PHYSICAL PROPERTIES AND CHEMICAL REACTIVITY OF ALTERNANT HYDROCARBONS AND RELATED COMPOUNDS. XXI.* ACID–BASE EQUILIBRIA OF POLYNUCLEAR PHENOLS AND AMINES

M.Tichý[a], R.Zahradník[b], J.A.Völlmin[c]** and W.Simon[c]

[a] *Institute of Industrial Hygiene and Occupational Diseases, Prague 10,*
[b] *Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague 2,*
[c] *Eidg. Technische Hochschule, Laboratorium für Organische Chemie, Zürich, Schweiz*

Relationships between experimental pK_a values of the title compounds and MO characteristics calculated by the Pople SCF procedure are presented and the effect of solvation energy is mentioned. The use of theoretical data to estimate changes of pK_a values due to the excitation of molecules to their first singlet excited states is discussed.

Dissociation of phenols and protonation of amines are well defined processes, therefore the measured pK_a values appear to provide suitable data against which a theoretical model could be judged. Several attempts have been reported[1-4] to correlate pK_a values of phenols and amines with quantum chemical data, however, these correlations are not as satisfactory as for some other processes[5]. In view of this we decided to employ a consistent set of experimental data for sufficiently large groups of these compounds. The reactions studied are as follows,

$$R{-}OH + LH \; \rightleftarrows \; R{-}O^- + LH_2^+ , \qquad (A)$$

$$R{-}NH_3^+ + LH \; \rightleftarrows \; R{-}NH_2 + LH_2^+ , \qquad (B)$$
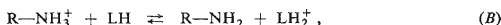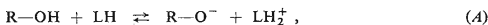
where R denotes an unsubstituted aryl and LH stands for solvent. From the point of view of the present computational achievements, the SCF π-electron energies (as defined by Pople) appear to be the most suitable theoretical data.

The subject of this paper is a comparison of the experimental pK_a values with the corresponding changes in the π-electron energies. Furthermore, we attempted to estimate changes in the pK_a values due to the excitation of the molecules to their first singlet excited states.

EXPERIMENTAL

The conditions of the spectrophotometric determination of pK_a values are listed below the Tables. SCF calculations have been described previously[6]. For these calculations we employed para-
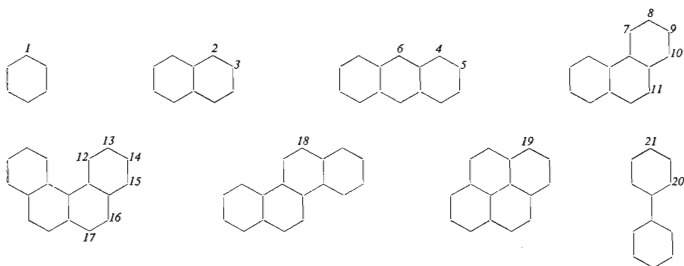
CHART

Survey of Investigated Substances

The Arabic Numbers *1—21* Denote the Position in which the Hydrocarbon is Substituted by a Functional Group (NH$_2$ or OH)
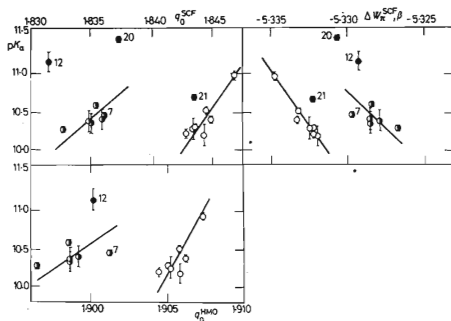

FIG. 1

Plot of pK_a Values of Aromatic Polynuclear Phenols Against Quantum Chemical Characteristics (ΔW_π^{SCF}, q_O^{SCF}, q_O^{HMO})

Full lines respect split of data according to classes[9] of positions: ○ (*0*), ◐ (*1*). Molecules having a sterically hindered functional group are indicated by numbers[2] (7, 12, 20, 21). By means of the short vertical lines, the errors of the pK_a values are vizualised. Data not included in the statistical treatment are indicated by full circles. The following empirical equations hold for the class 0:
pK_a = 344·43q_O^{HMO} — 646·48, *n* 7, *r* 0·841; pK_a = 222·22q_O^{SCF} — 399·51, *n* 7, *r* 0·903; pK_a = —294·12 ΔW_π^{SCF} —1558·03, *n* 7, *r* —0·970; for the class 1: pK_a = 137·17q_O^{HMO} —250·05, *n* 6, *r* 0·506; pK_a = 134·05q_O^{SCF} —235·56, *n* 6, *r* 0·630; pK_a = —195·31 ΔW_π^{SCF} —1030·29, *n* 6, *r* —0·540.

meters, which had been suggested in our study on electronic spectra of aromatic phenols and amines[7,8]. Further details on experimental data and calculations are presented in Tables I and II. For approximations involved in examination of correlations see ref.[5]. The compounds studied were consecutively numbered; these numbers appear in the Chart, the Tables and in the Figures.

RESULTS AND DISCUSSION

pK_a values determined experimentally are summarized in Table I, where changes in SCF π-electron energy and π-electron densities on exocyclic oxygen and nitrogen atoms are also presented. The application of π-electron energy changes has been generally accepted[3] as a justified approach and the adoption of the π-electron densities follows from the perturbation theory[1,2]. Experimental pK_a values are plotted against the theoretical data in Figs 1 and 2. The points identified by numbers (7, 12, 20, 21) refer to compounds bearing a sterically hindered functional group[2]. The data excluded from the statistical treatment are indicated by full circles.
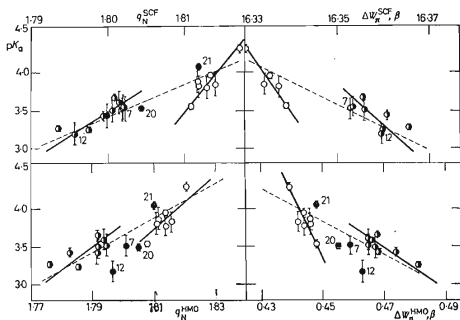

Fig. 2

Plot of pK_a Values of Aromatic Polynuclear Amines Against Quantum Chemical Characteristics (ΔW_π^{HMO}, ΔW_π^{SCF}, q_N^{HMO}, q_N^{SCF})

Dashed lines do not respect the differentiation of the data according to classes of positions. The values of ΔW_π^{HMO} were taken from ref.[2]. The following empirical equations hold for the class 0: $pK_a = 34.130 q_N^{HMO} - 58.024$, n 7, r 0.911; $pK_a = -86.957 \Delta W_\pi^{HMO} + 42.478$, n 7, r —0.869; $pK_a = 121.95 q_N^{SCF} - 217.26$, n 7, r 0.902; $pK_a = -88.496 \Delta W_\pi^{SCF} + 1449.48$, n 5, r —0.942; for the class 1: $pK_a = 29.762 q_N^{HMO} - 49.774$, n 8, r 0.759; $pK_a = -26.954 \Delta W_\pi^{HMO} + 16.137$, n 8, r —0.795; $pK_a = 62.500 q_N^{SCF} - 109.01$, n 11, r 0.830; $pK_a = -55.249 \Delta W_\pi^{SCF} + 907.17$, n 8, r —0.745; for the whole set $pK_a = 22.522 q_N^{HMO} - 36.892$, n 15, r 0.892; $pK_a = -22.026 \Delta W_\pi^{HMO} + 13.747$, n 15, r —0.861; $pK_a = 40.984 q_N^{SCF} - 70.357$, n 16, r 0.889; $pK_a = -28.249 \Delta W_\pi^{SCF} + 465.45$, n 11, r —0.873. The other details see Fig. 1.

It should be stated that in spite of the consistency and accuracy of the experimental data and the adoption of SCF π-electron energy changes, the result is not as satisfactory as we expected. Even so, one must differentiate between the different types of carbon atoms to which the substituents are attached (*i.e.* what we call classes 0

<small>TABLE I</small>

Experimental pK_a Values and Theoretical SCF Characteristics of Polynuclear Phenols and Amines

No	Experimental data		SCF Characteristics[a]			
	phenols[b]	amines[c]	phenols		amines	
			$\Delta W_\pi[-\beta]^d$	q_0	$\Delta W_\pi[\beta]^d$	q_N
1	10·97 ± 0·04	4·30 ± 0·04	5·335	1·847	16·330	1·817
2	10·59 ± 0·01	3·66 ± 0·05	5·328	1·835	16·356	1·801
3	10·51 ± 0·03	3·95 ± 0·03	5·333	1·845	16·336	1·814
4	10·28 ± 0·02	3·43 ± 0·06	5·327	1·833	16·361	1·797
5	10·21 ± 0·05	3·55 ± 0·02	5·332	1·843	16·339	1·811
6	—	(3·12)	5·318	1·820	16·391	1·779
7	10·46 ± 0·02	(3·52)	5·330	1·836	16·353	1·802
8	10·30 ± 0·03	(3·81)	5·332	1·844	16·337	1·812
9	10·40 ± 0·03	(3·84)	5·333	1·845	16·334	1·814
10	11·20 ± 0·03	(3·53)	5·329	1·836	16·354	1·802
11	(10·35)	(3·50)	5·329	1·835	16·356	1·801
12	(11·15)	(3·18)	5·329	1·832	16·360	1·796
13	(10·28)	(3·87)	5·333	1·843	—	1·812
14	(10·19)	(3·79)	5·332	1·844	—	1·813
15	(10·40)	(3·60)	5·329	1·836	—	1·802
16	(10·38)	(3·43)	5·328	1·835	—	1·800
17	(10·10)	(3·52)	5·329	1·836	—	1·802
18	—	3·24 ± 0·01	5·327	1·833	16·360	1·798
19	—	3·27 ± 0·01	5·324	1·831	16·366	1·794
20	11·46 ± 0·01	3·51 ± 0·03	5·331	1·837	—	1·805
21	10·69 ± 0·02	4·06 ± 0·03	5·332	1·844	—	1·812

[a] For the procedure and the parameters of the SCF calculations see refs[7,8]. [b] The pK_a values were determined by a spectrophotometric procedure using the solvent methanol/water 60%/40% (vol.). The values in the parenthesis were estimated using a correlation between our experimental data and the experimental data in ref.[11]: pK_a = pK_a^{11} −0·16, standard deviation $\sigma = \pm 0·08$. The data for 50% aqueous methanol solutions were published in the cited papers: 1—10·75 (ref.[10]), 3—10·15 (ref.[4]), 4—10·08 (ref.[4]), 5—10·05 (ref.[4]), 8—10·12 (ref.[4]), 9—10·17 (ref.[4]), 11—10·15 (ref.[4]). [c] The pK_a values were determined by a spectrophotometric procedure using the solvent methanol/water 60%/40% (vol.). The values in the parenthesis were estimated using a correlation between our experimental data and the experimental data in ref.[2]: pK_a = 0·782 pK_a^2 + 1·005, $\sigma = \pm 0·08$. [d] $\beta = -2·318$ eV.

and *1*)[9]. It is true that with data for amines we obtained a single statistically significant linear dependence; however, we had already found this in a previous approach using HMO method[2].

It is noteworthy that with sterically hindered amines the SCF data are superior to the HMO ones (compounds 7 and 12 in Fig. 2).

With some reaction series a considerable improvement in correlations is achieved on going from the HMO characteristics to the SCF ones; in particular the splitting up of data into partial linear dependencies according to classes of positions disappears[5]. Since this is not the case here, we were forced to consider another effect, *viz.* the differences in solvation energy changes accompanying dissociation or protonation for positions of classes 0 and 1. An anisotropic contribution to the total solvation energy can be estimated by means of the Born formula[12],

$$E_{\text{solv}} = \left(\sum_\mu \frac{q_\mu^2}{2r_\mu} + \sum_{\mu < \nu} \frac{q_\mu q_\nu}{r_{\mu\nu}} \right) \left(1 - \frac{1}{D} \right), \qquad (1)$$

where q_μ stands for the net charge in the position μ, r_μ stands for the effective radius of the atom μ, $r_{\mu\nu}$ is the distance between atoms μ and ν, and D is the effective dielectric constant of the solvent.

Computational costs represent a difficulty encountered here, as the charges in Eq. (*1*) have to be evaluated from the all valence shell electron calculations. As calculations of this type are rather time-consuming for aromatic polynuclear systems, we restricted our considerations to naphthalene derivatives. Although the results of these calculations (Table II) prohibit any simple quantitative interpretation, it is obvious that the estimated ΔE_{solv} is larger with compounds bearing a functional

TABLE II

Solvation Energy (Eq. (*1*))[a] of Isomeric Naphthols and Naphthyl Amines for Reactions (*A*) and (*B*)

No	E_{solv}, eV		ΔE_{solv}[b]		E_{solv}, eV		ΔE_{solv}[c]	
	naphthol	naphtholate	eV	[β][d]	amine	protonized amine	eV	[β][d]
2	—4·019	—10·135	—6·116	2·638	—2·686	—4·145	1·459	—0·630
3	—4·062	—10·241	—6·179	2·666	—2·598	—4·078	1·480	—0·639

[a] Net charge distribution was calculated by means of the extended Hückel method[13]. Dielectric constant for 60% aqueous methanol was estimated from those of water and methanol, *i.e.* 51·1. [b] $\Delta E_{\text{solv}} = E_{\text{solv}}$ (naphtholate) − E_{solv} (naphthol).   [c] $\Delta E_{\text{solv}} = E_{\text{solv}}$ (naphthylamine) − E_{solv} (protonized naphthylamine). [d] $1\beta = -2·318$ eV.

TABLE III
pK_a^s Values Estimated by the Förster's Cycle[14] Using Experimental and SCF LCI Theoretical Data[a]

No	Phenols A $\Delta\tilde{\nu}_{exp}$[b]	ΔpK_a	pK_a^s	Phenols B $\tilde{\nu}_{th}$[b]	ΔpK_a	pK_a^s	Amines A $\Delta\tilde{\nu}_{exp}$[b]	ΔpK_a	pK_a^s	Amines B $\Delta\tilde{\nu}_{th}$[b]	ΔpK_a	pK_a^s
1	-1.45	-3.1	7.9	-1.07	-2.3	8.7	-3.80	-8.0	-3.7	-4.18	-8.8	-4.5
2	-1.20	-2.5	8.1	-1.43c	-3.0	7.6	-1.45	-3.1	-0.1	-1.70	-3.6	0.1
3	-1.70	-3.6	6.9	-1.22	-2.6	8.0	-2.40	-5.1	-1.1	-3.34	-7.1	-3.1
4	-1.50	-3.2	7.1	-1.42	-3.0	7.3	-2.05	-4.3	-0.9	-2.62	-5.5	-2.1
5	-1.30	-2.7	7.5	-1.06	-2.2	8.1	-2.55	-5.4	-1.8	-2.08	-4.4	-0.8
6	—	—	—	—	—	—	—	—	—	-2.33	-4.9	-1.8
7	-1.30	-2.7	7.7	-1.48	-3.1	8.1	—	—	—	-2.36	-5.0	-1.5
8	-1.00	-2.1	8.2	-1.10	-2.3	9.1	—	—	—	-1.41	-3.0	0.8
9	-1.20	-2.5	7.9	-0.56	-1.2	8.5	-2.35	-5.0	-1.1	-2.00	-4.2	-0.4
10	-1.30	-2.7	8.5	-0.88c	-1.9	9.1	—	—	—	—	—	—
11	—	—	—	-1.02c	-2.2	—	-2.45	-5.2	-1.7	-1.24c	-2.7	0.8
12	-0.80	-1.7	9.5	—	—	—	-1.55	-3.3	-0.1	-2.31	-4.9	-1.7
13	-1.25	-2.6	7.6	—	—	—	-1.70	-3.6	-0.3	-1.26	-2.7	1.2
14	-0.85	-1.8	8.4	c	—	—	-1.25	-2.6	-1.2	-1.65c	-3.5	0.3
15	-0.70	-1.5	8.9	c	—	—	-1.15	-2.4	-1.2	-1.50c	-3.2	0.4
16	—	—	—	—	—	—	-1.65	-3.5	-0.1	-1.77	-3.7	-0.3
17	-1.65	-3.5	6.6	—	—	—	-2.10	-4.4	-0.9	-2.21	-4.7	-1.2
18	—	—	—	—	—	—	-1.30	-2.7	-0.5	-1.23	-2.6	0.6
19	—	—	—	—	—	—	-2.90	-6.1	-2.9	-2.59	-5.5	-2.2
20	-4.50	-9.5	2.0	-1.85	-3.9	7.6	-6.5	-13.7	-10.2	—	—	—
21	-2.95	-6.2	4.5	-0.84	-1.8	8.9	-3.9	-8.2	-4.1	—	—	—

[a] The values estimated from experimental data: differences between the longest-wavelength bands of electron absorption spectra of a base and a conjugated acid are used ($\Delta\tilde{\nu}_{exp}$); B the values estimated from LCI SCF characteristics[7,8], differences in wavenumbers of electron transitions from the ground state to the first excited state ($\Delta\tilde{\nu}_{th}$). The pK_a values are calculated for 23°C using the equation: $\Delta pK_a = pK_a^s = 2.111 \cdot 10^{-3}(\tilde{\nu}_B - \tilde{\nu}_{BH^+})$, $\tilde{\nu}$ in [cm^{-1}]; [b] The differences are given in 10^3 cm^{-1}. [c] With the base or with the conjugated acid (or with both) the first electron transition is not a $1 \rightarrow 1'$ transition. Wavenumbers calculated by the LCI SCF procedure, SCF π-electron energies and π-electron densities for the first excited singlet states of the molecules are available from the authors.

group in position 2 (class *0*) than with compounds, where a functional group is in position 1 (class *1*) (Figs 1 and 2). Thus the introduction of the solvation energy brings the straight lines for both classes nearer to each other. Here we content ourself with this qualitative statement; the attempts to treat solvation energies in a quantitative way will be the subject of another study.

A direct determination of pK_a values in the first excited singlet state (pK_a^s) from the effect of the pH of a medium on fluorescence spectra is time-consuming. Moreover, at least one partner of a conjugated acid–base pair has to emit fluorescence, which imposes major limitations in the choice of compounds. An alternate method was reported by Förster[14] for obtaining pK_a^s values. This method as well as the direct method were employed with polynuclear amines and phenols derived from benzene, naphthalene and anthracene[15-18].

Table III presents the results of calculations on the pK_a^s values. The aim of this attempt is to find whether the LCI SCF excitation energies can be employed to estimate pK_a^s values by means of the Förster's cycle[14], in a similar way as with experimental data. In one of the earlier papers[19] we reported the changes in pK_a values due to excitation for the series of polynuclear phenalenones; the values estimated by means of the Förster's cycle from the longest-wavelength bands in absorption spectra, the shortest-wavelength fluorescence bands, or considering the respective average were in fair agreement. Since many of the compounds under study exhibit no fluorescence, we employed only the absorption spectra. Table III shows that the trends in pK_a changes due to excitation are in agreement with the theoretical data for both series of compounds studied; values in refs[15-18] are of $2-4$ pK_a units lower. It is difficult to judge the merits of this theoretical approach for quantitative predictions. The difficulty stems from the fact that the pK_a^s values are estimated from absorption spectra which show vibrational fine structure in the case of the acid but not with the conjugated base or *vice versa*. From the footnote *a* in Table III it follows that an error $1\,000\ cm^{-1}$ in a difference of spectral maxima of both forms corresponds to two pK_a units. Nevertheless, the theoretical data can be used for predictions of trends and approximate magnitudes of pK_a changes due to excitation, *i.e.* for qualitative purposes or in favourable cases even for semiquantitative purposes; this holds also for experimental spectral data.

REFERENCES

1. Elliott J. J., Mason S. F.: J. Chem. Soc. *1959*, 2352.
2. Guha S., Zahradník R.: This Journal *32*, 2448 (1967).
3. Streitwieser A., jr: *Molecular Orbital Theory for Organic Chemists*. Wiley, New York 1961.
4. Rosenberg H. M.: Dissertation Abstr. *25*, 847 (1964).
5. Zahradník R., Chalvet O.: This Journal *34*, 3402 (1969).
6. Hochmann P., Zahradník R., Kvasnička V.: This Journal *33*, 3478 (1968).
7. Tichý M.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1966.
8. Tichý M., Zahradník R.: J. Phys. Chem. *73*, 534 (1969).

9. Koutecký J., Zahradník R., Čížek J.: Trans. Faraday Soc. *57*, 169 (1961).
10. Musso H., Mathies H. G.: Chem. Ber. *94*, 356 (1961).
11. Newman M. S., Blum J.: J. Am. Chem. Soc. *86*, 503 (1964).
12. Chalvet O., Daudel R., Jano I., Peradejordi F. in the book: *Modern Quantum Chemistry* (O. Sinanoglu, Ed.). Part 2, p. 165. Academic Press, New York 1965.
13. Hoffmann R.: J. Chem. Phys. *39*, 1307 (1963).
14. Förster T.: Z. Elektrochem. *54*, 42 (1950).
15. Weller A. in the book: *Progress in Reaction Kinetics* (G. Porter, Ed.). Part 1, p. 187. Pergamon Press, New York 1961.
16. Jaffé H. H., Jones H. L.: J. Org. Chem. *30*, 964 (1965).
17. Itoh R.: J. Phys. Soc. Japan *13*, 389 (1958).
18. Rotkiewicz K., Grabowski Z. R.: Trans. Faraday Soc. *65*, 3263 (1969).
19. Zahradník R., Tichý M., Reid D. H.: Tetrahedron *24*, 3001 (1968).

Translated by P. Čársky.