CONJUGATED RADICALS. XV.*

CORRELATION OF pK_a VALUES OF PROTONATED SUBSTITUTED NITROBENZENE RADICAL ANIONS WITH EXTENDED HÜCKEL MO DATA

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It was found possible to correlate the observed pK_a values of protonated nitrobenzene radicals with the electronic energy changes calculated by the Extended Hückel method. The slope of this dependence, which is close to that for parent closed shell nitrobenzenes and aliphatic C-acids, is discussed on the basis of the relationship between heats of atomization and Extended Hückel bonding energies of closed shell systems.

Standard HMO and SCF methods have been successful in providing an understanding of the relation between the structure of conjugated molecules and the protonation equilibria[1]. Recently an attempt was made[2] to employ the HMO method also for the interpretation of protonation equilibria of unsaturated ketyl radical anions. In spite of the rough approximations involved in that approach, a surprisingly good correlation was obtained. This encouraged us to attempt to interpret the pK_a values of substituted nitrobenzene radical anions measured by one of us (A. F.) previously[3]. In this case, however, the HMO method can hardly be employed, since the nitrobenzenes substituted by methyl, hydroxy, methoxy, cyano, carboxy, and nitro groups do not constitute one class of compounds, which is just what is demanded by the nature of each HMO treatment. We selected, therefore, the Extended Hückel Theory (EHT), which is free of such a restriction and, moreover, offers the following advantages: *1*. The actual MO calculations do not involve parameter problems because the original parameter set proposed by Hoffmann[4,5] has successfully been employed in various chemical applications, *2*. the protonated forms are parametrized in the same way as the dissociated species, *3*. the EHT being an all-valence electron method, the σ-bonding is explicitely accounted for.

CALCULATIONS

The calculations undertaken were of the extended Hückel type, following all computational details described in ref.[4] The parameters adopted are summarized in Table I. As there are no experiment-

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al estimates of the geometries of nitrobenzene radical anions, we used a known structure of nitrobenzene[6], combining it with a reasonable geometries of substituting groups for both dissociated and protonated radicals. In the latter the geometry assumed for the protonated nitro group is given in Fig. 1. In the usual theoretical approach to protonation equilibria the solvation energy and entropy changes are not explicitely taken into account but assumed to be in a linear relationship with the enthalpy changes throughout the whole series of the compounds under study. Under these circumstances the protonation equilibria

$$[RNO_2H]^{\cdot} \rightleftarrows [RNO_2]^{\cdot(-)} + H^{(+)}$$

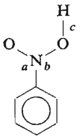
can be characterized by the following equation,

$$pK_a = a\,\Delta E + b\,, \tag{1}$$

where ΔE is the energy change accompanying the dissociation. In the actual approach ΔE is a difference in the EHT total energies of an unprotonated and protonated radical. For radicals the EHT total energy is defined as a sum orbital energies

$$E = 2\sum_{i=1}^{m-1} \varepsilon_i + \varepsilon_m\,. \tag{2}$$

Here index i runs over the closed shells and m refers to the open shell.



a = 1·21 Å
b = 1·41 Å
c = 0·98 Å
$\measuredangle ab$ = 124°
$\measuredangle bc$ = 103°

FIG. 1

Assumed Geometry for Protonated Nitrobenzene Radicals

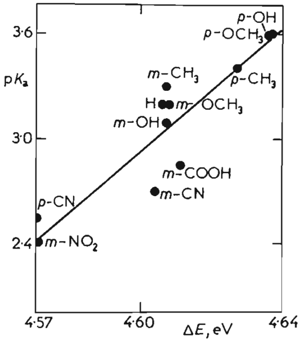


FIG. 2

Plot of pK_a Values for Protonated Nitrobenzene Radicals against the EHT Energy Changes

RESULTS AND DISCUSSION

The calculated results for nitrobenzene radical anions are given in Table II, together with the observed $\mathrm{p}K_a$ values. The statistical treatment of these data by the method of least squares permits to write Eq. (*1*) in the form

$$\mathrm{p}K_a = 16{\cdot}84\,\Delta E\,(\mathrm{eV}) - 74{\cdot}52\,, \qquad n = 11\,, \quad s = \pm 0{\cdot}16\,. \tag{3}$$

The respective plot is given in Fig. 2. A correlation of such a type should be examined whether it represents a special empirical relationship or whether it holds more generally. Therefore, it was of interest to us whether also the $\mathrm{p}K_{\mathrm{BH}^+}$ values of the

TABLE I

Parameters Adopted in the EHT Calculations[a]

Atom	$-I_s$	$-I_p$	Slater exp.
H	13·6	—	1·000
C	21·4	11·4	1·625
N	26·0	13·4	1·950
O	32·3	14·8	2·275

[a] From refs.[4,5]; ionization potentials I_s, I_p in eV.

TABLE II

Calculated ΔE and Observed $\mathrm{p}K_a$ Values for Protonated Substituted Nitrobenzene Radical Anions

Substituent	Obs.[3] $\mathrm{p}K_a$	Calc. ΔE, eV[a]	Substituent	Obs.[3] $\mathrm{p}K_a$	Calc. ΔE, eV[a]
H	3·2	4·606	*p*-OH	3·6	4·636
p-CH_3	3·4	4·628	*m*-OH	3·1	4·607
m-CH_3	3·3	4·607	*p*-CN	2·55	4·570
m-NO_2	2·4	4·571	*m*-CN	2·7	4·604
p-OCH_3	3·6	4·636	*m*-COOH	2·85	4·611
m-OCH_3	3·2	4·608			

[a] Eq. (*1*).

corresponding parent nitro compounds could be treated in a similar way. In the literature we found pK_{BH^+} values[7] for nitrobenzene, *m*- and *p*-nitrotoluene, and *m*-dinitrobenzene. The calculated EHT energy changes accompanying the protonation on the nitro group are presented in Table III. Fig. 3 shows that these data fit well the EHT correlation reported recently[8] for pK_a values of some aliphatic C-acids. A statistical treatment of the latter gives the following relationship:

$$pK_a = 17{\cdot}3\,\Delta E(\mathrm{eV}) - 78{\cdot}72\,, \qquad (4)$$

$$n = 8\,, \quad s = \pm 3{\cdot}55\,.$$

A similarity of the constants in Eqs (*3*) and (*4*) is encouraging, since it means that the EHT data give uniform results for the series of compounds rather different from the chemical point of view. It can be noticed that in the cited paper[8] the observed pK_a values range from 0–40, while in our case the pK_a difference between the strongest and the weakest conjugated acid is only 1·2. The slopes in Eqs (*3*) and (*4*) are close to a theoretical value of 16·9 for the slope in the relationship

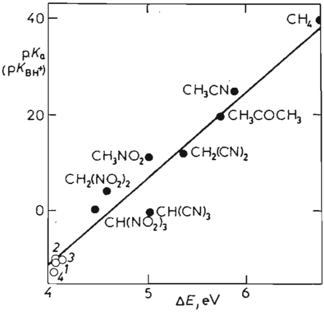


FIG. 3

Plot of pK_a Values for C-acids[8] and pK_{BH^+} Values of Nitrobenzenes[7] against the EHT Energy Changes

1 Nitrobenzene, *2* *m*-nitrotoluene, *3*-*p*-nitrotoluene, *4* *m*-dinitrobenzene.

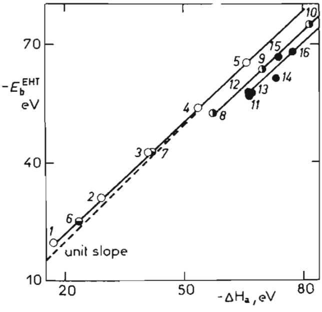


FIG. 4

Plot of Heats of Atomization against the EHT Bonding Energies

See footnotes in Table IV; *1*–*5* normal alkanes through pentane, *6* ethylene, *7* butadiene, *8* benzene, *9* toluene, *10* *m*-xylene, *11* nitrobenzene, *12* *m*-nitrophenol, *13* *p*-nitrophenol, *14* *m*-dinitrobenzene, *15* *m*-nitrobenzoic acid, *16* *p*-nitrotoluene.

$$-\log K = \frac{23{\cdot}052}{2{\cdot}303\, RT}\, \Delta G \tag{5}$$

for $T = 298$ K, ΔG being expressed in eV (1 eV = 23·052 kcal/mol). This implies

TABLE III

Calculated ΔE and Observed pK_{BH^+} Values for Substituted Nitrobenzenes

Substituent	Obs.[a] pK_{BH^+}	Calc. ΔE, eV
H	−11·0	4·046
m-CH_3	−10·6	4·047
p-CH_3	−10·1	4·078
m-NO_2	−12·6	4·045

[a] pK_{BH^+} values were obtained from conductometric data (pK_b) by means of the relation[7] $pK_{BH^+} = pK_b - 8{\cdot}07$.

TABLE IV

Heats of Atomization[a] ($-\Delta H_a$) and Calculated EHT Bonding Energies[b] ($-E_b$) for Some Hydrocarbons and Substituted Nitrobenzenes

Compound	$-\Delta H_a$, eV	$-E_b$, eV	Compound	$-\Delta H_a$, eV	$-E_b$, eV
Methane	17·23	19·61	Toluene	69·46	63·44
Ethane	29·27	30·87	*m*-Xylene	81·74	75·01
Propane	41·40	42·29	Nitrobenzene	66·03	56·55
Butane	53·57	53·69	*m*-Nitrophenol	66·24	58·36
Pentane	65·71	65·10	*p*-Nitrophenol	66·43	58·39
Ethylene	23·33	24·88	*m*-Dinitrobenzene	73·44	61·45
Butadiene	42·05	42·09	*m*-Nitrobenzoic acid	74·03	66·92
Benzene	57·19	51·87	*p*-Nitrotoluene	77·40	68·04

[a] Heats of atomization were obtained from heats of formation by adding the sum of heats of formation for the isolated atoms[9] ($\Delta H_f(H) = 52{\cdot}102$ kcal/mol, $\Delta H_f(C) = 170{\cdot}890$ kcal/mol, $\Delta H_f(N) = 113{\cdot}000$ kcal/mol, $\Delta H_f(O) = 59{\cdot}559$ kcal/mol). Heats of formation for hydrocarbons were taken from ref.[10], heats of atomization for nitro compounds were obtained from heats of combustion[11]. [b] EHT bonding energies of molecules were calculated from total EHT electron energies by subtracting the sum of the isolated atom energies for the component atoms of the molecule ($E(H, 1s) = -13{\cdot}6$ eV, $E(C, 2s^2\,2p^2) = -65{\cdot}6$ eV, $E(N, 2s^2\,2p^3) = -92{\cdot}2$ eV, $E(O, 2s^2\,2p^4) = -123{\cdot}8$ eV). For total EHT electron energies of hydrocarbons see ref.[4]

that throughout the whole series of the compounds under study the entropy and solvation energy changes are constant, *i.e.* $\varDelta\Delta S = 0$ and $\varDelta\Delta E_{\mathrm{solv.}} = 0$, but also the following equation must hold

$$\Delta H = \Delta E + \text{const}\,, \tag{6}$$

where ΔE is the energy change accompanying the dissociation calculated by the EHT method. In order to check this relationship, we plotted the observed heats of atomization for four groups of related compounds against the calculated EHT bonding energied (Table IV). The plots are seen, in Fig. 4, to have slopes very close to unity. The splitting into partial linear dependences according to classes of compounds reminds of various HMO correlations, the reason for this splitting being probably the same – the neglect of electronic repulsion. A somewhat less satisfactory correlation for the group of nitrobenzenes can be ascribed to the fact that these compounds do constitute a less homogeneous group than *e.g.* alkanes or methyl substituted benzenes. On the basis of Fig. 4 it can be anticipated that for protonated and dissociated forms of compounds constituting one group of chemically related systems one gets two separate linear dependences. Here the following possibilities can occur: *a*) both dependences have a unit slope; then providing $\varDelta\Delta S = 0$ and $\varDelta\Delta E_{\mathrm{solv}} = 0$, a linear correlation of $\mathrm{p}K_a$ against ΔE with a slope having the theoretical value 16·9 is obtained; *b*) both dependences are parallel but have slopes different from unity; then providing $\varDelta\,\Delta S = 0$ and $\varDelta\,\Delta E_{\mathrm{solv}} = 0$, the slope of a linear correlation $\mathrm{p}K_a$ *vs* ΔE differs from the theoretical value 16·9; *c*) for dependences having different slopes a nonlinear correlation $\mathrm{p}K_a$ *vs* ΔE can be expected.

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