STUDY OF THE AZO–HYDRAZONE TAUTOMERIC EQUILIBRIUM BY ELECTRONIC SPECTROSCOPY AND QUANTUM CHEMISTRY. II. HMO CALCULATIONS

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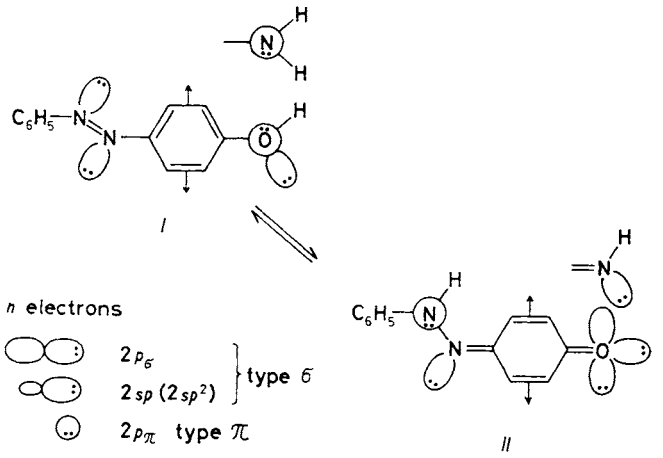
Dedicated to Prof. Jaromír Horák on the occasion of his 60th birthday.

Experimental data obtained in Part I of this work for *p*-hydroxy and *p*-amino derivatives of four arylazo compounds with different fused ring systems were correlated with some indices calculated by the simple HMO quantum chemical method in relation to the π-electron structure of the azo and hydrazone tautomers of the compounds studied. Mental fragmentation and the related stability of the systems expressed by Julg's aromaticity indices of the hydrocarbon fragments appeared to be basically different for the two tautomers.

As follows from the simplified formulas of the azo (*I*) and hydrazone (*II*) tautomers in Scheme 1, this tautomeric equilibrium is associated with a significant change in the electronic structure of the molecular pair concerned.



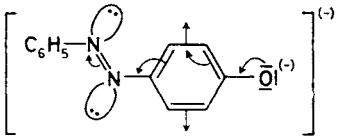
I ⇌ *II*

SCHEME 1

Since both tautomers possess virtually a planar arrangement, it is feasible, to a first approximation to identify the changes in the electronic structure of the ground electronic state with the changes in the π-electron distribution. In this work, this π-electron distribution and some related characteristics are calculated by the simple HMO quantum chemical method, and the experimental data obtained in Part I of this work by electronic absorption and fluorescence spectroscopy are interpreted in terms of this simple model. The parameters used, which are practically identical with those used by Kuder[1] and Kelemen[2], are given in Table I.

RESULTS AND DISCUSSION

Scheme 1 demonstrates that the tautomeric transition involves proton transfer between the proton donor *para* substituent (—OH, —NH_2) and one of the nitrogen atoms of the azo group. We assume that the planar arrangement is preserved in both tautomeric forms and changes in geometry are only due to the different π-electron distribution in the azo and hydrazone forms. Apart from the mechanism of proton transfer from the proton donor *para* substituent to one of the nitrogen atoms of the azo group, elimination of this proton from the substituent should be the easier the lower is the π-electron density at this substituent (see the resonance structure in Eq. (*B*) in Part I, showing the formation of the ion pair of the azo compound anion and the cation of the protonated molecule of the polar solvent), and the proton should bond to that nitrogen atom possessing a higher π-electron density. Protonation of one of the nitrogen atoms of the azo group can occur either in the molecule of the nonionized azo form of the compound, A—OH, or in the anion of the azo form, $A—O^-$. Possibility of this ionization giving rise to the azo form anion depends on the proton acceptor strength of the solvent used and on acidity of the corresponding hydrogen atom of the proton donor *para* substituent. Elimination of protons in proton acceptor polar solvents, however, is only feasible for the *p*-hydroxyazo compounds studied; the formed anion of the *p*-hydroxyazo compound azo form exhibits a pronounced tendency to π-electron density migration following Scheme 2, leading to an increase in the π-electron density and thereby, to an increased possibility of protonation at the α-nitrogen atom of the azo group giving rise to the hydrazone form H of the *p*-hydroxyazo compound (see equilibrium K_5



SCHEME 2

TABLE I

Parameters used for HMO calculations

Atomic core	Z_X[a]	δ_X[b]	k_{X-Y}[c]	X—Y bond
		Azo form		
C^+ (aromatic)	1	0·0	1·0	C—C (aromatic)
N^+ (pyridinic)	1	0·5	0·9	$\rangle C-\bar{N}=$
			1·0	$-\bar{N}=\bar{N}-$
HO^{2+} (hydroxylic)	2	2·0	0·8	$\rangle C-OH$
H_2N^{2+} (aminic)	2	1·5	0·8	$\rangle C-NH_2$
$(O^-)^{2+}$ (hydroxylate)[d]	2	1·4	1·0	$\rangle C-\bar{O}\vert^-$
		Hydrazone form		
C^+ (aromatic)	1	0·0	1·0	C—C (aromatic)
HN^{2+} (aminic)	2	1·5	0·7	$\rangle C-\bar{N}H-$
			0·7	$-\bar{N}H-\bar{N}=$
N^+ (pyridinic)	1	0·5	1·1	$\rangle C=\bar{N}-$
O^+ (carbonyl)	1	1·0	1·0	$\rangle C=\bar{O}$
HN^+ (iminic)	1	0·5	1·1	$\rangle C=\bar{N}H$
		Azo form dimer[e]		
$-\vdots N=$	1	0·7	0·9	$\rangle C-\vdots N=$
$-\bar{N}=$	1	0·5	1·0	$-\vdots N=N-$
$-OH\cdots$	2	1·8	0·8	$\rangle C-OH\cdots$
		Hydrazone form dimer[e]		
$-\bar{N}H\cdots$	2	1·3	0·7	$\rangle C-\bar{N}H\cdots$
$-\bar{N}=$	1	0·5	0·7	$-\bar{N}H\cdots$ $\bar{N}=$
$=O\cdots$	1	1·2	1·0	$\rangle C=\bar{O}\cdots$

[a] Number of π electrons contributed to conjugation by atom X; [b] constant in the expression for the effective Coulomb integral $\alpha_X = \alpha_C + \delta_X\beta$; [c] constant in the expression for the effective resonance integral $\beta_{X-Y} = k_{X-Y}\beta$; [d] ref.[3]; [e] a general expression for the effective Coulomb integral has been suggested[4] for the case of an intermolecular hydrogen bond: $\alpha_{XH\cdots} = \alpha_X - 0{\cdot}2\beta$ and $\alpha_{Y\cdots H} = \alpha_Y + 0{\cdot}2\beta$.

in Eq. (*B*) in Part I). HMO calculations gave evidence that both in the nonionized form and in the anion, it is the α-nitrogen atom of the azo form of the *p*-hydroxyazo compound that is better protonable (see Table II). From the discussion in Part I, however, it follows that hydrogen bonding between the proton donor *para* substituent of the azo form and molecules of proton acceptor polar solvents results in a stabilization of the azo form, which implies that only solute–solvent complexation takes place, with no formation of the anion of the azo form of solute and cation of the protonated molecule of solvent.

The relative stabilities of pairs of tautomers can be expressed by using the method of Baird and Whitehead[5]; the π-electron bonding energies of the azo form BE_A and of the hydrazone form BE_H are calculated as

$$BE_A = W_A - W'_A \qquad (1a)$$

$$BE_H = W_H - W'_H , \qquad (1b)$$

where W_A and W_H are the total π-electron energies of the azo and hydrazone forms, respectively, and W'_A and W'_H are the sums of energies of all π electrons localized at the $2p_\pi$ atomic orbitals of centres in conjugation in the two tautomeric forms. The difference $\Delta BE_{A-H} = BE_A - BE_H$ is a measure of stability of the species for mutually corresponding isoelectronic pairs of tautomers. For a comparison of stability of the tautomers in a fused ring system series with different numbers of π electrons, the bonding energies BE_A and BE_H have to be taken relative to this number of electrons, i.e., divided by the number of π electrons, *n*:

$$\Delta(BE/n)_{A-H} = BE_A/n - BE_H/n . \qquad (2)$$

TABLE II

π-Electron charge at the $-\bar{N}_\alpha=$ and $-\bar{N}_\beta=$ atoms in the azo groups of nonionized *p*-hydroxyazo compounds in the azo form and the corresponding anions. System labelling following Scheme 1 in Part I of this series

System	Nonionized azo form A—OH		Azo form anion A—O$^-$	
	$-\bar{N}_\alpha=$	$-\bar{N}_\beta=$	$-\bar{N}_\alpha=$	$-\bar{N}_\beta=$
A(OH)	−0·0814	−0·0607	−0·1037	−0·0604
B(OH)	−0·1072	−0·0651	−0·1390	−0·0667
C(OH)	−0·1178	−0·0685	−0·1525	−0·0711
D(OH)	−0·1545	−0·0758	−0·2005	−0·0815

These π-electron energy characteristics, which can be used for a classification of the relative stability of the tautomeric forms in dependence of the ring fusion patterns, are plotted in Fig. 1. The dependences of the quantity $\Delta(BE/n)_{A-H}$ on the size of the system (number of atoms in conjugation) or on the number of π electrons, n (the ring fusion plot) for *para* substitution by —OH and —NH_2 groups are identical in shape, they are, however, mutually displaced. It should be noted that if the $\Delta(BE/n)_{A-H}$ or ΔBE_{A-H} value is positive, the azo form is more stable than the hydrazone form, whereas the reverse is true if this value is negative. In terms of this criterion, it can be deduced that in the two series of *para* substituted derivatives of azo systems, the stability of the hydrazone form increases with increasing extent of ring fusion, which agrees with the experimental results obtained in Part I of this work. The stability of the system $D(X)$ ($B(X) \dashrightarrow D(X)$ ring fusion) in the two series is shifted markedly in favour of the hydrazone form as compared to the $A(X)$ to $C(X)$ systems. For the *p*-amino derivatives the stability of the azo form is generally higher than for the corresponding *p*-hydroxy derivatives. The $A(OH)$, $B(OH)$, $C(OH)$, $B(NH_2)$, $C(NH_2)$, and $D(NH_2)$ systems exist in both tautomeric forms whereas the $A(NH_2)$ system occurs virtually solely in the azo form and the $D(OH)$ system, in the hydrazone form. A marked change occurs on the $B(X) \dashrightarrow D(X)$ fusion, which from the topological point of view is a transition from the 1,4-system series to the 9,10-system series. The question, however, arises as to why the stability of the hydrazone form generally increases with the system growth, as is both observed experimentally (Part I) and obtained by HMO calculation.

Let us examine the π-electronic structure of the two tautomeric forms and consider the possible mental fragmentation of the systems. Fragmentation of a molecule can

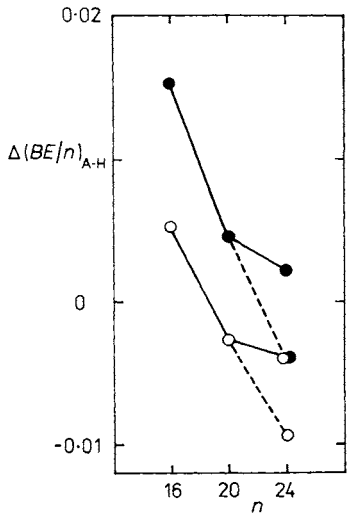
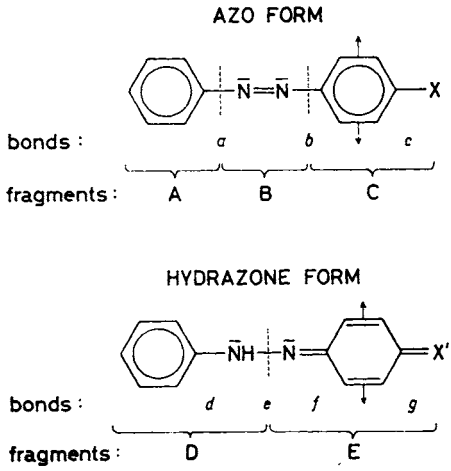


FIG. 1

Dependence of the quantity $\Delta(BE/n)_{A-H}$ for the simple azo–hydrazone equilibrium on the extent of ring fusion; n is the number of π electrons in the system, ○ *p*-hydroxy derivatives, ● *p*-amino derivatives

be thought in bonds with a highly single-bond character, separating the individual conjugated fragments. If exocyclic double bonds are formed in this manner in the aromatic fragments, extended conjugation results; these bonds will be therefore also considered (Scheme 3).



SCHEME 3

The azo form can be mentally fragmented in bonds *a* and *b* to obtain fragments A (benzene), B (azo group), and C (substituted (poly)nuclear aromatic fragment). Fragmentation of the hydrazone form is simpler, viz. in bond e giving fragments D (aniline) and E (poly)nuclear aromatic *p*-quinoneimine or *p*-diimine).

The π-electron bond orders in Table III demonstrate that the character of the mental fragmentation varies with benzene ring fusion neither for the azo nor for the hydrazone form. As the molecule grows in size, the mental fragmentation of the hydrazone form in bond e even becomes better justified, this bond acquiring more of a single-bond character; this holds true more for the *p*-amino derivatives. Bond *a* in the azo form and the corresponding bond *d* in the hydrazone form exhibit no dependence on the extent of ring fusion or on the proton donor *para* substituent used. A more marked dependence on the ring fusion is observed for bonds *b* and *c*, the latter also exhibiting the expected dependence on the *para* substituent: the π-electron bond order for the $>C-NH_2$ bond is higher than for the $>C-OH$ bond, which implies that *para* substitution by the amino group brings about a more pronounced extension of conjugation than *para* substitution by the hydroxy group. This can account for the experimentally established fact that in comparison to the *p*-hydroxy derivatives, *p*-amino derivatives are generally more stable in the azo form, which is also consistent with the energy criterion data. While for the azo forms

of the molecules studied, the π-electron bond order of the "single" *b* and *c* bonds increases slightly with extending ring fusion, for the hydrazone forms the π-electron bond order of the "single" bond e decreases. On the other hand, the π-electron bond order of the exocyclic "double" bonds of the hydrazone form (bonds *f* and *g*) increases, whereupon the conjugation of the hydrocarbon fragment extends with the formation of the *p*-quinoneimine or *p*-diimine fragment, the conjugation extension being more marked for the latter. The isomeric systems *C*(X) and *D*(X) (see Scheme 1 in Part I) are mutually rather different in both tautomeric forms. The π-electronic structure of system *C* approaches that of system *B* (both are 1,4-systems) whereas the π-electronic structure of system *D* (a 9,10-system) differs appreciably from that of system *B* although both systems *C* and *D* derive from system *B* by linear ring fusion.

The exocyclic "double" bonds *f* and *g* of the hydrazone form impart to fragment E and, particularly, the ring to which they are bonded a quinoid structure which, owing to the presence of localized "single" and "double" bonds, is generally less stable than the aromatic benzenoid structure of fragment C of the azo form. It should be noted, however, that fusion of a benzene ring to the quinoid ring of fragment E makes the partly quinoid structure of this fragment "more aromatic" (this effect is most pronounced for the symmetrical benzene ring fusion to the quinoid ring of system *D*); in this manner the hydrazone form is stabilized significantly.

A stabilizing factor for the azo systems in their azo form is the more or less aromatic structure of fragments A and C; a destabilizing factor is the high alternation of bond lengths in fragment B (localized "single" and "double" bonds of the azo group —N̄=N̄—) and the highly "single-bond" nature of bond *c*. For the hydrazone

TABLE III

π-Electron bond orders for the *a*, *b*, *c* bonds of the azo form and *d*, e, *f*, *g* bonds of the hydrazone form of molecules *A*(X) through *D*(X). Bond labelling following Scheme 3

System	Azo form			Hydrazone form			
	a	*b*	*c*	*d*	e	*f*	*g*
A(OH)	0·402	0·412	0·261	0·265	0·440	0·710	0·582
B(OH)	0·404	0·442	0·277	0·265	0·376	0·748	0·626
C(OH)	0·405	0·450	0·281	0·264	0·353	0·752	0·629
D(OH)	0·408	0·487	0·305	0·262	0·317	0·781	0·667
A(NH_2)	0·401	0·416	0·309	0·265	0·356	0·734	0·734
B(NH_2)	0·404	0·448	0·332	0·263	0·319	0·762	0·766
C(NH_2)	0·405	0·456	0·338	0·263	0·307	0·763	0·768
D(NH_2)	0·407	0·494	0·370	0·262	0·287	0·787	0·796

form, a stabilizing factor is the aromatic structure of the unsubstituted phenyl, and also the extension of conjugation of the (poly)nuclear hydrocarbon fragment by the exocyclic "double" bonds *f* and *g*. Destabilizing factors are the "single" bond *d* (virtually independent of ring fusion as well as of the *para* substitution) in fragment D and the more or less quinoid structure of fragment E, which, however, is made "partly aromatic" by the benzene ring fusion. Since both tautomeric forms are heteromolecules, alternation of the π-electron density takes place to various degrees

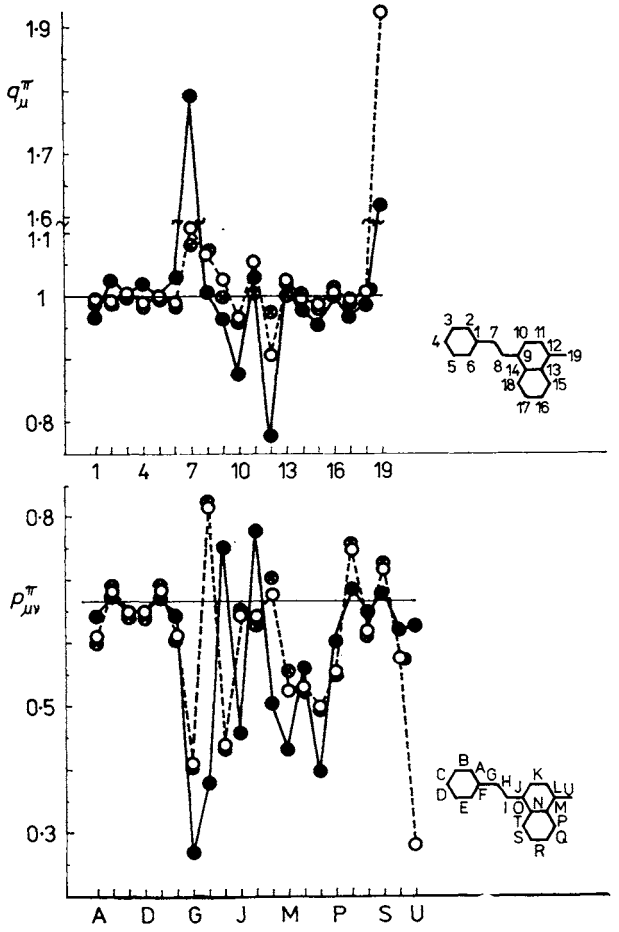


FIG. 2

Dependence of the π-electron density, q_μ^π, and π-electron bond order, $p_{\mu\nu}^\pi$, on the position of the centre and bond in the skeleton of 1-phenylazo-4-naphthol (system *B*(OH)). ○ azo form, ● hydrazone form, ⊗ unsubstituted azo compound (1-phenylazonaphthalene)

at their centres of conjugation, and this fact can be generally regarded as a destabilizing factor for both tautomeric forms, though to a different extent (Figs 2 and 3).

The plots in Figs 2 and 3 show the dependences of the π-electron densities and π-electron bond orders on the centre and bond positions in the $B(OH)$ and $B(NH_2)$ molecules in the two tautomeric forms. This sort of plots demonstrates that the proton donor *para* substituents have virtually no effect on the π-electron structure and only a minor effect with respect to the benzene ring fusion on the π-electronic density of fragment A (unsubstituted phenyl) of the azo form. The distribution of

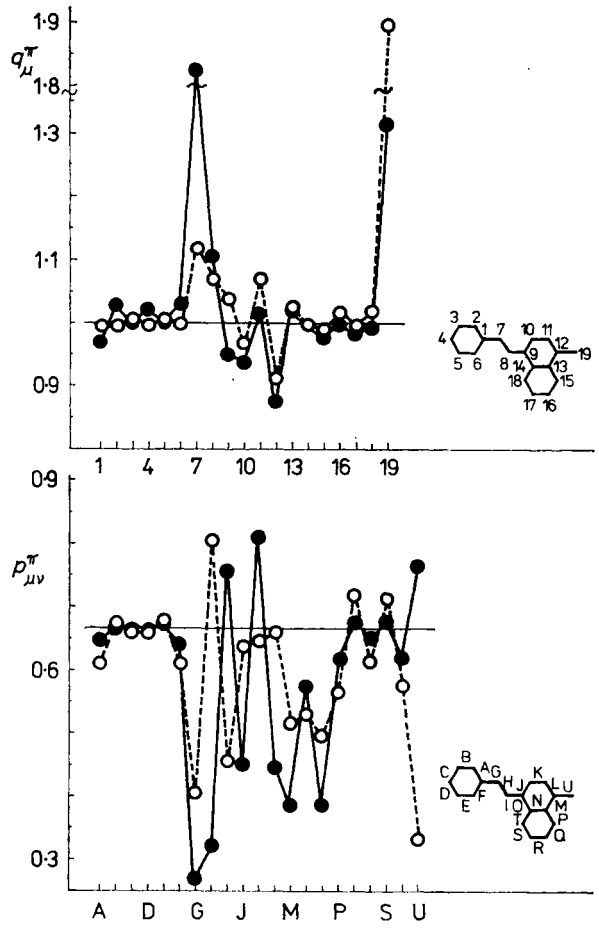


FIG. 3

Dependence of the π-electron density, q_μ^π, and π-electron bond order, $p_{\mu\nu}^\pi$, on the position of the centre and bond in the skeleton of 1-phenylazo-4-naphthylamine (system $B(NH_2)$). ○ azo form, ● hydrazone form

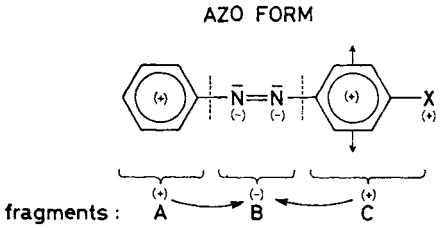
the π-electron charge at the unsubstituted phenyl of the azo form is such that in the ground electronic state this phenyl exhibits a positive charge, which decreases from the unsubstituted compound to the *p*-hydroxy to the *p*-amino derivatives and lowers considerably with extending ring fusion (Table IV). Fragment B (the azo group) of the azo form in the ground electronic state is a negative π-electron charge carrier (of the two nitrogen atoms, which both carry negative charges, the α-nitrogen carries a higher charge); this negative charge increases with the extent of ring fusion and for the *p*-amino deivatives is higher. Fragment C of the azo form in the ground electronic state is a positive charge carrier, both at the hydrocarbon part and at the proton donor *para* substituent; this positive charge increases with the extent of ring fusion (Table IV). Thus, with respect to their π-electron charge distribution, the *p*-hydroxyazo and *p*-aminoazo compounds in their azo form in the ground electronic state can be represented by Scheme 4.

TABLE IV

π-Electron charge of fragments in the azo and hydrazone forms of the substances studied

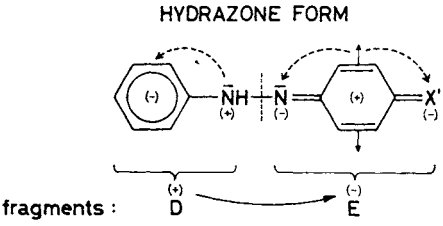
Fragment	*A*(OH)	*B*(OH)	*C*(OH)	*D*(OH)	*A*(NH_2)	*B*(NH_2)	*C*(NH_2)	*D*(NH_2)
				Azo form				
A	0·0534	0·0416	0·0362	0·0184	0·0502	0·0368	0·0307	0·0107
B	−0·1421	−0·1723	−0·1862	−0·2303	−0·1484	−0·1820	−0·1971	−0·2458
C	0·0887	0·1308	0·1501	0·2120	0·0983	0·1452	0·1663	0·2352
	0·0230	0·0572	0·0745	0·1256	0·0050	0·0381	0·0554	0·1053
—X	0·0658	0·0736	0·0756	0·0864	0·0933	0·1071	0·1109	0·1299
				Hydrazone form				
D	0·2175	0·1686	0·1525	0·1252	0·1553	0·1275	0·1198	0·1044
	−0·0272	−0·0397	−0·0438	−0·0504	−0·0435	−0·0502	−0·0521	−0·0556
—$\overline{N}$H—	0·2447	0·2083	0·1963	0·1756	0·1988	0·1777	0·1719	0·1600
E	−0·2174	−0·1686	−0·1523	−0·1251	−0·1553	−0·1275	−0·1197	−0·1043
—$\overline{N}$=	0·0937	−0·0049	−0·0469	−0·0996	−0·0513	−0·1075	−0·1290	−0·1547
	0·3426	0·4538	0·5101	0·5599	0·2304	0·2939	0·3255	0·3496
=X′	−0·6537	−0·6175	−0·6155	−0·5854	−0·3344	−0·3138	−0·3162	−0·2992

The hydrazone form in the ground electronic state is mentally separated into two fragments, of which fragment D is a carrier of a positive π-electron charge, which decreases with the extent of ring fusion, and fragment E is a carrier of a negative π-electron charge of equal magnitude. This charge is lower for the *p*-amino deriva-



SCHEME 4

tives than for the *p*-hydroxy derivatives. Fragment D is constituted by an unsubstituted phenyl and an amino group, —$\overline{\text{N}}$H—, where the former has a negative π-electron charge, which increases with the extent of ring fusion and is higher for the *p*-amino derivatives, and the latter has a positive π-electron charge, which decreases with the extent of ring fusion and is lower for the *p*-amino derivatives. Fragment E is constituted by an imine group, —$\overline{\text{N}}$=C$\diagdown$, a (poly)nuclear hydrocarbon fragment and a carbonyl ($\diagdown$C=$\overline{\text{O}}$) or imine ($\diagdown$C=$\overline{\text{N}}$H) group. Now, the (poly)nuclear hydrocarbon fragment carries a positive π-electron charge, which increases with the extent of ring fusion and is lower for the *p*-amino derivatives; the carbonyl or imine group carries a negative π-electron charge (lower at the imine group), decreasing with the extent of ring fusion; the imine group, —$\overline{\text{N}}$=C$\diagdown$, carries a negative π-electron charge (with one exception, viz. the *A*(OH) system), increasing with the extent of ring fusion and having a higher (negative) value for the *p*-amino derivatives. From the point of view of the π-electron distribution, the hydrazone form of the *p*-hydroxyazo and *p*-aminoazo compounds in their ground electronic state can be represented by Scheme 5.



SCHEME 5

Schemes 4 and 5 demonstrate that in the azo form in the ground electronic state, π-electron charge transfer occurs from fragments A and C (π-electron charge donors) to fragment B (π-electron charge acceptor); in the hydrazone form in the ground electronic state, π-electron charge transfer occurs from fragment D (its amine group —$\overline{\text{N}}$H—; π-electron charge donor) to fragment E, whose hydrocarbon part is actually also a π-electron charge donor whereas the carbonyl or imine groups are π-electron charge acceptors.

The dependences of the π-electron bond orders and densities on the bond and centre positions in the molecules of the azo and hydrazone forms of the compounds in their ground electronic state are rather different.

The stability can be also treated in terms of the quantitatively expressed aromaticity of the (poly)nuclear hydrocarbon parts of the fragments of the two tautomeric forms. This aromaticity index should relate directly to the π-electronic structure of the fragments. For this purpose we employed Julg's aromaticity indices[6] A_1, A_2 and their product A (Table V). In Julg's indices, allowance is made both for the bond length (π-electron bond order) alternation (A_1) and for the alternation of π-electron densities at centres in conjugation (A_2). For obtaining index A_1, Julg calculated the aromatic bond lengths (in nm) by the relation $d_{rs} = 0{\cdot}152 - 0{\cdot}019p_{rs}^{\pi}$; we employed a slightly modified formula, viz.

$$d_{rs} = 0{\cdot}1517 - 0{\cdot}0180p_{rs}^{\pi} \qquad (3)$$

which proved many times to give good results in our previous work. In this connection, Julg's value of $a = 225$ had to be replaced by $a = 250$.

It must be borne in mind that Julg's indices only apply to the (poly)nuclear hydrocarbon fragments of the two tautomeric forms and only then the indices A_1 and A_2 are consistent; index A_1 refers to the whole perimeter of the hydrocarbon fragment whereas index A_2 is a product of the indices for the individual benzene rings of this fragment (A_2', A_2'', A_2'''). Table V and Fig. 4 demonstrate that for the *p*-hydroxy derivatives, the total aromaticity index A of the (poly)nuclear hydrocarbon part of fragment C of the azo form decreases with increasing size of the molecule, whereas for the hydrazone tautomers (hydrocarbon part of fragment E) it increases slightly. For the *p*-aminoazo systems, the dependence for the azo form is virtually the same, whereas for the hydrazone tautomers the aromaticity of the (poly)nuclear hydrocarbon part of fragment E increases significantly with extending ring fusion. The total aromaticity index A of the unsubstituted benzene ring is virtually independent of the ring fusion patterns; for the *p*-hydroxy derivatives it is also independent of the tautomeric form whereas for the *p*-amino derivatives a slight dependence is observed. Since Julg's indices only refer to the hydrocarbon parts of the fragments, augmenting of the conjugated hydrocarbon fragment of the hydrazone tautomer with the —$\overline{\text{N}}$=C$\diagdown$ and $\diagup$C=$\underline{\text{O}}$ or —$\overline{\text{N}}$=C$\diagdown$ and $\diagup$C=$\overline{\text{N}}$H exocyclic "double"

bonds will have a significant stabilizing effect on the hydrazone tautomers, which will generally increase with extending ring fusion, as indicated by the π-electron bond order distribution (Figs 2 and 3).

Comparing the $C(X)$ and $D(X)$ isomers (1,4- and 9,10-systems, respectively), which have an identical number of centres in conjugation and are isoelectronic but differ in topology, we find that benzene ring fusion to the two sides of the *para* substituted benzene ring lowers the aromaticity of the polynuclear hydrocarbon fragment of system $D(X)$ in the azo form, from which a lowering of aromaticity of the entire $D(X)$ system with respect to the $C(X)$ system, or with respect to the $B(X)$ system due to the ring fusion, can be inferred. Fusion of benzene rings to the two

TABLE V

Julg's aromaticity indices A_1, A_2, and A of (poly)nuclear benzenoid fragments of the azo form (fragment A and the hydrocarbon part of fragment C) and the hydrazone form (hydrocarbon parts of fragments D and E) of the compounds studied

System	A_1		A_2		A	
	a	*b*	*a*	*b*	*a*	*b*
			Azo form			
A(OH)	0·996	0·994	1·000	0·982	0·996	0·976
B(OH)	0·996	0·979	1·000	0·966	0·996	0·946
C(OH)	0·996	0·978	1·000	0·971	0·996	0·950
D(OH)	0·996	0·977	1·000	0·956	0·996	0·934
$A(NH_2)$	0·997	0·993	1·000	0·980	0·997	0·973
$B(NH_2)$	0·996	0·979	1·000	0·968	0·996	0·948
$C(NH_2)$	0·996	0·978	1·000	0·887	0·996	0·867
$D(NH_2)$	0·996	0·983	1·000	0·950	0·996	0·934
			Hydrazone form			
A(OH)	0·999	0·917	0·998	0·932	0·997	0·855
B(OH)	0·999	0·943	0·996	0·920	0·995	0·868
C(OH)	0·999	0·949	0·996	0·916	0·995	0·869
D(OH)	0·999	0·953	0·994	0·915	0·993	0·872
$A(NH_2)$	0·999	0·877	0·996	0·980	0·995	0·859
$B(NH_2)$	0·999	0·924	0·992	0·975	0·991	0·901
$C(NH_2)$	0·999	0·935	0·994	0·975	0·993	0·912
$D(NH_2)$	0·999	0·944	0·994	0·976	0·993	0·921

[a] Fragment A for the azo form, hydrocarbon part of fragment D for the hydrazone form; [b] hydrocarbon part of fragment C for the azo form, hydrocarbon part of fragment E for the hydrazone form.

sides of the "quinoid" ring in compound $D(X)$ in the hydrazone form suppresses to a considerable extent the quinoid nature of this polynuclear hydrocarbon fragment (a destabilizing factor for the hydrazone form) as compared to the corresponding hydrocarbon part of fragment E in the azo system $C(X)$ in the hydrazone form.

Study of the ring fusion dependence of the partial aromaticity indices A_1 and A_2 (Fig. 5) revealed that the dependence of the total aromaticity index A of the (poly)-nuclear hydrocarbon part of fragment C of the azo form on the extent of ring fusion is dominated by the partial index A_2 of this fragment, whereas the corresponding dependence of this index A for the hydrocarbon part of fragment E of the hydrazone form is dominated by the partial index A_1 of this fragment; this applies to both substituents. Since index A_2 is obtained as the product of partial indices for the *para* substituted benzene ring and the fused benzene rings, all of them being less than or equal to unity, we have $A_2 \leqq A_2'$, where A_2' is the partial index for that benzene ring where the *para* substitution occurs. Thus, the A_2 value must decrease against A_2' or remain equal to it. From this point of view, the product form of index A_2

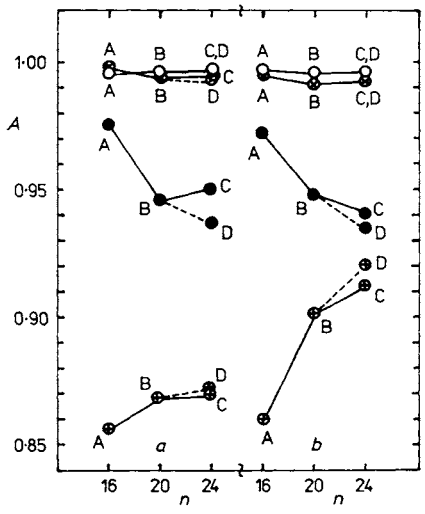


FIG. 4

Dependence of the total aromaticity index A on the extent of ring fusion; *a* *p*-hydroxy derivatives, *b* *p*-amino derivatives. Hydrocarbon fragment ⬡··· : ○ azo form, ⊗ hydrazone form; hydrocarbon fragment ···⬡···X : ● azo form, ⊕ hydrazone form

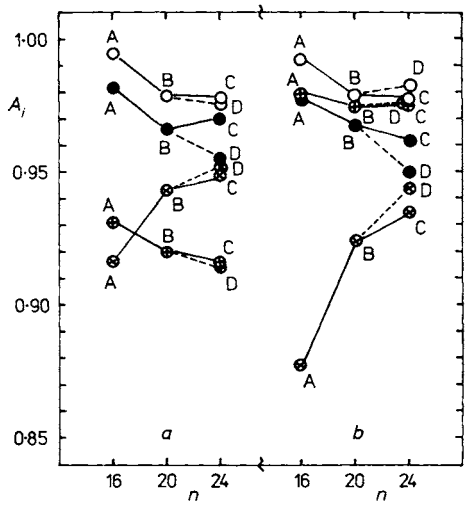


FIG. 5

Dependence of the partial aromaticity indices A_1 and A_2 for the (poly)nuclear hydrocarbon part of fragment C (azo form) and fragment E (hydrazone form), i.e., ···⬡···X *a* *p*-hydroxy derivatives, *b* *p*-amino derivatives. A_1: ○ azo form, ⊗ hydrazone form; A_2: ● azo form, ⊕ hydrazone form

with weight coefficients of all the partial indices (A_2', A_2'', A_2''') equal to unity is questionable. Since the relation for the partial index A_2 involves the squared difference between the π-electron densities of centres bonded by chemical bonds, the effect of the charge alternation is actually neglected. The different dominant effect of the partial indices A_1 and A_2 on the total index for the same (poly)nuclear hydrocarbon fragment in the two tautomeric forms also casts doubts on the product form of the total aromaticity index ($A = A_1A_2$) with weight coefficients equal to unity.

These quantitative results, though affected by the use of the simple quantum chemical method and by their relation to the hydrocarbon fragments only, indicate that the stability of the compounds in the azo form decreases with increasing extent of ring fusion whereas the reverse is true of the hydrazone form, irrespective of the nature of the proton donor *para* substituent.

Based on the theoretical results, the azo–hydrazone tautomeric equilibrium can be expected to be affected by a number of physico-chemical factors; this was also confirmed experimentally (Part I).

A detailed examination of the electronic absorption spectra of the *para* substituted azo compounds studied in hydrocarbon solvent and in ethanol at temperatures from 20°C down to −180°C (Part I) brought us to study the mechanism of proton transfer in solvents of this kind during the azo–hydrazone tautomeric transition. Instead of the so far assumed simple tautomeric equilibrium A ⇄ H, where A and H are the azo form and hydrazone form, respectively, in their monomeric forms, we suggest that a more complex equilibrium, viz.

$$\mathrm{A} + \mathrm{A} \rightleftarrows (\mathrm{AA}) \rightleftarrows (\mathrm{HH}) \rightleftarrows \mathrm{H} + \mathrm{H} \qquad (A)$$

is involved ((AA) and (HH) are the respective dimers). Formation of higher aggregates is not assumed in view of the low concentations used[7,8].

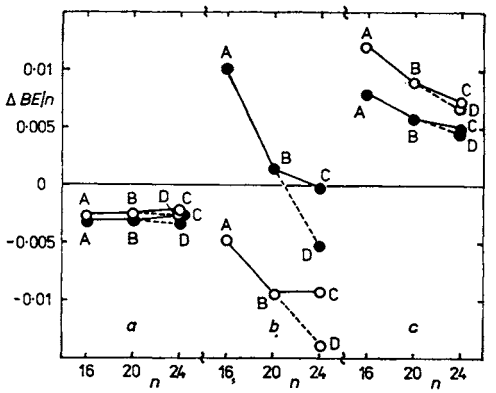


FIG. 6

Dependence of the $\Delta BE/n$ value on the extent of ring fusion *a* for the A + A ⇄ (AA) partial equilibrium, *b* for the (AA) ⇄ (HH) partial (tautomeric) equilibrium, *c* for the (HH) ⇄ H + H partial equilibrium. ○ *p*-hydroxy derivatives ● *p*-amino derivatives

Using the parameters given in Table I, we performed HMO calculations for the (AA) and (HH) dimers of the eight substances studied. In the HMO approach, however, the dimer is again treated as a molecule of the corresponding, slightly perturbed, monomer, which in turn implies that the results so obtained are consistent with those for the monomer in the azo or hydrazone form. Owing to this consistency, the aforementioned energy criterion could be also obtained for the partial equilibria A + A ⇄ (AA) (azo form monomer–dimer), (AA) ⇄ (HH) (azo–hydrazone dimer) and (HH) ⇄ H + H (hydrazone form dimer–monomer). The $(\Delta BE/n)_{A-AA}$ plots (Fig. 6*a*) exhibit nearly no dependence on the extent of ring fusion and a negligible dependence on the para substituent. The fact that the values are negative and nearly constant for all the compounds studied shows that within this quantum chemical model the A + A ⇄ (AA) equilibrium is shifted somewhat in favour of the (AA) dimer formation. The plots for the $(\Delta BE/n)_{AA-HH}$ quantity (Fig. 6*b*) exhibit a marked dependence both on the extent of ring fusion and on the *para* substitution; they resemble the plots for the simple A ⇄ H equilibrium in Fig. 1. For the *p*-hydroxyazo compounds this (AA) ⇄ (HH) tautomeric equilibrium is markedly shifted in favour of the hydrazone dimer, this shift being the larger the larger in size is the system concerned. For the *p*-amino compounds the equilibrium also shifts in favour of the (HH) dimer with increasing size of the system; the position of the plot with respect to the zero $(\Delta BE/n)$ value, however, shows that the $A(NH_2)$ system tends to remain in the (AA) form, systems $B(NH_2)$ and $C(NH_2)$ exhibit an approximately 1 : 1 (AA) ⇄ (HH) equilibrium and only for the $D(NH_2)$ system this partial equilibrium is shifted to the right side. The plots for the decomposition of the (HH) hydrazone form dimers to the monomers are shown in Fig. 6*c*. They exhibit dependences both on the ring fusion patterns and on the *para* substituent involved, this dependence, however, is less marked than that exhibited by Fig. 6*b*. This tendency to the decomposition of the dimer to the monomers increases with increasing size of the molecule; the $(\Delta BE/n)_{HH-H}$ values are all positive, hence, the (HH ⇄ H + H) equilibrium is shifted in favour of the dimer.

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