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TAUTOMERISM IN ARYLAZONAPHTHOLS BY DIPOLE MOMENT ANALYSIS[a]

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Abstract—The azo-hydrazone equilibrium in some arylazonaphthols has been studied by dipole moment measurements and HMO calculations. Results show that in 1,4-derivatives comparable amounts of both forms are present. The 1,2-derivatives appear to be essentially azo-compounds, but an overestimate of azo proportion cannot be excluded.

INTRODUCTION

The azo-hydrazone tautomerism in hydroxyazo compounds has been widely investigated by means of UV, IR and NMR spectroscopy.[1-7]

Recently, HMO calculations have been carried out on some hydroxyazo compounds to clarify the role of the aromatic ring size, H-bonding, solvent and substituent effect on the above tautomerism.[8]

A contribution presented to this problem is the dipole moment measurements and HMO calculations on some arylazonaphthols (Fig 1).

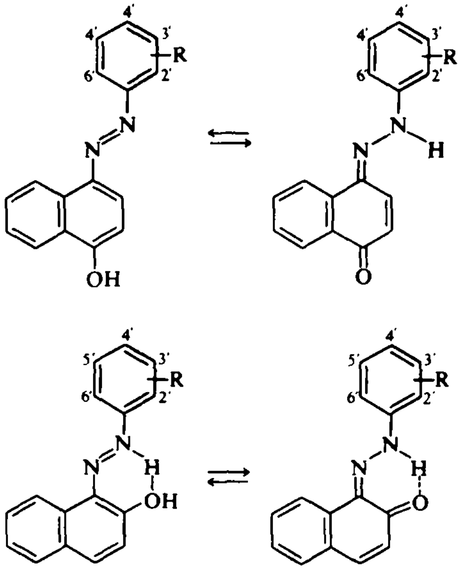

Fig 1.

EXPERIMENTAL

Electric moments were determined in dry benzene and dioxane solutions at 25° and 45° ± 0·05°. Dielectric constants were measured on a WTW Mod. DM 01 Dipolmeter ($\Delta\epsilon/\epsilon \simeq 10^{-5}$ at 2 MHz). The specific volumes were measured on an Ostwald pycnometer of about 10 ml capacity. The total solute polarization P_2 at infinite dilution was evaluated by the method of Halverstadt and Kumler.[9] The benzene dielectric constants at 25° and 45° were taken 2·2725 and 2·2350[10] respectively. The benzene density was obtained from the expression[11] $d = 0{\cdot}8737 + 1{\cdot}0688 \cdot 10^{-3} \cdot (25-t)$. The dielectric constant of dioxane was calculated from its capacity after calibrating the meter by pure benzene and air ($\epsilon = 1$); we obtained $\epsilon = 2{\cdot}2044$ and 2·1734 at 25° and 45° respectively. The densities of dioxane are taken 1·0277 at 25° and 1·0052 at 45°.[12] The terms α, β, ϵ_1, v_1 were evaluated by the mean square method. The solute molar refraction R_2 was evaluated from group and bond refractions. *o*'—, *m*'—, and *p*'—Me—, —Cl—, —OME—1-phenylazo-2-naphthols were prepared and purified as previously reported.[11]

1,2-*Naphthoquinone*-N-*diphenylhydrazone.* 0·01 M of 1,2-naphthoquinone in 50% AcOH was added to 0·01 M N-diphenylhydrazine hydrochloride in 50% AcOH. A violet soln was obtained from which a gummy substance was filtered off after about 10 min and washed with water. A benzene soln of this substance was eluated by EtOAc on neutral alumina. The product was crystallized from EtOAc, yield 40%, m.p. 175–6°. (Found: N = 8·65. Calc. N = 8·63%). λ_{max} = 478 nm, log ϵ = 4·33 in MeOH.

1,4-*Naphthoquinone*-N-*methylphenylhydrazone.* A concentrated abs EtOH soln of 2 g 1,4-naphthoquinone was added to 3 g N-methylphenylhydrazine hydrochloride in abs EtOH and stirred for 2 hr at the ice-temp. Then by adding water + ice a product precipitated which was purified by crystallization from ligroin, yield 50%, m.p. 119–20°. (Found: N = 10·72. Calc. N = 10·68%). λ_{max} = 457 nm, log ϵ = 4·39 in MeOH.

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Table 1. Dipole moments of arylazonaphthols and parameters for their evaluation

Compound	Solvent		α^a	$-\beta$	ϵ_1	v_1	R_2	P_2	μ
2-Naphthol	benzene	25°	2·029	0·377	2·2721	1·1443	42·3	88·0	1·49
	benzene	45°	1·855	0·377	2·2349	1·1730	42·3	86·0	1·51
	dioxane	25°	3·484	0·119	2·2027	0·9727	42·3	118·2	1·93
	dioxane	45°	3·172	0·146	2·1729	0·9945	42·3	112·7	1·92
1-Phenylazo-2-naphthol	benzene	25°	1·725	0·302	2·2725	1·1443	72·4	142·8	1·85
	benzene	45°	1·644	0·356	2·2351	1·1731	72·4	139·2	1·87
	dioxane	25°	1·761	0·144	2·2030	0·9730	72·4	131·1	1·69
	dioxane	45°	1·648	0·167	2·1724	0·9946	72·4	127·9	1·70
o'—Me	benzene	25°	1·078	0·341	2·2726	1·1444	77·1	115·9	1·38
	benzene	45°	1·046	0·403	2·2350	1·1730	77·1	112·7	1·36
	dioxane	25°	1·468	0·134	2·2033	0·9730	77·1	126·6	1·56
	dioxane	45°	1·436	0·147	2·1723	0·9945	77·1	127·0	1·61
m'—Me	benzene	25°	1·561	0·381	2·2717	1·1443	77·1	136·6	1·71
	benzene	45°	1·441	0·394	2·2345	1·1729	77·1	133·7	1·72
	dioxane	25°	1·874	0·087	2·2043	0·9728	77·1	147·7	1·86
	dioxane	45°	1·914	0·106	2·1723	0·9943	77·1	151·5	1·97
p'—Me	benzene	25°	1·746	0·270	2·2724	1·1443	77·1	154·4	1·94
	benzene	45°	1·685	0·309	2·2350	1·1730	77·1	152·8	1·99
	dioxane	25°	2·005	0·158	2·2042	0·9730	77·1	148·1	1·86
	dioxane	45°	1·998	0·170	2·1734	0·9945	77·1	150·6	1·96
o'—Cl	benzene	25°	3·271	0·311	2·2725	1·1441	77·3	244·0	2·85
	benzene	45°	3·068	0·358	2·2350	1·1728	77·3	237·3	2·89
	dioxane	25°	4·076	0·200	2·2032	0·9729	77·3	252·9	2·93
	dioxane	45°	3·671	0·183	2·1733	0·9943	77·3	242·2	2·93
m'—Cl	benzene	25°	2·083	0·370	2·2725	1·1444	77·3	176·0	2·20
	benzene	45°	1·992	0·341	2·2349	1·1728	77·3	179·0	2·30
	dioxane	25°	2·791	0·095	2·2033	0·9728	77·3	201·4	2·46
	dioxane	45°	2·714	0·105	2·1726	0·9942	77·3	202·1	2·55
p'—Cl	benzene	25°	1·964	0·353	2·2726	1·1444	77·3	171·1	2·14
	benzene	45°	1·910	0·396	2·2352	1·1731	77·3	170·0	2·20
	dioxane	25°	2·417	0·181	2·2039	0·9729	77·3	177·0	2·21
	dioxane	45°	2·358	0·225	2·1732	0·9946	77·3	175·4	2·26
o'—OMe	benzene	25°	1·487	0·277	2·2726	1·1445	78·8	149·7	1·86
	benzene	45°	1·513	0·348	2·2349	1·1731	78·8	149·6	1·92
	dioxane	25°	1·968	0·149	2·2028	0·9729	78·8	156·1	1·94
	dioxane	45°	1·957	0·211	2·1724	0·9947	78·8	154·6	1·99
m'—OMe	benzene	25°	1·932	0·296	2·2724	1·1444	78·8	171·4	2·12
	benzene	45°	1·839	0·315	2·2348	1·1729	78·8	170·0	2·18
	dioxane	25°	2·282	0·123	2·2041	0·9728	78·8	172·6	2·14
	dioxane	45°	2·273	0·166	2·1736	0·9946	78·8	173·1	2·22
p'—OMe	benzene	25°	2·637	0·311	2·2721	1·1441	78·8	207·0	2·50
	benzene	45°	2·377	0·278	2·2347	1·1727	78·8	202·4	2·54
	dioxane	25°	3·135	0·166	2·2026	0·9731	78·8	208·5	2·60
	dioxane	45°	2·929	0·151	2·1722	0·9945	78·8	205·7	2·57
1,2-Naphthoquinone-N-diphenylhydrazone	benzene	25°	8·760	0·302	2·2728	1·1444	98·6	615·7	5·03
	benzene	45°	8·004	0·329	2·2350	1·1731	98·6	589·3	5·06
	dioxane	25°	10·224	0·124	2·2044	0·9729	98·6	626·4	5·08
	dioxane	45°	9·496	0·176	2·1727	0·9947	98·6	602·5	5·12
1,4-Naphthoquinone-N-methylphenylhydrazone	benzene	25°	10·831	0·332	2·2716	1·1444	79·1	598·0	5·03
	benzene	45°	9·846	0·385	2·2340	1·1731	79·1	567·3	5·04
	dioxane	25°	12·080	0·099	2·2022	0·9728	79·1	589·2	4·99
	dioxane	45°	11·009	0·138	2·1716	0·9945	79·1	558·2	5·00
1,4-Naphthoquinone-N-diphenylhydrazone	benzene	25°	7·584	0·279	2·2727	1·1444	98·6	546·2	4·67
	benzene	45°	6·937	0·325	2·2353	1·1731	98·6	521·7	4·69
	dioxane	25°	8·691	0·222	2·2047	0·9730	98·6	535·2	4·62
	dioxane	45°	8·025	0·235	2·1738	0·9948	98·6	515·3	4·66

[a] $\alpha = \frac{d\epsilon_{12}}{dw_2}$; $\beta = \frac{dv_{12}}{dw_2}$; $\epsilon_1 = \lim_{w_2 \to 0} \epsilon_{12}$; $v_1 = \lim_{w_2 \to 0} v_{12}$; R_2 and P_2 solute molar refraction and total polarization, unit cc.

*1,4-Naphthoquinone-*N*-diphenylhydrazone*. To 0·01 M 1,4-naphthoquinone in 25 ml 50% AcOH was added 0·01 M N-diphenylhydrazine hydrochloride in 50% AcOH. The soln, turned violet, and was stirred for 1 hr. The filtered product was crystallized from EtOAc, yield 70–80%, m.p. 189–91°. (Found: N = 8·70. Calc. N = 8·63%). $\lambda_{max} = 462$ nm, $\log \epsilon = 4{\cdot}38$ in MeOH.

RESULTS AND DISCUSSION

Table 1 summarizes the present experimental data. It is evident that the moments are essentially the same in benzene and dioxane solutions, and that a 25° variations do not change appreciably the dipole moments both in benzene and dioxane solutions. The equilibrium constant K = [hydrazone]/[azo] is calculated by the equation:

$$\mu^2 = (1 - x) \cdot \mu_A^2 + x \cdot \mu_I^2$$

where μ is the experimental dipole moment, x the molar fraction of the hydrazone isomer, μ_A and μ_I the dipole moments of the azo and hydrazone isomers, respectively. These have been calculated as a vector composition of σ-moments, for which the usually accepted literature values were used, and π-moments calculated by the HMO method utilizing the parameters of Table 2, and the following bond lengths:

$C—C = 1{\cdot}39$ Å $C—N = 1{\cdot}43$ Å $N{=}N = 1{\cdot}25$ Å
$C{=}N = 1{\cdot}33$ Å $N—N = 1{\cdot}34$ Å $C—O = 1{\cdot}40$ Å
$C{=}O = 1{\cdot}26$ Å $C—CH_3 = 1{\cdot}49$ Å $C—Cl = 1{\cdot}74$ Å

Parameters for the substituents on the benzene ring and for the azo-group are those previously reported;[14] the k values for the bonds in the hydrazone conformation were calculated from bond lengths assuming proportionality between resonance and overlap integrals.[15] The h_O and k_{CO} parameters for the azo conformation are those which allow to reproduce the experimental dipole moment of 1-phenylazo-4-methoxynaphthalene (1·74 D at 25° in benzene[16]). The h_{NH} and h_O for the hydrazone isomer allow to reproduce the experimental moments of the hydrazone compounds in Table 1. In the *ortho* derivatives the probable rotation of the phenyl ring was accounted for around the C—N bond by considering the resonance integral β_{CN} to be a function of the twisting angle φ: $\beta_\varphi = \beta_0 \cdot \cos \varphi$, where φ is 25° in *o*′-methyl-, 31·5° in *o*′-chloro- and 40° in *o*′-methoxy-derivative.[14]

1-Phenylazo-4-naphthols. In Table 3 are reported the calculated dipole moments for the azo and hydrazone isomers, the hydrazone proportion in per cent, and the equilibrium constant for the various isomers. Results suggest that comparable amounts of both tautomers are present in this class of compound; the substituent effect on the position of the tautomeric equilibrium parallels the qualitative trend displayed by IR[17] and UV[2,18] spectroscopy. The quantitative datum which can be compared with our results is relative to *p*′-methoxy-1-phenylazo-4-naphthol for which a K = 0·25 in acetone-d_6 was found from NMR measurements.[1]

1-Phenylazo-2-naphthols. They appear to be essentially azo-compounds as can be seen from Table 4. These results can be compared with the NMR quantitative data relative to the 1-phenylazo-2-naphthol and to the *p*′-methoxy-1-phenylazo-2-naphthol; the former displays a 38% hydrazone proportion in hexane[19] and the latter a K = 1·54 in acetone-d_6.[1] Data coming from UV spectra seem to show that in these compounds both isomers are present in comparable amounts also in non-polar solvents,[20,21] but it is probable that the UV evidence overestimates the hydrazone concentration; in fact IR data for 1-phenylazo-2-naphthols show a diminution in the CO band intensity with respect to the 1,4-derivative which, at least in part, has been ascribed to a decrease in the hydrazone concentration.[17]

Our data for this class of compound seem to underestimate the concentration of the hydrazone

Table 2. Parameters used in the HMO treatment of azo-hydrazone tautomerism

Azo	Hydrazone	Substituent
$h_N = 0{\cdot}50$	$h_{NH} = 2{\cdot}00$	$h_{CH_3} = 1{\cdot}18$
$h_O = 2{\cdot}00$	$h_N = 0{\cdot}50$	$k_{CCH_3} = 0{\cdot}30$
$k_{CN} = 0{\cdot}72$	$h_O = 0{\cdot}45$	$h_{OCH_3} = 1{\cdot}20$
$k_{NN} = 0{\cdot}83$	$k_{CN} = 0{\cdot}72$	$k_{COCH_3} = 0{\cdot}60$
$k_{CO} = 0{\cdot}55$	$k_{C—N} = 0{\cdot}88$	$h_{Cl} = 2{\cdot}20$
	$k_{NN} = 0{\cdot}68$	$k_{CCl} = 0{\cdot}50$
	$k_{CO} = 0{\cdot}81$	

Table 3. Theoretical and experimental dipole moments and tautomeric equilibrium constants for 1-phenylazo-4-naphthols

Subst.	μ_A	μ_I	μ_{EXP}[a]	% I	K[c]
H	1·79	5·03	3·39	38	0·60
2′—OMe	1·67	6·14	5·30	72	2·63
6′—OMe	1·98	6·01		75	3·01
3′—OMe	2·09	5·18	3·69	41	0·70
5′—OMe	2·16	5·13		41	0·70
4′—OMe	1·98	5·49	2·63	11	0·13
2′—Me	1·92	4·81	2·95	26	0·35
6′—Me	2·04	4·74		25	0·33
3′—Me	1·69	5·09	3·24	33	0·50
5′—Me	1·81	5·01		33	0·50
4′—Me	1·61	5·28	2·91	23	0·30
2′—Cl	2·45	5·85	4·01	36	0·56
6′—Cl	2·00	6·11		36	0·56
3′—Cl	2·79	4·12	3·41	42	0·72
5′—Cl	2·44	4·48		40	0·67
4′—Cl	2·68	3·41	3·20[b]	69	2·20

[a] In benzene at 25° from reference 16.
[b] In dioxane at 25°.
[c] K = [hydrazone]/[azo].

Table 4. Theoretical and experimental dipole moments and tautomeric equilibrium constants for 1-phenylazo-2-naphthols

Subst.	μ_A[a]	μ_I	μ_{EXP}[b]	% (I)	K[c]
H	1·18	5·13	1·85	8	0·09
2′—OMe	1·17	4·00	1·86	14	0·17
6′—OMe	2·21	5·22			
3′—OMe	1·56	4·99	2·12	9	0·10
5′—OMe	1·88	5·39		4	0·04
4′—OMe	1·93	5·03	2·50	12	0·13
2′—Me	0·88	4·95	1·38	5	0·05
6′—Me	1·53	5·44			
3′—Me	0·92	4·75	1·71	10	0·11
5′—Me	1·54	5·30		2	0·02
4′—Me	1·34	4·90	1·94	9	0·10
2′—Cl	2·78	5·78	2·85	1·5	0·02
6′—Cl	1·14	3·60		59	1·41
3′—Cl	2·56	6·66	2·20		
5′—Cl	0·60	4·69		21	0·26
4′—Cl	1·60	6·10	2·14	6	0·06

[a] Calculated dipole moments values without inclusion of the hydrogen bonding effect.

[b] In benzene at 25°.

[c] K = [hydrazone]/[azo].

tautomer when compared with spectroscopic results. It must be pointed out, however, that in the calculations we have not taken into account the intramolecular H-bonding, which is present in these molecules, as is evident when we compare the dipole moments in benzene and dioxane solutions (Table 1).

Preliminary calculations carried out on the parent compound to account for this effect, by the Pullman method,[22] gave 1·85 and 5·44 D for μ_A and μ_I respectively, i.e. 100% azo-form, in contrast with any experimental evidence.

The failure of this approach can be attributed to the lack of an adequate model for the azo conformation. A possible molecular model for this might be 2-phenylazophenol (μ = 1·31 D[23]); but it was discarded because we ascertained, by means of HMO calculations, that the fusion of a second ring to the part of molecule bearing the OH group changes both entity and direction of the π-moment; besides it is not clearcut that this molecule is in the azo form at all.[20,21,24,25]

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