Ultraviolet — Visible Spectra of Azophenols:

# Absorption of the Hydrazone Form in the "Azo Region"

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The ultraviolet – visible spectra of the hydrazone tautomer of 4-(2',4'-dinitrophenylazo)-alkylphenols show two distinct absorption maxima, at about 383 – 402 and 417 – 440 nm, in tetrachloroethylene solution. The shorter-wavelength band occurs in the same region as the main band of the azo tautomer, and thus interferes with the detection of that form. Similar spectra are given by quinone 2'-nitrophenylhydrazones, and by the N-methyl derivatives of quinone 2'- and 4'-nitro- and 2',4'-dinitrophenylhydrazones. The longer-wavelength maximum is tentatively assigned to the degenerate transitions of the NH nitrogen lone pair to the nitro groups and the quinone oxygen, and the shorter-wavelength band is proposed to be the displaced, next-lower band among the four commonly found in dinitrophenylhydrazones.

Ever since the work of Kuhn and Bär[1] it has been generally assumed[2,3] that the hydrazone species (I) of the arylazophenol – quinone arylhydrazone tautomeric system absorbs at a longer ultraviolet – visible (UV) wavelength than the azophenol (II). *Vice versa*, it has been assumed that substances of this type are actually present as equilibrium mixtures of the two forms whenever the UV spectra of their solutions[4–7] or of the solids[6,7] show two bands at the appropriate positions. The assignment of the bands originally was deduced[1,4] from the spectra of the O- and N-methylated species, which represent unambiguous azo and hydrazone structures; later, it has been confirmed by relation to the infrared[7] and nuclear magnetic resonance[8,9] spectra. It will appear from the results reported below, however, that UV spectroscopy is less generally useful for detecting and studying tautomerism than was formerly believed: several quinone 2',4'-dinitrophenylhydrazones (DNPHs) and 2'-nitrophenylhydrazones (2'-NPHs), which are 100 % hydrazones according to infrared,[10] show two distinct UV maxima, the lower of which coincides with

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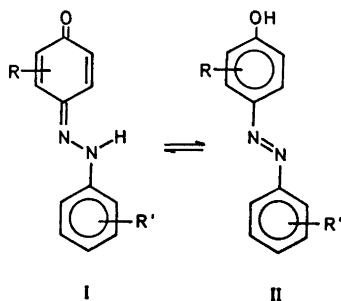
the maximum of the azo tautomer. This would induce the erroneous conclusion that a considerable proportion of the azo form were present.

EXPERIMENTAL

The preparation and purification of compounds Nos. *1 − 30, 36 − 39*, and *42 − 45* (Table 1) are described elsewhere.[10] The *N*-methyl hydrazones were prepared by treating the quinone with the appropriate 1-methyl-1-arylhydrazine [11] in hot, 2 N ethanolic hydrochloric acid (Nos. *32, 33, 36, 40, 46, 56*), or in anhydrous formic acid at room temperature (No. *31*), and purified by preparative-layer chromatography (PLC)[10] on silica gel. Oxidation of the hydrazine to *N*-methyl-mono- or -dinitroaniline, and demethylation of the hydrazone, were troublesome side reactions. The *O*-methyl azo compounds Nos. *34, 35, 41*, and *47* were made from the dinitrophenylazophenol with diazomethane in ether solution, followed by PLC.

Table 1. Ultraviolet − visible spectra of dinitrophenylazophenols and related compounds in tetrachloroethylene solution.

No.	R in I or II [a,b]	Lower band [c,d,e]		Higher band [d,e,f]		Int. ratio [g]	% NH [h]	$\Delta\lambda$ nm [f]
		λ nm [f]	$\varepsilon \times 10^{-4}$	λ nm [f]	$\varepsilon \times 10^{-4}$			
	$R' = 2',4'-(NO_2)_2$							
1	H	383		—			8	
2	2-Me	393	2.61	429	2.59	0.99	60	36
3	2-Et	393		430		1.04	64	37
4	2-Pr	394		433		1.09	68	39
5	2-Bu	394		435		1.19	84	41
6	2-Ph	394	1.87	—			4	
7	3-Me	392	2.08	(430)	(0.84)	0.40	25	(38)
8	3-Et	391	2.07	(427)	(0.59)	0.29	27	(36)
9	3-Pr	396	2.74	(432)	(0.67)	0.24	19	(36)
0	3-Bu	392		(428)		0.35	20	(36)
1	3-Ph	396	2.06	—			7	
2	3,5-Me₂	399		—			22	
3	3-Me-5-Et	402		—			15	
4	3-Me-5-Pr	395		—			14	
5	3-Me-5-Bu	402	2.40	—			14	

(Table 1, continued)

16	2,3-Me$_2$	398		434		1.18	80	36
17	2,5-Me$_2$	391		428		1.16	90	37
18	2-Me-5-Pr	392		427		1.12	89	35
19	2-Pr-5-Me	393	3.49	430	3.96	1.14	94	37
20	2-Bu-5-Me	393		430		1.14	91	37
21	2,5-Pr$_2$	396	2.06	432	2.34	1.14	93	36
22	2,5-Bu$_2$	395		431		1.09	97	36
23	2,3,5-Me$_3$	389		417		0.98	81	28
24	2,6-Me$_2$	397		437		1.25	95	40
25	2,6-Pr$_2$	400		440		1.24	98	40
26	2-Me-6-Bu	398		437		1.24	98	39
27	3-Cl-2,6-Pr$_2$	395	2.66	440	4.00	1.49	100	45
28	2,6-Bu$_2$	401	2.86	440	3.31	1.14	100	39
29	2,3,6-Me$_3$	399	4.02	435	4.56	1.16	100	36
30	2,3,5,6-Me$_4$	391	3.08	421	2.94	0.90	100	30
31	H N-Me-(I)	(345)		426		3.84		(79)
32	2-Pr-5-Me N-Me-(I)	346	0.79	448	1.20	1.72		102
33	2,6-Bu$_2$ N-Me-(I)	351		446		2.32		95
34	H O-Me-(II)	390		—				
35	2-Pr-5-Me O-Me-(II)	414		—				
	$R' = 2'$-NO$_2$							
36	3-Et	364	2.12	444	0.36	0.17	10	70
37	2-Pr-5-Me	399	2.35	449	1.82	1.28	82	50
38	2,6-Pr$_2$	395	1.96	457	3.22	1.64	93	62
39	2,6-Bu$_2$	395	1.69	457	2.56	1.49	100	62
40	2-Pr-5-Me N-Me-(I)	(368)		435		1.68		(67)
41	2-Pr-5-Me O-Me-(II)	375						
	$R' = 4'$-NO$_2$							
42	3-Et	378	3.94	—			0	
43	2-Pr-5-Me	387	1.99	—			0	
44	2,6-Pr$_2$	386	2.80	—			0	
45	2,6-Bu$_2$	386		(449)		0.21	4	(54)
46	2-Pr-5-Me N-Me-(I)	346		453		2.35		107
47	2-Pr-5-Me O-Me-(II)	391		—				

[a] Or in derivatives of I or II, as remarked. [b] Me = methyl; Et = ethyl; Pr = isopropyl; Bu = *tert*-butyl; Ph = phenyl. [c] Lower band of hydrazone form, or main band of azo form, or both. [d] Main band of hydrazone form. [e] ε is in 1 mol^{-1} cm^{-1}. [f] Values in parenthesis are geometrically resolved, submerged bands. [g] Intensity ratio higher/lower band. [h] Percentage of hydrazone form, according to infrared spectra (Ref. 10).

Compounds Nos. *48 − 55* were made in the usual way.[12] Of Nos. *52 − 55*, the main isomer (*trans*, or *E* [13]) was isolated by PLC, and its identity checked by infrared spectra in tetrachloroethylene solution. Compounds Nos. *48, 49,* and *51* probably are *E* isomers as obtained.[14,15] Compounds Nos. *57,*[16,17] *58,*[18,19] and *59* [20] were made according to published methods, and Nos. *60 − 62* by coupling of 2,4-pentanedione with the appropriate diazonium tetrafluoroborate [21] in acetic acid solution.

UV spectra were recorded of $2 − 5 \times 10^{-5}$ M solutions in Merck Uvasol tetrachloroethylene, or in Fluka *p.a.* acetonitrile, using a Beckman DB instrument and 10 mm quartz cells, usually at 25°.

Table 2. Ultraviolet − visible spectra of 2,4-dinitrophenylhydrazones in tetrachloroethylene solution.[a]

No. Carbonyl comp. and hydrazone[b]		para[c] band λ nm	ortho[c] band λ nm[d]	$\Delta \lambda$ nm[e]	Int. ratio[f]
48	2-Butanone DNPH	351	(425)	74	0.16
49	3-Methyl-2-butenal DNPH	371	(440)	69	0.21
50	Phorone DNPH	382	(453)	71	0.21
51	Benzaldehyde DNPH	366	(433)	67	0.22
52	2-Furaldehyde DNPH	374	(440)	66	0.21
53	Ethyl pyruvate DNPH	347	(393)	46	0.33
54	Methylglyoxal 1-mono-DNPH	338	(381)	43	0.42
55	Methylglyoxal 2-mono-DNPH	341	(390)	49	0.33

[a] Molar absorptivities were not determined. [b] Isomerism: *cf.* Experimental section. [c] Assignment: *cf.* text. [d] Values in parenthesis are for geometrically resolved, submerged bands. [e] $\lambda_{ortho} - \lambda_{para}$. [f] Intensity ratio *ortho/para* band, by graphical analysis.

RESULTS

The "azo" and "hydrazone" absorption regions (about 400 and 450 nm, respectively) of the series of dinitro compounds (Nos. *1−30*) are defined [1,4] approximately by the spectra of the *N*- and *O*-methyl compounds Nos. *31−35* (*cf.* Fig. 1: *31*, *32*, and *34*). Two bands are found in these regions in most of the compounds. The maxima are particularly well developed (*cf.* Fig. 1: *2*
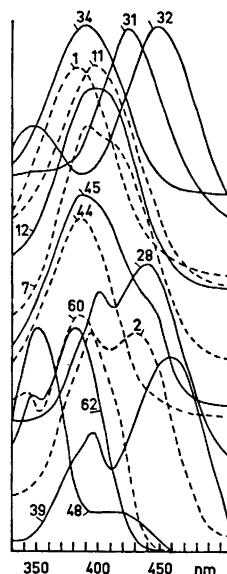

Fig. 1. Ultraviolet − visible spectra of quinone hydrazones and azophenols in tetrachloroethylene solution. Numbers refer to the tables. The spectra are vertically displaced for clarity. The absorbances are arbitrary.

and *28*) in compounds Nos. *2 − 5*, and *16 − 30*, which all contain much of the
hydrazone tautomer (60 − 100 %[10]). In these compounds, the lower
band (389 − 401 nm) is always the minor one (40 − 65 % relative intensity,
by graphical analysis), and it coincides fairly exactly with the band given by
the azo tautomer (394 − 402 nm). When less hydrazone is present, the higher
band is reduced in the same measure (Fig. 1: *7, 12, 11, 1*). When the molecule
is locked in the hydrazone structure by *N*-methylation (Nos. *31 − 33*), two
bands are still present, but the lower band is shifted towards the blue.

Two bands are found also in the compounds of the 2′-nitro series (Fig. 1: *39*);
here, the two regions are farther apart, and the lower band of the hydrazone
occurs some 20 nm higher than the azo band. With *N*-methyl (No. *40*), there
are still two similar bands.

In the 4′-nitro series, which are usually pure azo compounds,[10] there is a
single, practically symmetrical band in the azo region (Fig. 1: *44*). Only No. *45*
gives two additional shoulders (*cf.* Fig. 1), of which that at the higher wave-
length perhaps is due to the 4 % of hydrazone tautomer present,[10] as deduced
from the *N*-methyl derivative No. *46*. The latter, which has the hydrazone
structure, again shows two bands.

Two bands, very similar to those found in the quinone DNPHs and 2′-
NPHs, are also shown by di-heteroconjugated DNPHs and 2-NPHs,[22] as
exemplified by Nos. *60* and *62* (Table 3, and Fig. 1). The corresponding 4-
nitro compounds (No. *61*) show a single band, however.[22]

Table 3. Ultraviolet − visible spectra of hydrazones and azo compounds in acetonitrile
solution.

No.	Compound [a]	λ nm[b]; $\varepsilon \times 10^{-4}$ [b,c]				
33	2,6-Bu$_2$-benzoquinone	(222)	284	(348)	446	
	N-Me DNPH	d	d	d	d	
46	2-Pr-5-Me-benzoquinone	(258)	(296)	(355)	461	
	N-Me 4′-NPH	(0.86)	(0.76)	(0.76)	2.77	
56	Benzoquinone *N*-Me 4′-NPH	(236)	(260)	(295)	(342)	443
		(0.32)	(0.48)	(0.42)	(0.32)	3.13
57	2-Nitroazobenzene	229	(269)	316	435[e]	
		1.12	(0.70)	1.76	0.060	
58	2,4-Dinitroazobenzene	231	(260)	331	444[e]	
		1.14	(0.86)	2.19	0.078	
59	1-(2′,4′-Dinitrobenzeneazo)-	231	270	405		
	2,3-Me$_2$-butadiene	1.17	0.43	1.71		
60	2,3,4-Pentanetrione 3-(2′-NPH)	(228)	(244)	(278)	(330)	390
		(1.67)	(1.90)	(1.70)	(2.24)	2.99
61	2,3,4-Pentanetrione 3-(4′-NPH)	237	(297)	375		
		0.93	(0.26)	3.07		
62	2,3,4-Pentanetrione 3-(DNPH)	243	(275)	(337)	383	
		1.01	(0.74)	(1.01)	2.41	

[a] Abbreviations: *cf.* footnote *b* to Table 1, and text. [b] Values in parenthesis are for graphi-
cally resolved bands. [c] ε is in l mol^{-1}cm^{-1}. [d] Not determined. [e] $n \rightarrow \pi^*$ band.

DISCUSSION

Hydrazone spectra. Since DNPHs are derivatives of benzene, their spectra may generally be regarded as modified benzene spectra, where the bands are displaced and their intensity altered under the influence of the substituents.[23,24] More specifically, of the two bands found at long wavelengths in aliphatic and aromatic DNPHs (*cf.* Fig. 1: *48*), the main one has been considered to represent the charge-transfer transition from nitrogen 2 to the *para* nitro group (III), and the shoulder, the analogous transition to the *ortho* group (IV).[14]

III   IV   V   VI
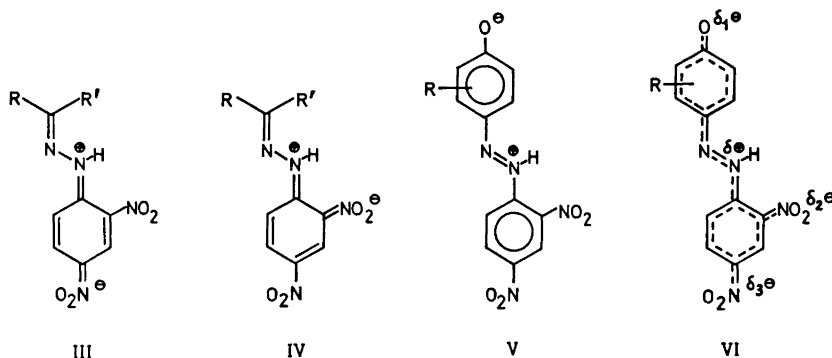
This assignment was based on the observation that 2-NPHs absorb at longer wavelengths, and with less intensity, than the corresponding 4-NPHs.[14] The similar spectra found in 2,4-dinitroaniline and its *N*-monoalkyl derivatives were interpreted in the same way.[25]

This assignment apparently cannot be applied uncritically to the spectra of quinone DNPHs, or di-heteroconjugated DNPHs of the type of No. *62*, since the minor band now occurs to the other side of the main band (*cf.* Fig. 1: *28*), and is sharper and stronger ($\Delta\lambda_{\frac{1}{2}} \approx 25$ nm; $40-65$ % rel. intensity) than that of ordinary DNPHs ($\Delta\lambda_{\frac{1}{2}} \approx 60$ nm; $20-25$ %). Moreover, according to the same interpretation [14] quinone 2'-NPHs and di-heteroconjugated 2-NPHs should give a single band only, whereas two bands are actually present (*cf.* Fig. 1: *39* and *60*).

Therefore, the main band of the quinone DNPHs is now proposed to arise from the degenerate transitions to the nitro groups and the quinone oxygen (III≡IV≡V), while the minor band probably is identical to the displaced, next-lower band among the four bands commonly occurring in DNPHs.[23]

As regards the main band, the assumption of overlap between III and IV finds support in the observation that the distance between the III and IV bands is noticeably shorter in mono-heteroconjugated (*cf.* Nos. *53−55*) than in ordinary saturated, unsaturated, or aromatic DNPHs (Ref. 23, and Table 2); hence, it may be expected to be still shorter in the quinone and di-hetero-conjugated DNPHs, in which the degree of conjugation is still higher. Further, since this overlap is obviously induced by the presence of the cross-conjugated quinone ring, the strongly electron-withdrawing quinone oxygen probably

takes part to some extent in the partial delocalisation; this leads to VI as a tentative structure of the ground state. The extension of the absorbing electron system beyond the C=N bond is indicated by the higher molar absorptivity and longer wavelength maxima of quinone DNPHs ($3-4 \times 10^4$; $420-440$ nm; cf. Nos. 24-27), compared to those of saturated DNPHs ($2-3 \times 10^4$, $350-370$ nm [23],[26]). Similarly, electron-attracting groups in para-position of aromatic DNPHs also lead to a slight increase in absorptivity.[14],[26],[27] An even more obvious example of degeneracy analogous to the excitation of VI is found in the single-band spectra of the probably completely delocalised anions of quinone [28] and mono-[22],[29] and di-heteroconjugated [22] DNPHs; this is contrasted by the anions of ordinary, nonheteroconjugated DNPHs, which give two bands.[23],[29],[30] The latter bands have been assigned to the separate transfers of charge to the two nitro groups.[30] The spectra of quinone DNPH anions are further discussed elsewhere.[28]

Structures similar to VI are proposed for the ground state of quinone 2'-NPHs, and for the N-methyl derivatives of quinone DNPHs, 2'-NPHs, and 4'-NPHs, to account for the main band in their two-band spectra. Similarly, excitation of VII explains the main band of the di-hetero-conjugated DNPHs, and analogous structures are adopted for the ground states of di-heteroconjugated 2-NPHs and 4-NPHs, e.g., Nos. 60 and 61.

As to the minor band, the next-lower band of ordinary DNPHs is proposed to be displaced to the close vicinity of the main band in the quinone DNPHs,

VII   VIII
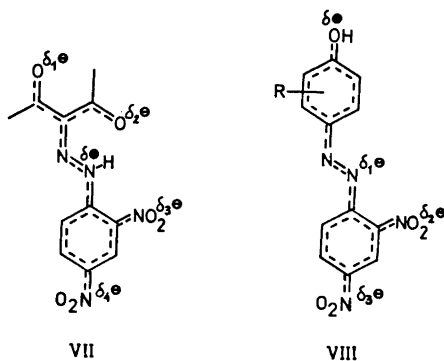
as a result of the presence of the cross-conjugated quinone oxygen. Similar shifts towards the red on introduction of unsaturation are observed for all the four bands usually given by DNPHs,[23] and the shift may be expected to be greater with heteroconjugation, as was found for the band distance discussed above. Since the minor band thus is probably due to a local transition in the substituted benzene ring, it should occur in 2-NPHs and 4-NPHs as well. The apparent lack of it in the di-heteroconjugated 4-NPHs (cf. No. 61) may be due to overlap with the main band, since the latter occurs at lower wavelengths than in the corresponding 2-NPHs and DNPHs (cf. Nos. 60-62), and introduction of a 4-nitro group in a 2-NPH (to give a DNPH) results in a red shift of the minor band (No. 60 vs. No. 62).

Azo spectra. The existence of a "single" band in the spectra of the azo tautomer (Nos. *1, 6, 11 – 15; cf.* Fig. 1: *1, 11*) seems to be characteristic of the azo structure, since the same is found in the *O*-methyl compounds (Nos. *34* and *35; cf.* Fig. 1: *34*) and in simple azo compounds (Nos. *57 – 59*). The absence of sp^3 electrons on nitrogen 2 excludes transitions of the types III and IV, whereas excitation of the sp^2 electrons $(n \rightarrow \pi^*)$ is forbidden.[31] A very weak band at about 440 nm due to the latter transition is found in the simple azo compounds Nos. *57* and *58*, but not in the other azo compounds examined, probably because it is masked by the main band.

The main band hence is probably the usual "conjugation" (K) band [24] of azo compounds, shifted to long wavelengths by the combination of electron-donating and -withdrawing substituents on the rings: the ground state may be represented by VIII, and on excitation, degeneracy between the transitions to the nitro groups and the strongly electron-attracting nitrogen 2 is postulated. The absence of the cross-conjugated oxygen atom characteristic of the hydrazone structure may explain the "absence" of a minor band close to the main band: the distance between the main band and the next-lower band is noticeably longer in the azo compounds (*cf.* Table 3).

It is noted that whereas 2-NPHs seem to absorb generally at longer wavelengths than 4-NPHs or DNPHs,[14] (*cf.* also Nos. *60 – 62*), this sequence is reversed in the case of azo compounds (*cf.* Nos. *35, 41, 47,* and Nos. *58, 59*). This perhaps is another indication that the main bands of the hydrazone and azo tautomers are of different origin.

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