Research Article

Journal of Physical Organic Chemistry

Received: 18 October 2011, Revised: 29 November 2011, Accepted: 2 December 2011,

(wileyonlinelibrary.com) DOI: 10.1002/poc.2905

Dicyanoaromatic radical anions as mixed valence species

Álvaro Moneo[a], M. Fernanda N. N. Carvalho[a] and João P. Telo[a]*

The reduction of nine symmetric dicyanoaromatic radical anions by sodium amalgam in the presence of cryptand[2.2.2] was studied using cyclic voltammetry and using optical and electron paramagnetic resonance (EPR) spectroscopies in two aprotic solvents. All radicals are charge-delocalized (Class III) mixed valence species, as shown by the weak solvatochromism of their low-energy optical bands and by the vibrational structure exhibited by most of the bands. The maximum of the low-energy optical transition decreases logarithmically with the number of bonds (*n*) between cyano groups in a series of p-phenylene-bridged radicals, from p-phenyl ($n = 5$) to p-quaterphenyl ($n = 17$), although the energy of the latter lies higher than the value predicted by the linear regression. The energy of this band decreases linearly with the cos^2 value of the torsion angle between phenyl rings in the spectra of biphenyl-4,4′-dicarbonitrile radical anion and their methyl-substituted derivatives. The fact that charge delocalization is maintained in radicals with non-Kekulé bridges, with unusually large bridges and with bridges with highly twisted biphenyl systems suggests that cyano charge-bearing units have small reorganization energies and induce high electronic couplings through the bridges. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: charge-transfer optical bands; conjugation; dicyanoaromatic radical anions; Marcus–Hush theory; organic mixed valence

INTRODUCTION

Mixed valence (MV) compounds are characterized by having two charge-bearing units (CBU) symmetrically attached to a bridge, and being at an oxidation level for which the charges at the CBU could be different. The Marcus–Hush two-state model [1–4] for electron transfer employs parabolas representing diabatic states with the charge on the left and on the right (traced curves on Fig. 1). These diabatic surfaces are allowed to interact through an electronic coupling term H_{ab}, producing the adiabatic energy surfaces shown as solid lines in Fig. 1. When the vertical reorganization energy (λ), which is the energy gap between the diabatic parabolas at their energy minima, exceeds $2H_{ab}$, the charge is instantaneously localized in one of the CBU, and the compound is charge-localized, or Class II in the Robin-Day classification. [5] As shown in Fig. 1, the lower energy surface for a Class II compound has double minima, and interconvertion between the two minima corresponds to the thermally-activated electron transfer between CBU. When $\lambda < 2H_{ab}$, there is only a single minimum in the ground state adiabatic energy surface, and the compound is delocalized (or Class III).

Class III and Class II compounds can usually be distinguished by their low-energy optical absorption band, often referred to as the intervalence band. In Class II systems, the vertical excitation from the ground state minimum is to a steeply sloping region of the upper energy surface, producing the typical wide and Gaussian shaped intervalence bands with no vibrational fine structure, typical of localized MV compounds. In delocalized Class III MV systems, the excited state has a minimum vertical from the ground state minimum, so the optical bands are narrow and often show vibrational structure.

Dinitroaromatic radical anions have been the subject of our studies on MV chemistry for the last several years.[6–15] A wide range of properties can be achieved by changing the nature of the aromatic bridge on these radicals. Radical anions with small bridges, where the two nitro groups are conjugated in what is often called a Kekulé substitution pattern, like p-dinitrobenzene or 2,6-dinitronaphthalene radical anions, are delocalized Class III MV species in all aprotic solvents studied. [6,7] Increasing the distance between nitro groups increases the $\lambda/2H_{ab}$ ratio and may result in localization of charge. 4,4′-dinitrobiphenyl and 4,4′-dinitrotolane are examples of Class II MV species in solvents that induce a high reorganization energy value. [8–11] Decreasing the conjugation (and hence H_{ab}) by the twisting around the central bond on substituted biphenyl bridges, as in 2,2′-dimethyl-4,4′-dinitrobiphenyl radical anion, also leads to localization of charge.[9,10] Dinitroaromatic radical anions with non-Kekulé substitution patterns like 1,3-dinitrobenzene, 2,7-dinitronaphthalene, or 2,7-dinitrodibenzodioxin radical anions have small enough H_{ab} values to make them localized Class II radicals in all solvents studied. [12–15]

Although there are several studies that explore the effects of the nature of the bridge on the properties of organic MV species, the same amount of effort have not been applied to the systematic study of the nature of the charge-bearing unit. Changing the bridge affects mostly the electronic coupling H_{ab}, but MV compounds with the same bridge and different CBU will differ both in the electronic coupling between the

---

* *Correspondence to: J. P. Telo, Centro de Química Estrutural, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: jptelo@ist.utl.pt*

a *Á. Moneo, M. Fernanda N. N. Carvalho, J. P. Telo*
Centro de Química Estrutural, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

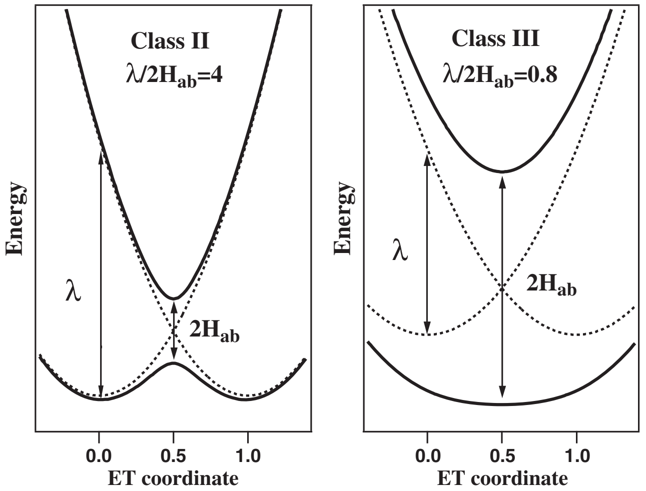


Figure 1. Marcus–Hush diagrams for localized (Class II, left-hand side) and delocalized (Class III, right-hand side) MV compounds using the frequently applied two-state model

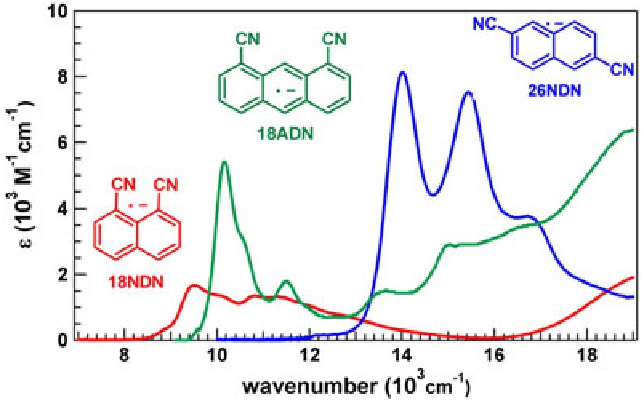


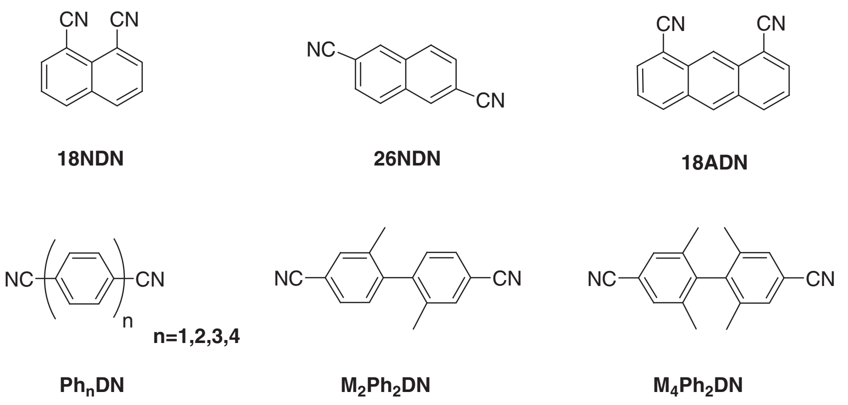
Figure 2. Optical spectra of **18NDN**, **26NDN**, and **18ADN** radical anions in MeCN at room temperature

CBU and the bridge and in the reorganization energy. In this work, we explore the MV chemistry of the dicyanoaromatic radical anions of Chart 1 and compare their properties with other MV compounds with similar bridges.

RESULTS AND DISCUSSION

The optical spectra of **18NDN, 26NDN**, and **18ADN** radical anions are shown in Fig. 2. The low-energy absorption bands are narrow and clearly have vibrational fine structure, showing that these radicals are delocalized Class III MV compounds. Although the term "intervalence band" is also used for Class III systems, in this case the Frank–Condon vertical transition does not involve a net charge transfer between CBU. Application of Marcus–Hush two-state model to Class III compounds implies that the energy of the vertical transition equals $2H_{ab}$, as shown in Fig. 1. A large number of studies use the E_{op} value of the lowest-energy (0,0) band of Class III MV compounds as an accurate measure of $2H_{ab}$. However, delocalized MV systems are symmetric, and the electronic transition shown in the right-hand side of Fig. 1 occurs between symmetric electronic states. This symmetry-forbidden transition should produce an optical band of very low intensity, which is clearly not the case of the bands shown in Fig. 2. As pointed out before, the two-state model does not apply unaltered to Class III MV compounds.[7,16] Nevertheless, although not being correct to assign it to $2H_{ab}$, E_{op} often decreases exponentially with the distance between the charge-bearing units, as expected for an electronic coupling, and in most cases, its change with the CBU substitution pattern somewhat accompany the predictable change in H_{ab}. For example, the energy of the (0,0) maximum occurs at 14,010 cm^{-1} for the conjugated **26NDN** radical anion, but at much lower energy (9500 cm^{-1}) for the non-conjugated **18NDN** (Fig. 2 and Table 1). Although with a shorter distance between CBU, the lack of direct resonance between the cyano groups in **18NDN**$^{\cdot-}$ causes a much smaller electronic coupling than in **26NDN**$^{\cdot-}$, and this effect is reflected in the relative values of E_{op}. The fact that the non-Kekulé **18NDN** radical anion is a delocalized Class III radical anion led us to prepare the also non-Kekulé **18ADN**. Increasing the distance between CBU should decrease H_{ab} and possibly induce charge localization. Surprisingly, not only the narrow optical band of **18ADN** radical anion shows it is still Class III but it also occurs at a higher energy than the one from the shorter **18NDN**. The difference between the first and the second reduction potentials (Table 1) is a measure of the electronic interaction between CBU. This difference is similar for both radicals, although higher for the 1,8-naphthalene-bridged radical, which is not consistent with **18NDN**$^{\cdot-}$ having a smaller E_{op}. This shows that the correlation of E_{op} with $2H_{ab}$ should be taken cautiously.

The low-energy optical bands of the oligo-(p-phenylene) dicarbonitrile radical anions on Fig. 3 show a typical decrease of E_{op}, with the distance between CBU. Terephthalonitrile (**Ph$_1$DN**)



18NDN **26NDN** **18ADN**

n=1,2,3,4

Ph$_n$DN **M$_2$Ph$_2$DN** **M$_4$Ph$_2$DN**

Chart 1. Dicyanoaromatic compounds studied in this work

Table 1. Cyclic voltammetry data (in V, vs Fc/Fc$^+$, Pt electrode) of dicyanoaromatic compounds, optical spectra data of their radical anions and calculated dihedral angle between phenyl rings

	Reduction	Potential		Optical	Spectrum	
Compound	$^{I}E^{o}_{1/2}$	$^{II}E^{o}_{1/2}$	$\Delta E^{o} = {}^{I}E^{o}_{1/2} - {}^{II}E^{o}_{1/2}$	E_{op} (cm^{-1})^{a}	ε (M^{-1} cm^{-1})^{a}	θ^{b}
18NDN	-1.92^{c}	-2.75^{d}	0.83	9500	1670	–
26NDN	-1.93^{c}	-2.70	0.77	14,010	8130	–
18ADN	-1.67	-2.37	0.70	10,160	5620	–
	-1.59^{e}	-2.37^{e}	0.78^{e}			
Ph$_1$DN	-2.00	-2.79^{d}	0.79	23,200	3427	–
Ph$_2$DN	-2.08	-2.54	0.46	13,230	21,300	10°
Ph$_3$DN	-2.17	-2.36	0.19	7680	13,850	16°
Ph$_4$DN	-2.27	–	<0.04	6820	10,070	20°
M$_2$Ph$_2$DN	-2.42	-2.72	0.30	10,090	7760	43°
M$_4$Ph$_2$DN	-2.71	-2.99^{d}	0.28	6600	5230	69°

[a] Maximum of the low-energy (0,0) band of the radical anion.

[b] Calculated dihedral angle between phenyl rings of the radical anions.

[c] In good agreement with the values in reference [38]

[d] Not reversible, value of $E_p/2$.

[e] Measured with a glassy carbon working electrode.

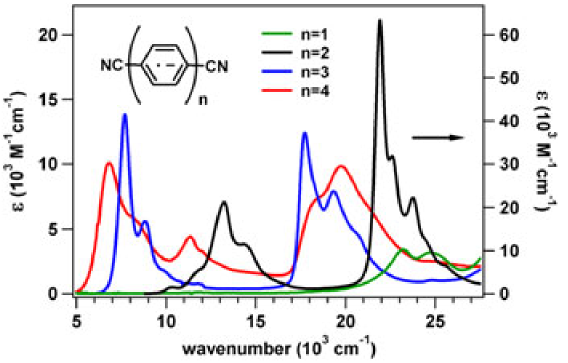


Figure 3. Optical spectra of radical anions from the oligo-(p-phenylene)dicarbonitriles **Ph$_1$DN** to **Ph$_4$DN** in DMF. The spectrum of **Ph$_2$DN** (right-hand side axis) is plotted with 1/3 the intensity of the other spectra (left-hand side axis). The band at 11300 cm^{-1} of **Ph$_4$DN$^{\cdot-}$** (red line) belongs to the dianion formed by disproportionation

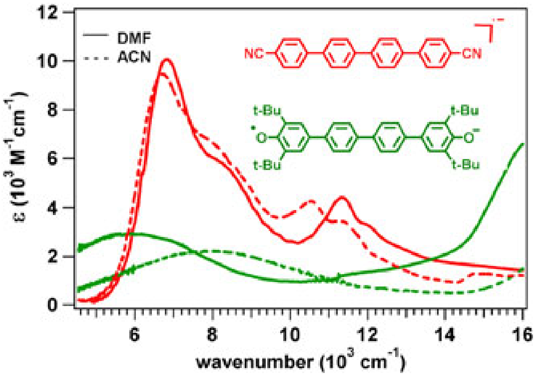


Figure 4. Comparison of the optical spectra of Class III **Ph$_4$DN** radical anion (red lines) with the Class II quaterphenylquinone radical anion (green lines) in dimethylformamide (full lines) and MeCN (traced lines).[20] The bands at 10,000–12,000 cm^{-1} on the **Ph$_4$DN$^{\cdot-}$** spectra belong to the dianion formed by disproportionation

radical anion absorbs mainly in the ultraviolet (UV), but the intervalence band shifts to lower energies with the increase of the bridge size. Surprisingly to us, all radicals are delocalized Class III systems, even the long quaterphenyl-bridged **Ph$_4$DN$^{\cdot-}$**, with 17 bonds connecting the CBU. Most examples of compounds with bridges of this size found on the literature are Class II MV systems. [17–19] Figure 4 compares the spectra of **Ph$_4$DN$^{\cdot-}$** in two solvents with the ones of the t-butyl-protected quaterphenyl quinone radical anion, which show a wide Gaussian-shaped band having a band maximum that is strongly dependent on solvent, as is typical of Class II mixed-valence compounds. [20] The maximum of the quinone band moves from 5890 cm^{-1} in dimethylformamide (DMF) to 7970 cm^{-1} in MeCN, a blue-shift of 2080 cm^{-1} compared with the small 100 cm^{-1} red-shift of the Class III **Ph$_4$DN** radical anion band maximum between the same two solvents. Localization of charge occurs because the reorganization energy increases (through its solvent component λ_S) and the electronic coupling decrease with the increase of distance between the CBU, eventually making the ratio $\lambda/2H_{ab}$ smaller than 1.

The decay of E_{op} with distance on Class III MV systems is normally exponential, and this has been one of the arguments to ascribe the energy of the optical transition to $2H_{ab}$. The data are fitted with the equation $\ln(E_{op}/2) = \text{constant} - \beta_N{\cdot}N/2$, where β_N is a dimensionless distance decay constant and N the number of bonds connecting the CBU. [21] A plot of ln ($E_{op}/2$) for radical anions **Ph$_1$DN** to **Ph$_4$DN** versus N is shown in Fig. 5. A linear fit with a decay constant of $\beta_N = 0.28$ is obtained for the first three N values ($N = 5$, 9, and 13), but the point for the 17-bonded **Ph$_4$DN** compound lies somewhat higher than what is predicted by the linear fit. The value of the decay constant is in good agreement with the $\beta_N = 0.30$ value found both for a series of Class III violene radical cations [22] and for a series of Class III quinone radical anions.[20]

The calculated (UB3LYP/6-31G*) twist angle at the central bond of the biphenyl bridge of **Ph$_2$DN$^{\cdot-}$** is 10°. The twist angle between phenyl rings increases to 16° for **Ph$_3$DN$^{\cdot-}$** and to an average of 20° for the longer **Ph$_4$DN$^{\cdot-}$**, so there is no reason to suspect that the attenuation of the decay of E_{op} with distance for

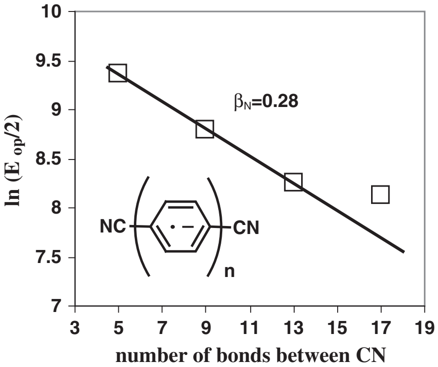


Figure 5. Plot of ln(E_{op}/2) versus the number of bonds N connecting cyano groups for the Class III radical anions **Ph_1DN** to **Ph_4DN**. The line shown is a fit for the first three points

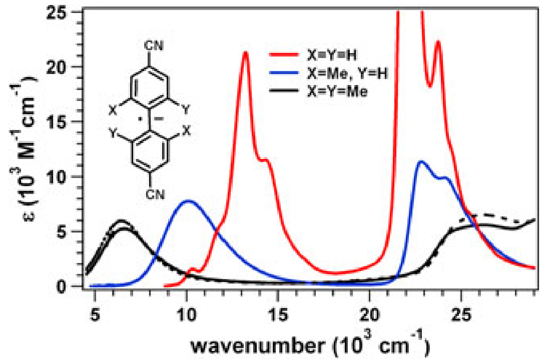


Figure 6. Comparison of optical spectra of **Ph_2DN**, **M_2Ph_2DN**, and **M_4Ph_2DN** radical anions in dimethylformamide (full lines) and of **M_4Ph_2DN** radical anion in MeCN (broken line). The full spectra of **$Ph_2DN^{\cdot-}$** is shown in Fig. 3

the 17-bonded **$Ph_4DN^{\cdot-}$** is due to some structural effect. According to superexchange theory, electron tunneling through the bridge is facilitated by low-energy gaps between the singly occupied molecular orbital (SOMO) of the donor (the reduced CN group in this case) and the lowest unoccupied molecular orbital of the bridge. In that case, the scheme of Fig. 1 is no longer valid because bridge-centered electronic surfaces have to be taken into account in a 3-stage model. In long-range electron transfer, as it occurs in DNA or in molecular wires, reduced bridge states (or oxidized states, in the case of hole-transfer) are effective intermediates, and an electron hopping process is achieved. Electron hopping is characterized by a very shallow distance dependence of the electron transfer rate. [23,24] The quaterphenyl-4,4‴-dicarbonitrile radical anion is Class III and effective electron transfer never occurs, but we suggest that, in this case, the bridge-donor energy gap is small enough to produce an electronic coupling that is higher than what the distance dependence plot would predict. In fact, it is 120 mV easier to reduce p-quaterphenyl ($E^0_{1/2} = -2.28$ V vs Ag/AgCl) than p-terphenyl ($E^0_{1/2} = -2.40$ V). [25] A similar effect was found in the Class III optical spectra of 4, 4′-dinitroazobenzene and 4,4′-dinitrostilbene radical anions. Although the distance between nitro groups is similar, the E_{op} value of the azobenzene-bridged radical is 1.48 times that for the stilbene-bridge radical. Introduction of the nitrogens in the bridge lowers the reduction potential for the bridge relative to that of the hydrocarbon bridge.[11]

In an attempt to induce charge localization, we prepared the dimethyl-substituted and the tetramethyl-substituted biphenyldicarbonitriles **M_2Ph_2DN** and **M_4Ph_2DN**. Introduction of the *ortho*-methyl groups in the biphenyl bridge will force some twisting around the central bond of biphenyl, which should decrease the electronic coupling. Theoretical calculations (UB3LYP/6-31G*) predict a dihedral angle between rings of 10° for the unsubstituted **Ph_2DN** radical anion, of 43° for the dimethylated **$M_2Ph_2DN^{\cdot-}$** and of 69° in the tetramethylated **M_4Ph_2DN** radical anion. The neutral compounds are more twisted than the parent radical anions, with a dihedral angle of 37° in **Ph_2DN** and both methylated neutral compounds **M_2Ph_2DN** and **M_4Ph_2DN** optimizing with orthogonal phenyl rings. Clearly, the radical anions allow a higher degree of steric hindrance in order to increase the resonance between rings.

The optical spectra of these radicals (Fig. 6) show that the maximum of the low energy band decreases with the degree of methyl substitution, as predicted by the two-state model, for which $E_{op} = 2H_{ab}$. This is accompanied by a loss of the vibrational structure, interestingly more severe in the second band than in the low-energy one. The absence of vibrational structure could suggest that the methylated radicals are delocalized Class II species. However, the widths at half height of the low-energy bands of **$M_2Ph_2DN^{\cdot-}$** and **$M_4Ph_2DN^{\cdot-}$**, $\Delta\bar{\nu}_{1/2} = 3570\,\text{cm}^{-1}$ and $\Delta\bar{\nu}_{1/2} = 3230\,\text{cm}^{-1}$, respectively, are smaller than the minimum width that Hush predicted for Class II bands, $\Delta\bar{\nu}^{\text{Hush}}_{1/2} = [16RT(\ln 2)\,E_{op}]^{1/2}$. This equation yields $\Delta\bar{\nu}^{\text{Hush}}_{1/2} = 4812\,\text{cm}^{-1}$ for **$M_2Ph_2DN^{\cdot-}$** and $\Delta\bar{\nu}^{\text{Hush}}_{1/2} = 3891\,\text{cm}^{-1}$ for **$M_4Ph_2DN^{\cdot-}$**. Moreover, changing the solvent from DMF to MeCN produces only minor changes in band maxima, as shown in Fig. 6 for the tetramethylated radical, indicating that both radicals are in fact delocalized Class III MV species. The two-state model assumes that $E_{op} = 2H_{ab}$, and the electronic coupling is predicted to depend on $\cos^2(\theta)$, where θ is the twist angle between any of the π orbitals along the conjugation path. Figure 7 shows a linear plot of E_{op} versus $\cos^2(\theta)$ for the radicals of Fig. 6, where θ is the calculated dihedral angle between the aromatic rings, confirming the theoretical prediction.

Cyclic voltammetry data (Table 1) show that the difference between the two reduction potentials, $\Delta E°$, varies according to the predictable change in H_{ab}. All the planar dicyano radical anions with 1,4-phenylene, 1,8- or 2,6-naphtylene or 1,8-anthracenylene bridges have large $\Delta E°$ values. $\Delta E°$ decreases with the distance between CBU in the oligo-(phenylene)dinitrile series. The longer

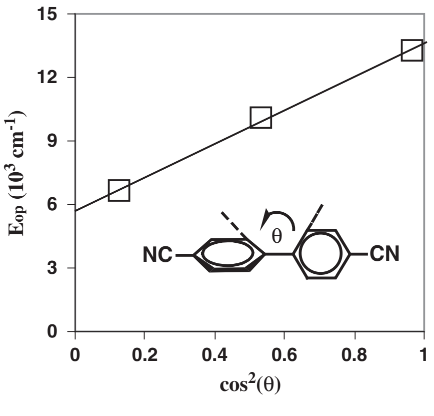
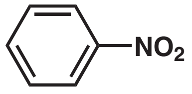


Figure 7. Dependence of the energy of the band maximum on the twist angle θ of the central bond of the biphenyl bridge for **Ph_2DN** (structure show in the inset), **M_2Ph_2DN** and **M_4Ph_2DN** radical anions

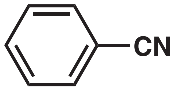
Ph_4DN shows an unresolved wave that probably correspond to a two-electron reduction. Unfortunately, controlled-potential electrolysis of this compound was accompanied by the precipitation of a highly insoluble product, which prevented electron counting. ΔE^{o} values in Table 1 are higher than in dinitro radical anions with the same bridges. For example, $\Delta E^{o} = 0.067$ V for 4, 4′-dinitrobiphenyl, [26] a much smaller value than the $\Delta E^{o} = 0.46$ V found for **Ph_2DN**. This shows that the electronic couplings in dicyano compounds are higher than in dinitro compounds with similar bridges. The value of ΔE^{o} also decreases with the twist angle between phenyl rings in the three compounds with biphenyl bridges, following the decrease in conjugation. A similar effect was recently found in a series of dicyanobiphenylcyclophanes. [27]

The fact that all the dicyanoaromatic radical anions presented in this work are charge-delocalized, even the ones with bridges that are supposed to induce a small electronic coupling is unexpected. Other organic MV radicals with similar bridges, like the quaterphenylquinone radical anion of Fig. 4, are charge-localized. The radical anion of 2,2′-dimethyl-4,4′-dinitrobiphenyl, which is the dinitro equivalent of **M_2Ph_2DN**, is Class II in DMF and MeCN with high λ values of 11,000 $cm^{-1}$and 12,800 cm^{-1}, respectively.[9] Charge-delocalization occurs when $\lambda/2H_{ab} < 1$, so these dicyano radicals, as argued below, must have reorganization energies smaller than the parent dinitroaromatic radicals and higher electronic couplings. Theoretical calculations show that the phenyl rings of the dicyano radical anions are less twisted than in the corresponding dinitro radical anions with the same bridges, which necessarily implies increased electronic couplings. At the UB3LYP/6-31G* level, the 4,4′-dinitrobiphenyl radical anion is calculated to have a twist angle of 19°, almost twice the one calculated for **$Ph_2DN^{\cdot-}$**. 4,4″-dinitroterphenyl has twist angles of 22°, bigger than the 16° value found for **$Ph_3DN^{\cdot-}$**. The same effect is found for radicals with the methylated biphenyl bridges, with 2,2′,6,6′-tetramethyl-4,4′-dinitrobiphenyl radical anion optimizing with a dihedral angle between rings of 77°, also bigger than the value of 69° found for the parent **$M_2Ph_2DN^{\cdot-}$**. Although these differences seem small, its effect in the electronic coupling is enhanced because of the dependence of H_{ab} on the $\cos^2(\theta)$.

The reorganization energy is normally considered to have a vibrational component λ_v, which depends upon the change of internal coordinates of the atoms, and a solvent component λ_s, which accounts for the change in solvation upon electron transfer. The internal component of the reorganization energy of both types of compounds can be compared using the four-point method of Nelsen. [28] λ is the energy of the vertical transition from the ground-state minimum shown in the left side of Fig. 1, and corresponds to an electron transfer between CBU with no change in geometry. Estimates of λ_v are obtained by computing the energy change between the radical anion calculated with the geometry of the neutral compound ($\mathbf{n}^-$) and the relaxed neutral ($\mathbf{n}^0$), and between the neutral calculated at the geometry of the radical anion ($\mathbf{a}^0$) and the relaxed radical anion ($\mathbf{a}^-$), that is, $\lambda_v' = \mathbf{a}^0 - \mathbf{a}^- + \mathbf{n}^- - \mathbf{n}^0$. Using benzonitrile and nitrobenzene as model, CBU yields the values shown below.



$$\lambda_v' = 4850\ cm^{-1}$$



$$\lambda_v' = 2460\ cm^{-1}$$

The internal component of the reorganization energy in electron transfer between benzonitrile units is almost half the value calculated for the transfer between nitrobenzene units. This difference was already predicted long ago by Formosinho using the intersecting-state model. [29]

The EPR spectra of the dicyano radical anions studied show small nitrogen coupling constants and large ring hydrogen coupling constants (see experimental part). The hydrogen atoms of the biphenyl-bridged **$Ph_2DN^{\cdot-}$** have hyperfine coupling constants of 1.79 G and 1.03 G in DMF. Because of the higher electron-withdrawing power of the nitro group, the hydrogen coupling constants are 1.18 G and 0.22 G in the parent 4, 4′-dinitrobiphenyl radical anion spectrum in the same solvent. The higher spin density on the bridges of the dicyano radical anions, as compared with the parent dinitro radical anions, forces the polyphenyl-bridges to have smaller twist angles to accommodate the extra resonance, increasing the electronic coupling. On the other hand, less spin density (and, therefore, less charge) on the CBU will make the solvent component of the reorganization energy smaller, because λ_s depends strongly on the change of the dipole moment upon electron transfer.

CONCLUSIONS

Marcus–Hush analysis of the optical spectra of nine dicyanoaromatic radical anions has shown that these mixed-valence species are charge-delocalized. Theoretical calculations show that the oligo-(p-phenylene)dicarbonitrile radical anions are less twisted than the dinitro radical anions with the same bridges, suggesting that the cyano charge-bearing unit induces higher electronic coupling energies throughout the bridges. Apparently, the lower electron-withdrawing power of the cyano group allows a higher charge density on the bridges, which results in higher electronic couplings. Estimates show that the vibrational component of the reorganization energy in the electron transfer between benzonitrile units is almost half the value calculated for the transfer between nitrobenzene units. The congruence of these factors explains the preservation of charge delocalization even in radicals with bridges that normally induce charge localization.

EXPERIMENTAL

Terephthalonitrile (**Ph_1DN**) and 4,4′-biphenyldicarbonitrile (**Ph_2DN**) were purchased from Aldrich and used as received.

Naphthalene-1,8-dicarbonitrile (18NDN)

This compound was prepared from acenaphthenequinone in two steps using published procedures. [30,31] mp = 239–240 °C (lit.[30] 230–231 °C). ^1H NMR (300 MHz; DMSO) δ 8.47 (d, 2H, $J = 7.6$ Hz), 8.35 (d, 2H, $J = 6.3$ Hz), 7.82 (m, 2H). ^{13}C NMR δ 138.5, 135.3, 132.9, 127.8, 127.1, 116.7, 107.0; ultraviolet–visible (UV–VIS) (MeCN) 323.5 nm (log $\varepsilon = 3.78$), 305.5 nm (log = 3.98); EPR (radical anion, MeCN) $a_{2N} = 0.53$ G, $a_{2H} = 6.05$ G, $a_{2H} = 4.35$ G, $a_{2H} = 0.14$ G.

Naphthalene-2,6-dicarbonitrile (26NDN)

2,6-dibromonaphthalene (2.2 g, 7.1 mmol) and cuprous cyanide (1.5 g, 16.7 mmol) were refluxed in dry *N*-methylpyrrolidinone under nitrogen atmosphere for 3 h. The mixture was cooled, poured into ice-water, and filtered. The solids were purified by elution with toluene from a column packed with silica to yield 0.96 g (76%) of a white solid. mp 306–307 °C; ^1H NMR (300 MHz; $CDCl_3$) δ 8.30 (d, 2H, $J = 1.2$ Hz), 8.02 (d, 2H, $J = 8.7$ Hz), 7.76

(dd, 2H, *J* = 8.7 and *J* = 1.2 Hz); ^{13}C NMR δ 134.0, 133.5, 129.8, 128.2, 118.2, 112.7; UV–VIS (DMF) 322 nm (log ε = 3.43), 306.5 nm (log ε = 3.27), 272.5 nm (log ε = 3.92), 261.5 nm (log ε = 4.00); EPR (radical anion, MeCN) $a_{2N} = 1.18$ G, $a_{2H} = 3.37$ G, $a_{2H} = 3.35$ G, $a_{2H} = 0.87$ G.

Anthracene-1,8-dicarbonitril (18ADN)

1,8-diiodoanthracene [32] (1 g, 2.3 mmol) was reacted with CuCN (0.5 g, 5.58 mmol) as described above to yield 0,45 g (60%) of yellow crystals; mp 300 °C (Lit [33] 300,5 °C); ^{1}H NMR (300 MHz; CDCl$_3$), δ 9.16 (s, 1H), δ 8.64 (s, 1H), δ 8.30 (dd, 2H, *J* = 8.7 and *J* = 1.2 Hz), δ 8.07 (dd, 2H, *J* = 6.9 and *J* = 1.2 Hz), δ 7.62 (dd, 2H, *J* = 8.7 and *J* = 6.9 Hz); UV–VIS (DMF) 406 nm (log ε = 3.72), 385 nm (log ε = 3.84), 364 nm (log ε = 3.78); EPR (radical anion, DMF) $a_{2N} = 0.28$ G, $a_H = 5.33$ G, $a_{2H} = 4.08$ G, $a_{2H} = 3.34$ G, $a_H = 3.23$ G, $a_{2H} = 0.28$ G.

Biphenyl-4,4′-dicarbonitrile (Ph$_2$DN)

UV–VIS (DMF) 280 nm (log ε = 4.49); EPR (radical anion, DMF) $a_{2N} = 0.28$ G, $a_{4H} = 1.79$ G, $a_{4H} = 1.03$ G.

Terphenyl-4,4″-dicarbonitrile (Ph$_3$DN)

This compound was prepared using published procedures. [34] mp > 303–306 °C (Lit[35] 299–300 °C); ^{1}H NMR (300 MHz; CDCl$_3$) 7.75 (AB, 8H), 7.72 (s, 4H); ^{13}C NMR δ 144.80, 139.57, 136.81, 132.89, 131.55, 128.10, 127.82, 118.93, 111.55; UV–VIS (DMF) 339.5 nm (log ε = 3.76). The complex EPR spectrum was not interpreted.

Quaterphenyl-4,4‴-dicarbonitrile (Ph$_4$DN)

To a stirred solution of 4,4′-dibromobiphenyl (0.42 g, 3,2 mmol) and tetrakis (triphenylphosphine)palladium(0) (0.1 g) in 10 ml of toluene was added under nitrogen atmosphere 5 ml of a 2 M aqueous solution of Na$_2$CO$_3$, followed by 4-cyanophenylboronic acid (0.5 g, 6.8 mmol) in 5 ml of methanol. The mixture was vigorously stirred at 80 °C for 24 h, filtered and the powder extracted with chloroform to yield 0.38 g of crude **Ph$_4$DN** (78%). The crude solid was purified by elution with toluene from a column packed with silica to yield 0.24 g (50%) of a white solid. mp 285–287 °C; ^{1}H NMR (500 MHz; Acetone-d6) 7.99 (d, 4H, *J* = 8.4), 7.93 (d, 4H, *J* = 8.4 Hz), 7.92 (s, 8H); ^{13}C NMR δ 144.98, 140.50, 138.44, 132.71, 127.77, 127.75, 127.60, 118.91, 111.08; UV–VIS (DMF) 306 nm (log ε = 4.23). The complex EPR spectrum was not interpreted.

2,2′-dimethylbiphenyl-4,4′-dicarbonitrile (M$_2$Ph$_2$DN)

2,2′-dimethyl-4,4′-dibromobiphenyl [35] (1 g, 0.29 mmol) was reacted with CuCN (0.47 g, 5.3 mmol) and the product purified as described previously to yield 0.35 g (65%) of a white solid. mp 112–113 °C (lit [36] 113 °C); ^{1}H NMR (300 MHz; CDCl$_3$) δ 7.6 (d, 2H, *J* = 0.6 Hz), 7.56 (dd, 2H, *J* = 7.8 Hz, *J* = 0.6), 7.17 (d, 2H, *J* = 8.7), 2.08 (s, 6H); ^{13}C NMR δ 144.63, 137.15, 133.86, 129.84, 129.68, 118.73, 112.27, 19.68. The complex EPR spectrum was not interpreted.

2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarbonitrile (M$_4$Ph$_2$DN)

4,4′-Dibromo-2,2′,6,6′-tetramethylbiphenyl[36] (0.71 g, 1.92 mmol) was reacted with CuCN (0.41 g, 4.6 mmol) and purified as described previously to yield 0.12 g (24%) of a white solid. mp 252–253 °C; ^{1}H NMR (300 MHz; CDCl$_3$) 7.46 (s, 4H), 2.09 (s, 12H); ^{13}C NMR δ 134.41, 136.77, 131.53, 118.95, 111.88, 19.66; UV–VIS (DMF) 283 nm (log ε = 3.44), 274 nm (log ε = 3.47). EPR (radical anion, DMF) $a_{2N} = 0.34$ G, $a_{4H} = 1.52$ G, $a_{12H} = 0.69$ G.

Radical anions were prepared in vacuum sealed glass cells equipped with an EPR tube and a quartz optical cell. The concentration of the samples was determined spectrophotometrically before reduction using the UV data earlier. Reduction was achieved by contact with 0.2% Na–Hg amalgam. A large excess of Cryptand [2.2.2] was used to sequester the sodium counter-ion.

Cyclic voltammetry (CV) and controlled potential electrolysis (CPE) were performed in Bu$_4$NBF$_4$/DMF (0.1 M) using a Pt wire (CV) or a Pt-gauze (CPE) as working electrodes. Potentials were measured versus Fc/Fc$^+$ (internal reference) at 200 mV/s. A potentiostat/galvanostat Radiometer Analytical Voltammetry PST050 VoltaLab® (72 rue d'Alsace 69627 Villeurbanne Cedex Lyon France) equipment was used for VC and CPE studies.

Theoretical calculations were performed using Gaussian 03. [37]

Acknowledgements

We thank Dr. Alexandra Antunes for the use of the 500 MHz NMR facility, Professor Dennis Evans (Purdue University, IN, USA) for providing a sample of 2,6-dibromonaphthalene, and Professor José Paulo Farinha for the use of a Shimadzu UV/Vis/NIR spectrometer. Support by Fundação Para a Ciência e Tecnologia through its Centro de Química Estrutural and Projects PEst-OE/QUI/UI0100/2011 and PTDC/QUI-QUI/101433/2008 is gratefully acknowledged.

REFERENCES

[1] R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966–978.

[2] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265–322.

[3] N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 391–444.

[4] N. S. Hush, *Coord. Chem. Rev.* **1985**, *64*, 135–157.

[5] M. B. Robin, P. Day, *Adv. Inorg. Radiochem.* **1967**, *10*, 247–422.

[6] S. F. Nelsen, A. E. Konradsson, M. N. Weaver, J. P. Telo, *J. Am. Chem. Soc.* **2003**, *125*, 12493–12501.

[7] S. F. Nelsen, M. N. Weaver, J. I. Zink, J. P. Telo, *J. Am. Chem. Soc.* **2005**, *127*, 10611–10622.

[8] R. M. Hoekstra, J. P. Telo, Q. Wu, R. M. Stephenson, S. F. Nelsen, J. I. Zink, *J. Am. Chem. Soc.* **2010**, *132*, 8825–8827.

[9] J. P. Telo, S. F. Nelsen, Y. Zhao, *J. Phys. Chem. A* **2009**, *113*, 7730–7736.

[10] S. F. Nelsen, K. P. Schultz, J. P. Telo, *J. Phys. Chem. A* **2008**, *112*, 12622–12628.

[11] S. F. Nelsen, M. N. Weaver, J. P. Telo, *J. Am. Chem. Soc.* **2007**, *129*, 7036–7043.

[12] J. P. Telo, A. Moneo, M. F. N. N. Carvalho, S. F. Nelsen, *J. Phys. Chem. A* **2011**, *115*, 10738–10743.

[13] J. P. Telo, A. S. Jalilov, S. F. Nelsen, *J. Phys. Chem. A* **2011**, *115*, 3016–3021.

[14] S. F. Nelsen, M. N. Weaver, A. E. Konradsson, J. P. Telo, T. Clark, *J. Am. Chem. Soc.* **2004**, *126*, 15431–15438.

[15] J. P. Telo, M. C. B. L. Shohoji, B. J. Herold, G. Grampp, *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 47–51.

[16] S. F. Nelsen, M. N. Weaver, Y. Luo, J. V. Lockard, J. I. Zink, *Chem. Phys.* **2006**, *324*, 195–201.

[17] C. Lambert, G. Nöll, *J. Am. Chem. Soc.* **1999**, *121*, 8434–8442.

[18] S. V. Rosokha, D.-L. Sun, J. K. Kochi *J. Phys. Chem. A* **2002**, *106*, 2283–2292.

[19] S. Barlow, C. Risko, S.-J. Chung, N. M. Tucker, V. Coropceanu, S. C. Jones, Z. Levi, J.-L. Brédas, S. R. Marder, *J. Am. Chem. Soc.* **2005**, *127*, 16900–16911.

[20] S. F. Nelsen, M. N. Weaver, J. P. Telo, *J. Phys. Chem. A* **2007**, *111*, 10993–10997.

[21] G. L. Closs, J. R. Miller, *Science* **1988**, *240*, 440–447.

[22] S. F. Nelsen, H. Q. Tran, M. A. Nagy, *J. Am. Chem. Soc.* **1998**, *120*, 298–304.

[23] O. S. Wenger, *Inorg. Chim. Acta* **2009**, *374*, 3–9.

[24] M. Cordes, B. Giese, *Chem. Soc. Rev.* **2009**, *38*, 892–901.

[25] K. Meerholtz, J. Heinze, *Electrochim. Acta* **1996**, *41*, 1839–1854.

[26] N. A. Macías-Ruvalcaba, J. P. Telo, D. H. Evans, *J. Electroanal. Chem.* **2007**, *600*, 294–302.

[27] D. Vonlanthen, A. Rudnev, A. Mishchenko, A. Käslin, J. Rotzler, M. Neuburger, T. Wandlowski, M. Mayor, *Chem. Eur. J.* **2011**, *17*, 7236–7250.

[28] S. F. Nelsen, S. C. Blackstock, Y. Kim, *J. Am. Chem. Soc.* **1987**, *109*, 677–682.

[29] S. J. Formosinho, *J. Chem. Soc. Perkin Trans 2* **1988**, 1209–1212.

[30] G. Ege, E. Beisiege, *Synthesis* **1974**, 22–23.

[31] J. B. Wright, *J. Org. Chem.* **1964**, *29*, 1905–1909.
[32] M. Goichi, K. Segawa, S. Suzuki, S. Toyota, *Synthesis* **2005**, 2116–2118.
[33] H. Woldmann, R. Stengl, *Chem. Ber.* **1950**, *83*, 167
[34] M. A. Ismail, R. K. Arafa, R. Brun, T. Wenzler, Y. Mao, W. D. Wilson, C. Generaux, A. Bridges, J. E. Hall, D. W. Boykin, *J. Med. Chem.* **2006**, *49*, 5324–5332.
[35] A. Helms, D. Heiler, G. McLendon, *J. Am. Chem. Soc.* **1992**, *114*, 6227–6238.
[36] W. Theilacker, W. Ozegowski, *Chem. Ber.* **1940**, *73*, 33–40.
[37] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, (Revision D01), Gaussian, Inc., Wallingford CT, **2005**.
[38] P. D. Astudillo Sánchez, D. H. Evans, *J. Electroanal. Chem.* **2011**, *660*, 91–96.