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Charge Localization in a 17-Bond Mixed-Valence Quinone Radical Anion

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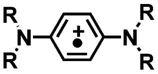
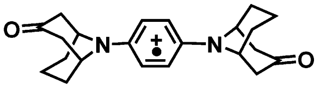
Optical spectra in dimethylformamide are reported for the radical anions of benzoquinone, its tetramethyl and tetrachloro analogues, and tetra-ortho-alkyl derivatives of biphenyl, stilbene, terphenyl, quadriphenyl, and 1,4-bis(2-phenylethenyl)benzene quinones. The first absorption bands for all but the quadriphenyl quinone show vibrational fine structure, demonstrating that they are delocalized (Class III) mixed-valence compounds. The quadriphenyl quinone radical anion shows a wide Gaussian-shaped band having a band maximum that is strongly dependent on solvent, typical of localized (Class II) mixed-valence compounds. The simple O charge-bearing unit of these compounds maintains charge delocalization in examples with unusually large bridges.

Introduction

Derivatives of *p*-phenylenediamine radical cation ($\mathbf{1}^+$ $\mathbf{PD}^+$) were the first organic radical ions ever isolated,[1] and more recently have been recognized as the prototypical organic Robin−Day[2] Class III (delocalized) intervalence compounds.



$\mathbf{1}^+$ $\mathbf{PD}^+$



$\mathbf{2}^+$ $\mathbf{(k33N)_2PH}^+$

$\mathbf{3}^-$ $\mathbf{BQ}^-$

Intervalence compounds are characterized as having two charge-bearing units (**M**) attached to a bridge (**B**), and being at an oxidation level for which the charges at **M** could be different. Class III compounds have charge delocalization, with the same charge at each **M** group. The Marcus−Hush two-state model[3] employs horizontally displaced parabolas representing diabatic states with charge on the left and the right (the dashed curves in Figure 1). These diabatic surfaces interact with an off-diagonal electronic coupling term V_{ab}, producing the adiabatic energy surfaces shown as solid lines in Figure 1. When V_{ab} is small compared to the vertical reorganization energy λ, which is the energy gap between the diabatic parabolas at their energy minima, charge is instantaneously localized, and the compound is Class II. As shown in Figure 1a, the lower energy surface for a Class II compound has double minima, and vertical excitation is to a steeply sloping region of the upper energy surface, precluding the presence of a vibrational fine structure in their optical spectra.[4] When V_{ab} exceeds $\lambda/2$, there is only a single minimum in the ground-state adiabatic energy surface, and the compound is delocalized (Class III), so the first excited state has a minimum vertical from the ground-state minimum (Figure 1b). We believe that Creutz first explicitly noted that the two-state model requires that V_{ab} is half the transition energy for a delocalized case.[5] Because $\mathbf{PD}^+$ derivatives show vibrational fine structure and the band maximum corresponds to the 0,0 band, we thought that the electronic coupling V_{ab} could be determined especially accurately for it and related compounds, and have discussed both observed and calculated structural effects on V_{ab} using these and related compounds.[6,7] The two-state model interpretation is routinely used in calculations of V_{ab}, often with reference to pioneering papers by Larsson.[8] We more recently carried out a detailed study of the resonance Raman, absorption, and emission spectra of the tetraalkyl-substituted $\mathbf{PD}^+$, $\mathbf{2}^+$, also reporting a V_{ab} calculated using the two-state model.[9]

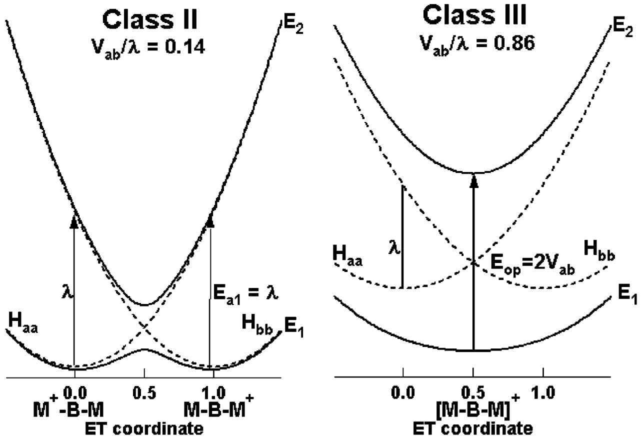


Figure 1. Marcus−Hush diagrams for localized (Class II) and delocalized (Class III) intervalence compounds.

The present work concerns *p*-benzoquinone radical anion ($\mathbf{3}^-$ $\mathbf{BQ}^-$), and related compounds with larger π systems, which are π isoelectronic with diaminoaromatic radical cations, have much simpler charge-bearing units (single oxygen atoms), and bear a negative overall charge. The close electronic relationship between *p*-phenylenediamine radical cations and quinone radical anions was already pointed out by Michaelis in his 1935 review of semiquinones.[10] These radical anions are unstable in air and are thus considerably more difficult to handle experimentally than intervalence radical cations.

Results and Discussion

Optical Spectra. The optical spectra of $\mathbf{BQ}^-$ and the seven quinone radical anions $\mathbf{4}^-$−$\mathbf{10}^-$

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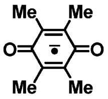
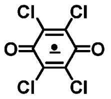
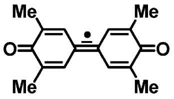


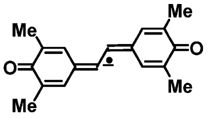
4$^-$ **M$_4$Q**$^-$



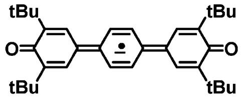
5$^-$ **Cl$_4$Q**$^-$



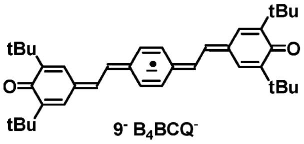
6$^-$ **M$_4$Q$_2$**$^-$



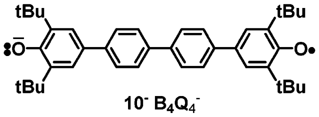
7$^-$ **M$_4$SQ**$^-$



8$^-$ **B$_4$Q$_3$**$^-$

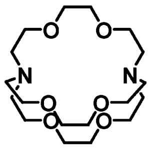


9$^-$ **B$_4$BCQ**$^-$



10$^-$ **B$_4$Q$_4$**$^-$

have been studied in dimethylformamide (DMF) containing an excess of cryptand[2,2,2] **11**, to sequester the sodium counterion.



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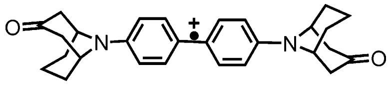
Their optical spectra show that all but **10**$^-$ are delocalized (Class III) compounds with equivalent oxygens. Ortho methyl group protection sufficed for convenient stability of the neutral forms and radical anions of diquinone (**M$_4$Q$_2$**) and stilboquinone (**M$_4$SQ**), but neutral tetramethyl triquinone proved to be rather unstable, so the tetra-*tert*-butyl compounds were studied instead for the larger and less stable systems **B$_4$Q$_3$**, **B$_4$Q$_4$**, and the bis(cyclohexadienylideone)-substituted quinodimethane **9**.

Figure 2 compares the spectra of the five-bond-bridged **3**$^-$ **BQ**$^-$ and **2**$^+$ **(k33)$_2$PD**$^+$,[9] and the nine-bond-bridged **12**$^+$ **(k33N)$_2$BI**$^+$ and **6**$^-$ **M$_4$Q$_2$**$^-$. They resemble each other remarkably in shape, considering their rather large differences in structure and charge, demonstrating that their similar π systems are indeed the important consideration for their optical spectra.



12$^+$ **(k33N)$_2$BI**

Figure 3 compares the optical spectra of the three five-bond-bridged quinones studied. The substituted compounds **4**$^-$ and **5**$^-$ show larger band widths than **3**$^-$, and only quite indistinct vibrational features appear in their first large absorption bands. Significant absorption is observed at lower energy than the first large band, increasing in intensity in the order **3**$^-$ < **4**$^-$ < **5**$^-$.

Figure 4 compares the effect of increasing bridge size in the series **3**$^-$, **6**$^-$, and **7**$^-$, while Figure 5 compares that of the triquinone **8**$^-$ **B$_4$Q$_3$**$^-$ with the latter two of Figure 4. The absorptions appear at lower energy as bridge size is increased for these 9, 11, and 13-bond-bridged quinone radical anions, and the spectra have narrower lines than those for **BQ**$^-$. They show a rather comparable, partially resolved vibrational structure in both the first and second oxidation bands. The fine structure demonstrates that they are delocalized (Class III) systems, because localized intervalence compounds have extremely broad, nearly Gaussian-shaped bands that are characteristic of transitions to strongly sloping curves of excited-state energy surface that do not have a minimum close in geometry to that of the ground state (see Figure 1a).

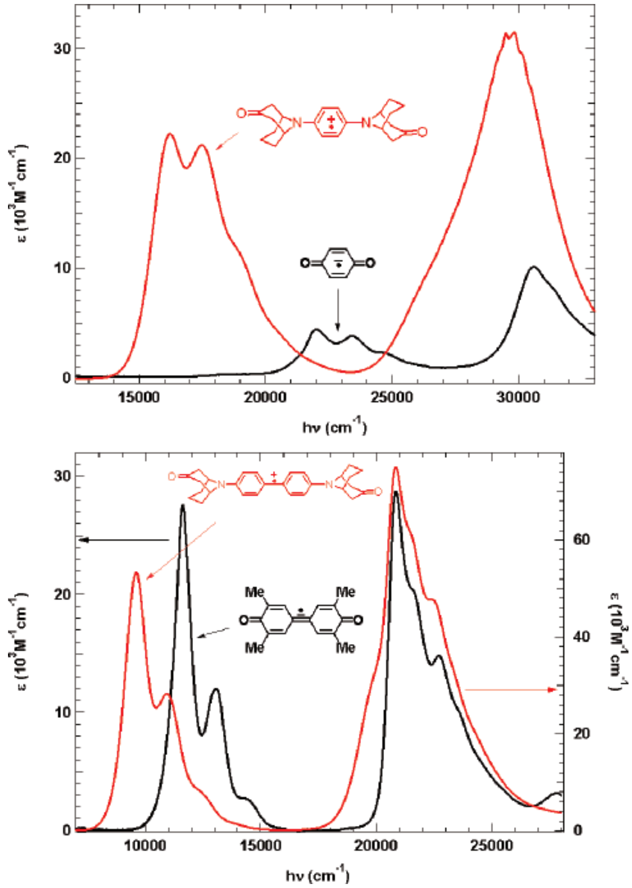


Figure 2. Comparison of optical spectra of nitrogen-centered radical cations and oxygen-centered radical anions having five connecting bonds (**2**$^+$ and **3**$^-$, left panel) and nine connecting bonds (**12**$^+$ and **6**$^-$).

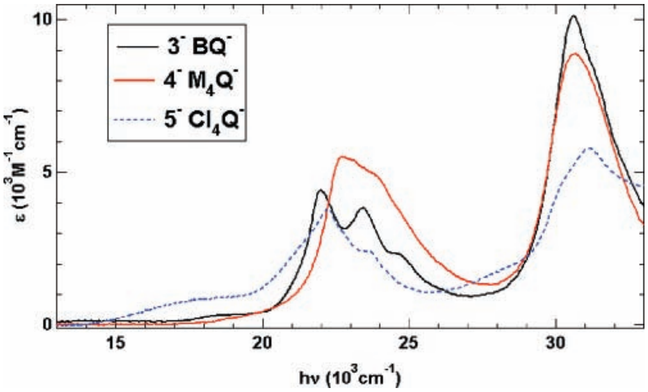


Figure 3. Optical spectra of **3**$^-$ **BQ**$^-$, **4**$^-$ **M$_4$Q**$^-$, and **5**$^-$ **Cl$_4$Q**$^-$ in DMF.

The spectra of the two 17-bond-bridged compounds, **9**$^-$ (**B$_4$BCQ**$^-$) and **10**$^-$ (**B$_4$Q$_4$**$^-$) are compared in Figure 6. Both their neutral forms and radical anions are rather unstable, and we do not doubt that the ϵ values shown, which assume 100% yield of the radical anion, are overestimated. The spectrum of **9**$^-$ resembles that of the smaller systems, and is that of a delocalized compound. That of **10**$^-$, however, shows the broad, nearly Gaussian band shape of a Class II, localized compound. The band maxima observed for these compounds are summarized in Table 1.

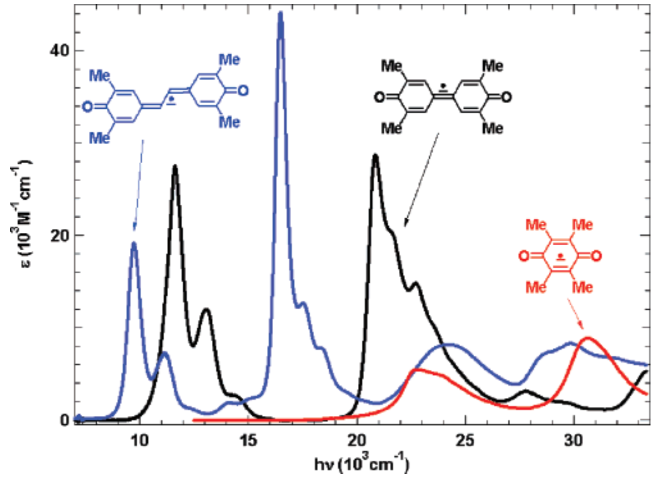


Figure 4. Optical spectra of 4^- **M$_4$Q$^-$**, 6^- **M$_4$DQ$^-$**, and 7^- **M$_4$SQ$^-$** in DMF.

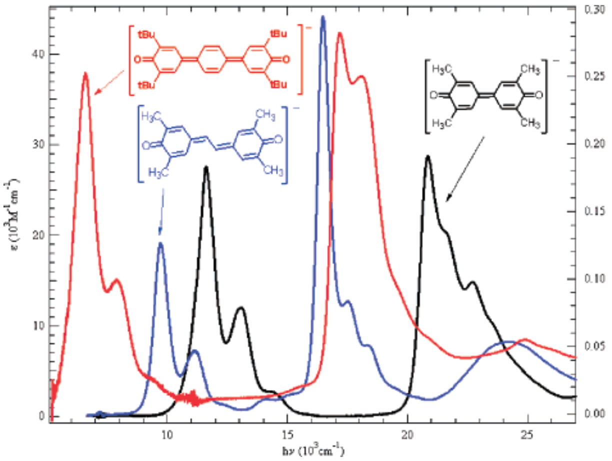


Figure 5. Optical spectra of 6^- **M$_4$Q$_2$$^-$**, 7^- **M$_4SQ^-$**, and 8^- **B$_4Q_3$$^-$** in DMF.

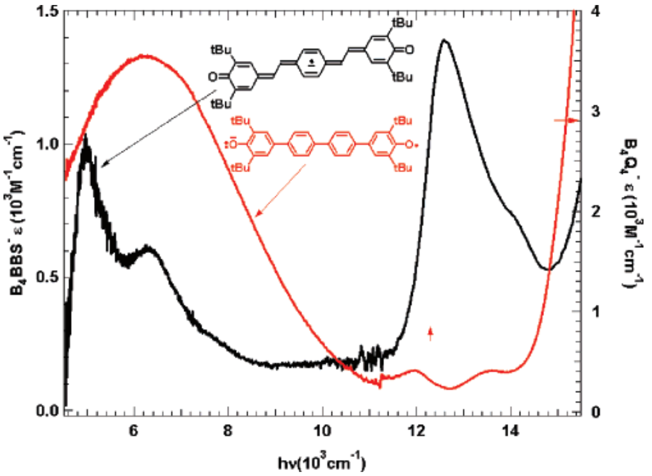


Figure 6. Optical spectra of 9^- **B$_4$BCQ$^-$** and 10^- **B$_4$Q$_4$$^-$** in DMF.

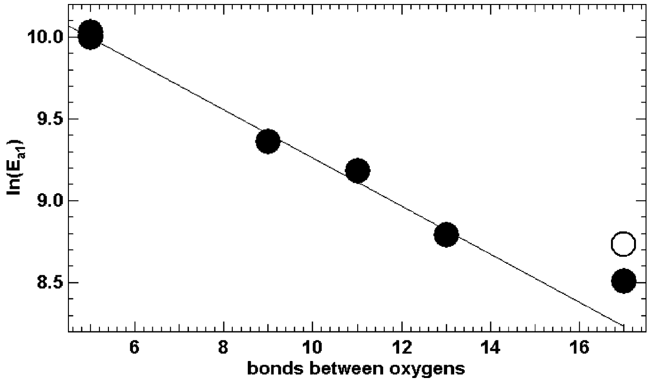


Figure 7. Plot of ln(E_{a1}) versus the number of bonds between the oxygens for the delocalized compounds 3^- to 9^- (filled circles) along with a regression line for 3^- to 8^-. The data for the localized 10^- are shown as the open circle.

TABLE 1: Observed Lowest Transition Energies (cm^{-1}) in DMF

		observed	
radical anion	bonds between O	E_{a1}	E_{a2}
3^- BQ$^-$	5	22000	30600
4^- M$_4$Q$^-$	5	22700	30700
5^- Cl$_4$Q$^-$	5	22200	31150
6^- M$_4$Q$_2$$^-$	9	11630	20860
7^- M$_4$SQ$^-$	11	9710	16450
8^- B$_4$Q$_3$$^-$	13	6570	17200
9^- B$_4$BCQ$^-$	17	4960	12600
10^- B$_4$Q$_4$$^-$	17	∼6200	

Electronic Coupling. The lowest energy large bands for Class III intervalence compounds (the E_{a1} values in Table 1) have traditionally been called "the intervalence band", and their energies are interpreted using the two-state model, for which $V_{ab} = 1/2E_{a1}$.[5] As expected for an electronic coupling, E_{a1} is assumed to be $2V_{ab}$ and ln(V_{ab}) to be proportional to the number of connecting bonds in systems like these. As shown in Figure 7, a plot of ln(E_{a1}) versus the number of bonds between O is nearly linear, as expected for the behavior of V_{ab} for the delocalized systems 3^-−9^-. The points for both the stilboquinone 7^- and its higher analogue 9^- lie noticeably higher than that for the mono-, bi-, and triphenyl compounds, possibly influenced by twisting at phenyl−phenyl bonds of the latter. The ln(E_{a1}/2) regression line is 10.06(±0.05) − 0.149(±0.006)n, where n is the number of bonds connecting the charge-bearing units. This slope corresponds to a β_{bond} value of 0.30, where β is the coefficient in an exponential coupling relationship formulated as $V_{ab} = V_{ab}° \exp(-\beta_{bond}(n - 1)/2)$.[11] This is the same value we obtained for amino-substituted Class III radical cations in our previous work using the same method.[6]

Nevertheless, there is a problem with the interpretation of E_{a1} as $2V_{ab}$. As discussed in detail elsewhere,[12] the transition represented by E_{a1} is between states of different symmetry, so it is not simply determined by a single electronic coupling. Furthermore, the two-state model does not apply unaltered to Class III compounds, because there are two diabatic **M** combination orbitals, which, for Class III compounds, are the symmetric and antisymmetric combinations of the individual **M** group orbitals (simply the p orbitals at the two oxygens for the quinone examples considered here) relative to a plane bisecting the molecule. They interact separately with the symmetric and antisymmetric bridge diabatic orbitals, as shown in Figure 8. Because of the 1/E dependence of orbital mixings, the bridge orbitals that have reasonable overlap with the **M** orbitals and are closest in energy will interact most strongly with the bridge orbitals. Therefore, we suggest that the two-state model does not give reasonable electronic couplings for Class III intervalence compounds, and should not be used to extract electronic couplings, despite the fact that the variation of numbers extracted in this way with the electron-transfer distance is reasonable.

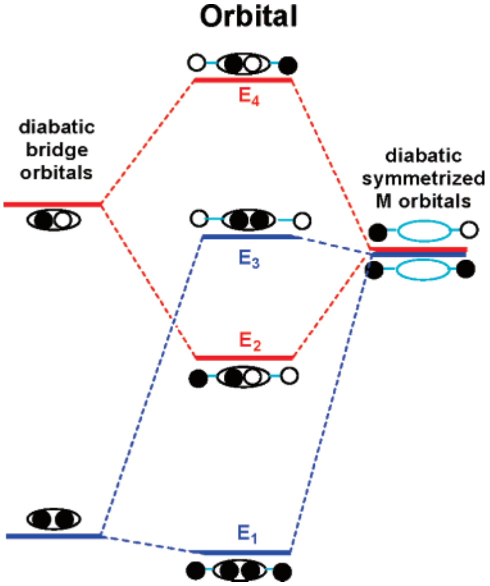


Figure 8. Orbital interaction diagram for a delocalized intervalence compound for which symmetric and antisymmetric bridge orbitals interact with the charge-bearing unit symmetric and antisymmetric orbitals.

Charge Localization in $\mathbf{B_4Q_4}^-$. The localized **10**$^-$ lies distinctly too high relative to the line in Figure 7 for it to be consistent with the delocalized examples (although it should be pointed out that the band maximum for the nearly Gaussian-shaped **10**$^-$ is far higher than the 0,0 transition energy, which is what has been plotted for the delocalized cases). λ increases with molecular size, because its solvent component λ_s increases. As expected for a Class II system, where E_{a1} represents λ, the band maximum for **10**$^-$ increases by 1360 cm^{-1}, to 7660 cm^{-1}, in the higher λ_s solvent, acetonitrile. However, the widely used dielectric continuum theory equation does not properly describe how λ (as measured by the band maximum) changes in localized mixed-valence compounds, either with distance or with solvent, as demonstrated by studies of a series of mixed-valence bis-hydrazine radical cations.[13]

$\mathbf{B_4Q_4}^-$ is calculated to be delocalized using the B3LYP/6-31G* level of theory. This is not surprising because of the well-known tendency for density functional theory calculations to overemphasize the stabilization provided by delocalization.[14] In the systems closest to the examples studied here, B3LYP calculations incorrectly predict charge-delocalization for the iso-π-electronic aromatic-bridged bishydrazine intervalence radical cations.[15] Nevertheless, these calculations do rationalize a significantly lower V_{ab} for $\mathbf{B_4Q_4}^-$ than for $\mathbf{B_4BCQ}^-$, because considerably more twisting is predicted in the bridge of the former compound. Because V_{ab} is proportional to overlap, and overlap should depend on the product of the cos ϕ values for twisting at each bond, more twisting will lower V_{ab}. There are four CC bonds about which twisting is calculated to occur for $\mathbf{B_4BCQ}^-$ (those that would be single bonds in a C$-$O single bond representation such as that shown for $\mathbf{B_4Q_4}^-$) but the ϕ values obtained were small (1.2$-$1.4°), and the product of the cos ϕ values is 0.999. For $\mathbf{B_4Q_4}^-$ the calculated ϕ values at the three CC bonds linking benzene rings were 25.3, $-$23.9, and 25.3°, leading to a cos ϕ product of 0.75. Furthermore, the calculated ϕ values will be unrealistically small for $\mathbf{B_4Q_4}^-$ because of the overemphasis of stabilization provided by delocalization, so the actual drop in V_{ab} for $\mathbf{B_4Q_4}^-$ should be even larger.

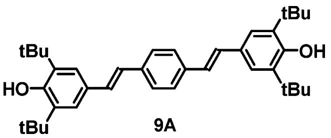
Applying the two-state model with $V_{ab} = \ln(E_a/2)$, the line for the $n = 5-13$ examples shown in Figure 7 predicts V_{ab} for $\mathbf{B_4Q_4}^-$ at 1880 cm^{-1} (for $n = 17$). Because it is a Class II intervalence compound, the E_{a1} of 6300 cm^{-1} for $\mathbf{B_4Q_4}^-$ is λ, and since $\lambda/2$ is greater than the V_{ab} estimation, the two-state model successfully predicts charge localization. However, $E_{a1}/2$ cannot represent a reasonable measure of electronic coupling for these systems, as pointed out above, and the other $n = 17$ compound, $\mathbf{B_4BCQ}^-$, is delocalized. As discussed in a paper on localized dinitroaromatic compounds that are near the Class II, Class III borderline, these also give anomalously small values of V_{ab} when analyzed with the Hush model,[16] but the strongly trapped 2,7-dinitronaphthalene radical anion produces an appropriate V_{ab} to rationalize the observed electron-transfer barrier measured by electron spin resonance (ESR).[17]

Conclusions

The vibrational fine structure observed in the optical spectra for three five-bond-bridged quinone radical anions (we use n, the number of bonds between the oxygen atoms), their analogues with 9, 11, and 13 bond-bridges, and the 17 bond-bridged **9**$^-$ $\mathbf{B_4BCQ}^-$, show that these systems are delocalized mixed-valence compounds. Charge localization does not occur in the series studied until the 17-bond-bridged system **10**$^-$ $\mathbf{B_4Q_4}^-$, establishing the single-atom charge-bearing unit M = O$^{\bullet-}$ as a particularly effective one for maintaining high electronic coupling relative to reorganization energy. Because these systems have both symmetric and antisymmetric **M** combination orbital pairs that must interact separately with symmetric and antisymmetric bridge orbitals, the simple two-state theory should not be used for consideration of the electronic couplings in these delocalized intervalence compounds.

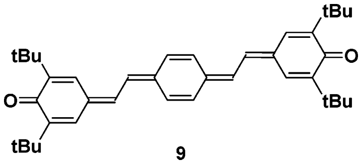
Experimental

Commercial **BQ**, $\mathbf{M_4Q_4}$, and $\mathbf{Cl_4Q_4}$ were recrystallized before use. $\mathbf{M_4Q_2}$,[18] $\mathbf{M_4SQ}$,[18] $\mathbf{B_4Q_3}$,[19] and $\mathbf{B_4Q_4}$[20] were prepared as previously described. Preparation of samples: Radical-anions were prepared in vacuum-sealed glass cells equipped with an ESR tube and a quartz optical cell. Reduction of the 30$-$330 μM solutions in DMF was achieved by contact with 0.2% Na$-$Hg amalgam in the presence of an excess of [2,2,2] cryptand.



9A

1,4-bis[2-(4-Hydroxy-3,5-di-*tert*-butylphenyl)ethenyl)]benzene (9A). A 1.5 g portion of 1,4-bis(2-bromoethyl)benzene and 0.25 g of magnesium turnings were refluxed in dried tetrahydrofuran (THF) until all the magnesium was consumed (12 h). To this solution of the Grignard reagent was added at 25 °C a solution of 2.3 g of 2,6-di-*t*-butyl-1,4-benzoquinone in 20 mL of dry THF. After 1 h at reflux, 20 mL of water was added, and the mixture was acidified with dilute sulfuric acid and again refluxed for 1 h. The aqueous mixture was extracted with ether, and the residue after evaporation of the solvent was separated by column chromatography on silica. The strongly fluorescent (under UV) band of the product was eluted with dry cyclohexane, giving 0.85 g (31%) of **9A** as a white solid: mp 256$-$258 °C (pet. eth.); IR (CCl_4), 3640 (sharp), 3020, 2960, 1420 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.48 (s, 36H), 7.07 (d, 2H, $J = 16.5$ Hz), 7.23 (d, 2H, $J = 16.5$ Hz), 7.44 (s, 4H), 7.55 (s, 4H). ^{13}C NMR (300 MHz, acetone-d_6) δ 30.6, 35.2, 124.2, 125.7, 126.0, 127.3, 129.9, 130,1, 137.8, 138.4, 154.9; Anal. Calc. for $C_{38}H_{50}O_2$: C, 84.71; H, 9.35. Found: C, 84.34; H 9.24. Subsequent elution afforded unreacted 2,6-di-*t*-butyl-1,4-benzoquinone.



9

7,8-bis(2,6-Di-*tert*-butyl-2,5-cyclohexadiene-4-ylidene-1-one-7-yl)quinodimethane (9). A solution of 0.5 g of the diphenol **9A** in 70 mL benzene was shaken twice with a solution of 6.0 g of $K_3Fe(CN)_6$ and 5 g KOH in 50 mL of water. The intensely blue organic phase was washed with water, dried, and evaporated in vacuum at 30 °C, yielding 0.37 g (75%) of **9** as green crystals (mp 204−206 °C (dec)). The compound is unstable and should be protected from light and kept in a refrigerator; UV−vis (benzene) 609 nm ($\log \epsilon = 4.3$); IR (CCl_4), 3001, 1632, 1616, 1568, 1361, 1253 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.17 (s, 18H), 1.28 (s, 18H), 6.70 (d, 2H, $J = 9.6$ Hz), 6.85 (s, 2H), 7.06 (d, 2H, $J = 9.6$ Hz), 7.35 (s, 2H), 7.37 (d, 2H, $J = 16.5$ Hz), 7.55 (d, 2H, $J = 16.5$ Hz); ^{13}C NMR (300 MHz, acetone-d_6) δ 30.6, 35.4, 36.0, 127.6, 128.3, 131.4, 132.0, 132.4, 135.9, 139.9, 147.4, 149.0, 149.5, 186.8; Anal. Calc. for $C_{38}H_{48}O_2$: C, 85.03; H, 9.01. Found: C, 84.85; H, 8.70.

Theoretical calculations were done using Gaussian 98.[21]

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