ACTA CHEMICA SCANDINAVICA 27 (1973) 1645–1652

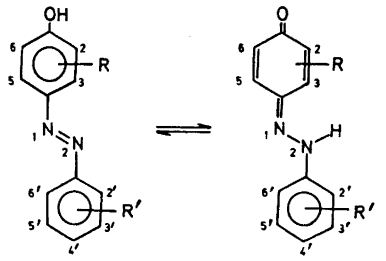
Tautomerism of Mono- and Dinitrophenylazo-alkylphenols

PAUL JUVVIK and BJØRN SUNDBY*

Chemical Institute, The University of Bergen, N-5000 Bergen, Norway

The tautomerism between azophenolic and hydrazonic structures of 4-(2′,4′-dinitrophenylazo)-alkylphenols in tetrachloroethylene solution has been studied by infrared spectroscopy. The tautomeric composition varies between 0 and 100 % hydrazone according to the alkyl substitution. The alkyl groups increase the hydrazone proportion apparently by inductive effects. Large groups in both *meta* positions to hydroxyl sterically prevent formation of the hydrazone and destabilise the azo form. The corresponding 4-(2′-nitrophenylazo)-alkylphenols parallel the dinitro series, but with slightly lower contents of hydrazone. 4-(Phenylazo)- and 4-(4′-nitrophenylazo)-alkylphenols are all pure azo, except 4-(4′-nitrophenylazo)-2,6-di-*tert*-butylphenol (4 % hydrazone). The main conditions for stabilising the hydrazone form appear to be, the presence of a 2′-nitro group, and the presence of one or better two alkyl groups *ortho* to hydroxyl. Appreciable amounts of hydrazone are not formed unless both conditions are fulfilled.

Through the years the tautomerism between *p*-arylazophenols (I) and *p*-quinone arylhydrazones (II) has been investigated extensively on compounds derived from phenols, anthranols, and particularly naphthols. The work has been dealt with in a number of reviews.[1–6] On basis of the early work [7–10] compounds from the phenol series were long assumed to exist in the azo form only.[1,2,11,12]



I II

* Present address: Division of Chemical Oceanography, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada.

Later studies by proton magnetic resonance (PMR)[13,14] have shown that substitution by nitro on the phenyl ring of 4-phenylazophenols results in the appearence of the hydrazone form. Similar effects have been found in azoanthranols[15] and azonaphthols.[9,16] A recent PMR study of phenylazophenols[17] indicates that the hydrazone form is favoured by a "push-pull" substitution of electron-donating groups on the phenol ring and withdrawing ones on the other ring: for the first time the existence of 100 % hydrazonic compounds in the phenylazophenol series was reported.

The tautomerism of 4-(2′,4′-dinitrophenylazo)-alkylphenols and mononitro analogs has now been studied in tetrachloroethylene solution, and the tautomer composition was found to vary strongly with the substitution pattern of alkyl. The slight solubility of many of the compounds in this solvent precluded recording of the PMR spectra, but most of the compounds are sufficiently soluble to give good quality infrared spectra in the OH and NH stretch region, provided long-path cells are used.

EXPERIMENTAL

Compounds. Most of the compounds were prepared by diazo-coupling of the corresponding phenols. Compounds 1, 20, 27 – 33, 35 – 37, 39 – 41, 47, and 48 were prepared from the quinone and the appropriate hydrazine in aqueous ethanol containing a little hydrochloric acid. The crude products usually contained numerous impurities in small amounts, which could not be removed by recrystallisation. All compounds were purified by repeated preparative layer chromatography on 1 – 1.5 mm layers of Merck Kieselgel PF_{254}, using chloroform or dichloromethane, or mixtures of petrol ethers or toluene with acetone, dioxane, esters, ethers, *etc.*, as solvents. The 3,5-dialkyl compounds partially decomposed on the layer; the extent of decomposition increased with increasing size of alkyl. 3,5-Di-*tert*-butylphenol coupled quantitatively to the *ortho* product.

Spectra. Infrared spectra were recorded with Unicam SP 100 and SP 200G instruments. Solutions in tetrachloroethylene were measured at 25° in 8.3 mm cells at $2-4\times10^{-3}$ M concentration to obtain the C=O band, and in 41 mm cells at $2-6\times10^{-4}$ M concentration to obtain the OH and NH bands. Spectra of the least soluble compounds (Nos. 1, 6, 7, 11, 12, 17, 18, 32, 33) were recorded with saturated solutions ($1-2\times10^{-4}$ M) up to 100° in electrically heated 41 mm cells. The intensities of the NH and OH stretching bands are given in Table 1 as *apparent* molar absorptivities ε_{app} calculated from the total concentration.

CALCULATIONS

The percentage of hydrazone tautomer (% NH) in tetrachloroethylene solution was estimated from the 3300 cm^{-1} NH and 3600 cm^{-1} OH stretching bands using eqn. (1).

$$\% \text{ NH} = 100A_{NH}/(A_{NH} + \alpha_{av}A_{OH}) \quad (1)$$

A_{NH} and A_{OH} are the band absorbances, and $\alpha_{av} = \varepsilon_{NH\,av}/\varepsilon_{OH\,av}$ is the ratio between the average molar band absorptivities of selected reference compounds with a 100 % hydrazone (Nos. 28 – 31 and 37) or azo (Nos. 38 – 40) structure. With the reference compounds mentioned, $\varepsilon_{NH\,av} = 121$; $\varepsilon_{OH\,av} = 298$; and $\alpha_{av} = 0.406$. This method was chosen because it to some extent corrects for casual impurities; this is not attained when one tautomer is determined by difference.

Table 1. Infrared spectral data and tautomer composition of 4-(substituted phenyl)-azophenols and related compounds in tetrachloroethylene solution.

No.	R in I ⇌ II,[a] or hydrazone	C=O[b] cm^{-1}	NH cm^{-1}	NH ε_{app}	OH cm^{-1}	OH ε_{app}	% NH	4-Nitroso-R-phenol: % oxime in $CDCl_3$ (Ref.)
	R′ = 2′,4′-dinitro							
1	H	0	3292	11	3590	310	8	83[18]
2	2-Me	1619	3301	72	3598	119	60	97.9[18]
3	2-Et		3301	70	3596	96	64	98.7[18]
4	2-Pr		3301	79	3595	91	68	98.8[18]
5	2-Bu	1620	3301	85	3590	40	84	99.4[18]
6	2-Ph		3298	6	3539	315	4	
7	3-Me		3300	29	3592	218	25	97[22]
8	3-Et		3300	27	3593	182	27	
9	3-Pr		3297	24	3589	252	19	
10	3-Bu	1616sh	3299	25	3589	246	20	99[22]
11	3-Ph		3295	8	3591	252	7	
12	3,5-Me_2		3328	31	3587	264	22	94[22]
13	3-Me-5-Et		3333	19	3593	262	15	
14	3-Me-5-Pr	1617sh	3331	17	3592	268	14	
15	3-Me-5-Bu		3332	18	3591	274	14	
16	3,5-Pr_2[c]		0		3608	(254)	0	
17	2,3-Me_2	1619	3302	93	3597	58	80	
18	2,5-Me_2		3303	104	3597	29	90	
19	2-Me-5-Pr	1618	3302	93	3594	30	89	
20	2-Pr-5-Me	1616	3302	93	3594	14	94	> 99.8[22]
21	2-Bu-5-Me	1620	3301	95	3605	22	91	> 99.8[22]
22	2,5-Pr_2		3300	92	3589	18	93	
23	2,5-Bu_2	1620	3300	94	3591	7	97	
24	2,3,5-Me_3	1618	3333	124	3593	73	81	
25	2,6-Me_2	1622	3301	99	3605	12	95	> 99.9[18]
26	2-Me-6-Bu	1618	3301	93	3613	6	98	
27	2,6-Pr_2	1616	3298	120	3601	5	98	
28	3-Cl-2,6-Pr_2	1616	3297	115	0		100	
29	2,6-Bu_2	1615	3300	109	0		100	> 99.94[18]
30	2,3,6-Me_3		3303	114	0		100	> 99.8[22]
31	2,3,5,6-Me_4	1625	3332	132	0		100	
32	1,4-Naphthoquinone DNPH		3302	135[d]	0		100[d]	
33	2-Me-1,4-naphthoquinone		3306	83[d]	0			
	4-DNPH		3366	36[d]	0		100[d]	
	R′ = 2′-nitro							
34	3-Et		3296	9	3587	213	10	
35	2-Pr-5-Me		3297	102	3587	57	82	
36	2,6-Pr_2	1612	3297	99	3602	18	93	
37	2,6-Bu_2	1616	3304	133	0		100	
	R′ = 4′-nitro							
38	3-Et		0		3563	322	0	
39	2-Pr-5-Me		0		3592	282	0	
40	2,6-Pr_2		0		3602	291	0	
41	2,6-Bu_2		3352	8	3628	429	4	

Table 1. Continued.

	Miscellaneous					
42	4-Ph-azophenol		0	3596	328	0
43	4-Ph-azo-2,6-Pr_2-phenol			3607	224	0
44	4-Ph-azo-2,6-Bu_2-phenol		0	3632	326	0
45	4-(2′-Tolylazo)-2,6-Bu_2-phenol		0	3635	336	0
46	4-(3′-nitro-Ph-azo)-2,6-Bu_2-phenol		0	3630	497	0
47	Thymoquinone 4-(*N*-Me-DNPH)	1643				
48	2,6-Bu_2-quinone 4-(*N*-Me-DNPH)	1654				

[a] Me = methyl; Et = ethyl; Pr = isopropyl; Bu = *tert*-butyl; Ph = phenyl; Cl = chloro. [b] sh = shoulder. [c] Unstable. [d] At 100°C.

This procedure involves at least two factors of uncertainty: α_{av} may change if the range of reference compounds is changed; and the true α of a given tautomeric compound may be different from α_{av}. However, similar uncertainties are inherent also with other methods employing reference standards.[12,15,18] It is assumed that for the present purpose the % NH obtained is sufficiently accurate. Owing to the crudeness of the method the simple molar absorptivity was found to be a satisfactory measure of peak intensity, instead of the more accurate but also more cumbersome, triangular area[1] or similar integrated expressions. The results parallel those of Hofer and Uffmann[17] in deuteriochloroform solution as far as the compounds are in common (Nos. 2, 25, 41, 44); this confirms the applicability of the method as a supplement to PMR. The method can be used only with a fixed 2′-substituent since ε_{NH} is strongly influenced by variations in the strength of the hydrogen bond N – H···2′-group.

RESULTS AND DISCUSSION

Solution spectra. The molar absorptivity of the OH band of the pure azo compounds (Nos. 38 – 40; *cf.* also No. 41) varies considerably with the substitution on the phenol ring, and the same was found with the NH band of the pure hydrazonic compounds (Nos. 28 – 34 and 37; *cf.* also Nos. 18, 24, 26, 27, 35). It was not possible, however, to detect any correlation between absorptivity and type, number, or position of alkyl. Similarly no general trends are apparent in the frequencies of the OH or NH bands *vs.* alkyl substitution pattern or tautomeric equilibrium position.

Solution spectra in the carbonyl region 1800 – 1600 cm^{-1} were investigated only for selected compounds. In most cases there is a triple band in the region 1646 – 1597 cm^{-1}. The intensity of the second of these peaks (1625 – 1612 cm^{-1}) follows that of the NH band, and it is therefore assigned to the C = O stretching vibration. As expected the position of this band in quinone dinitrophenylhydrazones is somewhat lower than in less negatively substituted quinone phenyl-

hydrazones.[1] *N*-Methylation (Nos. 47, 48) raises the C=O frequency, as expected.

The sharp, medium intensity band found at 3100 cm^{-1} in dinitrophenylhydrazones and attributed to the dinitrophenyl C–H stretching band,[19] is discussed elsewhere.[20]

In the 2′-nitro series the C=O band seems to overlap completely with a band at 1612–1616 cm^{-1} representing other double bond vibrations, since the presence of this band is not dependent on the NH band. In the 4′-nitro series it is not possible to determine the C=O band position owing to the almost complete lack of hydrazone tautomer in these compounds.

Tautomerism in low-polar solution. Early investigators [7–10] did not find spectral evidence for the existence of the hydrazone form in simple phenylazophenols, and the parent 4-phenylazophenol even does not react with carbonyl reagents or diene components.[21] Introduction of 2′,4′-dinitro substituents onto the phenyl ring of 4-phenylazophenol develops the ability to react with these reagents.[21,22] It was not surprising, therefore, to find a noticeable equilibrium amount (*ca.* 8 %) of hydrazone tautomer in this compound (No. 1, Table 1). Further substitution of alkyl on the phenol ring in the dinitro series raises the percentage of hydrazone relative to No. 1, but to different degrees depending on the type, number, and position of alkyl (*cf.* Table 1).

(1) 2-Alkylation of compound No. 1 results in a significant increase of the hydrazone proportion, and the proportion increases even more upon 2,6-dialkylation.

(2) 3-Alkylation of compound No. 1 results in a moderate increase of the content of hydrazone; this is reduced upon 3,5-dialkylation.

(3) With mixed alkylation 2-alkyl dominates over 3- or 3,5-alkyl, *i.e.*, there is always a high proportion of hydrazone.

(4) Increasing size of 2- or 2,6-alkyl rapidly increases the content of hydrazone.

(5) Increasing size of 3- or 3,5-alkyl has little effect upon or reduces the hydrazone proportion.

(6) Introduction of phenyl in 2- or 3-position has little effect upon or slightly reduces the content of hydrazone, relative to No. 1.

Although only a small number of sample compounds were investigated in the two mononitro and other series, the results seem to bear out the following trends.

(7) In the 2′-nitro series the effects of alkyl closely follow those observed in the 2′,4′-dinitro series, but with a slightly lower content of hydrazone. Only the 2,6-di-*tert*-butyl derivative (No. 37) was found to be 100 % hydrazonic.

(8) In the 4′-nitro series the hydrazone form could not be detected, except in the 2,6-di-*tert*-butyl derivative (No. 41).

(9) In the non-nitro series (Nos. 42, 43, 46), 3′-nitro series (No. 48), and 2′-methyl series (No. 51) no hydrazone was detected.

Results published by Hofer and Uffmann,[17] but not stated explicitly by them, substantiate observations (1), (4), (7), and (8).

Steric hindrance by alkyl in 2- or 2,6-position toward formation and solvent stabilisation of the phenolic group at C_1 could at first glance explain observa-

tions (1) and (4). However, the 96 % azophenolic character of No. 41 shows that these factors are not important in low-polar solvents. Instead, inductive effects must be considered (see below). In more polar solution steric effects seem to be more important.[17]

4-Nitroso-3-alkylphenols are known to exist in the *anti* configuration,[23] and the same is to be expected when dinitrophenylazo is substituted for nitroso (Nos. 7 – 10). The steric conditions at the nitrogen bridge in these compounds therefore should closely correspond to those in No. 1, and their slightly higher content of hydrazone must be ascribed to the inductive effect of the 3-alkyl group.

The steric effect of two alkyl groups in 3,5-position should be more pronounced. Space-filling models show that a *syn*-methyl substituent (Nos. 12 – 15) forces the amino hydrogen of the hydrazone form some 30° out of plane. However, even this steric destabilisation of the hydrazone structure cannot be serious, since the hydrazone content of Nos. 12 – 15 is still higher than that of No. 1.

With increasing size of both 3,5-substituents the steric hindrance at the 4′-position more than counteracts the inductive effect: the 3,5-diisopropyl derivate No. 16 shows no tendency to hydrazone formation. The increasing instability with increasing size of alkyl in the series Nos. 12 – 16 also indicates a strong interaction between the alkyl groups and the lone pair electrons on the nitrogens. This interaction is carried to the extreme with 3,5-di-*tert*-butyl: the *para*-coupling product is non-existent.

Observations (8) and (9) indicate that the inductive and mesomeric effects are not important in the formation of hydrazone; of the two effects the mesomeric is probably the stronger one. It probably acts by reducing the electron density on the hydroxyl oxygen whereby the relative density on nitrogen 2 is increased; this facilitates overlap between the two ring electron systems, increases the tendency of the nitrogen to hybridise, and increases the ability of the nitrogen to capture a hydrogen. Since the effect is weak (obs. 8), however, the higher hydrazone content in the 2′-nitro and dinitro series, relative to the 3′- and 4′-nitro series, probably is due mainly to stabilisation of the hydrazone form by chelation of the NH hydrogen with the 2′-nitro group. The importance of this presumed bonding of NH has been noted previously in 4-arylazo-l-naphthols with 2′-nitro, -methoxy, and -chloro substituents,[1] and it is further discussed in a subsequent paper.[24]

The hydrazone-promoting effect of 2-alkyl *vs.* 3-alkyl is striking. As noted previously this is not usually due to differences in steric requirements, and hence mainly inductive effects must be responsible. Since the inductive property is independent of the position to which the group is attached, the different effect in the two positions must be due to a different ability of the ring to accept the influence of the group. Although a good explanation of this is difficult to conceive, it may be pointed out that when acting from the 2-position a positive inductive effect can better contribute to an increase of electron density on nitrogen 2 than when acting from the 3-position; this increase of charge may facilitate hybridisation of the nitrogen, *etc.* Similar positional differences have been observed with various conjugated systems: it is inferred from published data [18,23] that 2- or 2,6-alkylated 4-nitrosophenols show a

greater tendency to exist in the quinone oxime form than the corresponding 3- or 3,5-analogs (*cf.* Table 1). *p*-Substituents in the β-phenyl groups of tetracyclones influence the infrared stretching frequency of the carbonyl group, whereas *p*-substituents in the α-phenyl groups do not.[25] In the 4-(4′-nitrophenylazo)-phenol series anions of 2-alkylated members absorb at higher wave lengths than 3-alkylated in basic medium, as judged from the colours formed with diethylamine on TLC plates.[26]

Comparison of Nos. 37 *vs.* 44 and 36 *vs.* 43 demonstrates that in the absence of the stabilising NH···nitro bonding, the effect from the alkyl groups is too weak to create any hydrazone. *Vice versa*, in the absence of alkyl, particularly 2- or 2,6-alkyl (*e.g.*, Nos. 25 – 29 *vs.* 1), the NH···nitro stabilisation loses much of its significance. In a "push-pull" cooperation, however, the two effects are able to displace the tautomeric equilibrium to the hydrazone side.

Only two compounds from the naphthol series were investigated (Nos. 32 and 33). The latter was exceedingly difficult to chromatograph, and its purity can be questioned. Due to low solubility in tetrachloroethylene the infrared spectra were obtained at 100°C. Both compounds seem to be 100 % hydrazonic, as expected from the general trend, naphthol series > phenol series.

Comparison of the tendencies of 4-(dinitrophenylazo)-alkylphenols and 4-nitroso-alkylphenols to assume the quinonoid structure (Table 1) indicates that the effect of the dinitrophenylhydrazono group is weaker than that of the oximo group.

REFERENCES

1. Morgan, K. J. *J. Chem. Soc.* **1961** 2151.
2. Zollinger, H., *Diazo and Azo Chemistry. Aliphatic and Aromatic Compounds*, Interscience, New York 1961, p. 322.
3. Schündehütte, K. H. In Müller, E., Ed., *Houben-Weyl's Methoden der organischen Chemie*, Georg Thieme, Stuttgart 1965, Vol. 10/3, p. 213.
4. Ershov, V. V. and Nikiforov, G. A. *Russ. Chem. Rev.* **35** (1966) 817.
5. Kitaev, Yu. P., Buzykin, B. I. and Troepol'skaya, T. V. *Russ. Chem. Rev.* **39** (1970) 441.
6. Bershtein, I. Ya. and Ginzburg, O. F. *Russ. Chem. Rev.* **44** (1972) 97.
7. Kuhn, R. and Bär, F. *Ann.* **516** (1935) 143.
8. Brode, W. R. and Herdle, L. E. *J. Org. Chem.* **6** (1941) 713; *Chem. Abstr.* **35** (1941) 7828.
9. Ospenson, J. N. *Acta Chem. Scand.* **4** (1950) 1351; **5** (1951) 491.
10. Burawoy, A. and Chamberlain, J. T. *J. Chem. Soc.* **1952** 3734.
11. Hadži, D. *J. Chem. Soc.* **1956** 2143.
12. Bekárek, V., Dobás, J., Socha J., Vetešník, P. and Večeřa, M. *Coll. Czech. Chem. Commun.* **35** (1970) 1406.
13. El-Dakhakhny, M. *Ann.* **685** (1965) 134.
14. Kaul, B. L., Nair, P. M., Rao, A.V.R. and Venkataraman, K. *Tetrahedron Letters* **1966** 3897.
15. Bansho, Y., Saito, I., and Miyamae, T. *Kogyo Kagaku Zasshi* **67** (1964) 177; *Chem. Abstr.* **61** (1964) 5817.
16. Burawoy, A., Salem, A. G. and Thompson, A. R. *J. Chem. Soc.* **1952** 4793.
17. Hofer, E. and Uffmann, H. *Tetrahedron Letters* **1971** (35) 3241.
18. Norris, R. K. and Sternhell, S. *Austral. J. Chem.* **22** (1969) 935.
19. Jones, L. A., Holmes, J. C. and Seligman, R. B. *Anal. Chem.* **28** (1956) 191.
20. Juvvik, P. *To be published.*
21. Lauer, W. M. and Miller, S. E. *J. Am. Chem. Soc.* **57** (1935) 520.

22. Borsche, W., Müller, W. and Bodenstein, C. A. *Ann.* **472** (1929) 201; *Chem. Abstr.* **23** (1929) 4679.
23. Uffmann, H. *Z. Naturforsch.* **22b** (1967) 491.
24. Juvvik, P. *To be published.*
25. Jones, R. N., Sandorfy, C. and Tucker, D. E. *J. Phys. Radium* **15** (1954) 320.
26. Juvvik, P. and Sundby, B. *J. Chromatogr.* **76** (1973) 467.

Received November 16, 1972.