

Acid Strengths of Some Dinitrophenylazo-alkylphenols

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The acid strengths of thirty 4-(2',4'-dinitrophenylazo)-alkylphenols, tautomeric with alkylquinone 2',4'-dinitrophenylhydrazones, have been measured in 50 % aqueous dimethyl sulfoxide solution. For 29 of the compounds, pK_a was between 7.33 and 8.69. 3-Chloro-2,6-diisopropyl-1,4-benzoquinone 4-(2',4'-dinitrophenylhydrazone) probably is the most strongly acidic hydrazone recorded (pK_a 5.91).

The change of colour which occurs when 2,4-dinitrophenylhydrazones (DNPH's) are treated with bases¹ forms the basis of much work on the analysis of carbonyl compounds.^{2,3} The colour produced, and the NH acid strength of the hydrazones, are both influenced by the structure of the substituents on the carbonyl carbon atom.⁴ *Vice versa*, knowledge of the acid strength is of interest in identification work. The literature records pK_a values of some saturated^{4,5} and unsaturated⁴ aliphatic, unsubstituted aromatic,⁴⁻⁶ and some other⁴ DNPH's, and of a series of DNPH's of substituted benzaldehydes and acetophenones.⁶ Since different solvents were used in these works, the values can be compared only *via* compounds which are common to the series, *e.g.*, benzaldehyde DNPH. On this basis, the pK_a values of the various DNPH's lie between about 9.4 and 12.4, referred to 50 % aqueous dioxane as solvent,⁶ and with benzaldehyde DNPH at 10.90.⁶

2-Methylnaphthoquinone 4-DNPH has been measured at pK' 4.1 in ethanol containing 10 % of chloroform:⁴ this corresponds to pK_a 10.2 in 50 % dioxane. The 4-(2',4'-dinitro-6'-chlorophenylhydrazone) of thymoquinone seems to be somewhat more acidic, as indicated by its pK_a of 8.33 in aqueous ethanol.⁷ It has also been observed that some chloroquinone DNPH's dissolve in neutral ethanol with blue or green colours,⁸ and that some alkylquinone DNPHs move as greenish spots on neutral silica gel thin-layer chromatograms;⁹ this indicates partial dissociation, and a higher acidity than of the DNPH's mentioned above.

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The acid strengths of a series of alkylquinone DNP_H's have now been determined in 50 % aqueous dimethyl sulfoxide (DMSO) solution. The chromatographical properties⁹ of the compounds and their tautomerism with dinitrophenylazo-alkylphenols^{10,11} have been discussed elsewhere. For brevity, the compounds are referred to below as DNPAP's (dinitrophenylazophenols), without regard to their actual structure in the solvent used.

EXPERIMENTAL

The preparation and purification of the compounds have been described before.¹⁰ The method used for determining the pK_a values is a simplification of a standard spectrophotometric method.^{6,12} The simplification involves omitting the buffer solutions and instead adjusting the sample pH by adding small amounts of base or acid, and measuring the pH directly in the cuvette with a combination electrode. The advantages of the method include more rapid measurements, extremely low ionic strength, and reduced consumption of solvent, without sacrifice in accuracy.

Measurements. Stock solutions were prepared containing about 0.4 mg of compound in 2 ml of pure DMSO (Fluka). The alkaline spectrum was recorded (Beckman DB or DB-GT instruments at 25°) of a sample made by diluting 50–100 μ l of stock solution to 2 ml with 50 % (v/v) DMSO in a 1 cm cuvette, and injecting 5 μ l of 10⁻² N potassium hydroxide in 50 % DMSO. The amount of sample was adjusted to give an absorbance of about 0.8 at the maximum absorbance wavelength. The acid spectrum was recorded using a fresh sample of the same concentration and containing 5 μ l of 10⁻² N hydrochloric acid in 50 % DMSO.

To obtain readings in the intermediate pH range, microliter amounts of 10⁻³ N potassium hydroxide in 50 % DMSO was injected into a fresh sample to give an absorbance of about 0.2 at the alkaline maximum wavelength. The pH then was measured in the cuvette (Radiometer pH-meter Type 28, with glass/calomel electrode GK 2321 C), and immediately afterwards, the exact absorbance was read. More base then was injected to increase the absorbance slightly, *etc.* Between readings, the electrode was blotted with tissue paper. Four to eight readings were taken in the 0.2–0.7 absorbance range. After each series, the electrode was rinsed with water, wiped dry, and immersed in an aqueous buffer (Beckman pH 7.00; Radiometer pH 4.65 and 9.22) until the correct reading was obtained, usually after 5 sec. Rinsing with water and drying was repeated when returning to a new sample; the response time now was $\frac{1}{2}$ –2 min. The sample was stirred magnetically during the pH-measurements (Bel-Art Spectrophotometric Cell Stirrer), and the stirrer was left in the cuvette during the spectral readings.

The slightly soluble Nos. 28 and 31 could not be measured accurately owing to precipitation at low or intermediate pH values. No. 31 was measured at a greater dilution in a 4 cm cuvette. By starting from the alkaline side, it was possible to obtain an approximate pK_a value for No. 28. Owing to the precipitation, the full spectrum of No. 28 could not be obtained in acid solution.

Calculations. The apparent pK_a values (Table 1) were calculated from the usual buffer equation,^{6,12} assuming all activity coefficients equal to unity. The deviation within each series of readings, and between duplicate series, was ± 0.08 to 0.02 pK_a unit.

RESULTS AND DISCUSSION

Spectra. Depending on the alkylation pattern, the DNPAP's show one or two absorption bands in acid solution. No. 1 and the mono- and 3,5-dialkyl compounds (Nos. 2–15) give a single band below 406 nm. A single band, but now at 412–427 nm, is also given by the 2,3- and 2,5-substituted compounds (Nos. 16–23), whereas the 2,6-alkylated compounds (Nos. 24–30) show two bands, at 383–400 and 443–456 nm. The latter two bands may indicate the presence of a tautomeric mixture of azo and hydrazone forms, or the com-

Table 1. Apparent pK_a values and spectral data of 4-(2',4'-dinitrophenylazo)alkylphenols, or alkyl-1,4-benzoquinone 4-(2',4'-dinitrophenylhydrazones), in 50 % aqueous dimethyl sulfoxide.

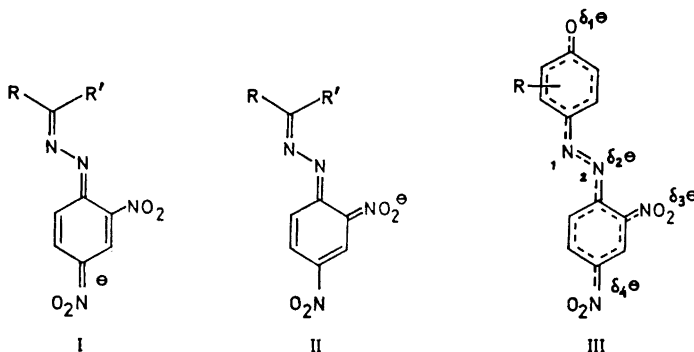
No.	Alkyl, ^a or full name	λ_{HA} nm ^b	ϵ_{HA}^c $\times 10^{-4}$	λ_{A^-} nm	ϵ_{A^-} $\times 10^{-4}$	$\epsilon_{A^-}/\epsilon_{HA}$	pK_a
1	H	387	2.12	553	3.85	1.82	8.05
2	2-Me	400	2.01	580	4.94	2.46	8.04
3	2-Et	402	2.12	590	5.07	2.39	8.04
4	2-Pr	403	2.06	595	5.21	2.53	8.00
5	2-Bu	405	2.07	604	6.11	2.95	8.27
6	2-Ph	402	1.70	586	4.24	2.49	7.92
7	3-Me	402	1.97	575	4.15	2.11	7.95
8	3-Et	402	2.06	577	4.92	2.39	8.11
9	3-Pr	404	2.15	575	4.63	2.15	7.66
10	3-Bu	405	1.94	592	4.62	2.38	8.27
11	3-Ph	398	1.59	564	3.31	2.08	7.63
12	3,5-Me ₂	402	2.18	566	4.02	1.85	8.01
13	3-Me-5-Et	403	2.27	564	4.47	1.97	8.28
14	3-Me-5-Pr	402	1.78	564	3.68	2.07	8.37
15	3-Me-5-Bu	406	1.60	576	4.00	2.50	8.27
16	2,3-Me ₂	412	2.03	603	5.50	2.71	8.13
17	2,5-Me ₂	417	2.03	599	5.50	2.71	7.86
18	2-Me-5-Pr	414	2.00	593	5.10	2.55	8.06
19	2-Pr-5-Me	417	2.19	596	6.26	2.86	8.10
20	2-Bu-5-Me	421	1.67	601	5.06	3.03	8.31
21	2,5-Pr ₂	417	2.20	598	6.28	2.86	7.99
22	2,5-Bu ₂	427	1.75	614	6.72	3.84	8.69
23	2,3,5-Me ₃	412	1.85	596	4.63	2.50	8.53
24	2,6-Me ₂	(383) 443	1.37	604	4.22	3.08	7.46
25	2-Bu-6-Me	(400) 455	2.57	612	5.78	2.28	7.68
26	2,6-Pr ₂	(399) 454	2.80	612	7.50	2.68	7.33
27	3-Cl-2,6-Pr ₂	(394) 452	3.33	606	6.10	1.83	5.91
28	2,6-Bu ₂	^d 456	2.78	613	8.04	2.89	8.4 ^g
29	2,3,6-Me ₃	(397) 453	2.81	610	6.08	2.19	7.95
30	2,3,5,6-Me ₄	(392) 445	2.02	608	4.59	2.27	8.59
<i>DNPH's of:</i>							
31	Benzaldehyde	402	2.83	472 ^e	3.25 ^e	1.15	11.48
32	Phorone	400	2.63	475 ^f	2.27 ^f	0.87	13.36

^a Me=methyl; Et=ethyl; Pr=isopropyl; Bu=*tert*-butyl; Ph=phenyl. ^b Values in parentheses are graphically resolved, submerged bands. ^c Main band only. ^d Unresolved, submerged band present (*cf.*, Experimental). ^e Submerged band at 550 nm ($\epsilon \approx 1.44 \times 10^4$). ^f Submerged band at 568 nm ($\epsilon \approx 1.37 \times 10^4$). ^g Approximate value (*cf.*, Experimental).

pound may exist entirely in the hydrazone form, which is known¹³ to give two bands. The intermediate position of the single band of Nos. 16–23 suggests it to be composed of two overlapping, closely spaced bands. By comparison with determinations of the tautomeric composition of similar com-

pounds in other solvents,^{10,14} Nos. 1 and 6–15 probably are pure azo in 50 % DMSO; Nos. 2–5 and 16–26 tautomeric mixtures; and No. 28, perhaps also Nos. 27, 29, and 30, pure hydrazones. The tentative assignments of the two bands of the hydrazone and the single band of the azo form in tetrachloroethylene solution have been discussed before.¹³ The same assignments apply also to the present spectra in acid, 50 % DMSO.

In basic solution, ordinary DNPH's give two bands (*cf.* Fig. 1: A), which have been assigned to the separate transfers of charge to the two nitro groups



(I–II).² This assignment does not fit the single band given by the DNPAP anions, except if one assumes degeneracy between the transitions corresponding to I and II. The consistent occurrence of a single band, independent of the probable tautomeric composition (Fig. 1: 1, 14, 19, 28), thus indicates structure III for the mesomeric, common anion in the ground state. This structure is supported by the long wavelengths of absorption in basic solution relative to saturated DNPH's (about 440 nm^{2,4}), and by the ratio between the absorptivities in basic and acid solution, which is about 2–4 for the DNPAP's *vs.* about 1 or less for saturated DNPH's.^{4,6}

Alkylation in 2- and 2,6-position leads to a red-shift of the absorption maximum in basic solution, relative to 3- and 3,5-alkylation. This resembles the effect of alkyl on the tautomeric composition in tetrachloroethylene solution,¹⁰ where 2- and 2,6-alkyl lead to much higher contents of hydrazone than do 3- and 3,5-alkyl. Probably the redshift is caused by the larger partial charge on nitrogen 2 with 2- and 2,6-alkyl, as was assumed for the contents of hydrazone.¹⁰ If so, the basic absorption wavelength of a given DNPAP, relative to a definitely non-hydrazonic DNPAP (*e.g.*, No. 1 in 50 % DMSO), may be taken as a measure of the tautomeric composition.

Acidities. Recalculation of the acidity values given by Timmons,⁴ which are in fact $-pK'_b$ values, using phorone DNPH (No. 32) as a reference compound, gives 10.5–13.5 as the probable range of pK'_a of his series of aliphatic and aromatic DNPH's when transferred to 50 % DMSO. Similar calculations on the values given by Jones and Mueller⁶ indicate 11.0–12.2 as the probable range for their aromatic DNPH's in 50 % DMSO. In this relation the DNPAP's are more acidic by 1.8 pK'_a units or more.

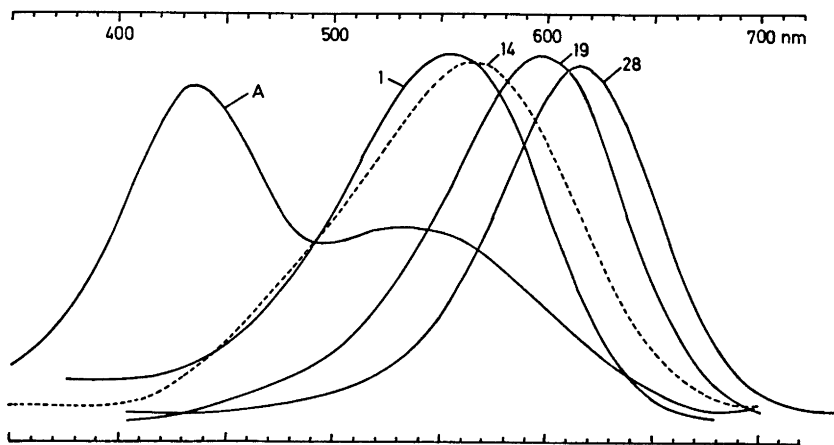


Fig. 1. Ultraviolet-visible spectra of dinitrophenyl-hydrazones and dinitrophenylazo-phenols in alkaline, 50 % aqueous dimethyl sulfoxide solution. Numbers refer to Table 1. A = 2-Butanone 2,4-dinitrophenylhydrazone.

Owing to the limited solubility of the DNPAP's in 50 % DMSO, it was not possible to determine the tautomeric composition and, hence, the acid strengths of the individual tautomers¹⁵ with any certainty. A detailed discussion of substituent and positional effects of the alkyl groups therefore is not worthwhile. However, chlorine (No. 27) exerts the ordinary inductive effect, which seems to be effectively transmitted across the C=N-N bridge: No. 27 probably is the most strongly acidic DNPH recorded, being at least 4.6 pK_a units more acidic than ordinary DNPH's, and 1.4 units more than No. 26.

Similarly, the mesomeric effect of the C=O group of the hydrazone Nos. 24-26 and 28-30 is transmitted to the NH group, as judged from their higher acidities relative to ordinary DNPH's. On the other hand, No. 32 is about 2 units less acidic than saturated DNPH's: in the absence of C=O conjugation, C=C conjugation decreases, rather than increases, the acidity. Thus, the conclusions of Jones and Mueller,⁶ that mainly the dinitrophenyl group is responsible for the acidity of DNPH's, and that transmission across the hydrazone bridge does not occur with any great facility, seem to be valid only for hydrazones without inductive or mesomeric groups.

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