

THE CORRELATIONS AND QUANTUM CHEMICAL INTERPRETATIONS OF SOME MOLECULAR PROPERTIES OF SEVERAL *p*-PHENYLENEDIAMINES AND RELATED COMPOUNDS

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Quantum chemical calculations of various *p*-phenylenediamines and related compounds are correlated with different molecular properties, such as electrochemical $E_{1/2}$ -values, ionization potentials, pK -values, UV-VIS spectra, the activation energies of the homogeneous electron self-exchange rates, and the synproportionation constants. All correlations are in good agreement with the predictions of simple HMO-theory.

In a previous paper¹, it was shown that it is possible to deduce a set of HMO-Coulomb perturbation parameters $h(NR_2)$ for various *p*-phenylenediamines from ESR spectra. Basing on these parameters several molecular data can be calculated and compared with experimental ones. So the rates of the alkaline and acid deamination of various *p*-phenylene quinonediimines could be interpreted as an orbital and charge controlled or only orbital controlled reactions, respectively².

This paper shows the validity of simple HMO-calculations for the interpretation of the different molecular and thermodynamic properties of *p*-phenylenediamines.

EXPERIMENTAL

The preparation and purification of the substances (Table I) and solvents used were described elsewhere¹. The UV-VIS spectra were recorded with a Pye Unicam SP 1700 spectrometer. The $E_{1/2}$ -values were measured with a rotating gold disc electrode arrangement and have accuracy of ± 15 mV (ref.³). Tetraethylammonium perchlorate (0.03 mol l^{-1}) was the supporting electrolyte and a Ferrocen/Ferrocinium system⁴ the reference electrode. Mostly the depolarisator concentration was $1 \cdot 10^{-3} \text{ mol l}^{-1}$. The solvent CH_3CN was dried over molecular sieve (3Å) ($1\text{Å} = 10^{-10} \text{ m}$) and saturated with argon.

QUANTUM CHEMICAL CALCULATIONS

All calculations were carried out according to the Hückel-MO procedure⁵. The spin densities of the radical cations were calculated by Mc Lachlan's method modified for radical cations

(POL-2)¹. Within this method the energy eigenvalues E_j^{π} are given by

$$E_j^{\pi} = \alpha_C + x_j \beta_{CC}, \quad (1)$$

where α_C is a Coulomb integral. β_{CC} is a resonance integral and x_j is an energy eigenvalue coefficient.

For different amino groups, the Coulomb and resonance integrals are given by

$$\alpha_N = \alpha_C + h(\text{NR}_2) \beta_{CC} \quad (2)$$

$$\beta_{CN} = k_{CN} \beta_{CC}. \quad (3)$$

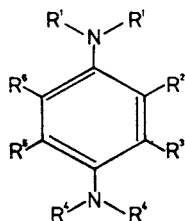
The following $h(\text{NR}_2)$ -parameters are obtained from related experimental ESR spectra¹:

$$h(\text{NH}_2) = 1.26, \quad h(\text{N}(\text{CH}_3)_2) = 0.99, \quad \text{and} \quad h(\text{N}(\text{C}_2\text{H}_5)_2) = 0.88;$$

k_{CN} is set equal to 1, according to the planar structure of the radicals. The ring methyl groups are regarded as an inductive perturbation with $h(\text{CCH}_3) = -0.3$ (refs^{5,6}). The chlorine atoms are represented by $h(\text{Cl}) = 2.25$ and $k_{\text{CCl}} = 0.4$ (ref.⁷). The quantum chemical calculations were done using a CYBER 173 computer at the Rechenzentrum of the University Erlangen.

TABLE I

The used *p*-phenylenediamines, related compounds, and their energy eigenvalue coefficients $x_j(\text{HOMO})$



| Compound | | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | R ⁶ | $x_j(\text{HOMO})$ |
|-------------------------------------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|--------------------|
| <i>p</i> -phenylenediamine | <i>I</i> | H | H | H | H | H | H | 0.360 |
| N,N-dimethyl-(<i>I</i>) | <i>II</i> | Me | H | H | H | H | H | 0.301 |
| N,N-diethyl-(<i>I</i>) | <i>III</i> | Et | H | H | H | H | H | 0.271 |
| 2,3,5,6-tetramethyl-(<i>I</i>) | <i>IV</i> | H | Me | Me | H | Me | Me | 0.268 |
| N,N,N',N'-tetramethyl-(<i>I</i>) | <i>V</i> | Me | H | H | Me | H | H | 0.250 |
| N,N,N',N'-tetraethyl-(<i>I</i>) | <i>VI</i> | Et | H | H | Et | H | H | 0.199 |
| 9,10-diaminoanthracene ^a | <i>VII</i> | — | — | — | — | — | — | 0.066 |
| N,N,N',N'-tetramethylbenzidine | <i>VIII</i> | — | — | — | — | — | — | 0.308 |
| 3-methyl-(<i>II</i>) | <i>IX</i> | Me | H | Me | H | H | H | 0.279 |
| 3,5-dimethyl-(<i>II</i>) | <i>X</i> | Me | H | Me | H | Me | H | 0.259 |
| 3-methyl-(<i>III</i>) | <i>XI</i> | Et | H | Me | H | H | H | 0.252 |
| 3,5-dimethyl-(<i>III</i>) | <i>XII</i> | Et | H | Me | H | Me | H | 0.233 |

^a Ref. ⁴⁵.

RESULTS

Calculated molecular data. The eigenvalues of energy x_j are listed in Table I.

Electrochemical $E_{1/2}$ -values. The oxidation of a *p*-phenylenediamine (R) to a semi-quinone radical cation ($S^{\dot{+}}$)



can formerly be regarded as a removal of an electron from the highest occupied molecular orbital (HOMO). Maccol⁸ and Hoijtink⁹ found for the first time a linear dependence between $E_{1/2}$ and the respective x_j

$$E_{1/2} = a + x_j b. \quad (4)$$

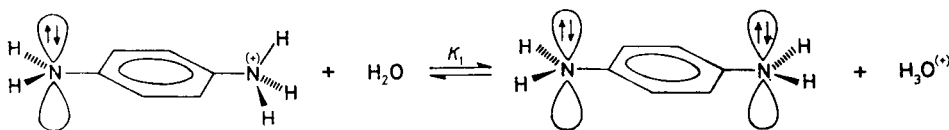
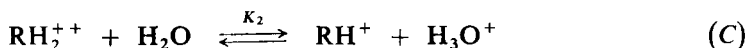
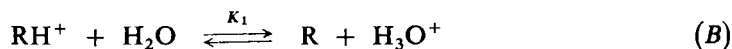
Up to now many proofs of this well established relation have been given in the literature¹⁰⁻¹². Eq. (4) is only valid under the justifying assumption that the diffusion coefficients of R and $S^{\dot{+}}$ are nearly equal and that all changes of reaction entropy are of the same order of magnitude. Table II shows the experimental $E_{1/2}$ -values measured in CH_3CN . In Fig. 1 the linear relation from Eq. (4) is shown.

Ionization potentials. IP Koopman's theorem¹³ predicts a linear dependency of the HMO - energy expressed by x_j on the ionization potential IP.

$$-IP = \varepsilon_j(\text{HOMO}) = \alpha + x_j \beta \quad (5)$$

The reorganization of the electron in the radical and the difference in the correlation energy between R and $S^{\dot{+}}$ are neglected in this consideration. Table II displays the photoelectronically measured IP-values, which are of greater accuracy than IP-values determined from charge-transfer spectra. The validity of Eq. (5) is shown in Fig. 1, too.

The pK-values. For the protonation of the *p*-phenylenediamines the following Brønsted equilibria are valid¹⁴ (see Scheme 1).



SCHEME 1

TABLE II

The $E_{1/2}$ -values, vertical ionization potentials IP_{vert} , first and second protonation constants pK_1 and pK_2 and 1L_a -bands. Homogeneous electron-self exchange rates and $\Delta G_{\text{ex}}^*(293)$ and the π -energies of different monoprotonated *p*-phenylenediamines

| Compound | $E_{1/2}^a$ mV | IP_{vert} eV | pK_1 | pK_2 | ν cm^{-1} | $k_{\text{ex}} \cdot 10^{-8}$ $\text{l mol}^{-1} \text{s}^{-1}$ | $\Delta G_{\text{ex}}^*(293)$ kJ mol^{-1} | $\Delta E_{\pi} - 2\alpha$ β |
|----------|-------------------|--------------------------|-------------------|-------------------|---------------------------|--|---|---------------------------------------|
| I | -107 | 7.50 ^b | 6.20 ^k | 2.70 ^p | 31 750 | 3.2 ± 0.2 | 15.7 | 2.864 |
| | | 7.34 ^e | 6.40 ^l | 2.89 ^s | | | | |
| | | 7.58 ^f | 6.44 ^m | | | | | |
| II | -147 | 7.10 ^b | 6.40 ^l | 2.38 ^l | 31 650 | 6.7 ± 0.2 | 14.1 | 2.383 |
| | | 6.97 ^g | 6.51 ⁿ | 2.60 ^t | | | | |
| | | | 6.32 ^o | 2.62 ^o | | | | |
| | | | | 2.85 ^p | | | | |
| III | -164 | 6.95 ^u | 8.00 ^l | 2.38 ^l | 31 250 | — | — | 1.926 |
| | | 6.81 ^h | 8.04 ^p | 2.67 ^p | | | | |
| | | | 8.30 ^r | 2.95 ^r | | | | |
| IV | -227 | 7.00 ^b | 6.11 ^q | — | 22 000 | 8.8 ± 0.3 | 13.2 | 2.760 |
| V | -234 | 6.80 ^b | 6.54 ^q | 2.20 ^u | 31 050 | 11.7 ± 0.8 | 12.9 | 2.377 |
| | | 6.75 ^l | | 2.68 ^v | | | | |
| VI | -331 | 6.95 ^b | 8.28 ^q | — | — | $25.2 \pm ?$ | 11.1 | 2.174 |
| IX | -117 | 6.55 ^j | — | — | — | — | — | — |

^a ref. 3; photoelectronic measurements³⁰; ^c ref. 17; ^d ref. 18; ^e ref. 28; ^f ref. 31; ^g ref. 32; ^h ref. 33; ⁱ ref. 34; ^j ref. 35; ^k ref. 36; ^l ref. 20; ^m ref. 37; ⁿ ref. 38; ^o ref. 39; ^p ref. 40; ^q ref. 14; ^r ref. 41; ^s ref. 42; ^t ref. 43; ^u ref. 3; ^v ref. 44.

For the protonation of R the π -conjugation of an exocyclic N-atom is lost and therefore the π -system of RH^+ differs from that of R not only by the number of π -electrons but also in the total π -energies E_π .

Under the simple HMO considerations RH^+ can be compared with the respective aniline, because one of the π -conjugations is blocked. For example E_π (aniline) is given by $8\alpha + 10.916\beta$, whereas $E_\pi(\text{PPD}) = 10\alpha + 13.800\beta$. The difference in the total π -energies of *p*-phenylenediamines and the respective anilines $\Delta E_\pi - 2\alpha = E_\pi(\text{PPD}) - E_\pi(\text{aniline})$ should be in relation with the $\text{p}K_1$ -values. The correlation in Fig. 2 shows that the assumption about the obstruction of one N-center can be helpful for the interpretation of the $\text{p}K$ -values.

The double protonated RH_2^{++} systems are given in the same way by a simple 6π -system. The difference $\Delta E_\pi - 2\alpha = E_\pi(\text{RH}_2^{++}) - E_\pi(\text{RH}^+)$ should be constant for all comparable compounds and therefore the $\text{p}K_2$ -values should also be constant for all derivatives. The experimental $\text{p}K_2$ -values in Table II manifest this prediction.

UV-VIS spectra. It is well known, that one of the long wave bands of a UV-VIS spectra the so-called 1L_x -band is a $\pi - \pi^*$ - transition in the *p*-phenylenediamine systems^{15,16}. This transition can be described (within the framework of the HMO-method) by the following relation

$$h\nu/c = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} = (x_{\text{J}} - x_{\text{J}+1}) \beta. \quad (6)$$

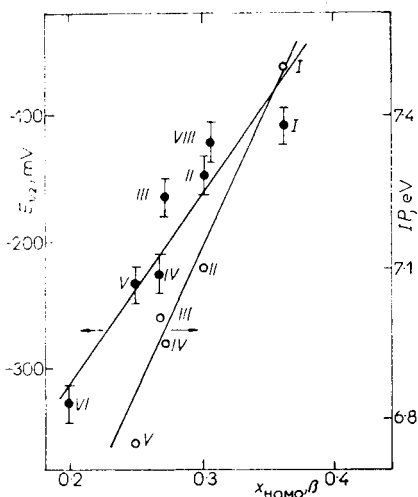


FIG. 1
Dependence of $E_{1/2}$ and IP on the eigenvalue coefficients of the HOMO

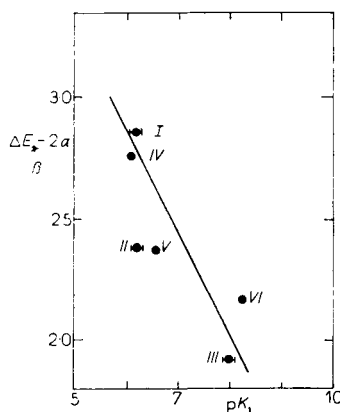


FIG. 2
The relation between the π -energies and the $\text{p}K_1$ -values of different *p*-phenylenediamines

Therefore a correlation between \bar{v} and $x_j - x_{j+1}$ should exist. Fig. 3 shows the correlation according to Eq. (6). A more detailed discussion is given in refs^{27,28,19}.

The homogenous electron-self exchange rates k_{ex} . Recently^{17,18}, we measured extensively the rate constants of the homogeneous electron self exchange reactions, according to Eq. (D)

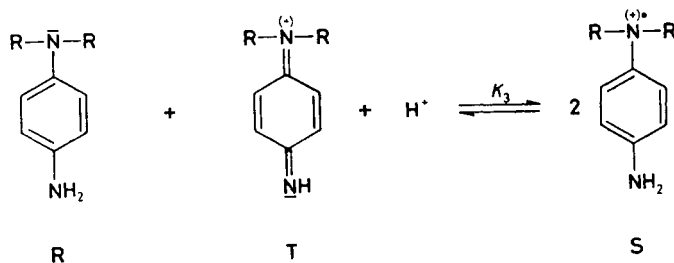


by ESR line broadening effects.

It was shown that the rate constants corrected for diffusion can be interpreted in terms of the Marcus' theory, including some modifications¹⁹.

The rate constants k_{ex} measured in CH_3CN are listed in Table II. The correlation of $-RT \ln(k_{ex}/Z_0 T^{1/2}) = \Delta G_{ex}^*(293)$ (with $Z_0 = (2r)^2 N_L(8RT/m)^{1/2}$; r = molecular radius, m = reduced mass) and the energy eigenvalues x_j are actually good and indicate that the energy required to remove the electron from R may play an important role in determining the electron transfer rate constant, see Fig. 4.

The synproportionation constants K_3 . The semiquinone radicals of the *p*-phenylenediamines S^{\dagger} disproportionate in aqueous solutions according to Scheme 2



SCHEME 2

where the equilibrium constant K_3 is given by

$$K_3 = \frac{[S^{\dagger}]^2}{[R][T^+][H^+]}. \quad (7)$$

The constant K_3 can be determined spectrophotometrically²⁰ Hush and Blackledge²¹ described the free energy change ΔG_D accompanying the disproportionation and supposed that ΔG_D consists of the following main contributions

$$\Delta G_D = \Delta E_r + \Delta E_{solv}, \quad (8)$$

where ΔE_r is the repulsion energy and ΔE_{soliv} is the solvation energy change. ΔE_r is the sum of different terms, the inner-shell energy ΔE_i , the change in σ -electron energy ΔE_σ and the change in π -electron energy ΔE_π .

$$\Delta E_r = \Delta E_i + \Delta E_\sigma + \Delta E_\pi \quad (9)$$

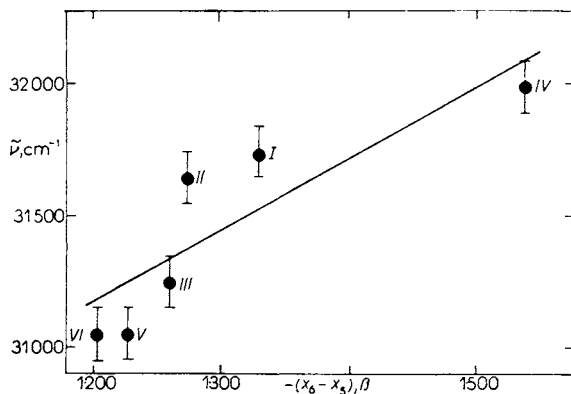


FIG. 3

The dependence of $\tilde{\nu}$ (1L_a -bands) on the difference between the HOMO and LUMO orbital ($x_6 - x_5$)

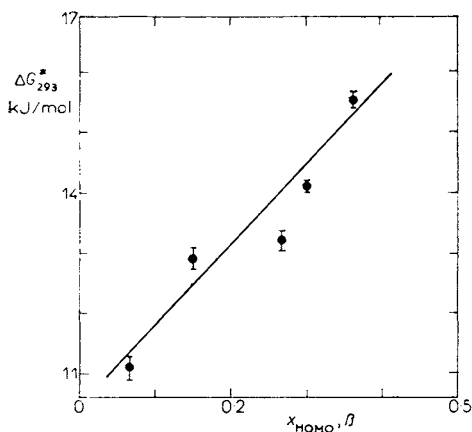


FIG. 4

The activation energies of the homogenous electron exchange reactions $\Delta G^*(293)$ depends on x_{HOMO}

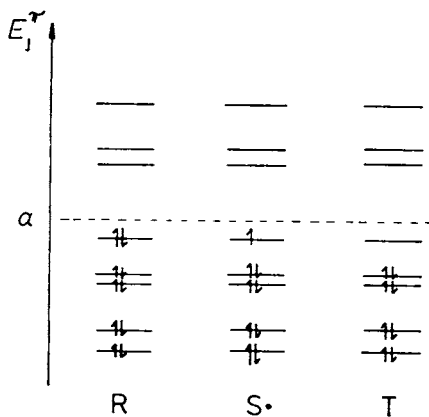


FIG. 5

Orbital scheme of the reduced (R), semioxidized ($S^{\cdot+}$) and total oxidized (T) *p*-phenylenediamines

We assume that the ΔE_σ , ΔE_i , and ΔE_{solv} are nearly constant for all investigated compounds and therefore the total energy change is mainly determined by the π -electron contribution. If we furthermore adopt the usual assumption that ΔH_D depends linearly on ΔS_D , we can write

$$\Delta G_D = \Delta H_D - T \Delta S_D, \quad (10)$$

$$\Delta G_D = -RT \ln K_3, \quad (11)$$

$$\Delta H_D \sim -\log K_3, \quad (12)$$

where

$$\Delta H_D = \Delta E_i + \Delta E_\sigma + \Delta E_{\text{solv}} + \Delta E_\pi. \quad (13)$$

With the assumptions described above follows:

$$\log K_3 \sim \Delta E_\pi. \quad (14)$$

The change of π -electron energy can be expressed by

$$\Delta E_\pi = 2\Delta E_\pi^S - \Delta E_\pi^T - \Delta E_\pi^R \quad (15)$$

and according to Eq. (4)

$$\log K_3 \sim \Delta E_\pi^R + \Delta E_\pi^T - 2\Delta E_\pi^S. \quad (16)$$

Unfortunately the term $\Delta E_\pi^R + \Delta E_\pi^T - 2\Delta E_\pi^S$ is zero in the simple HMO-framework. This is caused by the neglect of the electron repulsion term in the HMO-Hamiltonian, see Fig. 5. To solve the problem SCF-methods must be used.

According to Hush²¹ and Zahradník²² the change in π -electron energy is represented by the electron repulsion I_{JJ} in the SOMO (single occupied molecular orbital) of the semiquinone S^\ddagger

$$I_{JJ} = \Delta E_\pi^R + \Delta E_\pi^T - 2\Delta E_\pi^S, \quad (17)$$

where I_{JJ} is commonly given by

$$I_{JJ} = \iint \psi_J(1) \psi_J(2) \frac{e_0^2}{r_{12}} \psi(1) \psi_J(2) dV_1 dV_2. \quad (18)$$

Considering the LCAO-approximation of the MO's

$$\psi_J = \sum_{\nu} c_{J\nu} \phi_{\nu} \quad (19)$$

one can write

$$I_{JJ} = \sum_{\mu} \sum_{\nu} c_{J\mu}^2 c_{J\nu}^2 \gamma_{\mu\nu}, \quad (20)$$

where $\gamma_{\mu\nu}$ represents the electron repulsion integral over the atomic orbitals $\phi_{\mu,\nu}$. Basing on the fact that $\gamma_{\mu\nu}$ decrease rapidly with the distance of the centers μ and ν only repulsions integrals for one center and neighbouring centers were retained.

TABLE III

Experimental synproportionation constants K_3 and repulsions integrals I_{JJ} ($J = 5$) calculated from Eq. (22)

| Compound | $\log K_3$ | I_{55}^a |
|------------|------------|------------|
| <i>II</i> | 7.924 | 3.748 |
| <i>III</i> | 8.491 | 2.932 |
| <i>IX</i> | 7.079 | 3.595 |
| <i>X</i> | 6.699 | 3.513 |
| <i>XI</i> | 7.716 | 2.796 |
| <i>XII</i> | 7.279 | 2.780 |

^a Calculated with $IP(C) = 11.22$ eV, $\gamma_{CC} = 10.53$ eV (ref.²²), $IP(NH_2) = 26.70$ eV, $\gamma_{NN} = 17.44$ (ref.²³), $IP(CH_3)_2 = 25.70$ eV, $\gamma_{NN} = 16.80$ eV (refs.^{24,25}), $\gamma_{NN}(N(C_2H_5)_2) = 16.56$ eV (ref.²⁶); $1 \text{ eV} \cong 96.4868 \text{ kJ mol}^{-1}$.

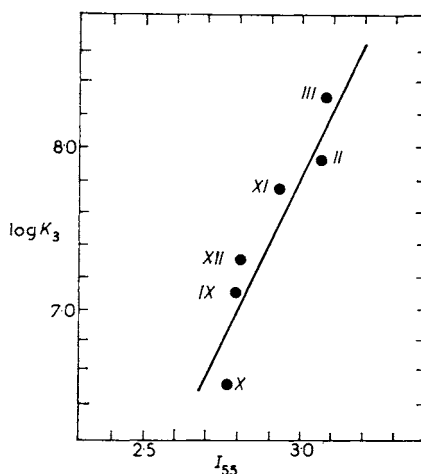


FIG. 6

The correlation between $\log K_3$ and I_{55}

Under such conditions I_{JJ} can be expressed by

$$I_{JJ} = \sum_{\mu=v} c_{J\mu}^2 c_{Jv}^2 \gamma_{\mu v}. \quad (21)$$

Matagata and Nishimoto²⁴ evaluated the $\gamma_{\mu v}$ -integral in which I_{μ} and A_{μ} stand for the ionization potential and the electron affinity of the center μ , respectively

$$I_{JJ} = \sum_{\mu} c_{J\mu}^4 (I_{\mu} - A_{\mu}) + \sum_{\mu} \sum_{v} c_{J\mu}^2 c_{Jv}^2 \frac{a}{b + 2a/(I_{\mu} + I_v - A_{\mu} - A_v)} \quad (22)$$

with: $a = 14.3986$ and $b = 1.4$.

In Table III the calculated I_{55} ($J = 5$)-values are listed together with the experimental K_3 values. Fig. 6 shows the correlation according to Eqs (16) and (17).

CONCLUSION

This paper shows that several molecular properties of various *p*-phenylenediamines can be interpreted in terms of quantum chemical HMO-calculations, at which the perturbation parameters $h(\text{NR}_2)$ are derived from experimental ESR-spectra.

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