambert, S. Amthor and J. Schelter, *J. Phys. Chem. A*, 2004, **108**, 6474, C. Lambert, C. Risko, V. Coropceanu, J. Schelter, S. Amthor, N. E. Gruhn, J. C. Durivage and J.-L. Brédas, *J. Am. Chem. Soc.*, 2005, **127**, 8508.
14 M. A. Fox, B. Le Guennic, R. L. Roberts, D. A. Brue, D. S. Yufit, J. A. K. Howard, G. Manca, J.-F. Halet, F. Hartl and P. J. Low, *J. Am. Chem. Soc.*, 2011, **133**, 18433.
15 H. Block and U. Lechner-Knoblauch, *Z. Naturforsch.*, 1985, **40b**, 1463.
16 O. S. Wenger, *Inorg. Chim. Acta*, 2009, **374**, 3; O. S. Wenger, *Acc. Chem. Res.*, 2011, **44**, 25.