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AN IMPROVED PPP π-ELECTRON PARAMETERIZATION FOR CYANOAROMATICS

APPLICATION TO PREDICTIONS OF SPECTRAL AND OTHER PHYSICAL PROPERTIES

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Abstract—Electronic spectra, ionization and reduction potentials, and dipole moments of representative cyanoaromatics have been simulated with a single PPP calculational scheme contrary to previous π-electron treatments. This was achieved by altering the standard cyano PPP parameterization such that the N atom becomes substantially more electronegative and the nitrile carbon slightly more electropositive. *Ab initio* STO 4-31G results were the model for the proposed modifications. Application of this approach to a wide range of cyano-containing electron deficient, "push-pull" and anionic molecules demonstrates its utility in physical properties predictions, and offers a correct theoretical basis for a number of unusual spectral observations in which simple resonance considerations fail.

The cyano function has been used widely as a strong electronegative group in conjugated molecules. A vast experimental data base exists on its role in altering a number of standard physical properties of π-electronic systems such as electronic spectra, ionization potentials, reduction potentials, electron affinities and dipole moments in the ground and excited states. Despite this, no unifying set of Pariser–Parr–Pople (PPP) π-electronic parameters have been developed and widely tested for this group.

Two classes of parameters have suggested in the literature and received limited application: (1) A standard set based on electronegativities of neutral atoms as developed by Hinze and Jaffé,[1] which offered good spectral predictions on simple aromatic nitriles.[2,3] (2) A more "electronegative" scheme which was employed in spectral descriptions of charge-transfer complexes[4] and electron affinity calculations.[5] The two parameter sets are displayed in Table 1.

However upon further investigation, we have found that the standard set of cyano parameters yielded poor predictions for ionization potentials and dipole moments of simple aromatic nitriles including benzonitrile. On the other hand the "electronegative" treatment failed to give reasonable spectral results for these molecules, although ionization potentials and dipole moment† values were found to be acceptable. Some typical data are displayed in Table 2.

Parameter development

Thus, we began a search to develop a more universal set of PPP π-electron cyano parameters. Initially as in a previous study on the nitro function,[7] we started by considering the results of valence-electron and *ab initio* calculations on small model compounds as a more realistic basis for simulation. However, contrary to the nitro study, it was found that CNDO/2[8] and *ab initio* calculations at the STO-3G level[9] gave poor values for the dipole moments of simple compounds such as HCN and acrylonitrile. Furthermore CNDO/2 predicted an ionization potential destabilization for cyano-containing species such as acrylonitrile and benzonitrile compared to their parent hydrocarbons,[10] a finding which is reminiscent of the standard cyano PPP parameter set. On the other hand we observed that more sophisticated STO 4-31G[11] results gave the proper trends. The major difference between the STO 4-31G charge densities and those of the other techniques was that a higher dipole moment was induced in the cyano function with the nitrogen atom being quite negatively charged.

With this basis and considering the need to incorporate a more realistic θ-$\bar{\pi}$-core charge distribution into the framework of the π-electron method,[7] we systematically varied the PPP π-electronic parameters for the cyano atoms. Our goal was to reproduce the electronic spectra, ionization potentials and ground-state dipole moments of some representative aromatic nitriles subject to the con-

Table 1. Cyano parameter summary

Scheme	Atom (θ Charge)	$\gamma_{\mu\mu}$ (eV)	V.S.I.P. (eV)	β_{C-N}(eV)
(a)"Standard"	C(+ 1.0)	11.13	- 11.16	- 3.25
	N(+ 1.0)	12.52	- 14.18	
(b)"Electronegative"	C(+ 1.0)	10.09	- 12.69	- 3.35
	N(+ 1.0)	11.52	- 16.18	
(c) Proposed	C(+ 1.1)	11.05	- 12.00	- 3.45
	N(+ 0.9)	12.75	- 15.20	

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†The lone pair moment of the nitrogen atom has been assessed to contribute on the order of 1 D.[6] A value of 0.8 D was used in calculations.

Table 2. Comparison of cyano PPP parameterizations predictions

Compound-Method	λ_{max} (intensity)[a] t_1	t_2	Ionization[b] Potential (eV)	Dipole Moment (D)
Benzonitrile				
(a) "Standard"	265(0.01)	224(0.57)	9.24	2.5
(b) "Electronegative"	289(0.01)	267(0.68)	9.56	3.96
(c) Proposed	266(0.01)	226(0.54)	9.57	3.95
(d) Exptl.[c]	273(2.8)	225(4.1)	9.78	3.93
4-Aminobenzonitrile				
(a) "Standard"	279(0.11)	266(1.40)	7.18	5.62
(b) "Electronegative"	292(0.00)	314(0.83)	8.18	5.90
(c) Proposed	283(0.02)	266(0.77)	8.15	5.82
(d) Exptl.[c]	-	270(4.26)	8.30	5.96

[a] λ_{max} in nm. Theoretical intensity as oscillator strengths; Exptl. as log ϵ_{max}.

[b] Relative to 9.23 eV for benzene.

[c] References to exptl. results given in Tables 3, 4 and 8.

straint that the charge density for acrylonitrile resembled that of STO 4-31G calculations.

The best set of resultant parameters is given in Table 1. A comparison of this suggested PPP set and the two in the literature for select physical properties of some aromatic nitriles is displayed in Table 2. This scheme appears to incorporate the best features of each of the other approaches. It is noteworthy that the sum of the "proposed" valence state ionization energies for the cyano C and N atoms is intermediate between the standard and "electronegative" schemes. However, whereas the nitrogen V.S.I.P. is considerable greater in magnitude than the extrapolated Hinze-Jaffé value, the corresponding carbon number is less in magnitude than its interpolated V.S.I.P, of −12.40 eV.[7] This feature allows a simultaneous reproduction of all the experimental properties in Table 2. Furthermore, this proposed scheme mimics fairly well the STO 4-31G charge densities on acrylonitrile. Therefore, a program was undertaken to apply this cyano treatment to additional aromatic nitriles of theoretical interest.

Computational procedures

The basic SCF-MO-CI π-electron PPP method using the semiempirical parameter scheme proposed by Nishimoto and Forster,[12] in which the two-center repulsion integrals are calculated by the Nishimoto–Mataga[13] method, was employed in this study. Calculational details are given in an earlier paper.[7]

In addition, for many compounds it was necessary to include the role of solvent explicitly in order to compare the theoretical spectral predictions with available experimental data, which often were limited to polar solvents such as ethanol. This was necessary since the raw calculational output should correspond to a gas phase or nonpolar media result, whereas a number of the molecules are highly resonating-dipoles or "push–pull" structures, and experience substantial solvent spectral shifts, similar to p-nitroaniline [λ_{max}(hexane) 322 nm → (ethanol) 370 nm] and p-nitro-dimethylaniline [λ_{max}(hexane) 340 → (ethanol) 388 nm].† Fortunately, these absorption maxima differences in two solvents, S_1 and S_2 can be assessed theoretically via the following quantum mechanical expression:[14]

$$V_1 - V_2 = \frac{k}{A}(\mu g - \mu e)\mu g\left[\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{\epsilon_2 - 1}{\epsilon_2 + 2}\right] \quad (1)$$

where:

V_1 = absorption max in solvent 1
V_2 = absorption max in solvent 2
k = constant
A = molecular size of solute
μg = ground state dipole moment of solute
μe = excited state dipole moment of solute
ϵ = dielectric constant of solvent.

All quantities except μg, μe and k are known experimentally, while μg and μe can be calculated theoretically by the PPP method which produces good ground-state and excited-state[7,15,16] dipole moment predictions. Thus, to compare ethanol to nonpolar media spectra a new variable k′ was defined

$$k' = k\left[\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{\epsilon_2 - 1}{\epsilon_2 + 2}\right] \quad (2)$$

and scaled to duplicate the p-nitroaniline and p-nitrodimethylaniline spectral trends ($k' = 320\ \mathrm{cm}^{-1}$).

RESULTS

(a) *Spectra of electron-deficient benzonitrile derivatives*

The results of PPP π-electronic spectral calculations for a series of electron-deficient cyano benzenoid molecules are compared with the corresponding experimental values in Table 3. In general the compounds display a weak band in the 265–310 nm region and more pronounced absorption between 220–255 nm. These maxima correspond to the classical ${}^1L_b \leftarrow {}^1A$ and ${}^1L_a \leftarrow {}^1A$ transitions respectively. The ability of the theoretical calculations to reproduce both the location and the relative intensities of the bands is excellent. For example in the dicyano series, 1,4-dicyanobenzene is predicted to have its spectrum

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†All non-referenced spectral data reported in this paper were obtained by the author.

Table 3. Absorption spectra of electron-deficient benzonitrile derivatives

Compound		Exptl. λ_{max} (ϵ_{max})	Calcd. λ_{max} (oscillator strength)
Benzonitrile	t_1	273(2.8)[a]	266(0.01)
	t_2	225(4.1)	226(0.54)
1,2-Dicyanobenzene	t_1	283(3.1)[b]	276(0.04)
	t_2	232(4.0)	241(0.32)
1,3-Dicyanobenzene	t_1	281(2.4)[b]	274(0.01)
	t_2	229(3.9)	229(0.24)
1,4-Dicyanobenzene	t_1	284(3.1)[b]	278(0.04)
	t_2	235(4.3)	242(0.92)
1,2,4,5-Tetracyanobenzene	t_1	308(3.6)[c]	290(0.08)
	t_2	256(4.2)	256(0.51)
	t_3	223(4.8)	219(1.9)
TCNQ	t_1	~ 400(strong)[d]	437(1.9)

[a] Heptane, Ref. 6.
[b] Methanol, O. E. Polansky and M. A. Grassberger, Monatsh. Chem., 94, 647 (1963).
[c] Ethanol, A. Zweig, J. E. Lehnsen, W. G. Hodgson, and W. H. Jura, J. Am. Chem. Soc., 85, 3937 (1963).
[d] Dimethoxy ethane, H. T. Jonkman and J. Kommandeur, Chem. Phy. Let., 15, 496 (1972).

red-shifted the most and be the most intense relative to benzonitrile and the other two dicyano isomers, in agreement with observation. Furthermore, contrary to the multi-substituted nitrobenzenes,[7] the 1,2- and 1,3-dicyanobenzene $^1L_a \leftarrow {}^1A$ spectral transitions are found to be bathochromatic to benzonitrile calculationally and experimentally. Calculations on tetracyanobenzene displays all the observed trends in that its long-wavelength absorption is both the most red-shifted and intense (totally contrary to s-trinitrobenzene which had the weakest $^1L_b \leftarrow {}^1A$ band), and is tri-banded with its short-wavelength transition being the most hypsochromic and strongest in this series.

(b) *Spectra of "push-pull" cyanoaromatics*

A more challenging spectral problem is offered by the introduction of electron donors into the cyano-containing molecular framework leading to classical "push–pull" systems. As discussed earlier, the experimental results are affected strongly by solvent interactions, and where applicable the spectral shifts induced by polar solvents have been included explicitly in the calculations employing the procedure outlined earlier.

Mono-aminobenzonitrile spectral data are presented in Table 4. The cyano group can be considered a reasonably weak conjugative electron-poor function. For example, in nonpolar media the intense $^1L_a \leftarrow {}^1A$ band is found at 322 nm (hexane) and 284 nm (heptane)[17] for *p*-nitroaniline and *p*-aminoacetophenone respectively. Theoretically the bathochromaticity of these dipolar nitrile aromatics is suppressed since it is the C atom of the cyano function rather than N which experiences the more substantial growth in charge upon excitation, and the electronegativity of the cyano carbon is of reduced character.†

Within the amino-substituted series, the m-NH_2 derivative is found to be red-shifted relative to its *p*-analogue, an observation which is contrary to simple resonance considerations. Our MO data correctly predicts this result as well as the transitional properties of the *ortho* isomer. Further, the relative intensities are duplicated very well by calculations with the *para* derivative being the most intense.

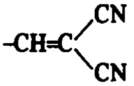
Chromophoric extension of these push–pull benzenoid species can be induced by incorporation of a vinyl linkage into the molecular structure. A sizable experimental spectral data base exists for multi-substituted cyanovinyl resonating aromatics,[18] and representative results are shown in Table 5. It is observed that the dicyanovinyl function  $-CH{=}C(CN)_2$ is an electron-deficient auxo-

Table 4. Absorption spectra of aminobenzonitrile compounds

Compound	λ_{max} (os.st.)	Expt λ_{max} (log ε)
o-Aminobenzonitrile	312 (0.19)	315 (3.57)[a]
m-Aminobenzonitrile	309 (0.11)	308 (3.43)[a]
p-Aminobenzonitrile	283 (0.02)	270 (4.26)[a]
	266 (0.77)	
p-Dimethylaminobenzonitrile	300 (0.04)	289s (4.37)[b]
	285 (0.79)	280 (4.46)

[a] A. deCorville and L. Kerisit, Compt. rend., 262, 362 (1966).
[b] T. Matsuo, et.al., Bull. Chem. Soc. Jap., 41, 2849 (1968).

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†For example, $Q_{S0} \rightarrow Q_{S2}$ for *p*-aminobenzonitrile: C-1 (carbon adjacent to cyano) −0.075 → +0.010, C-2 +0.035 → −0.057, C-3 −0.072 → +0.043, C-4 +0.033 → −0.036, Nitrile C +0.350 → +0.150, Nitrile N −0.417 → −0.535, and NH_2 +0.184 → +0.438.

Table 5. Absorption spectra of "push–pull cyanoaromatics

Compound	Calcd. Cyclohexane → Alcohol λ_{max} (os.st.)	Exptl. $\lambda_{max}(\epsilon_{max})$	Solvent
4-$Me_2NC_6H_4CHCHCN$	338(1.06) → 365	366(4.7)[a]	EtOH
3-$Me_2NC_6H_4CHCHCN$	360(0.10) → 388	-	
4-$Me_2NC_6H_4CHC(CN)_2$	382(0.87) → 420	432(4.7)[b]	EtOH
3-$Me_2NC_6H_4CHC(CN)_2$	418(0.08) → 460	444(3.3)[c]	EtOH
4-$Me_2NC_6H_4C_2(CN)_3$	440(0.67) → 501	514(4.6)[b]	EtOH
3-$Me_2NC_6H_4C_2(CN)_3$	488(0.05) → 553	537(3.1)[c]	EtOH
4-Dimethylaminostilbene (4-DMAS)	338(1.34) → 348	349(4.5)[d]	EtOH
4'-CN-4-DMAS	359(1.44) → 388	387(4.6)[d]	80% EtOH
3'-CN-4-DMAS	343(1.30) → 362	363(4.5)[d]	80% EtOH
4'-CN-4-aminobiphenyl	302(1.10) → 320	325(4.3)[e]	80% EtOH
1 (μg = 6.8; μ_e = 15.5)	431(0.42) → 470	472(4.0)[f] Red	2-Ethoxy-EtOH
2 (μg = 10.4; μ_e = 8.9)	402(0.80) → 395	Yellow[f]	

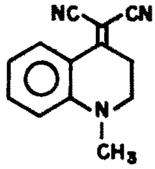
[a] E. Lippert and W. Luder, J. Phys. Chem., 66, 2430 (1962).
[b] Ref. 18.
[c] W. A. Sheppard and R. M. Henderson, J.Am.Chem.Soc., 89, 4446 (1967).
[d] M. Syz and H. Zollinger, Helv. Chem. Acta, 48, 517 (1965).
[e] E. Czerwinska-Fejgin and W. Polaczkowa, Roczniki Chem., 40, 429 (1966).
[f] Ref. 20.

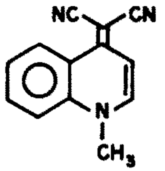
chrome which is substantially more effective than even the nitro group. Calculations confirm this behavior. The spectral shifts caused by sequential cyano substitution onto the vinyl group are successfully handled by the theoretical technique. Similar to the benzenoid case, longer wavelength absorption of the meta derivatives are observed throughout the series, as noted by Griffiths.[19] The PPP data display this quality but tend to overestimate the spectral differences. The extinction characteristics are also in very good agreement with experiment.

More typical spectral trends are observed for the 4-dimethylaminostilbene chromophere. In this series, as resonance principles dictate, 4'–CN is substantially bathochromatic relative to 3'–CN in 80% alcohol. Calculations correctly predict this behavior (Table 5), and show the 4'-analogue is inherently red-shifted independent of environment. Polar media enhance this effect. Further, the slightly increased absorption of the 4'–CN derivative is simulated by the PPP approach.

The spectral properties of 4'-cyano-4-aminobiphenyl are in good agreement with experiment, in that the spectral maximum is at a substantially longer wavelength than its benzene analogue, despite the non-planar character of the biphenyl species (Table 5).

An interesting example where simple resonance considerations fail to predict spectral characteristics of "look-alike" molecules is provided by a comparison of the two dicyanovinyl species 1 and 2. Despite their structural similarities and the fact 2 represents a more conjugative molecule, 1 is red in color whereas 2 is yellow. A rationale based on charge-separated forms has been suggested to account for these observations.[19,20] MO data, which are given in Table 5, support this argument. The calculations predict that 1 behaves like a typical "push-pull" molecule in that the intramolecular charge-transfer form dominates in the excited state. Thus substantial excited-state stabilization is introduced in polar solvents or the crystal state. On the other hand 2 is predicted to be highly-polar in its ground state, and thus should display a hypsochromic shift in more polar surroundings, characteristic of certain merocyanine dyes.[21] Thus, the effects of environment enhance considerably the spectral differences in these two molecules. Interestingly the calculations predict the ionization potentials and electron affinities of these two species should be nearly identical despite their spectral variations.


1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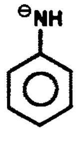
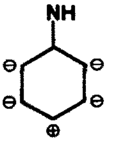
(c) *Spectra of anilide anions*

The absorption characteristics of nitrile-containing anilide anions were also investigated. Analysis of the spectra of a series of such anions reveals unexpectedly that the 4-cyano derivative absorbs 100 nm hypsochromatically to its 3-cyano isomer, and is even ~50 nm blue-shifted relative to the 3-chloroaniline anion,[22] which should represent a reasonable spectral model for the unsubstituted parent. Calculations were employed to attempt to understand these dramatic observations. MO results are given in Table 6, and are in satisfactory agreement with experiment including intensity characteristics. Upon further analysis of the theoretical output, one finds large charge density changes upon excitation in the anilide anion. The three lowest electronic states of this species can be represented by the following dominant forms:


S_0


S_1


S_2

Table 6. Properties of anilide anions

Derivative		Exptl. $\lambda_{max}(\epsilon_{max})$	Calcd. λ_{max}(os.st.)	pK_{HA}[a]	Calcd. I.P.
3-Chloro	t_1	386(3.4)	360(0.09)	25.63	3.55
	t_2		270(0.59)		
4-Cyano	t_1	337(4.6)	350(0.95)	22.68	4.2
	t_2		345(0.07)		
3-Cyano	t_1	447(3.4)	490(0.07)	24.64	3.9
	t_2		310(0.16)		

[a] Ref. 22.

Therefore the 447 nm band in the 3-cyano anion is associated with the near-visible long-wavelength band in the anilide parent, whereas the intense 337 nm absorption in the 4-cyano isomer originates from the S_2 UV transition. Finally, acid strength can be successfully correlated with ionization potential for these anions (Table 6) with 4-cyanoaniline being the strongest acid in this series despite its anion's lack of color.

(d) *Physical properties of cyanoaromatics*

1. *Dipole moments.* Results of "adjusted" calculated moments for the ground and select excited-states of representative cyanoaromatics are compared with available experimental data in Table 7. For the ground state values the agreement is acceptable after consideration of the inherent theoretical errors introduced by the $-NH_2$ and $-N(CH_3)_2$ groups.† The enhanced conjugative resonance interaction observed for the "push–pull" molecules beyond that of the summation of their respective donor and acceptor components is reproduced very well by the calculations. For example, experimentally the dipole moment of *p*-aminobenzonitrile is 0.5 D greater than that of aniline and benzonitrile, whereas calculationally 0.45 D is obtained. Also the MO results correctly predict that the dipole moment of 2-cyanonaphthalene is greater than the 1-cyano isomer despite its reduced conjugation onto the ring [i.e. πB.O. (2-cyano) = 0.286, πB.O. (1-cyano) = 0.296], as has been observed with electron-rich naphthalenes.[23]

Because of the strong electronegativity properties of the cyano function, there have been meaningful efforts to experimentally determine the excited-state dipole moments for a number of nitrile-containing dipolar molecules. Three different techniques[25] have been employed: spectroscopic methods, fluorescence polarization and electric dichroism. Results are compiled in Table 7. In general the agreement theory and experiment is very good especially considering the large variations from one experimental technique to the next, and even within the same method as determined by different investigators. The following observations can be made:

(a) The substantially different experimental μe for *p*-dimethylaminobenzonitrile as found by fluorescence polarization (11.1 D) and spectroscopic methods (23, 15.7 D)[25] can be understood theoretically by assuming that the former technique is measuring the first excited-state moment (calc. $\mu e_1 = 10.5$ D), whereas the spectroscopic experiments are following the intense charge-transfer transition (calc. $\mu e_2 = 16.5$ D) which involves the second excited-state.

(b) The calculations overestimate the excited-state dipole moment of 4′-CN-4-aminobiphenyl. Theoretically it was found that the more nonplanar this compound is made, the greater μe becomes.

(c) Differences between the dipole moments for

Table 7. Ground and excited-state dipole moments of cyanoaromatics

Compound	μg[a]	Spectroscopic	μ_x Fluorescence[f] Polarization	Electric[g] Dichroism	Calcd.
p-Aminobenzonitrile	5.96 (5.72)[b]	-	-	-	S_1 8.0 S_2 14.4
p-Dimethylaminobenzonitrile	6.55 (6.15)	23[c] 15.7[d]	11.1	-	S_1 10.5 S_2 16.5
$4\text{-}Me_2NC_6H_4CHCHCN$	6.75 (6.7)	14[c]	-	14	S_1 18.2
4′-CN-4-aminobiphenyl	6.0 (6.3)	-	15.3	-	S_1 19.5
4′-CN-4-dimethylaminostilbene	7.0 (6.9)	29[c] 21[d] 21[e]	21.2	20.0	S_1 21.2

[a] Exptl. values from Ref. 25. [b] Calcd. μg values in ( ). [c] Ref. 26.
[d] L. Bilot and A. Kawsky, Ref. 25. [e] N. G. Bakhshiev, Ref. 25.
[f] J. Czekalla and K. Meyer, Ref. 25 [g] Ref. 25.

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†The point charge dipole moments calculated by the PPP scheme for aniline and N,N-dimethylaniline are 0.6 K and 0.75 D greater than the experimental values of 1.53 D and 1.61 D[23] respectively. Charge distributions are poorly represented when these nitrogen-containing groups are treated as a single charge center as confirmed by *an initio* calculations.[24] In order to account for these difficulties it was decided to reduce the resultant calculated ground and excited-state dipole moments of compounds containing these functions by the amounts given above.

Table 8. Polarographic reduction potentials

Compound	ϵ_{LUMO}(eV)	Calcd.[a] $E_{1/2}$ (V.)	Polarographic[b] $E_{1/2}$ (V.)
Benzonitrile	-2.10	-2.68	-2.74
1,2-Dicyanobenzene	-2.71	-2.07	-2.12
1,3-Dicyanobenzene	-2.53	-2.25	-2.17
1,4-Dicyanobenzene	-2.82	-1.96	-1.97
4-Aminobenzonitrile	-1.69	-3.09	-3.12
4-Nitrobenzonitrile	-3.41	-1.37	-1.25
1,2,4,5-Tetracyanobenzene	-3.66	-1.12	-1.02
TCNE	-4.40	-0.38	-0.17
TCNQ	-5.02	+0.24	-0.19

[a] Eq. 3. [b] Ref. 29.

dimethylamino and amino analogues accentuated in the excited state. Experimental data on nitro species display this behavior and confirm this prediction.[25]

(d) The approach of Lippert[26] seems to yield dipole moment values which are in substantial disagreement with the other spectroscopic and experimental techniques and the theoretical treatment.

2. *Reduction potentials.* Considerable success has been acheived in relating ϵ_{LUMO} as determined by π-electronic methods to experimental reduction potentials[27,28] and electron affinities[5] for conjugative molecules. Our results for a number of cyano-containing species are presented in Table 8. The following relationship between calculated ϵ_{LUMO} and polarographic reduction potential $E_{1/2}$ is proposed:

$$E_{1/2} = -\epsilon_{LUMO} - 4.78, \qquad (3)$$

and gives an excellent correlation. The only compounds for which sizable errors are observed are TCNE and TCNQ. However, the experimental measurements for these two compounds are suspect in the original work.[29] Further "reorganization energy"[30] may be substantially different in these two cases than for the benzenoid molecules. These calculations do suggest on the basis of ϵ_{LUMO} values that TCNQ has greater electron-acquiring capabilities than TCNE. Continuing controversy surrounds this issue.[5,31]

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