420. *Absorption Spectra and Structure of Some Solid Hydroxyazo-compounds.*

By D. HADŽI.

Infrared and electronic spectra were investigated of solid 1-phenylazo-2-naphthol, 2-phenylazo-1-naphthol, 4-phenylazo-1-naphthol, their deuterated analogues, as well as of the *O*-methyl derivatives. Infrared spectra of *o*- and *p*-phenylazophenol were also investigated. The last two compounds have been found to exist as true azo-compounds, whereas both types of spectra indicate that the naphthalene derivatives exist in the solid state either as pure phenylhydrazones (1 : 4-naphthaquinone monophenylhydrazone) or as mixtures of both tautomeric forms.

INVESTIGATIONS of the electronic spectra of arylazonaphthols in solution have demonstrated that these compounds exist in the true azo-form along with the tautomeric phenylhydrazone form.[1-4] It has been shown also that both *o*- and *p*-azophenols appear in the azo-form only, irrespective of the solvent.[2] In contrast to the very extensive work on solutions, the investigations of the structure of solid hydroxyazo-compounds are limited to a few isolated infrared spectra.[5-7] Therefore a more complete investigation appeared desirable. It was hoped that the infrared spectra would reveal some structural details of the groups involved in the tautomeric changes, besides bringing additional evidence for the gross structure of these interesting compounds.

In this investigation, infrared spectra were recorded of *o*- and *p*-phenylazophenol, 1-phenylazo-2-naphthol, and 2- and 4-phenylazo-1-naphthol, and of their OD analogues. Some nitrophenylazonaphthols were studied too, but since their spectra had no particularly

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[1] Burawoy and Markowitsch, *Annalen*, 1933, **503**, 180; 1934, **504**, 71.
[2] Kuhn and Bär, *ibid.*, 1935, **516**, 143.
[3] Ramart-Lucas, *Bull. Soc. chim.*, 1944, **11**, 75.
[4] Burawoy, Salem, and Thompson, *J.*, 1952, 4793.
[5] Druckrey, Schmähl, and Dannenberg, *Naturwiss.*, 1952, **39**, 393.
[6] Le Fèvre, O'Dwyer, and Werner, *Austral. J. Chem.*, 1953, **6**, 341.
[7] Dolinsky and Jones, *J. Assoc. Off. Agric. Chem.*, 1954, **37**, 167.

interesting features they will not be discussed separately. The investigation includes the spectra of some reference compounds, such as the *O*-methyl derivatives of azonaphthols, and naphthaquinones. The spectra were recorded with substances in the solid state, but where solubility permitted, also in solution. Since the infrared spectra did not yield clear-cut results in all instances, it was necessary to resort to the electronic spectra of the solids.

The region between 1700 and 1400 K is most promising for the distinction between the azo- and the hydrazone structure. Here are expected the bands due to the C=O and C=N groups which characterise the hydrazone form, as well as those due to the stretching of the –N=N– group of the azo-form. However, the absorption of the latter is usually much less characteristic than that of the former. The region of the OH and NH stretching vibrations should be of little use, since it is not easy to distinguish the respective bands, particularly if the compounds appear in the hydrogen-bonded form. The OH and NH bending vibrations give rise to rather characteristic bands in certain circumstances, particularly when compared with analogous deuterium-substituted compounds.[8,9] It might be expected that the region of the out-of-plane vibrations of aromatic hydrogen atoms would be useful too for diagnostic purposes, but a close examination of the bands in the spectra of the naphthaquinones and a number of appropriately substituted naphthalenes has shown that too many bands overlap in this region for useful conclusions to be drawn.

Description of Spectra.—In the spectrum of the solid *p*-phenylazophenol a strong and broad band appears at 3120 K (Fig. 1). In solution in carbon tetrachloride this band is replaced by a sharp one at 3600 K. The large wave-number of this band in solution, and the broadening in the solid state due to hydrogen bonding, leave little doubt as to its assignment to the OH stretching mode. The corresponding ν(OD) band appears at 2340 K (solid). The bands between 1600 and 1400 K (Fig. 3*a*) can be accounted for by ring and aromatic CH vibrations. Corresponding bands with little change of position are observed (Fig. 3*c*) in the *O*-methyl derivative of this compound. The absorption band due to the azo-group should fall also in this region, but it is difficult to decide which band in the present spectra should be attributed to this vibration in particular. Deuterium substitution (Fig. 3*b*) causes the very significant shift of a band from 1235 to 990 K. The new band seems to be slightly less strong than the disappearing one. Similar shifts have been observed with a number of phenolic compounds, and the bands attributed to a vibration mode roughly described as the in-plane bending of the COH and COD groups respectively.[8] This pair of bands is important for the subsequent discussion; some minor changes of band positions after deuteration were observed in addition but adequate explanation for them is lacking as yet. The differences in the spectra of the basic compound and its *O*-methyl derivative can be accounted for by the effect of the replacement of the hydrogen by a methyl group. The band attributed to the OH bending is lacking in the ether spectrum, and the strong band at 1250 K replaces that at 1280 K. Both bands are due to the C–O stretching.[10]

Instead of the strong ν(OH) band in the spectrum of the *para*-isomer, the *ortho*-isomer has a weak and very broad absorption (Fig. 2) extending from about 3000 to 2400 K. Similar broad absorption bands, due to the stretching of OH groups in chelated structures, have been described before.[8,9] No traces of free OH absorption appear near 3600 K in the dilute chloroform solution. The broad absorption is overlapped by a sharp band near 3040 K, due to the stretching of aromatic CH, and by some smaller subsidiary maxima. These are probably due to overtones and are brought out by the relative thickness of the layer. The other important features of the spectrum (Fig. 3*d*) correspond to those described with the *para*-isomer. Particularly interesting is the shift of the band from 1277 to 1015 K after deuteration (Fig. 3*e*). The assignment is analogous to that given in the previous case.

The high wave-number region of the spectrum of 4-phenylazo-1-naphthol bears a weak and sharp band at 3240 K (Fig. 1). In chloroform solution (2-mm. cell), a weak and sharp band appears at 3360 K, and a slightly broader and stronger one at 3260 K. Because of

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[8] Hadži and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 911.

[9] Bratož, Hadži, and Rossmy, *ibid.*, 1956, **52**, 464.

[10] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

FIG. 1.

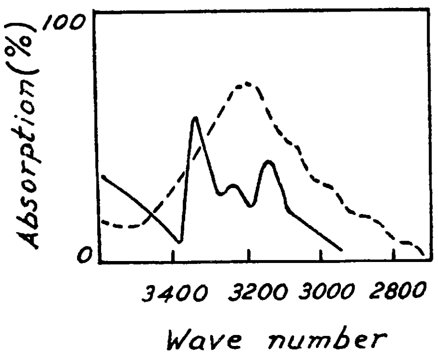

FIG. 2.

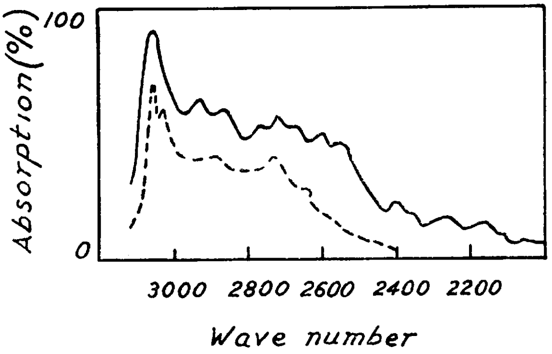

FIG. 1. *Infrared spectra of solid 4-phenylazophenol* * (*broken*) *and 4-phenylazo-1-naphthol* (*full line*).

FIG. 2. *Infrared spectra of 2-phenylazophenol* (*broken*) *and 1-phenylazo-2-naphthol* (*full*) *in* CCl_4 *solution.*

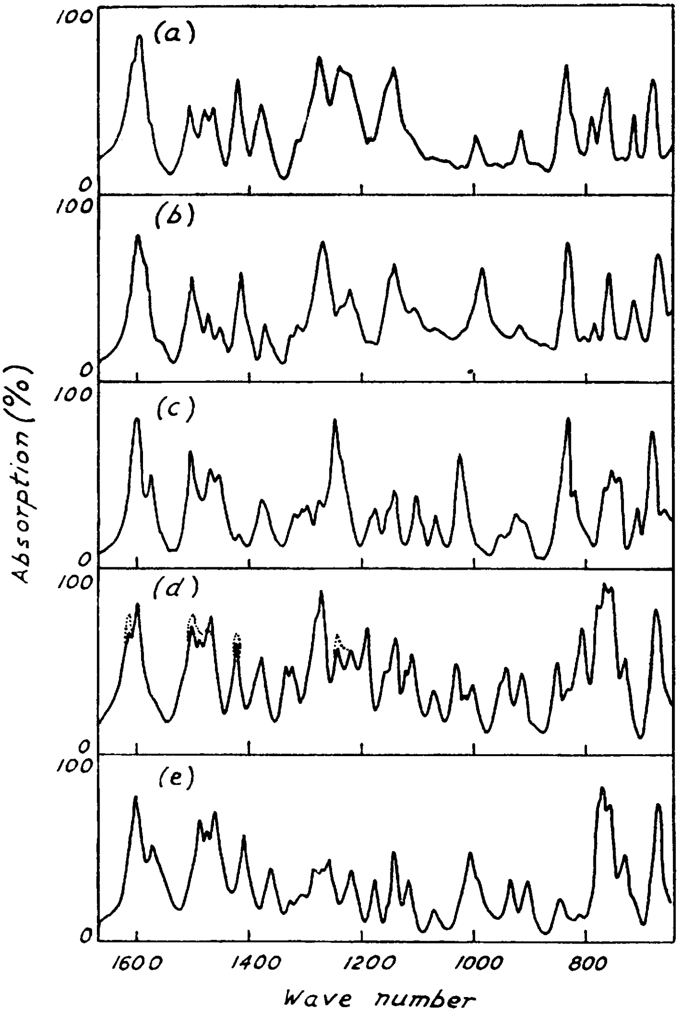

FIG. 3. *Infrared spectra of solid phenylazophenols and derivatives:* (*a*) *4-phenylazophenol;* (*b*) *its deuterium analogue;* (*c*) *its O-methyl ether;* (*d*) *2-phenylazophenol* (*dotted: solution in* $CHCl_3$); (*e*) *its deuterium analogue.*

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* The names used for designating the compounds are not intended to describe their true structure.

its sharpness in the associated state (solid and moderately diluted solution), and the relatively small wave-number in the free state (3360 K) these bands may be safely assigned to an NH stretching mode. The bands due to associated OH groups are usually much broader whereas free OH groups absorb at larger wave-numbers (cf. the spectrum of solid *p*-azophenol).

The region 1650—1500 K contains two interesting features (Fig. 4). First, the strong band observed at 1615 K is missing in the spectrum of 4-phenylazo-1-methoxynaphthalene (Fig. 4*c*). This makes its assignment to the C=O stretching very probable. Secondly, there is a very strong and broad band at 1538 K. A similar band is not observed in the spectrum of *p*-phenylazophenol, and it is also lacking in the spectrum of 4-phenylazo-1-methoxynaphthalene. But even more significant is the shift of this band to 1500 K after deuteration (Fig. 4*b*). The position of the band suggests that it is due to the stretching of a bond having largely double-bond character, but the shift indicates clearly that a motion of the hydrogen atom, probably a deformation, is involved in this vibration mode. NH bending vibrations in secondary amines, hydrazines, etc., have been associated [11] with bands near 1200 K. However, it may be expected that the neighbourhood of double bonds would considerably influence the absorption frequency of this vibration, and several examples of the interaction of NH vibrations with the vibrations of adjacent bonds having more or less double-bond character have been noted in this laboratory. For example, in pyridine hydrochloride a strong band at 1532 K is severely reduced in intensity after deuterium substitution, and a very strong and broad band appears instead at 1488 K. Less marked but related intensity changes and shifts of bands in this region have been observed in several ketone phenylhydrazones, and in the β-benzylaminobenzylideneacetophenone. The spectra of these compounds will be dealt with in a subsequent paper. A similar change in spectrum on deuteration to that observed with the present compound is found also with secondary amides. The well known amide-II band near 1550 K is replaced in deuterated amides by another near 1480 K, of similar intensity. The amide-II band is now commonly ascribed to a vibration involving the asymmetric stretching of the CO·NH group, coupled with the NH bending.[12] Accordingly, the band near 1500 K in the

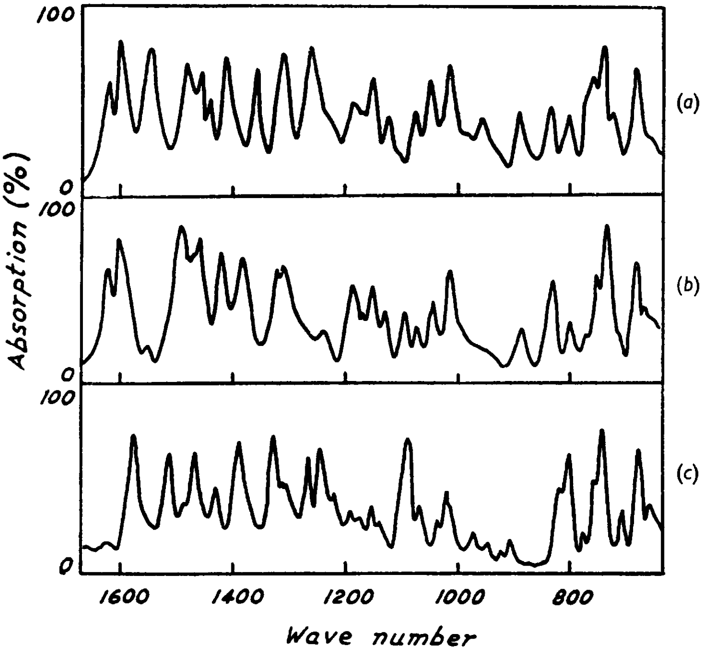

FIG. 4. *Infrared spectra of: (a) 4-phenylazo-1-naphthol; (b) its deuterium analogue; (c) its O-methyl ether.*

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[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 219.

[12] Fraser and Price, *Nature*, 1952, **170**, 490.

present spectrum is attributed to a combined vibration, involving the NH bending and some skeletal stretching motion. It must be largely influenced by the skeletal bonds, since even in the homologous series of phenylhydrazones a considerable variability is observed in the positions and the intensities of the bands in this region, and other bands affected by the exchange for deuterium.

Features sensitive to deuterium substitution and important for diagnostic purposes are expected in the range 1300—1000 K. In the present case, a very strong band disappears from 1263. It appears to be replaced by a band of low intensity at 1092 K. Deuterated amides also show a more or less strong intense new band near 1000 K on deuteration, while a band near 1200—1250 K is reduced in intensity. The case of amines and secondary hydrazines has been already mentioned, having bands due to NH bending near 1250 K. Thus, the band at 1263 K in the present case is tentatively assigned to an NH bending mode. Complications may arise again from the coupling with skeletal modes, as occurs with amides.

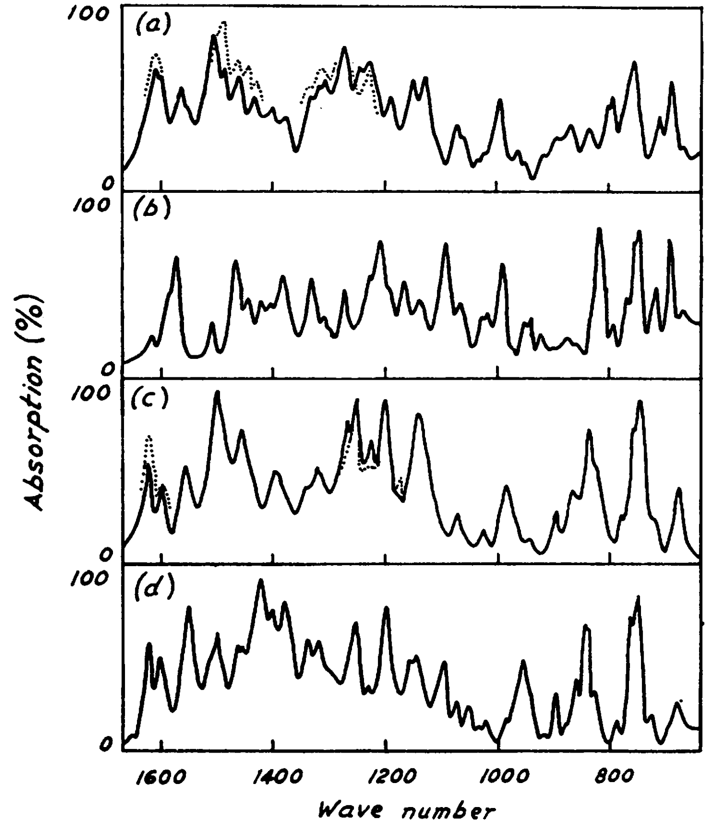

Fig. 5. *Infrared spectra of:* (*a*) *2-phenylazo-1-naphthol;* (*b*) *its O-methyl ether;* (*c*) *1-phenylazo-2-naphthol;* (*d*) *its deuterium analogue.* Dotted lines: solution in CCl_4.

The spectra of 2-phenylazo-1-naphthol, its deuterated analogue, and the *O*-methyl derivative bear the same relation to each other as those of 1-phenylazo-2-naphthol, and therefore one of each derivative is reproduced in Fig. 5. The spectra of both basic compounds have a weak and very broad absorption centred at about 2900 K (Fig. 2), similar to that noted in the spectrum of *o*-phenylazophenol. No particularly strong band appears near 1600 K, but there is a marked difference in absorption in this region between the basic compounds and their *O*-methyl derivatives. The bands at larger wave-numbers are lacking in the spectra of the latter, but stronger bands appear at lower wave-numbers (1575 and 1590 K respectively). Consequently, the bands at 1612 and 1615 K respectively in the two compounds may be due to carbonyl groups. The most prominent feature is gain the bands near 1500 K, which behave in precisely the same way as the analogous band in the previously discussed compound, except for a slightly larger shift on deuterium substitution (about 70 wave-numbers). The interpretation of this band follows the same line as above. It differs from the one given previously by Le Fèvre *et al.*,[6] who attributed the band near 1500 K in the spectrum of 2-phenylazo-1-naphthol to a phenyl ring vibration. The appearance of a similar band in the spectrum of the copper complex of the same compound must be a fortuitous coincidence. Le Fèvre's assignment does not explain the absence of the band in the *O*-methyl derivative, or the shift on deuteration. On comparison of the spectra of both *ortho*-isomers with that of the 1 : 4-isomer and the respective deuterium-substituted analogues, it may be noted that in the former two cases a larger number of bands is subject to change after deuterium substitution. Interesting is the appearance of a strong band near 1000 K. It resembles the band due to OD bending in phenols, but it might be also an ND bending, for some reason stronger than in the 1 : 4-isomer.

In order to facilitate the comparison with the electronic spectra, the infrared spectra of solutions in carbon tetrachloride were recorded (dotted in the figures). They do not differ essentially from the spectra of the solids, the main difference being in the stronger bands near 1615 K and the reduction of some bands near 1250 K. The spectrum of the molten 1-phenylazo-2-naphthol is the same as that of the solution.

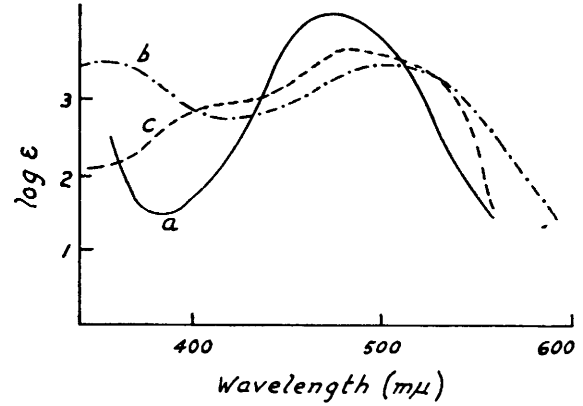

FIG. 6. *Electronic spectra of*: (*a*) *4-phenylazo-1-naphthol* (*full line*); (*b*) *2-phenylazo-1-naphthol* (— · — ·); (*c*) *1-phenylazo-2-naphthol* (— — —). Solids pressed in KBr.

Electronic Spectra.—The spectrum of the " 4-phenylazo-1-naphthol " (Fig. 6*a*) presents a single peak at 470 mμ whereas those of 2-phenylazo-1-naphthol (Fig. 6*b*) and 1-phenylazo-2-naphthol (Fig. 6*c*) have two maxima each (486, 410 and 500, 360 mμ). The peak of the 1 : 4-isomer and the long-wave maxima of the other two compounds are attributed to the quinonehydrazone form, whereas the short-wave maxima are due to the azo-chromophore. These assignments have been sufficiently discussed by previous authors.[1–3] For the present purpose it is noteworthy that the general character of the electronic absorption of the solids corresponds to that of solutions in polar solvents. However, it must be emphasised that the extinctions in the case of the spectra of the solids have a relative significance only, since the uniformity of thickness and scattering of the light by the pressed potassium bromide discs cannot be guaranteed.

Discussion.—The infrared spectra of both phenylazophenols correspond to what is expected of phenolic compounds. This is in agreement with the conclusions drawn from their electronic spectra. The problem of the structure of the so-called 4-phenylazo-1-naphthol is also clearly solved from both the electronic and the infrared spectra. The latter give evidence for the presence of a carbonyl group and an NH group, so the compound is in the phenylhydrazone form. The band attributed to the C=O group is at relatively small wave-numbers, the carbonyl band of 1 : 4-naphthaquinone being found at 1675 (solution) by Fuson, Josien *et al.*,[13] and at 1668 K (solid) in this laboratory. The hydrogen bonding is expected to reduce this value. Since the position of the NH stretching band indicates only moderately strong bonding, the shift should not exceed a few tens of

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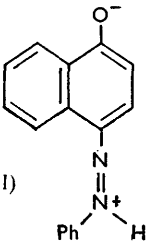
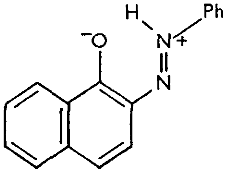
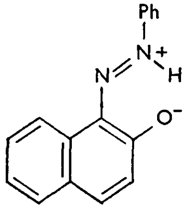
[13] Josien, Fuson, Lebas, and Gregory, *J. Chem. Phys.*, 1953, **21**, 331.

wave-numbers. The position observed thus indicates that the double-bond character of the carbonyl group is considerably reduced. Structures of the type (I) seem to play an important rôle in the state of the compound.


(I)


(II)


(III)

It is difficult to draw reliable conclusions as to the structure of phenylazo-1- and -2-naphthol from the infrared spectra alone. The band near 2900 K does not permit distinguishing between the stretching of an NH or OH group. Although OH groups usually form stronger hydrogen bonds, with subsequent large shifts and broadening of the band, the NH · · · O group has been stated [14] to give rise to very weak and broad absorption in the stretching region, like the presently observed one. However, the presence of any absorption near 2900 K indicates that the proton does not occupy a symmetrical position between O and N. Also, internal salt-formation is very improbable in view of the weakness of the band.

The bands near 1600 K can hardly be taken as characteristic carbonyl bands, since these are usually very strong. The position is lower than in 1 : 2-naphthaquinone, which has the carbonyl band at 1657 K. The lowering is due in part to the chelation, but structures of the type (II) and (III), respectively, may contribute to the reduction of the double-bond character of the C=O group. Similar atypical carbonyl bands have been observed also in other cases, *e.g.*, the tropones.[15]

The most important band for diagnostic purpose is the one near 1500 K. Since it is present neither in the *O*-methyl derivatives nor in the azophenols, but appears in the 1 : 4-naphthaquinone monophenylhydrazone, it must be connected with the hydrazone structure, and assigned as above. This conclusion is in agreement with the electronic spectra of both compounds. However, the electronic absorption indicates that the azo-form too is present in the solid in substantial amounts. The infrared spectrum does not exclude the presence of the azo-form, neither does it furnish strict proof of it. Strong hydrogen bonding is certain in the azo-form, as the example of *o*-phenylazophenol shows; hence the bonded OH band would not show up separately. The absorption of the azo-groups is difficult to identify. An indication that both NH and OH groups exist is given by the number of bands in the region 1300—1000 K, subject to change after deuterium substitution, more such bands being observed than in the case of 1 : 4-naphthaquinone phenylhydrazone. This difference cannot be explained in terms of symmetry differences or similar simple causes. However, this evidence alone is not sufficient, and the conclusion that both forms exist in the solid is based on the evidence from electronic spectra. This conclusion is rather surprising, since, to the best of our knowledge, substances exhibiting tautomerism in solution are in one form only in the crystalline state. As examples may be quoted benzoyl- and furoyl-phenylacetonitriles. Both form keto–enol equilibria in solution,[16] but in the solid state the first compound is fully enolised whereas the second is ketonic.[17] A microscopic examination of the crystals of each 1 : 2-naphthaquinone phenylhydrazone excludes the possibility of a mixture of two sorts of crystals, and probably the *X*-ray diffraction patterns could reveal more about the arrangement of the two types

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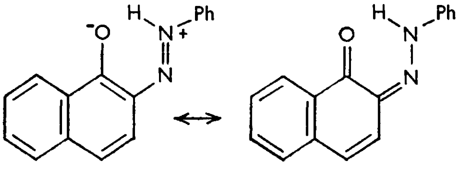
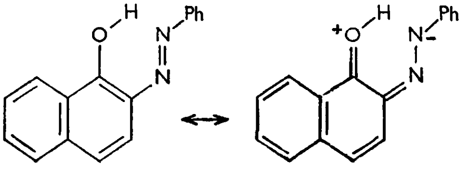
[14] Cromwell, Miller, Johnson, Frank, and Wallace, *J. Amer. Chem. Soc.*, 1949, **71**, 3337.
[15] Tišler, Thesis, Ljubljana, 1955.
[16] Russell and Mentha, *J. Amer. Chem. Soc.*, 1955, **77**, 4245.
[17] Chase and Walker, *J.*, 1953, 3518.

of molecule in the crystals, but it would not necessarily give an unambiguous result. The two types of molecule—the hydrazone and the azo—have probably very similar bond lengths in view of the resonance between the structures (II) and (V) on the one hand and (IV) and (VI) on the other. Moreover, the proton is expected to change its position (from O to N) with time, and thus the two types of molecules would give on the time average a single set of bond dimensions.



(II) (IV)



(V) (VI)

Experimental.—Some of the substances were given by Dr. A. Burawoy or by Imperial Chemical Industries Limited, Dyestuffs Division; others were prepared in this laboratory. The *O*-methyl derivatives were prepared by Charrier's method.[18] The exchange with D_2O was effected by dissolving the substances in dioxan (dried by refluxing over sodium) and adding some D_2O. The precipitated substance was filtered off and dried. All operations were performed in a micro-flask designed to exclude atmospheric moisture. The infrared spectra were recorded with a Perkin-Elmer Model 21 spectrometer, equipped with a rock-salt prism. The solid substances were made into mulls with mineral oil or hexachlorobutadiene. Some of the substances were pressed with potassium bromide into discs, in order to match the conditions used in recording the electronic spectra. In general, the mulling technique gave spectra of better quality. The electronic spectra were taken with a Beckman DU spectrometer. A holder was constructed to hold potassium bromide discs of 12-mm. diameter. These were prepared by grinding the solid together with the bromide or by sprinkling powdered bromide with an acetone solution of the substance. The results were identical in the two cases.

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[18] Charrier and Casale, *Gazzetta*, 1914, **44**, 228.