On the Question of Tautomerism of
Solid Dinitrophenylazo-alkylphenols

PAUL JUVVIK and BJØRN SUNDBY*

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

Infrared spectra indicate that many solid 4-(2′,4′-dinitrophenyl-azo)-alkylphenols exist as tautomeric mixtures with alkyl-1,4-benzo-quinone 2′,4′-dinitrophenylhydrazones. There is also some indication that both tautomers are packed into a common crystal lattice. 2,5-Diisopropylquinone 2′,4′-dinitrophenylhydrazone was isolated in two interconvertible, solid modifications of seemingly different tautomeric composition.

Arylazonaphthols are known to exhibit tautomerism in solution (*cf.* Refs. in a previous paper[1]). Infrared studies of 1-phenylazo-2-naphthol,[2] 2-phenylazo-1-naphthol,[2] and 4-phenylazo-1-naphthols[3] as potassium bromide discs seem to indicate the existence of tautomeric mixtures (*cf.* Formula II) also in the solid state, contrary to the rule of thumb that one type of molecule only may be packed into a crystal lattice.[2] Application of X-ray methods has led to a similar conclusion:[4] one of the two crystalline modifications of 4-phenylazo-1-naphthol is mainly hydrazonic, the other azophenolic.

Arylazophenols have been much less thoroughly studied, and to the best of the authors' knowledge, nothing is known of their structure in the solid state. In the present paper the infrared spectra of solid dinitrophenylazo-alkylphenols [II, R = alkyl(s); R′ = 2′,4′-(NO₂)₂] are discussed from the tau-tomerism point of view; this work is closely related to a study of the tau-tomerism in tetrachloroethylene solution.[1]

EXPERIMENTAL

Preparation and purification of the mono- and dinitrophenylazoalkylphenols II have been mentioned elsewhere.[1]

Compound 16 (Table 1) was isolated from the preparative-layer chromatogram in the form of a dark, red-brown oil which solidified on standing. M.p. about 165° (dec.); solid

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

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IR-spectrum, Fig. 1a. On rubbing in the presence of a little solvent (petroleum ether 40 − 60° and dichloromethane were tested) the solid rapidly and quantitatively passed into a yellow modification: m.p. 165° (dec.) after turning brown at about 150°; solid IR-

Table 1. Infrared spectral data and probable tautomer composition of solid 4-(mono- and dinitrophenyl)-azophenols.

No.	R in II[a]	cm⁻¹ stretch (KBr discs)[b]			Tautomer composition[c]
		C=O	NH	OH	
	R′ = 1′,4′-dinitro				
1	H		0	3475s,b	A
2	2-Et	1613	3292w	3510w	M
				3420m	
				3180m,b	
3	2-Pr		0	3445s,b	A
4	2-Bu		0	3474s,b	A
5	3-Me		3290w	3180s,b	M
6	3-Et	1615	3288m	3120s,b	M
7	3-Bu		3274m	3090s,b	M
8	3,5-Me₂		0	3458s,b	A
9	3-Me-5-Et	1616sh	3311m	3110m,b	M
10	3-Me-5-Pr		0	3335m,b	A
				3557w,b	
11	2,3-Me₂		3295w	3360m,b	M
12	2,5-Me₂		3280m	3110s,b	M
13	2-Me-5-Pr		3292w	3090s,b	M
14	2-Pr-5-Me		3315w	3280m,b	M
15	2-Bu-5-Me		3272	3120s,b	M
16a	2,5-Pr₂ brown mod.	1616s	3295w	3410w,b	M
				3110m,b	
16b	2,5-Pr₂ yel. mod.	1617s	3295m	3405b	M
17	2,5-Bu₂	1618s	3301w	3160s,b	M
18	2,3,5-Me₃		3307m	3080s,b	M
19	2,6-Me₂	1615s	3290m		H
20	2-Me-6-Bu	1614s	3296s	3520m,b	M
21	2,6-Pr₂	1613s	3285s		H
22	2,6-Bu₂	1616s	3290s		H
23	2,3,6-Me₃	1617s	3300s		H
24	2,3,5,6-Me₄	1614sh	3332s		H
	R′ = 2′-nitro				
25	3-Et		0	3415s,b	A
26	2-Pr-5-Me	1612[d]	3293w	3130s,b	M
27	2,6-Pr₂	1612[d]	3295w	3395s,b	M
28	2,6-Bu₂	1612s	3301s		H
	R′ = 4′-nitro				
29	3-Et		0	3415s,b	A
30	2-Pr-5-Me		0	3455s,b	A
31	2,6-Pr₂		0	3235w,b	A
				3520s,b	
32	2,6-Bu₂		3296w	3420w,b	M
				3596w	

[a] Me=methyl; Et=ethyl; Pr=isopropyl; Bu=*tert*-butyl. [b] w=weak; m=medium; s=strong; b=broad; sh=shoulder. [c] A=azo; H=hydrazone; M=tautomeric mixture. [d] C=O+C=C (see text).
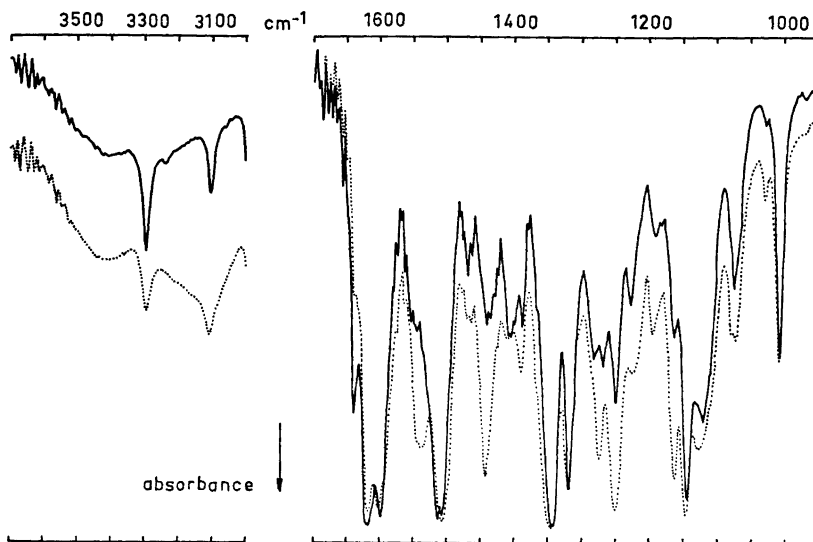
Fig. 1. Infrared solid spectra as KBr pellets. (*a*): Brown (···; No. 16*a*) and (*b*): yellow (——; No. 16*b*) modifications of 2,5-diisopropylquinone 2′,4′-dinitrophenylhydrazone. The broad bands at about 3420 cm⁻¹ are partially due to moisture. In the 3700 − 3000 cm⁻¹ region the spectra are vertically displaced for clarity; in the 1700 − 950 cm⁻¹ region they have a common base line.

spectrum, Fig. 1*b*. Both solids are stable in a dry condition. The reverse transformation could be brought about by dissolving the yellow form in, *e.g.*, dichloromethane and rapidly evaporating to dryness; on rubbing or standing, the solvent-free, brown oil solidified to a brown solid as before. Several of the other compounds were tested in a similar way, but could not be induced to undergo such transformations.

Infrared spectra were recorded with Unicam SP 100 and SP 200G instruments on potassium bromide pellets containing 0.5 − 1 % w/w of the solid compounds. Some spectra (*cf.* Fig. 2) were recorded at elevated temperatures up to 190°, using a specially constructed pellet holder fitting into a Beckman-RIIC variable temperature unit.

Electronic spectra (Fig. 3) were recorded with a Beckman DB instrument on well-ground, glass-clear potassium bromide pellets pressed from 30 − 50 µg of substance in 200 mg of salt.

RESULTS

Infrared spectra. Some of the dinitrophenylazo-alkylphenols show a strong OH band but no NH band (Fig. 4*a*), and hence are probably pure azo in the solid state (Nos. 1, 3, 4, 8, 10, 25, 29 − 31). Others apparently lack any OH band, whereas the NH band is as sharp and strong as in aliphatic dinitrophenylhydrazones (Fig. 4*b*); these are pure hydrazones (Nos. 19, 21 − 24, 28). Nos. 11, 16*b*, 20, 27 show a more or less well-defined NH-band at the ordinary frequency 3300 cm⁻¹,[5] together with a broad band at higher frequencies clearly due to bonded OH (Fig. 4*c*); these compounds apparently are tautomeric mixtures. In some instances (Nos. 2, 5 − 7, 9, 12 − 15, 16*a*, 17, 18, 26, 32)
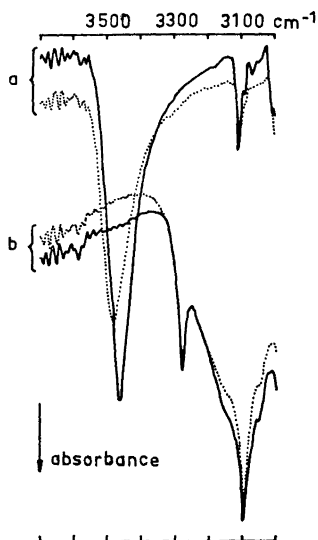
Fig. 2. Infrared solid spectra as KBr pellets. (*a*): 2-*tert*-butylquinone 4-(2',4'-dinitrophenylhydrazone) (No. 4) at 25° (——) and at 180° (···). (*b*): 2,5-dimethyl-quinone 2',4'-dinitrophenylhydrazone (No. 12) at 25° (——) and at 150° (···). Spectra (*b*) are vertically displaced for clarity.
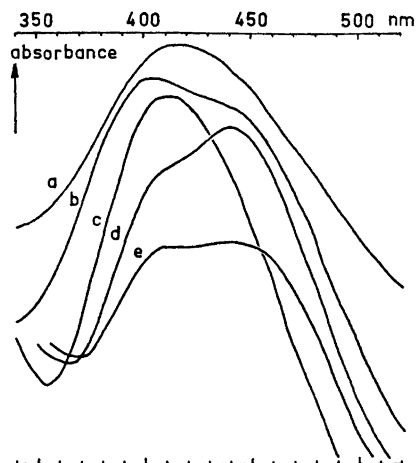
Fig. 3. Ultraviolet-visible solid spectra as KBr pellets (*a*): 4-(2',4'-Dinitrophenyl-azo)-3-methylphenol (No. 5). (*b*): 2,3,5,6-Tetramethylquinone 2',4'-dinitrophenyl-hydrazone (No. 24). (*c*): 4-(2',4'-Dinitro-phenylazo)-3-methyl-5-isopropylphenol (No. 10). (*d*): 2,6-Diisopropylquinone 4-(2',4'-dinitrophenylhydrazone) (No. 21). (*e*): 2,5-Di-*tert*-butylquinone 2',4'-dinitro-phenylhydrazone (No. 17). The spectra are vertically displaced for clarity.

the broad maximum comes below the NH position, and its nature (bonded OH, bonded NH, or both) then is more indeterminable (Fig. 4*d*). The width of the band ($\Delta v_{\frac{1}{2}}$ several hundred cm^{-1}) indicates, however, that much bonded OH is present, and hence also these compounds are tautomeric mixtures.

In the carbonyl region the dinitro compounds show a complex band centred at about 1610 cm^{-1}. One of the main peaks in this band, at 1612 – 1620 cm^{-1}, is missing in just the five compounds which also lack the NH band (Nos. 1, 3, 4, 8, 10), and hence this particular peak may be assigned to the C = O stretching vibration. Regrettably the partial overlap with the other bands restricts the diagnostic value of the C = O band of dinitrophenylazophenols to a mere qualitative confirmation of what may be deduced from the NH bands and only to cases where much hydrazone is present. The C = O band positions, in the solid DNPAP's are essentially the same as in tetrachloroethylene solution.[1]

In the 2'-nitro compounds the C = O band apparently overlaps completely with the higher one (1612 – 1614 cm^{-1}) of two bands representing the double bond vibrations, and in the 4'-nitro series the nearly systematic lack of
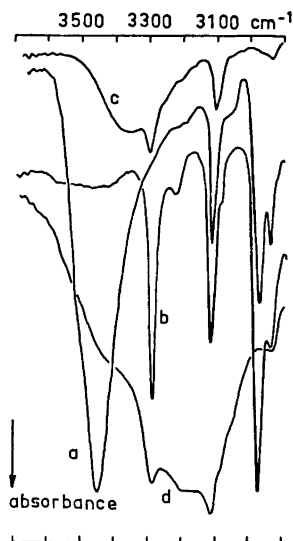
3500 3300 3100 cm⁻¹

Fig. 4. Infrared solid spectra as KBr pellets. (*a*): 2-Isopropylquinone 4-(2′,4′-dinitrophenylhydrazone) (No. 3). (*b*): 2,6-Diisopropylquinone 4-(2′,4′-dinitrophenyl-hydrazone) (No. 21). (*c*): 2,3-Dimethyl-quinone 2′,4′-dinitrophenylhydrazone (No. 11). (*d*): 4-(2′,4′-Dinitrophenylazo)-3-methylphenol (No. 5). The spectra are vertically displaced for clarity.

hydrazone[1] makes the assignment of a C=O band fortuitous.

Electronic spectra. Ultraviolet-visible (UV) spectra of the solids in the form of potassium bromide pellets have been used in the phenylazonaphthol series for confirming the presence of the azo form;[2] the positions of the UV azo and hydrazone maxima were found to fall at about the same wavelengths as in relatively polar solution. When this technique was applied to selected compounds of the present series (Fig. 3) no correspondence with the infrared spectra could be found: there is a single maximum in the azo region whether IR indicates absence (No. 10) or presence (No. 9) of NH; two UV bands appear, with the azo band the larger one (Nos. 22 and 24) or the smaller one (No. 21), even when IR shows no OH bands at all; or the azo and hydrazone bands are of about the same intensity (No. 17), whereas IR indicates only small amounts of NH. This behaviour is explained by the observations that the hydrazone tautomer of some 2′-nitro- and 2′,4′-dinitro-phenylazo-alkyl-phenols,[6] quinone *N*-methyl 2,4-dinitrophenylhydrazones,[6] and strongly conjugated, aliphatic DNPH's[7-9] shows two UV bands in the "azo" and "hydrazone" regions in low-polar as well as high-polar solution. It must be concluded, therefore, that unless interpreted with extreme care, UV spectra are useless for detecting or confirming tautomerism in solid nitrophenyl-azophenols.

DISCUSSION

There are two possible explanations of the presence of both tautomers in the solid state: two kinds of crystals may be present in admixture, or the molecules of both tautomers may be packed into the same crystal lattice. In the case of 1,2-naphthoquinone hydrazones Hadži[2] found no evidence of two

types of crystals. This is perhaps more obvious with 1,2- (I) than with 1,4-(II) derivatives, since in the former a dynamic tautomerism may take place by an intramolecular hydrogen-transfer mechanism without
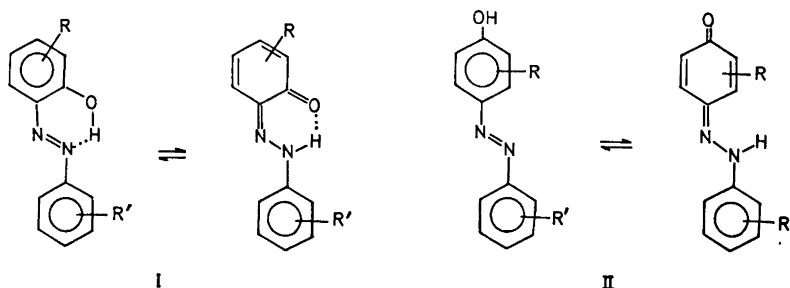
significant variation of molecular dimensions or orientation. However, the 1,4-tautomers differ mainly in the position of the small, active hydrogen, and also these should be sufficiently similar to allow for packing into a common lattice. 2,4-Dinitrophenylhydrazones are notorious of exhibiting polymorphism and forming solid solutions.[10,11]

The assumption of mixed crystal lattices is supported by the IR data discussed above, and by the observation that No. 16 occurs in two inter-convertible modifications. The properties of the two forms in the dissolved state (chromatography, IR-, and UV-spectra) are identical, as expected, whereas the IR solid spectra are clearly different (Fig. 1). The spectra indicate that the yellow modification (16b) contains much hydrazone, and the brown one (16a), considerably less. Thus both modifications probably are tautomeric mixtures, differing only in composition and stability. At room temperature the yellow, more hydrazonic form is the thermodynamically more stable one; at about 150° the azo form appears to be formed spontaneously. This is consistent with the relative stabilities found in similar tautomeric systems.[12]

The lack of relationship between the tautomeric compositions in tetra-chloroethylene solution and in the solid state is notable. Nos. 2, 11, 13, 14, 17, 26, and 27 are predominantly azophenolic in the solid state, whereas in solution they are $64-97 \%$ hydrazonic.[1] Even more striking are Nos. 3, 4, 8, 25, 29, and 30. These solids have practically identical spectra in the $3800-3000$ cm^{-1} region (cf. Fig. 4a) which indicate complete absence of hydrazone. In solution, however, Nos. 3 and 4 contain 68 and 84 % of hydrazone, against 10, 0, and 0 % in Nos. 25, 29, and 30.[1] Moreover, the spectra of Nos. 3, 4, and 8 are radically different from those of the other 2- and 3,5-alkylated dinitro compounds (Nos. 2, 9, 10; cf. Fig. 4c and d), which in solution contain 68, 15, and 14 % of hydrazone,[1] respectively. These lacks of relationship may be explained by different possibilities of intermolecular hydrogen bonding in the compounds. The various types of bonding ($> N-H\cdots O=$; $\geqslant N\cdots H-O-$; $> N-H\cdots$nitro; $-O-H\cdots$nitro; $\geqslant N-H\cdots O-H$; etc.) and their relative amounts in a given compound probably depend on, among other things, the steric conditions imposed by the alkyl substituents in one molecule on the

various donating and accepting centres in the neighbouring molecules. This also influences the tautomeric composition.

If this assumption of a mixed, tautomeric crystal lattice is correct, the question arises whether the tautomeric equilibrium is static or dynamic on a molecular scale. The stability of the yellow form of No. 16 up to $150°$ and the lack of significant changes in the solid spectra of other sample compounds up to some $190°$ (cf. Fig. 2) seem to give preference to the static version. The high conversion temperature indicates a high energy of activation of the hydrogen transfer reaction, hydrazone → azo. Consequently the tautomerically active bonds $> N - H \cdots O =$ and $\geqslant N \cdots H - O -$ are probably inactive at lower temperatures. The other types of bonding $(- O - H \cdots \text{nitro}, \text{ etc.})$ are tautomerically fixed and require complete rearrangement of the crystal lattice, or melting, to allow for transition of the hydrogen.

Infrared spectroscopy certainly is not the ideal method for an exhaustive study of tautomerism in solid azophenols. It appears from the results above, however, that Hadži's doubt [2] that an X-ray examination would yield nothing else than the average structure is too pessimistic, and that X-ray work in this field should be encouraged.

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