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1450, 1175, 965 cm^{-1}; ^{1}H NMR δ 1.02 (t, J = 7.3 Hz, 6 H, 2 CH_3CH_2), 1.81 (sext, J = 7.3 Hz, 4 H, 2 $CH_3CH_2CH_2$), 2.81 (t, J = 7.3 Hz, 4 H, 2 $CH_3CH_2CH_2$); MS m/e (relative intensity) 43 (42), 55 (22), 71 (20), 127 (100), 140 (19), 154 (M^+, 2), 155 (M^+ + 1, 3). Anal. Calcd for $C_8H_{14}N_2O$: C, 62.30; H, 9.15; N, 18.17. Found: C, 62.27; H, 9.12; N, 18.09.

2-*n*-Propyl-5-isopropyl-1,3,4-oxadiazole (4d): bp 102–104 °C (17 mm); IR (neat) ν 2950, 2860, 1580, 1555, 1450, 1185, 1140 cm^{-1}; ^{1}H NMR δ 1.02 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.38 (d, J = 6.8 Hz, 6 H, 2 CH_3Ch), 1.81 (sext, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 2.81 (t, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 3.17 (m, 1 H, CH_3CH); MS m/e (relative intensity) 43 (60), 55 (32), 71 (25), 127 (100), 140 (26), 154 (M^+, 2), 155 (M^+ + 1, 6). Anal. Calcd for $C_8H_{14}N_2O$: C, 62.30; H, 9.15; N, 18.17. Found: C, 62.14; H, 9.32; N, 18.03.

2-Methyl-5-phenyl-1,3,4-oxadiazole (4f): bp 123–125 °C (3 mm), mp 67–69 °C; IR (KBr) ν 1580, 1480, 1445, 1250, 780, 710, 690 cm^{-1}; ^{1}H NMR δ 2.62 (s, 3 H, CH_3), 7.40–8.09 (m, 5 H, *Ph*); MS m/e (relative intensity) 43 (52), 77 (47), 90 (53), 104 (44), 105 (61), 160 (M^+, 100). Anal. Calcd for $C_9H_8N_2O$: C, 67.48; H, 5.03; N, 17.49. Found: C, 67.49; H, 4.95; N, 17.48.

2-*n*-Propyl-5-phenyl-1,3,4-oxadiazole (4g): bp 141–143 °C (3 mm); IR (neat) ν 2970, 2875, 1570, 1550, 1485, 1445, 1005, 710, 690 cm^{-1}; ^{1}H NMR δ 1.06 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.88 (sext, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 2.90 (t, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 7.37–8.09 (m, 5 H, *Ph*); MS m/e (relative intensity) 43 (49), 77 (33), 90 (43), 105 (59), 160 (100), 188 (M^+, 23). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.17; H, 6.50; N, 14.73.

2-Isopropyl-5-phenyl-1,3,4-oxadiazole (4h): bp 130–132 °C (3 mm); IR (neat) ν 2980, 2875, 1565, 1550, 1485, 1450, 1070, 710, 690 cm^{-1}; ^{1}H NMR δ 1.45 (d, J = 6.8 Hz, 6 H, 2 CH_3CH), 3.27 (m, 1 H, CH_3CH), 7.37–8.10 (m, 5 H, *Ph*); MS m/e (relative intensity) 43 (100), 77 (46), 90 (41), 105 (92), 117 (54), 188 (M^+, 79). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.13; H, 6.49; N, 14.67.

2,5-Diphenyl-1,3,4-oxadiazole (4j): mp 139–140 °C (lit.[12] mp 141 °C). The material that was isolated was identical to an authentic sample of **4j** prepared by the dehydration of 1,2-dibenzoylhydrazine by PPA.[19] **4j**: IR (KBr) ν 1550, 1485, 1445, 1070, 785, 710, 685 cm^{-1}; ^{1}H NMR δ 7.48–8.20 (m, 10 H, *Ph*); MS m/e (relative intensity) 77 (49), 90 (41), 105 (100), 165 (71), 166 (39), 222 (M^+, 93).

Supplementary Material Available: Characterization data for **1h–l**, **2a,c–e,g,h**, and **3g,i–k** (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(19) Fitton, A. O.; Smalley, R. K. *Practical Heterocyclic Chemistry*; Academic: New York, 1968; p 38.

PPP-MO Calculations Predict Spectra of Quinone and Imide Anion Radicals

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Received October 15, 1991

PPP-MO calculations were used to calculate the electronic structure of quinone and imide anion radicals, including diquinones, diimides, and *N*-cyanoimine derivatives of quinones. The results were used to correlate electronic excitation spectra which extend from 400 to 1600 nm, ESR spectra, and electrochemical reduction potentials. Comparison with ab initio calculations is made.

Semiquinones, the anion radicals of quinones, are important species in biology, medicine, and chemistry.[1] It is surprising, therefore, that little attention has been given to molecular orbital calculations on these species. Work from this laboratory has recently explored the unusual properties of radical anions derived from diquinones,[2,3] diimides,[4] and the *N*-cyanoimine derivatives of quinones.[5] Of particular interest were the optical spectra which showed electronic absorption bands in the NIR region, often beyond 1000 nm. We wished to use MO theory to calculate the wavelength of these bands in order to predict which anion radicals would be of interest before they were synthesized. In addition we wished to confirm the origin of these long-wavelength bands, confirm the structure of the anion radicals by ESR spectroscopy, and predict the reduction potentials at which the anion radicals would be formed.

Some time ago extensive MO studies of π-orbital levels and spectra of neutral quinones appeared.[6,7] In principle these levels could be used to predict some of the quantities of interest here. As part of our work on semiquinones we have reported ab initio calculations.[3] These are high-quality calculations with large basis sets, which sometimes included configuration interaction (CI). Even so, the electronic transition energies did not accurately reflect

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(1) See for example: (a) *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; J. Wiley: New York, 1974. (b) *Function of Quinones in Energy Conserving Systems*; Trumpower, B. L., Ed.; Academic: New York, 1982. (c) Moore, H. W.; Czerniak, R.; Hamdan, A. *Drugs Exp. Clin. Res.* **1986**, *12*, 475. (d) Schreiber, J.; Mottley, C.; Sinha, B. K.; Kalyanaraman, B.; Mason, R. *J. Am. Chem. Soc.* **1987**, *109*, 348. (e) Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S.; Hurley, J. K.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1988**, *110*, 1733.

(2) (a) Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1987**, *109*, 6560. (b) Jozefiak, T. H. Ph.D. Thesis, University of Minnesota, 1989. (c) Almlöf, J.; Feyereisen, M. W.; Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1990**, *112*, 1206. (d) Forkner, M. W.; Rak, S. F.; Miller, L. L. *Synth. Met.* **1990**, *36*, 65.

(3) Jozefiak, T. H.; Almlöf, J.; Feyereisen, M. W.; Miller, L. L. *J. Am. Chem. Soc.* **1989**, *111*, 4105.

(4) Rak, S. F.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1990**, *55*, 4794.

(5) Rak, S. F.; Liberko, C. A.; Miller, L. L. *Synth. Met.* **1991**, *42*, 2365. Liberko, C. A.; Miller, L. L. *Chem. Mat.* **1990**, *2*, 339.

(6) Nepras, M.; Fabian, J.; Titz, M. *Collect. Czech. Chem. Commun.* **1981**, *46*, 20. Titz, M.; Nepras, M. *Int. J. Quant. Chem.* **1979**, *16*, 543 and references cited therein including: Titz, M.; Nepras, M. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2674.

(7) Pullman, B.; Diner, S. *J. Chim. Phys.* **1958**, *55*, 212.

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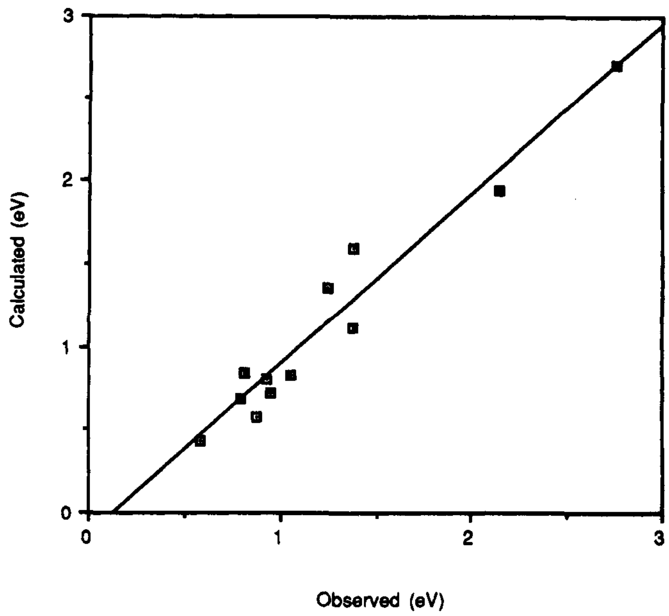

Figure 1. Comparison of long-wavelength transition energies for anion radicals.

experiment. Semiempirical PPP-MO calculations[8] are quite successful for calculating transition energies of closed shell species and are widely used for prediction of visible[9] and NIR[10] dye colors. These SCF calculations treat only the π-electrons, but for that reason they are very efficient. Here, we demonstrate that closed-shell PPP calculations are surprisingly useful for predicting the properties of the open-shell anion radicals.

Method

The calculations were done on a Zenith ZKB-2 microcomputer with program number QCMP054 purchased from Quantum Chemistry Program Exchange. The standard parameters were used to calculate the electronic structures of the neutral molecules. The program provides π–π^* transition energies for the neutral molecules, calculated with CI.

The π^*–π^* transition energies for the anion radicals were taken as the difference between the SCF energies of the LUMO and next highest orbital of the neutral molecule. No CI was used. In the text, anion radical orbitals are defined as SOMO (singly occupied molecular orbital, the neutral molecule LUMO), while the next highest orbital is defined as the anion radical LUMO. For calculations of a_H the McConnell equation, $a_H = qc^2$, was used where q = 27 G and c^2 is the electron density at the atom of interest in the SOMO.

Perturbations on the diquinones and diimides were calculated by stretching the carbonyls on one end while constricting the carbonyls on the other end by 2% of the original bond distance. The overlap integrals were likewise adjusted by decreasing or increasing their values by 2% respectively.

Results and Discussion

Electronic Absorption Spectra. Of primary interest to us was prediction of the long-wavelength absorption spectra of anion radicals. The anion radicals of diquinones and diimides have bands in the NIR region which are of practical as well as theoretical interest. Because these transitions have $\epsilon > 10^3$ it has been proposed that they originate from π^*–π^* transitions. It seemed possible, therefore, that the PPP method would be useful. By simply taking the difference between the SCF orbital energies for the SOMO and LUMO it was found that useful predictions could be made (Table I). Figure 1 shows the linear correlation (r = 0.98) of theory and experiment for the thirteen anion radicals derived from quinones, imides, and *N*-cyanoimines. Typically, the calculated transition energy is 0.2 eV smaller than the experimental value. Since there is an enormous spread of wavelength maxima (400–1600 nm), the success is especially remarkable. This success reinforces previous conclusions that all these transitions are π^*–π^*.

Table I. PPP-Calculated and Observed Long-Wavelength Transition Energies

			π–π^* neutral[a] (eV)		π^*–π^* radical anion[b] (eV)	
	SOMO	LUMO	calcd	obs	calcd	obs
1	−3.76	−1.06	4.19	4.34[d]	2.70 (3.57)[a]	2.76[c]
2	−3.42	−1.47	3.94	3.79[d]	1.95 (2.07)[a]	2.07[c]
3	−4.28	−3.16	2.92	3.83[e]	1.12 (2.06)[a]	1.38[c]
4	−3.86	−3.18	3.67	3.52[f]	0.69 (1.29)[a]	0.79[c]
5	−3.52	−2.72	4.08	3.70[f]	0.80 (1.50)[a]	0.93[c]
6	−3.63	−3.19	3.28	2.84[f]		
7	−3.48	−3.21	3.09	2.49[f]		
8	−3.15	−2.75	3.43	2.93[g]		
9	−3.08	−1.72	4.38	3.84[d]	1.36	1.24[f]
10	−3.31	−2.39	3.40	3.06[d]		
11	−2.97	−2.39	3.78	3.14[d]		
12	−3.78	−3.07			0.72	0.95[c]
13	−3.49	−2.66			0.83	1.05[i]
14	−3.26	−1.83	4.04	3.88[g]	1.43	1.72[g]
15	−3.65	−2.81	4.00	3.65[g]	0.84	1.14[g]
16	−4.81	−1.65	3.32	3.43[h]		
17	−4.14	−2.54	3.65	3.85[h]	1.59	1.37[i]
18	−3.97	−2.26	2.84	2.70[h]		
19	−4.08	−2.45	3.64	3.42[h]		
20	−4.78	−3.94	3.50	3.54[i]	0.84	0.82[j]

[a] Including CI. [b] Difference in orbital energies for neutral. [c] References 2c and 3. [d] Hartman, H.; Lorenz, E. Z. *Natur. Forschg.* **1951**, *7A*, 360. [e] Yoshino, S.; Hayakawa, K.; Kanematsu, K. *J. Org. Chem.* **1981**, *46*, 3841. [f] Reference 2b. [g] Reference 4. [h] Aumuller, A.; Hunig, S. *Liebigs Ann. Chem.* **1986**, 142. [i] Liberko, C. A. Unpublished results. [j] Reference 5.

Based on these results it was of interest to try to predict the π–π^* absorption maxima of the neutral compounds. Using the PPP method, especially with CI, the correlation was not good. Experimental data came from three solvents, DMF, CH_2Cl_2, and CH_3CN, but that does not seem to be the problem since the data sets from any one solvent also did not correlate well. No effort was made to change the parameters of the calculation to improve the fit. It is simply noted that it is surprising that the calculation works better for anion radicals than for the neutrals for which it was designed.

ESR Hyperfine Coupling Constants. It is interesting that there are not good calculations of semiquinone ESR spectra in the literature. Indeed, although INDO calculations are usually useful for ESR, the method is not very successful for simple semiquinones.[11] The coupling constants come from PPP calculations through use of the McConnell equation, and the value q = 27 G was chosen. The results for several quinone and imide anion radicals for which the ESR spectra have been reported in Table II are correlated in Figure 2. The results are quite satisfactory since the correlation coefficient is 0.99. It is noted

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(8) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466.

(9) See for example: Griffiths, J. *Dyes Pigments* **1982**, *3*, 211.

(10) Fabian, J.; Zahradnik, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677.

(11) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 4201. Miller, L. L. Unpublished work.

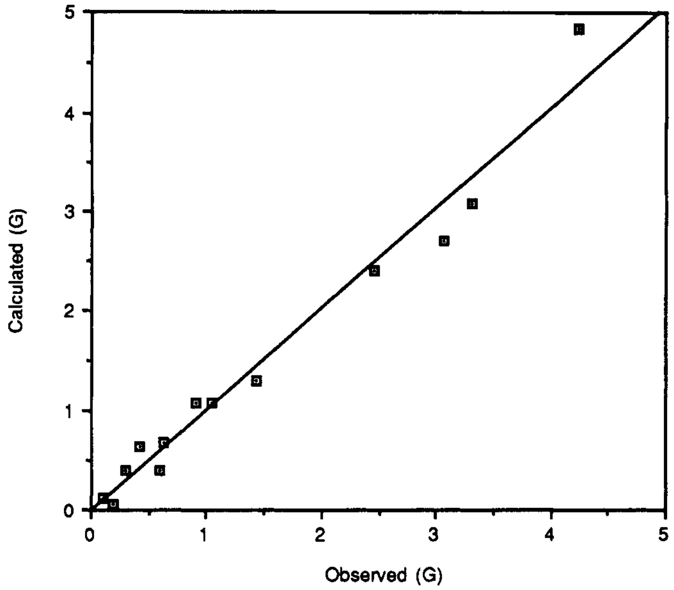

Figure 2. Comparison of ESR a_H values for quinone and imide anion radicals.

Table II. Calculated and Observed Hyperfine Splittings

proton[a]	calcd a_H	obs a_H
1a	2.39	2.45[b]
2a	3.09	3.31[c]
2b	0.40	0.60[c]
2c	0.80	0.63[c]
3a	0.63	0.41[b]
4a	1.07	0.90
6a	1.30	1.42[b]
6b	0.11	0.11[b]
8a	2.71	3.07[d]
8b	4.83	4.24[d]
9a	1.07	1.05[b]
	0.40	0.30[b]
15a	0.06	0.19[e]
16a	2.03	2.01, 1.63[f]
16b	2.07	
17a	0.57	0.40, 0.52[f]
17b	0.60	
17c	1.15	0.85, 0.63[f]
17d	0.83	
18a	1.30	1.27[f]
18b	0.59	0.29[f]
18c	0.83	0.61[f]
19a	0.64	0.37[f]
19b	0.88	0.72, 0.94[f]
19c	0.91	

[a] Number refers to compound, letter to specific proton as defined on the structural formula. [b] Reference 2b. [c] Stone, W. E.; Maki, A. H. *J. Chem. Phys.* **1962**, *36*, 1944. [d] Reference 13. [e] Rak, S. F. Unpublished results. [f] Gerson, F.; Gescheidt, G.; Mockel, R.; Aumuller, A.; Erk, P.; Hunig, S. *Helv. Chim. Acta* **1988**, *71*, 1665.

that this method does not predict the hyperfine couplings at positions lying on MO nodes.

Calculations of a_H values for *N*-cyanoimines were also performed, and there was a linear correlation, $r = 0.96$, of experiment and theory (Figure 3). Less satisfactory were the absolute values. The calculations overestimated a_H on average by about 0.2 G. It was deemed unwise to search for parameters which would improve the agreement, but which would be limited to ESR.

Electrochemical Reduction Potentials. Electrochemical reduction potentials for the neutral quinones, imides, and *N*-cyanoimine derivatives were correlated with the energy of the SOMO of the anion radical (Figure 4). Experimental data are apparent $E°$ values from cyclic voltammetry, using DMF solvent referred to a SCE reference electrode. The intercept, slope, and $r = 0.93$ are quite similar to the values obtained for other correlations of this type.[12]

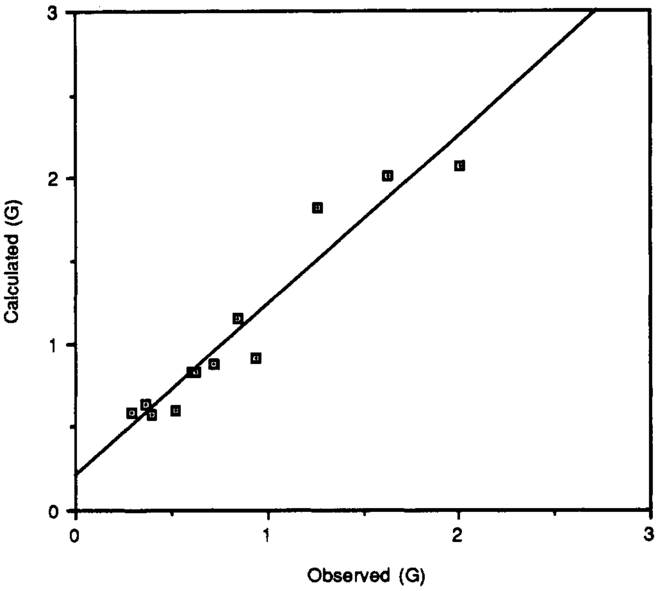

Figure 3. Comparison of ESR a_H values for *N*-cyanoimine anion radicals.

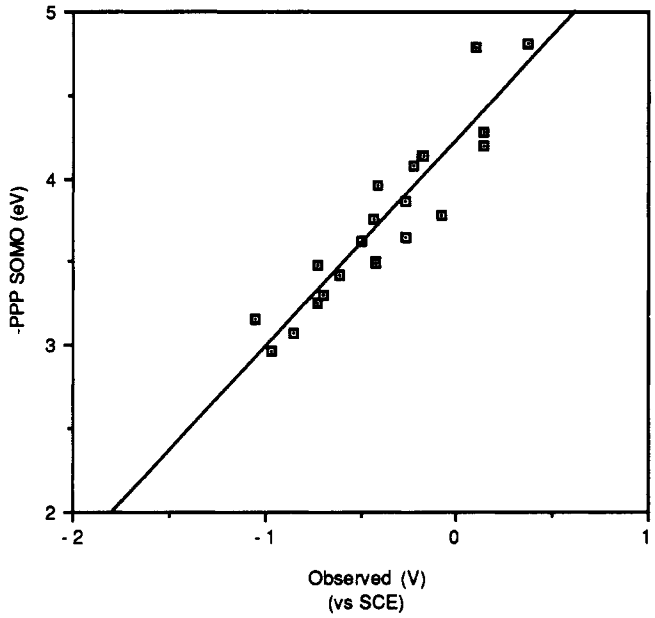

Figure 4. Comparison of SOMO energies and $E°$ values.

Comparison with ab Initio Calculations and the Question of Electron Localization. The properties of diquinone anion radicals **1–5** have been studied previously using ab initio calculations.[2,3] This method gave a good account of ESR coupling constants and qualitative correlations with observed absorption maxima and reduction potentials. Shown in Table I in parentheses are calculated transition energies for the long-wavelength bands of anion radicals. Comparison of these ab initio values with PPP values shows that PPP is superior as a quantitative tool. Beyond that, however, it is important to note that with one exception, **8**, the two calculational methods give the same orbitals as the HOMO, SOMO, and LUMO. Considering the large number of orbitals in these molecules that is not an insignificant accomplishment.

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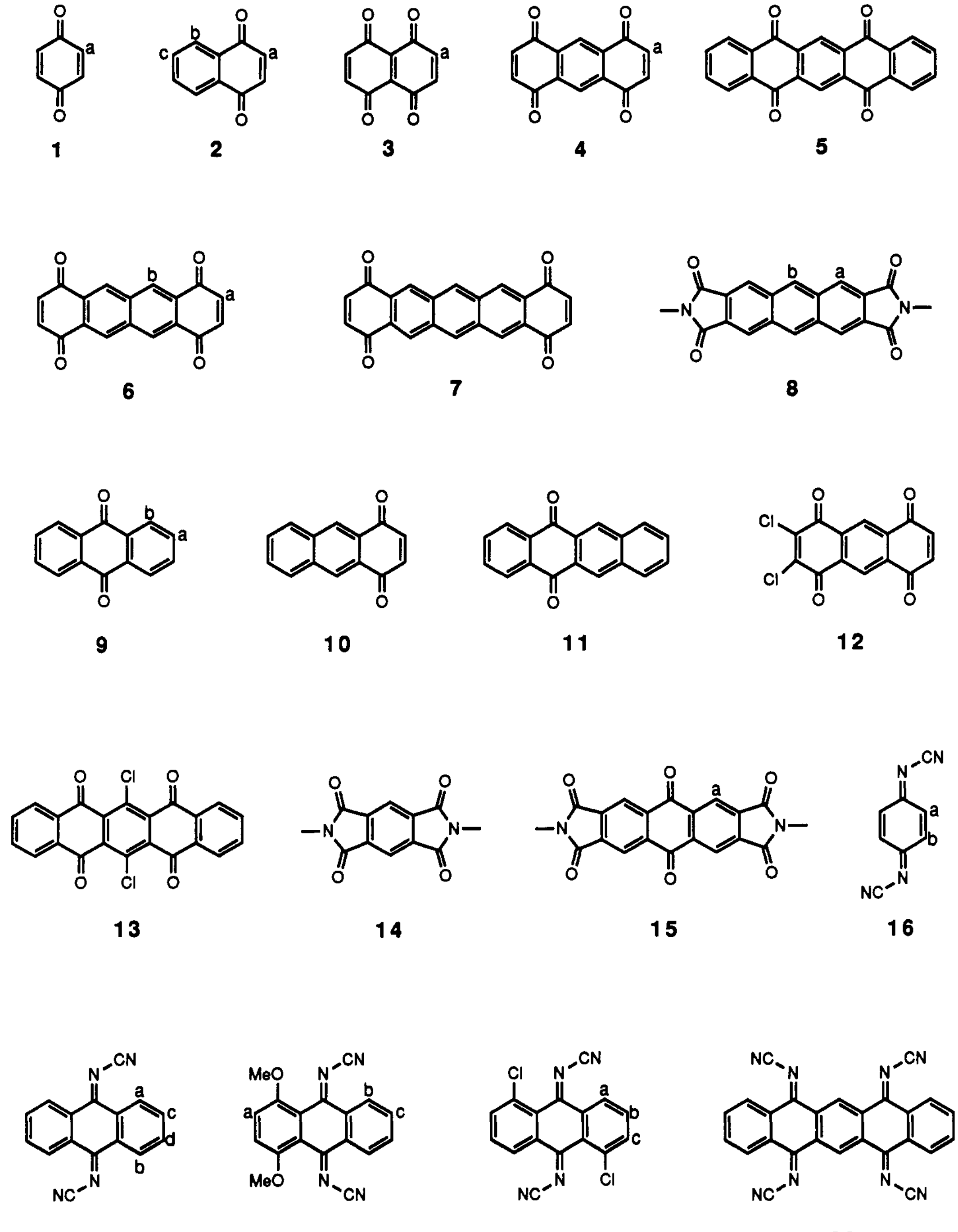
(12) Zuman, P. In *Substituent Effects in Organic Polarography*; Plenum: New York, 1967.

Chart I



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

The use of ab initio calculations has been important in understanding the electronic structure of the "stretched" diquinone anion radicals **6** and **7**.[3] The calculations suggested that the odd electron of these anion radicals was localized on one quinone or the other. This has recently been confirmed using a derivative of **7**.[13] ESR spectra showed that at room temperature the odd electron was hopping rapidly between the two quinones, while at 200 K it was localized on one quinone. Because their electronic structures are localized and PPP gives delocalized structures, anion radicals **6** and **7** were not included in the correlations of Figures 1 or 2.

Since localization is intimately associated with geometry changes, it was of interest to see if perturbation of the structures would lead to "localization" as defined by large changes in electron density[3] calculated by the PPP method. As the carbon oxygen bonds of one quinone are stretched there is an increase of electron density in that quinone at the expense of electron density at the other end. We first calculated electron densities for symmetrical delocalized anion radicals. The SOMO electron densities on the carbonyl groups of **5**, **6**, and **7** are found to be the same within ±2% (Table III). We then perturbed the structures by 2% and recalculated the electron densities. The change in SOMO electron density on the carbonyl groups was much larger for **7** than for **5**. To make a more valid comparison, Table III shows the percent change in q delocalized $(\Delta q/q) \times 100$ summed for all the carbons and oxygens on one side of the molecule. In the case of **5** the change is minimal, but **7** shows a 30% shift of electron density to one end. Since **5** is thought to be delocalized,

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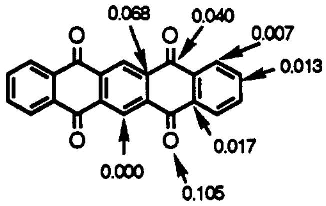
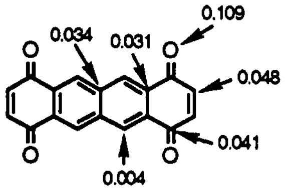
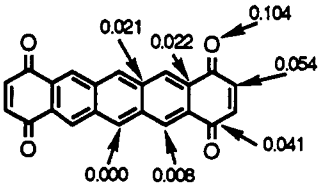
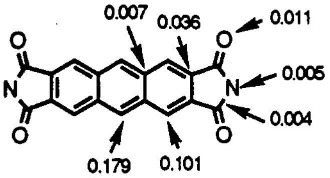
(13) Rak, S. F.; Miller, L. L. *J. Am. Chem. Soc.*, in press.

Table III. Change in SOMO Electron Density[a]

anion radical SOMO q values	$(\Delta q/q) \times 100$
 **5**	8.8
 **6**	18
 **7**	30
 **8**	1.7

[a] Carbonyl bonds lengthened by 2% on the left side of the molecules and compressed by 2% on the right side. The change in electron density (Δq) was computed for each side by summing the q values at all the carbons and oxygens on one side and subtracting the unperturbed values.

while **6** and **7** are localized, PPP results qualitatively mimic the experimental results and the results found using ab initio calculations.

A species of special interest is the anion radical of the stretched diimide **8**, derivatives of which have been shown by ESR to have delocalized structures. PPP calculations give a good account of the ESR coupling constants and confirm that much of the odd electron density lies in the anthracene bridge. Ab initio calculation gives a different SOMO orbital[14] and, therefore, does not give appropriate coupling constants. Consider now the question of odd-electron localization in anion radical **8**. In this case (Table III) stretching the carbonyl groups of the imides does not lead to any significant change in the electron density. This agrees with experiment which shows that odd-electron localization is not favorable.

These results lead us to some simple understanding of the electron localization phenomenon. If the carbonyls are far apart and there is high electron density on these groups in the delocalized SOMO (as in **7**), electron localization is possible. If the SOMO has high electron density on the bridge as in **8**, localization is unlikely. In the PPP method this can be explored by perturbing the carbonyls to see if there is a large change in electron density.

Conclusions

The method is quite sufficient to predict long wavelength transition energies, hyperfine coupling constants, and $E°$ values. The most interesting aspect is the calculation of the electronic spectra of open-shell anions using closed-shell calculations without CI. Two factors seem important. (1) Differences in orbital energies for the neutral are a good approximation to differences in state energies for the anion radicals. This is, in fact, predicted from Koopmans' theorem,[15] which states that the optimal MOs for the $2N$ electron closed-shell neutral are to first order also the optimum MOs of the $2N + 1$ and $2N - 1$ electron species (radical anion and cation) and that the state energy of species obtained by adding (subtracting) an electron to the kth MO of the neutral is given by the energy of the neutral plus (minus) the kth orbital energy. (2) CI is unnecessary because in contrast to the situation for closed shell molecules, these $\pi^*-\pi^*$ anion radical transitions involve open-shell ground and excited states. It can be postulated that the loosely held odd electron interacts with the other electrons and the nuclei to a similar extent in ground and excited states, so that the CI normally used to get accurate results is unnecessary.

Acknowledgment. This work was supportd by the National Science Foundation. L.L.M. was a Paul J. Flory, IBM Fellow, and C.A.L. was a Dow Fellow in 1990. The relevance of Koopmans' theorem was suggested by a reviewer.

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[14] Almlöf, J. Private communication.

[15] Koopmans, T. *Physica* 1933, *1*, 104.