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NMR Spectroscopy of Azo Dyes

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The known NMR spectroscopy data on different types of synthetic azo and polyazo dyes, including metal complexes, are correlated. The fundamentally new opportunities in the NMR spectroscopy of ^{1}H, ^{13}C, and ^{15}N nuclei in solving problems of structural chemistry in this field of industrial chemistry are demonstrated.
The bibliography includes 124 references.

CONTENTS

I. Introduction 941
II. Characteristics in studying azo dyes by NMR spectroscopy 941
III. Hydroxyazo dyes 944
IV. Aminoazo compounds 946
V. Labile hydroxyazo dyes. Tautomerism 947
VI. Azo derivatives of naphtholsulphonic acids 949
VII. Polyazo dyes 950
VIII. Formazan dyes 951
IX. Complex compounds of azo dyes with metal ions 952

I. INTRODUCTION

In relation to the practical application of synthetic dyes in chemistry and technology, azo compounds X−N=N−Y probably constitute the most important, diverse, and structurally ramified class of compounds.[1-5] Formazans −N=N−C(X)=N−NH− are also starting to be used actively in the chemistry of dyes.[5] While NMR spectroscopy as a powerful instrument for research into the molecular structure of compounds in solution and in the solid state is used for analysis of the structure and properties of azo dyes, the scale of its practical application falls short of the potentialities of this very same physical method and the number of unresolved problems in the chemistry of synthetic dyes. The first and until now only reviews on the NMR spectroscopy of synthetic dyes, primarily in its simplest form, appeared in the middle of the 1970's,[6,7] and they do not include the complete range of methods and wealth of opportunities which characterises the NMR spectroscopy of recent years. On the other hand, the chemistry of synthetic dyes is a forerunner of contemporary industrial chemistry and is frequently based on outdated concepts about the structure of some of its members, although many problems can be solved and have already been solved by means of NMR spectroscopy.

An attempt is made in the present work to correlate the existing NMR data on the structure and properties of azo dyes in solution and in the solid state and also on the methods of using NMR spectroscopy to resolve problems of structural chemistry in this area of chemistry.

Ideas about the actual structure of aromatic azo dyes in solution developed in spiral fashion, as so often happens, and NMR spectroscopy made a significant contribution to the solution of this problem and in a number of cases played a decisive role. By about 1970 the collection of NMR spectroscopy data obtained[8-20] (equally using other methods, see, for example one review[21]) contributed quite considerably to the understanding of the structure of these compounds in solution.[15] However, only in the last 15−17 years has the role of NMR spectroscopy in solving problems of azo dye chemistry become really significant.

The fact cannot be ignored that the structural problems of the chemistry of azo dyes and formazans are essentially inseparable from such fundamental chemical concepts as intramolecular hydrogen bonding, azo−quinone hydrazone tautomerism, internal rotation in molecules, complex formation of azo dyes with metal ions, and so forth. We have naturally taken this into account.

The aim of the present review is to show how the problems of the chemistry of synthetic azo dyes and formazans can be seen in the light of the existing information and potential applications of contemporary NMR spectroscopy. We believe that such a type of examination will be of some use to specialists working in this field of chemistry.

II. CHARACTERISTICS IN STUDYING AZO DYES BY NMR SPECTROSCOPY

(a) NMR Spectroscopy of Different Nuclei in Solution

^{1}H NMR spectroscopy has provided information about the structure of azo dyes in solution,[8-19, 22-49] including those containing a heterocyclic fragment.[34-39] In particular, information about the shielding of mobile protons in OH, NH, and SH groups, which are very frequently encountered in azo dyes, has proved productive. These and other findings provide definite information on intramolecular hydrogen bonding[8,11,18,27] and the tautomeric state[9,49] in azo dyes, on their protonation[12,13,16] and complex formation with metal ions,[28-33] and make it possible to build up initial ideas about their structure and transformations in solution.

In recent years, starting with one report,[50] a large amount of data has been obtained on the NMR spectroscopy of ^{13}C nuclei. These atoms constitute the skeleton of aromatic azo dyes and the information obtained is therefore especially useful. From the information available,[50-104] including that on compounds that do not contain functional hydroxy or amino groups,[50,81-93] it is possible to have

some idea about the electron distribution in the molecules,[50,88,89] to determine the barriers of internal rotation about the

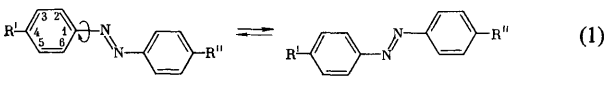


bond,[84,85] and to consider questions concerning the formation and cleavage of intramolecular hydrogen bonds in azo dyes,[59,62] the presence or absence of tautomerism in them,[70–74, 99, 101, 103, 104] and the spectral distinctions between *cis*- and *trans*-isomers.[90,91,93,100] All this information provides the necessary basis for an unequivocal interpretation of the ^{13}C NMR spectra of many types of azo dyes, including those containing heterocyclic groups.[66–69] It also provides the basis for making calculations to predict ^{13}C NMR spectra and computer knowledge of previously unstudied or newly synthesised dyes. There is also NMR information on dyes which has been obtained on ^{15}N,[93–109] ^{14}N,[20] and ^{17}O [19] nuclei; but the practical study of ^{15}N and ^{17}O nuclei at the present time is not yet as easy as it has become for ^{13}C and ^{1}H.

The NMR spectroscopy results on synthetic azo dyes are not limited to information on the shielding of their nuclei. In order to determine the structure and tautomeric state of the molecules, the results of studying various types of spin-spin coupling constant have been used, for example, mainly for ^{15}N-labelled molecules.[14,15,101, 103,106] Other techniques included in the arsenal of contemporary NMR spectroscopy have also been used—isotope effects,[94,96] temperature-dependent NMR spectra,[14,15,27] analysis of solvation effects,[62,72] two-dimensional spectroscopy,[104] and NMR titration.[57,58,64]

(b) NMR in the Solid State and Other Applications

The study of azo dyes in the solid state using high-resolution NMR spectroscopy started only in recent years.[77–80] Thus, in the first study of this type,[77] splitting of the signals from the *ortho*- and *meta*-carbon atoms was found in the solid state when the ^{13}C NMR spectra of *trans*-azobenzene and a large number of its *p,p'*-substituted derivatives (I) ($R' = R'' = H$, CH_3, OH, COOH, etc.) were studied. The overall range of differences ($\Delta\delta$) in the shielding of nuclei amounted to 13–18 p.p.m. for C(2,6) and 1.5–3 p.p.m. for C(3,5), and are thus virtually no different from what was observed in solution. The informative nature of high-resolution ^{13}C NMR spectroscopy in the solid state was demonstrated[77] when the first real example—the azo dye Disperse Orange—was studied. However, it should be emphasised that a more productive application of this branch of NMR spectroscopy is associated with solving the question concerning the unequivocal interpretation of NMR spectra, and the first steps in this direction have already been taken in the study[78] of the ^{13}C NMR spectra of Pigment Red 57:1 and for some other dyes that are azo derivatives of 2-naphthol (Pigments Red 1, 3, and 6).[80]



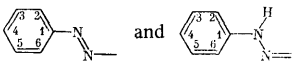
(1)

(I)

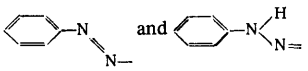
We can indicate other examples of using NMR spectroscopy that are important for the chemistry and technology of azo dyes such as analysis of the reaction of azo dyes with a substrate material,[45,46,52, 65,110] including those forming a mesomorphic phase[46] and investigation of their photo- and thermal isomerisation.[43,44,111] The aggregation of azo dye molecules in solution, and so on, has been examined.[48] All these reports undoubtedly constitute no more than the beginning of a wide range of research work which is expected to appear in the very near future, taking into account the progress in NMR spectroscopy in creating very new, extremely effective, and informative research methods.

(c) Distinguishing Features of NMR Spectroscopy in Determining the Structure of Azo Dyes in Solution

One of these is directly related to the problem concerning the effect of the azo group on shielding of ^{13}C nuclei in the aromatic ring of the diazo component of azo dyes. Thus, fairly recently the basic possibility of differences in the ^{13}C NMR spectra of the phenylazo group in two fixed and structurally distinct positions was



demonstrated.[51] This fragment was subsequently used[66,69] as a convenient diagnostic instrument in the unequivocal determination of the structure of azo dyes using NMR (in azo derivatives of 5-pyrazoline,[63,99] chromotropic acid,[55] H-acid,[61] the simplest hydroxyazo compounds used to synthesise metal-complex dyes,[59] and so forth). Moreover, this method has been successfully used for a qualitative assessment of the position of the azo–quinone hydrazone tautomeric equilibrium in azo dyes (for example, azo derivatives of 2-naphthol,[72,99] violet acid,[63] etc.). It transpired that the



groups differ markedly and clearly with respect to their shielding of carbon nuclei. When changing from a phenylazo to a phenylhydrazone group there is an upfield shift in signals from C(1), C(2), and C(4) (by ~11, 7, and 5 p.p.m. respectively). Of course, in the chemistry of synthetic azo dyes the phenyl group itself is not used so much as mono- and poly-substituted aromatic groups with the most diverse forms of substitution (depending on the problem). An appropriate correlation[109] showed that other, more commonly used aryl groups of diazo components that contain a particular substituent in the benzene ring (SO_3Na, Cl, COOH, NO_2, etc.) or a combination of certain substituents can also be used successfully for identification of the structure and conversions of azo dyes using ^{13}C NMR.

Another distinguishing feature also relates to the problem of differentiating the azo and quinone hydrazone forms of azo dyes using NMR when some hydroxy derivative of benzene, naphthalene, or anthracene acts as the azo component during their synthesis. The ^{13}C NMR signal from the carbonyl group in different types of quinoid structures is known to occur at much lower field than the signal from the $^{13}C–OH$ group in corresponding aromatic hydroxy compounds.[109] This fact was used for unequivocal identification of azo dyes in the quinone hydrazone form (examples such as arylazo derivatives of 2-naphthol,[66,67,72] chromotropic acid,[55,56] H-acid,[61] etc.) or in the azo form (examples such as derivatives of phenol,[51,52,62,64] resorcinol,[62] and 2-naphthol,[59,72] etc.).

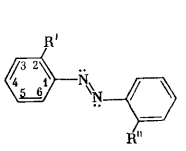
(d) Internal Rotation About the C—C Single Bond

The azophenyl fragment is known to be nonlinear in the gas phase and in the crystalline state a planar structure is the most favourable. The ^{13}C NMR spectra of *para*-substituted azobenzene (I), obtained under normal conditions, show, however, that in solution the pairs of nuclei of the *ortho*-carbon atoms C(2,6) as well as the pairs from the *meta*-carbon atoms C(3,5) are equivalent.[50,77] At low temperatures in inert solvents nonequivalence also does not occur either in the C(2,6) pair or the C(3,5) pair.[84] Thus, the available NMR data suggest a fairly rapid (relative to the time scale of NMR spectroscopy) internal rotation about the single C—N bond [reaction (1)]. This rotation is accompanied by averaging out of the shielding of these nonequivalent pairs of carbon nuclei (and, naturally, the hydrogen nuclei in ^1H NMR).

In recent years the conditions for slowing down process (1) were found when the ^{13}C NMR spectra of azobenzene derivatives in solution were studied.[84,85] The authors identified the conditions for structural modification of compounds (I) that would make it possible to increase the double-bond character of the C—N bond and slow down the internal rotation (1) accordingly. This can be achieved by the introduction of an $N(CH_2CH_3)_2$ substituent, which is often used in disperse azo dyes, at a position *para* to the azo group. As a result, in the ^{13}C NMR spectrum at a sufficiently low temperature in inert media it is possible to observe the signals from C(2) and C(6) separately ($\Delta\delta$ = 18 p.p.m.) as well as the signals from C(3) and C(5) ($\Delta\delta$ = 1.7 p.p.m.). The increase in rotation barrier about the C—N bond is determined, as the NMR data showed, not so much by steric factors as by electronic factors. In this case the electronic requirements necessary for slowing down the rotation about the C—N bond are different for the substituents acting from different sides of molecule (I). Process (1) is retarded by the introduction of an electron-donating group R′ = $N(CH_2.CH_3)_2$ on the aromatic ring side and also by the increase in electron-withdrawing capacity of the R″ group (in the series $N(CH_2.CH_3)_2$, H, NO_2) at the *para* position of the other benzene ring on the azo group side.

(e) Conformational Properties of Azophenyl Fragment

It is possible by means of NMR spectroscopy to determine unequivocally the structure of azo dyes of type (II) in solution, where groups R do not form intramolecular hydrogen bonds with a nitrogen atom.

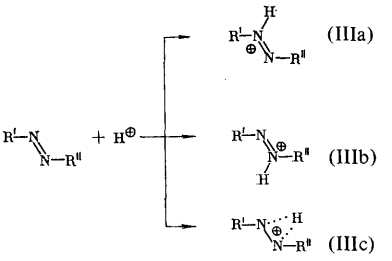


(II)

In fact, by introduction of *ortho* substituents and retardation of the internal rotation about the C—N bond, changes in shielding of the C(2) and C(6) nuclei in the ^{13}C NMR spectrum of compounds (II) take place in opposite directions. In the low-temperature splitting of the signal that corresponds to the C(2,6) nuclei in the high-temperature spectrum, the signal from the C(2) atom, which occupies the *cis* position relative to the unshared electron pair of nitrogen, is shifted downfield by about 8 p.p.m., while the signal from the C(6) atom, which occupies the *cis* position relative to the N=N bond, is shifted upfield by about 9 p.p.m.[84,85] This effect occurs in solution and at normal temperatures if the respective structural changes are made to azobenzene.[77] In particular, for 2,2′-dimethylazobenzene the C(6,6′) signal is shifted upfield by about 7.5 p.p.m. in comparison with unsubstituted azobenzene, which is clear evidence for the occurrence of only one out of three possible conformations, namely, conformation (II), R′ = R″ = CH_3. Similar results were also obtained for a wider range of compounds (II) (R′ = R″ = AlK[79]). Neither the interpretation nor the prediction of ^{13}C NMR spectra of new or previously unstudied azo dyes is possible without taking this fact into consideration.

(f) Protonation and Deprotonation of Azo Dyes

The NMR data can resolve unequivocally questions about the structural changes in aromatic and aliphatic azo dyes that occur when they are protonated in strong acid media and also deprotonated in alkaline media.



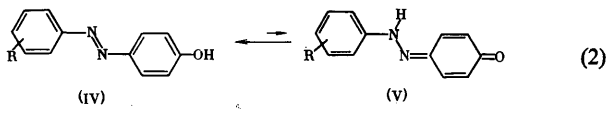
(IIIa) (IIIb) (IIIc)

In principle, the intermediates that are formed on protonation of azo dyes can have the form of (IIIa—c). NMR spectroscopy data[12,13] obtained using symmetrical model azo compounds with R′ = R″ = Ar as an example indicate that in the protonated form the aryl rings become nonequivalent (the NMR signals from indicative groups in both rings are nonequivalent). This suggests an asymmetric type of addition of the proton to the azo group. Similar results were obtained when R′ = R″ = tert-C_4H_9.[12] Thus with these results the concept of a symmetrically protonated azo structure (IIIc) can be rejected. The choice between the asymmetric structures (IIIa) and (IIIb) when R′ ≠ R″ is wholly related to the properties of the electronic effect of the R′ and R″ groups on the N=N fragment.

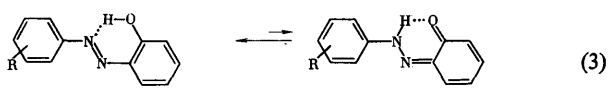
Results that are just as fundamental are given by NMR data, in particular for ^{13}C nuclei, when the consequences of deprotonation of molecules are studied (NMR titration).[64,109] The use of NMR titration to clarify the results of this chemically and industrially not infrequent situation, which occurs on alkali treatment of azo dyes, provided the answer to a number of questions concerning the structure in solution of azo derivatives of phenol,[62,64] resorcinol,[62,64] 1-naphthol,[64] and chromotropic acid.[57,58] Turning to the problem, for example, about the tautomeric form of azo dyes, ^{13}C NMR was successfully used to demonstrate, in particular, the possible occurrence of three conceivable situations during NMR titration—retention of the azo form (in phenol derivatives), its transformation from the azo to the quinone hydrazone form (in resorcinol derivatives), and its transformation from the quinone hydrazone to the azo form (in one of the 4-derivatives of 1-naphthol).[64] Even more complex situations were observed in the NMR studies of a series of azo derivatives of chromotropic acid.[57,58]

III. HYDROXYAZO DYES

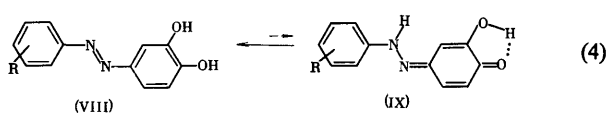
Hydroxyazo compounds constitute a considerable portion of the total number of azo dyes and include those acting as ligands in metal-complex dyes. The azo group in them is not only a chromophore but also a necessary component with an O-N type of coordination unit, because of the presence of a hydroxy substituent in the azo component.



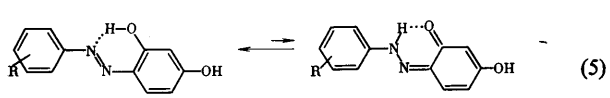
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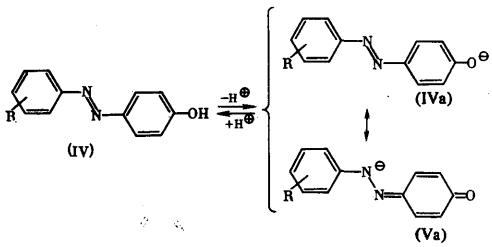
(4)



(5)

With regard to the question of the structure of hydroxyazo derivatives of benzene, which from a general hypothetical viewpoint can be represented as a mixture of products that make up tautomeric equilibria (2)–(5), there is extensive coverage on NMR in the literature. The ^{1}H,[8,14,15,17,25] ^{13}C,[59,77,99] and ^{15}N[105] NMR data suggest, however, that if diphenyl mono- and di-hydroxyazo compounds do not undergo special modification and the media conditions do not lead to complete removal of a hydroxyl proton, they only have the azo structure in solution. In other words, tautomeric equilibria (2)--(5) are shifted almost completely to the left. In fact, for each type of structure (IV), (VI), (VIII), and (X) the pattern of frequencies of ^{13}C NMR signals from the hydroxyphenyl fragment from compound to compound remains one and the same.[59] The ^{13}C NMR signal from the C–OH group, the most important in terms of identification, with allowance made for the electronic effect of the azo group in the spectra of compounds (IV), (VI), (VII), and (X) occurs in the same region as the C–OH signal of nonionised phenol: in (IV) $\delta_{C(4)}$ ~159–162.5 p.p.m.; in (VI) $\delta_{C(2)}$ ~150–154 p.p.m.; in (VIII) $\delta_{C(4)}$ ~146–147 p.p.m.; in (X) $\delta_{C(2)}$ ~153–160 p.p.m. and $\delta_{C(4)}$ ~163–166 p.p.m. These ^{13}C NMR findings can be used as a distinguishing feature in establishing the structure of the hydroxyphenylazo fragment in newly studied dyes.

In azo compounds (IV), by extrapolation from the conformational data, the proton signal from the *para*-hydroxy group in the ^{1}H NMR spectrum occurs at comparatively low field (δ_{OH} ~7.5–10 p.p.m.), and this suggests that it has a fairly acidic nature. Shielding of the hydroxy proton depends on both the properties of the substitutuent R and the properties of the medium.



In the anion form of compound (IV) the azo form (IVa) can be retained in principle, although on deprotonation it can be transformed at a given stage to the quinone hydrazone form (Va), as has been observed sometimes,[4] and these forms can be completely discrete rather than being two ways of writing the same intermediate structure. From the ^{13}C NMR data[62,64] obtained for the industrially important compounds (IV) with SO_3Na substituents at the *meta* position, however, it follows from the phenolate anions formed from them that in the spectra there are no fundamental differences from the corresponding anions not containing azo groups. Thus, there are no grounds for proposing the formation of the quinone hydrazone form (Va) during ionisation of azophenols.

However, the experimental data examined were obtained using the simplest examples of compounds (IV). Structural complexity of the molecules at times leads to unexpected results. An example of this is provided by the conditions identified[10,23,24,51] for shift of equilibrium (2) to the right and the existence of quinone hydrazone tautomer (V) in a series of 4-hydroxy derivatives of specifically substituted azobenzenes.

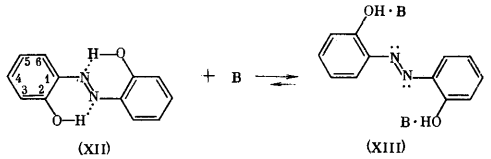
The authors[23,24] introduced electron-withdrawing substituents into the diazo component of 4-hydroxyazobenzene and electron-donating substituents into the azo component. In solutions of most of the compounds in aprotic solvents two tautomeric forms are observed separately in the ^{1}H NMR spectra—both the azo (IV) and quinone hydrazone (V) forms. Their identification was carried out by ^{1}H NMR and the ratio of tautomers was determined by integration. The ^{1}H NMR data obtained can be used to formulate the factors that determine the shift of the azo–quinone hydrazone tautomeric equilibrium (20) in either direction.

On changing from *para*- (IV) to *ortho*-hydroxy compounds (VI) the signal from the hydroxy proton is shifted downfield by 3 to 4 p.p.m. (when R = H, for example, depending on the properties of the medium and the concentration of the compound its chemical shift δ_{OH} = 12.0–12.9 p.p.m..[8,9,11,17] The magnitude of this shift is determined by the nature of the medium and the electronic and steric effects of substituents. This change in shielding of the hydroxy proton on going from (IV) to (VI) is due to the formation of a fairly strong intramolecular hydrogen bond C–O–H...N= in the respective azo structures.

Further changes in chemical shift of the hydroxy proton could be due to its intramolecular transition of NH/OH hydrogen bonding relating to the basic possibility of forming quinone hydrazone (VII). However, in reality, it hardly occurs at all in the compounds examined.

Interesting results have been obtained in studies of 2,2′-dihydroxyazobenzene (XII) using NMR. ^{1}H NMR data obtained at fairly low concentrations, which exclude the effect of aggregation, indicate that the compound has an azo structure in solution (δ_{OH} = 12.0 p.p.m. in inert media).[8,11] The same conclusion is reached when ^{13}C NMR spectroscopy is used.[59] However, when acetone-d_6

is used as the solvent instead of $CDCl_3$, in the ^{13}C NMR spectra of this compound there is a shift of the C(6) signal upfield by ~2.5 p.p.m. This fact is related to cleavage of the O–H...N intramolecular hydrogen bond in some of the molecules, in other words, there is a given shift of equilibrium (6) to the right. As a result, some of the molecules acquire a sterically more favourable conformation (XIII), in which the bulky *ortho*-substituent is aligned not in the direction of the N=N double bond but in the direction of the unshared electron pair of the nearest nitrogen atom. The average picture is recorded spectroscopically.



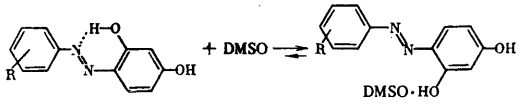
(XII) (XIII) (6)

The maximum upfield shift of C(6) that occurs assuming conformation (XIII) is more than ~8 p.p.m., and this effect occurs only in DMSO when cleavage of the intramolecular hydrogen bond occurs for all the molecules of 2,2′-dihydroxyazobenzene.[109]

In the ^{13}C NMR spectrum of 2,4-dihydroxyazobenzene—the simplest of the azo compounds (X) with a resorcinol azo component (R = H)—the pattern of frequencies of the ^{13}C signals is that expected for the azo structure and is due to the electronic effect of two hydroxy and one azo group[5] taking into account some effect from the intramolecular hydrogen bond.

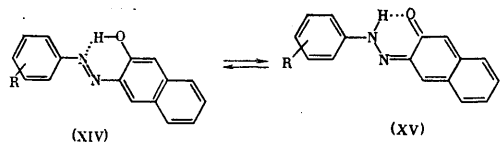
The same result is also shown by the introduction of an ^{15}N label into the compound at the N_β position.[15] The NMR signal of the proton at lower field (in this compound two hydroxy signals with δ_{OH} = 11.0 and 12.4 p.p.m. are observed), as also before introduction of the label, again proves to be a singlet over a wide temperature range although for equilibrium (5) it should have split into a doublet with the $^1J_{^{15}N-^1H}$ spin-spin coupling constant being greater the higher the content of quinone hydrazone tautomer (XI) in the mixture of (X) and (XI).

A feature of compounds of type (X) is that when acetone or alcohol is replaced by a powerful solvating medium such as DMSO, there is a marked upfield shift, which is almost the maximum possible, of the signal corresponding to C(6).[62] It is due to the replacement of an intramolecular by an intermolecular hydrogen bond with solvent, and, as a result, to the almost complete displacement of equilibrium (7) to the right and the adoption of a more favourable conformation by the compounds under these conditions:

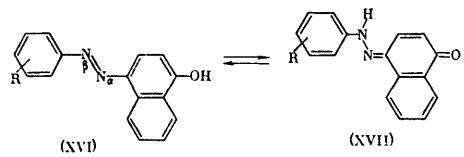


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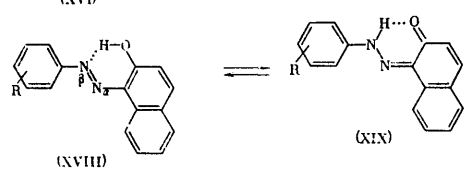
In phenyl-naphthol azo dyes, 1-naphthol or 2-naphthol act as the azo component. In principle they can participate in azo–quinone hydrazone equilibria (8)–(11). This class of compounds has been used and studied in the chemistry of azo dyes especially often.[1-5] However, in actual fact, when the equilibrium is significantly displaced in one or other direction, apparently only azo structures (XIV) and (XVI) can be identified as stable structures of this type—and then with reservations. The compounds that make up equilibrium (8) can in principle adopt both the azo form (XIV) and the quinone hydrazone form (XV). However, as it follows from the ^1H NMR data, in $CDCl_3$ they have the azo structure (XIV) (the value δ_{OH} = 12.1 p.p.m.[11] is consistent only with this type of structure). The question concerning the structure of these compounds in aqueous media remains open for the time being. Investigation of the ^1H NMR spectra of 1-benzeneazo-4-naphthol, in particular, analysis of the shape of the signal from the hydroxy proton when an ^{15}N label was introduced into the N_β position of the azo group showed[10,15] that in organic solvents this compound exists in the azo form (XVI) (R = H). ^{13}C NMR spectra obtained in nonaqueous media when R = *o*-OH are also consistent with the azo structure.[59] With regard to the possible shift of equilibrium (9) to the right in aqueous media, this question requires special consideration.



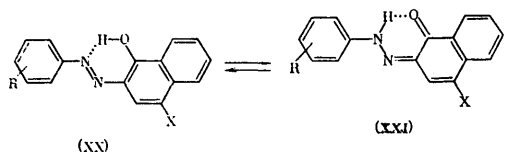
(XIV) (XV) (8)



(XVI) (XVII) (9)

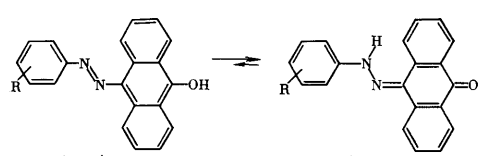


(XVIII) (XIX) (10)



(XX) (XXI) (11)

In one study[112] using ^1H NMR, the possibility of equilibrium (9) being displaced to the right (in acetone, where R = H) was discussed. However, this treatment was based on an analysis on the signal observed in solution with δ_{OH} = 3.59 p.p.m. (corresponding to an impurity, as has been revealed[70]) and consequently on an incorrect assignment of the main signal with δ_{OH} = 10.2 p.p.m. to the quinone hydrazone form (XVII), although in reality it belonged to the azo form of this compound (XVI).

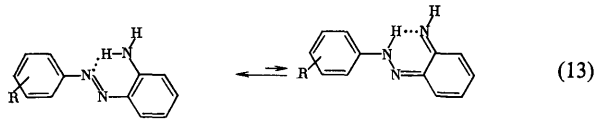


(XXII) (XXIII) (12)

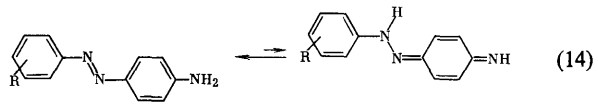
The last example from the number of basically distinct, stable aromatic hydroxyazo systems is 9,10-anthraquinone phenylhydrazone. According to ^1H [15] and ^{14}N [20] NMR data, this compound exists in the quinone hydrazone form (XXIII) (equilibrium (12) displaced to the right). Conformation of this is provided by the appearance of a $^{15}N-^1H$ spin-spin interaction in the ^1H NMR spectrum with a coupling constant that is independent of the temperature.

IV. AMINOAZO COMPOUNDS

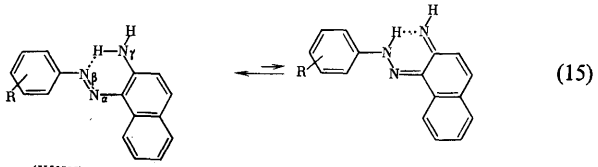
The conditions for formation of an iminoquinone hydrazone structure among aromatic aminoazo dyes is less favourable compared to hydroxyazo dyes as a result of the lower acidity of the NH proton compared to the OH proton and as a result of the differences in geometry for configuration of the proton in a hydrogen bond. Positive indications of the azo structure in aminoazo dyes are given by both ^1H [27,41] and ^{13}C [60,70,101] NMR spectroscopy data.



(13)

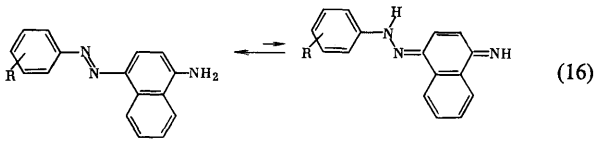


(14)

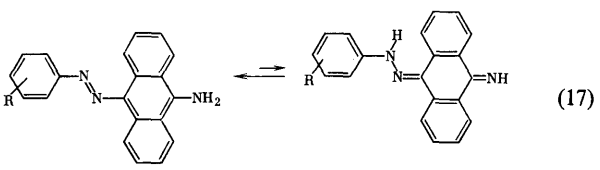


(15)

(XXIV)



(16)

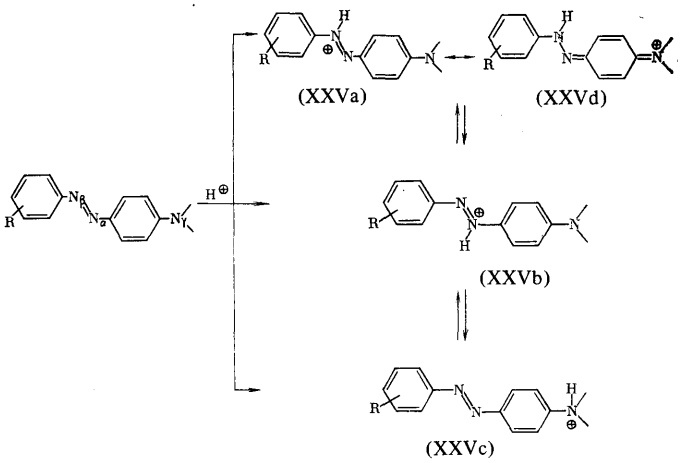


(17)

According to ^1H NMR data,[27] in the dye Fat Yellow AB (XXIV) (R = H) and in azo dyes (XXIV) in general it is the shielding of the NH proton that participates in intramolecular hydrogen bonding that suggests an azo structure, namely a complete displacement of the hypothetical equilibrium (15) to the left. At fairly low temperatures the signals from the protons of the amino group in (XXIV) are split; the proton contained in the N–H...N hydrogen bond has a shift δ_{NH} = 10–10.2 p.p.m., while the free proton has δ_{NH} = 5–5.3 p.p.m. On the other hand, in iminoquinone hydrazone structures the NH proton is shifted to lower field (δ_{NH} = 14 to 16 p.p.m.). The fact that both NH protons in these compounds are located precisely on N_γ was confirmed[27] by the introduction of an isotopic label N_γ = ^{15}N. In this case both the NH_2 protons are split by the ^{15}N nucleus with approximately the same constant. Accordingly, introduction of a ^{15}N isotope to replace N_β did not lead to splitting of the NH proton.

The ^{13}C NMR data[60,70,101] gave the same results. As was demonstrated in one study,[101] the azo structure actually occurs not only in substituted azobenzenes, where equilibria (13) and (14) could be assumed, but also in more complex compounds in which the amino group is joined to naphthalene or anthracene aromatic systems [hypothetical equilibria (15)–(17)]. In the ^{13}C NMR spectrum of the phenylazo derivative of aminoanthracene, for example, as in a number of related compounds, the chemical shifts of the different nuclei in the characteristic phenylazo group are clearly consistent with the azo structure of the $C_6H_5-N=N-$ fragment, namely, with the complete displacement of equilibrium (17) to the left. It is significant that the spectrum of the naphthylamine fragment of (XXIV) is the same regardless of the properties of the substituent R in the phenylazo group.[60,70,101] In this case the frequency pattern of the ^{13}C NMR signals from the naphthylamine fragment is consistent with its azo structure and is not satisfactorily interpreted on the basis of the iminoquinone hydrazone structure. The lack of dependence of the shielding of the NH proton participating in hydrogen bonding on the properties of substituent R was also observed in the ^1H NMR spectra of these compounds.[27]

Let us examine the NMR spectroscopy data on *para*-aminoazobenzene derivatives. Introduction of an amino group leads to a situation where in *para*-aminoazobenzene itself (Disperse Diazo Claret) and in dyes of this type in general (Fat Soluble Yellow 2G, Methyl Organe, etc.) that have three basic centres N_α, N_β, and N_γ, three monoprotonated structures (XXVa–c) that differ according to the site of proton attack, including two isomers (XXVa) and (XXVb) that are asymmetrically protonated on the azo group, can in principle occur:



(XXVa) (XXVd)

(XXVb)

(XXVc)

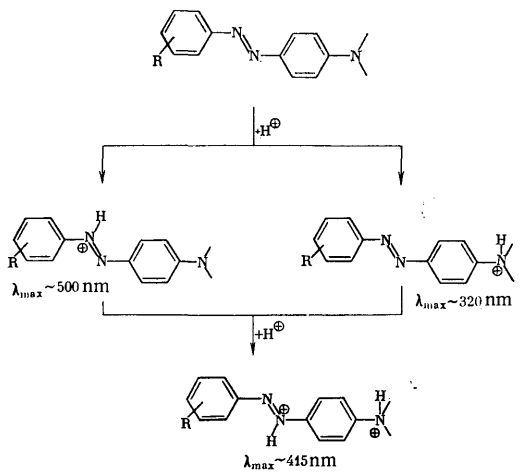
There is an interesting debate[1,2,21] over the interpretation of the spectroscopic data on the protonation of aromatic aminoazo dyes. It is based on the suggestion of the possible occurrence in these compounds of tautomerism of the form:



There has also been a discussion on the question concerning the addition site of a proton to the azonium cation—either to the α- or β-position.

These problems can be resolved almost completely using the NMR data. In weakly acid media these derivatives form one or both monocations—ammonium salt (XXVc) and one of the azonium salts. Making use of the arguments of NMR spectroscopy we can, in addition to ^1H NMR studies,[12,13,16] also indicate other works,[88,95]

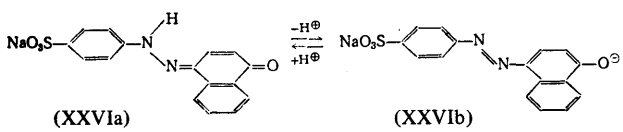
where a sample of Disperse Diazo Claret enriched with ^{15}N was analysed on its ^{13}C and ^{15}N nuclei. The authors showed that in a weakly acid medium the proton adds on either to N_γ or to N_β. The first isomer predominates in solution, while in the second isomer the distribution of electron density corresponds precisely to azonium structure (XXVa) and not to mesomeric structure (XXVd). Thus, on the basis of a direct NMR experiment, two questions are resolved—the site of addition of the proton to the azo group (N_α or N_β), namely, identification of cation (XXVa) or (XXVb), and the structure of the azonium cation formed. Addition of the proton to N_β is evidently due to the orienting effect of the *para*-amino group. In strong acid media there is a structural transformation in the dication formed, and the second proton is found to be added not to N_β but to N_α. Taking into account these results, protonation of Disperse Diazo Claret and related azo dyes can be represented as follows:



V. LABILE HYDROXYAZO COMPOUNDS. TAUTOMERISM.

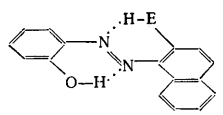
From the four phenylnaphthol hydroxyazo systems (8)–(11), usually a given limiting tautomeric form does not occur in the two depicted in equilibria (10) and (11) but there is an azo–quinone hydrazone tautomeric equilibrium. Conditions can be selected when tautomeric system (9) also becomes labile; NMR data relating to the preferred formation of the azo form for this was given above.

When Orange I (structure (XVI)/(XVII), R = *p*-SO_3Na) was studied using ^{13}C NMR, it was found[65] that the chemical shift of the C(4) nucleus was 186.3 p.p.m. (probably in D_2O). Although the authors[65] interpreted the results in favour of the azo structure (XVI), the magnitude of the shielding of C(4) objectively indicates the quinone hydrazone structure (XVII), namely, the complete displacement of equilibrium (9) to the right. A subsequent study of this dye using NMR showed[64] that the change of colour it undergoes in an alkaline medium is due to conversion (18), which occurs by deprotonation, namely, transformation of neutral quinone hydrazone form (XXVIa) to the ionised azo form (XXVIb).

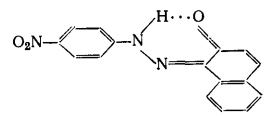


(XXVIa) yellow (XXVIb) red (18)

Arylazo derivatives of 2-naphthol constitute a large group of azo dyes (Fat Soluble Orange, Fat Soluble Orange 2K, Pigment Red G, Fat Soluble Dark Red, Chrome Violet K, Acid Orange G, Pigment Scarlet, etc.) that are not without significance in dye chemistry and are very interesting from the methodical viewpoint. It is not possible to assign a definite structure to these azo dyes but they should be regarded as forming azo–quinone hydrazone equilibrium (10). This equilibrium has been studied by NMR in relatively greater detail than the others—under different conditions and using various techniques of NMR spectroscopy.[8,10,14,15,19,20,49,59,70–74,80,99,106] Thus, when 1-benzeneazo-2-naphthol (Fat Soluble Orange dye; structure (XVIII), R = H) was studied, it was found[8] that the signal from the hydroxy proton was shifted downfield by ~3 p.p.m. relative to *ortho*-hydroxyazobenzene and 2,2′-dihydroxyazobenzene. Although an explanation for this effect was given in terms of azo structure (XVIII) (assuming that a stronger C–O–H...N hydrogen bond is formed in (XVIII) than in *ortho*-hydroxyazobenzenes), such an explanation could not be the only one since in the absence of any substantial structural changes in comparable hydroxyazo compounds that include the same type of intramolecular hydrogen bonding the magnitudes of the effect found[8] are too high. An alternative conclusion followed from ^{17}O NMR findings,[19] which indicated a certain double-bond character of the C–O bond, namely, some displacement of equilibrium (10) to the right. In other words, the downfield shift of the signal from the OH proton that occurs in compounds of type (XVIII) is due not so much to the increase in strength of the COH...N bond as to its change of form (C–O–H...N → C=O...H–N), namely to the development of azo–quinone hydrazone tautomerism (10). In subsequent NMR studies[10,14,15,20,49,59,70–74,80,99,106] the authors started precisely from this point and studied the dependence of the position of equilibrium in tautomeric system (10) on different factors such as the temperature of the solvent, type of medium, and changes in structure of the azo dye.



(XXVII) a) E = O, b) E = NH



(XXVIII)

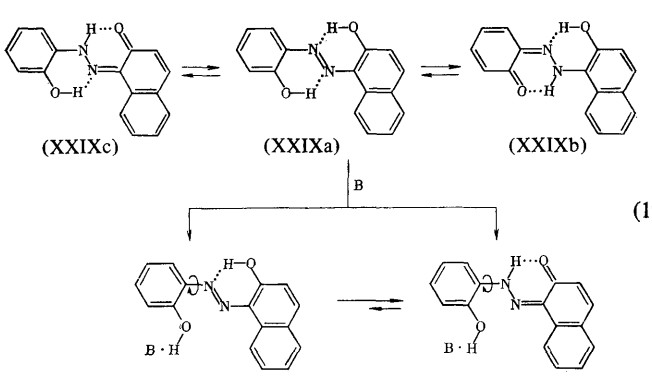
In particular, examples of the limiting tautomeric forms of these compounds—(XXVII) and (XXVIII)—were found, according to the ^{13}C NMR data.[59,70,109] In compounds (XXVII), studied in the polar but nonsolvating medium of chloroform, the experimental chemical shifts of the C(2) and C(4) nuclei ($\delta_{C(2)}$ ~153–155.8 p.p.m.; $\delta_{C(4)}$ ~133–136 p.p.m.) are similar to those calculated for a proposed azo structure. Here equilibrium (10) is displaced to the left and stabilisation of the azo form is achieved by two O–H...N hydrogen bonds that are similar in structure in (XXVIIa) or by the combination of different hydrogen bonds N–H...N and O–H...N in (XXVIIb). The dye Pigment Red G, on the other hand, has the quinone hydrazone structure (XXVIII), as is indicated by the value of the chemical shift $\delta_{C(2)}$ ~180 p.p.m., which is characteristic of the ketone group in the quinonoid ring, as well as by the significant change in chemical shift of C(4) ($\delta_{C(4)}$ = 143.5 p.p.m.). For this dye equilibrium (10) is displaced to the right.

Several NMR methods have been suggested for qualitative and quantitative determination of the position of the tautomeric equilibrium in system (10): a) from the change in proton chemical shift δ_{OH},[10,20] and also $\delta_{H(3)}$ and $\delta_{H(8)}$;[70] b) from the change in δ_{14_N}

chemical shift of the N_β atom, which participates in the hydrogen bond (since the NMR signal in this case is measured under conditions of $^{14}N-\{^1H\}$ double resonance, these determinations are evidence for a six-membered ring of the hydrogen bond with N_β, as is depicted in (XIX), and not a five-membered ring with N_α;[20] c) from the changes in chemical shift of $^{15}N_\beta$ and $^{15}N_\alpha$ and also the direct spin-spin coupling constants $^1J_{15_{N-1_H}}$ and $^1J_{15_{N-15_N}}$ (due to the low content of natural ^{15}N isotope, a ^{15}N isotopic label was introduced for the measurements in these studies;[14,15,106] d) from the changes in chemical shifts of ^{13}C nuclei of specific atoms in the system, those most sensitive to its changes of state.[71,72,99] All these methods require a knowledge of the measured radiospectroscopic parameter for the limiting positions of the tautomeric system—for the pure azo form and for the definitely proved quinone hydrazone form—and assume a linear dependence of the measured parameter on the content of tautomers in the mixture.

Results[71,72,99] indicate that ^{13}C NMR spectroscopy is particularly successful in determining the ratio of the individual tautomers (XVIII) and (XIX) and the equilibrium constant of (10). One modification of this method is suitable for studying the temperature dependence of the position of tautomeric equilibrium [using the data on the change in chemical shifts of some types of ^{13}C nuclei of the unsubstituted benzene ring in 2-benzeneazo-2-naphthol (Fat Soluble Orange) or, generally, a substituted but fixed phenyl ring and a naphthol residue]. The effect of structural factors on the position of equilibrium (10) is more convenient to study from the shifts in the structurally invariable part of the molecule, namely, from the changes in shifts of the C(2), C(3), and C(4) nuclei of the naphthalene ring in relation to the substituents in the benzene ring, since the variation in shielding of ^{13}C nuclei in these positions is more sensitive to structural changes in the molecules.[71,72] Structures (XXVIIa) (studied in chloroform) and (XXVIII) can be used as reference compounds.

Dihydroxyazo compound (XXIX) (Eriochrome Violet C), which is one of a series of compounds for which equilibrium (10) is possible and one of the main types of dye,[1-5] deserves special consideration. According to the ^{13}C NMR data,[59] this compound in chloroform has only the azo structure (XXIXa) and there were no indications that the quinone hydrazone forms (XXIXc) and (XXIXb) existed under these conditions. Thus, equilibrium (19) does not actually occur in nonsolvating media.

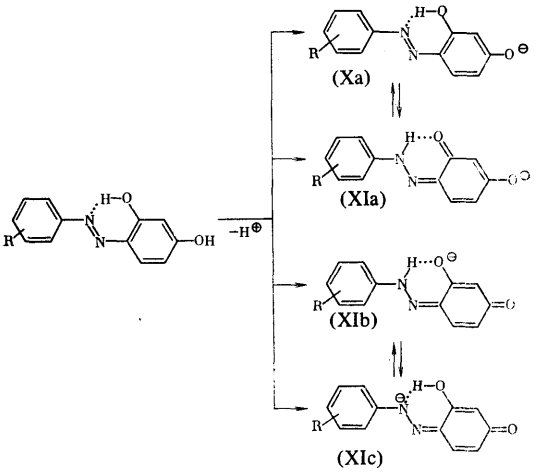


(19)

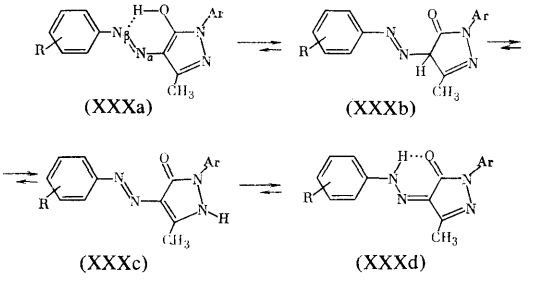
The displacement of the azo—quinone hydrazone equilibrium for compound (XXIX) towards azo structure (XXIXa) is apparently due to the formation of two O—H...N hydrogen bonds of similar structure. In one study[72] an attempt was made to find a solvation method (as opposed to a structural method) for conversion of the fixed tautomeric azo form to the corresponding tautomeric equilibrium.

It transpired that when chloroform was replaced by acetone and even more so by DMSO, the ^{13}C NMR spectrum of the compound changed considerably. Instead of the fixed tautomer (XXIXa), an equilibrium such as (19) occurs in solvating media. Strongly solvating media B that have basic properties promote the cleavage of one of the two hydrogen bonds (the weaker one), as a result of which in the compound with the remaining hydrogen bond the stabilisation conditions are virtually the same as those in other compounds with a substituent at the 2-position that does not form a hydrogen bond with the N=N group. Consequently, most of the molecules undergo a change in the type of hydrogen bond (N...H—O—C → N—H...O=C).

As has already been stated, resorcinol azo dyes in the neutral form have azo structure (X). However, a tautomeric conversion to the quinone hydrazone form was found in alkaline media by elimination of the primary, more acidic proton of the *para*-hydroxy group that does not participate in hydrogen bonding.[62,64]



The NMR spectroscopy data for azo dyes of type (X) (Sudan G, R = H; Azo Violet, R = *p*-NO_2; Resorcinol Yellow, R = SO_3Na) indicate that a quinonoid carbonyl group with chemical shift $\delta_{13_{C=O}}$ = 185—186 p.p.m. is formed in an alkaline medium. Thus, azo form (Xa) can be excluded as the monoanion state of resorcinol azo derivatives; in an alkaline medium they have one of the quinone hydrazone structures (XIa—c). From NMR titration curve graphs that were obtained[64] for compound (X), where R = *m*-SO_3Na, it was possible to make a more definite choice in favour of *para*-quinoid structure (XIb).

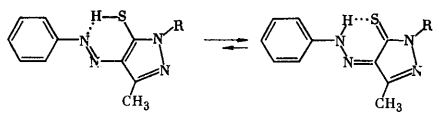


(20)

For dyes with a pyrazolone azo component, azo structure (XXXa) is to be expected from a traditional viewpoint.[5] An alternative approach with regard to possible tautomerism requires not just two

but four tautomeric forms (XXXa–d) to be considered for equilibrium (20). The "hybrid" forms (XXXb) and (XXXc), however, were ruled out many years ago by the first NMR studies (in the ^1H NMR spectrum of certain arylazo derivatives of 1-phenyl-3-methyl-5-pyrazolone, signals due to CH and NH protons not involved in hydrogen bonding were absent).[34–37] From the value of the chemical shift of the proton participating in NH/OH hydrogen bonding in nonsolvating media (δ_H = 13.5–13.8 p.p.m.[34,36]) and the changes in the ^1H NMR spectrum of the compound when it underwent N- and O-methylation it was possible to conclude further that out of the two more traditional tautomeric forms (XXXa) and (XXXd) keto form (XXXd) actually occurs in arylazo derivatives of 5-pyrazolone.[10,34,36] Confirmation of this was obtained[15,106] by introduction of a ^{15}N label into the β-position. In the ^1H and ^{15}N NMR spectra in chloroform there was a doublet which suggested the existence of a $^{15}N-^1H$ bond as part of the hydrazone form (XXXd).

The ^{13}C NMR data[54,63,99] are consistent with these results. Without dependence on the properties of the substituent in the aromatic diazo component and in the N-aryl azo component, the ^{13}C NMR spectra of the pyrazolone skeleton are only consistent with quinone hydrazone form (XXXd) for all the azo dyes based on 5-pyrazolone that have been studied, including the simplest, Fat Soluble Yellow 3 (R = H and Ar = C_6H_5) and more complex ones such as Acid Yellow Fast (R = H and Ar = p-$NaO_3SC_6H_4$), etc. These results can also be used to analyse the ^{13}C NMR spectra of other dyes of this class that have not previously been studied or have recently been synthesised.



(21)

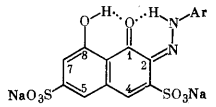
(XXXIa) (XXXIb)

The results are similar for azo derivatives of 5-thiopyrazolone. It follows from the ^1H NMR data[47] that the hydrogen atom involved in NH/SH hydrogen bonding occurs at very low field (δ_H = 16.68 p.p.m. when R = C_6H_5 and 16.20 p.p.m. when R = CH_3). This result together with the ^{13}C NMR data[54] clearly suggest that these compounds have quinone hydrazone structure (XXXIb) (in other words, the hypothetical equilibrium (21) is displaced to the right), although the azo structure (XXXIa) was preferred by the authors of one study.[47]

VI. AZO DERIVATIVES OF NAPHTHOLSULPHONIC ACIDS

Azo derivatives of 1-naphthol- and 2-naphthol-sulphonic acids (Nevile and Winther's acid, Schaeffer's acid, G- and H-acids, etc.) and also 1-8-dihydroxynaphthalene-3,6-disulphonic acid (chromotropic acid) and 1-hydroxy-8-aminonaphthalene-3,6-disulphonic acid (H-acid)[1–5] occupy a position of important practical significance. Study of them by means of ^1H and ^{13}C NMR spectroscopy is essentially only beginning,[52,53,55–58,61,63–65,104] and the ^{13}C NMR data obtained for the initial naphtholsulphonic acids[113–115] is proving to be effective for this.

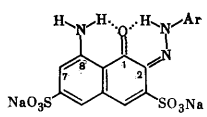
In the past it happened that in the studies devoted to dyes such as monoazo derivatives of chromotropic acid, the azo form of these compounds was usually a fundamentally accepted principle, and this transition has been preserved until recently. The structure and properties of both types of monoazo-substituted H-acid obtained under alkaline and acidic conditions and of monoazo-substituted Schaeffer's acid, G-acid, Violet acid, and others have also only been considered in terms of the azo structure.[5] The ^{13}C NMR spectroscopy data obtained for monoazo-substituted chromotropic and H-acids,[55–58,61,104] and equally for other compounds of this particular type,[52,53,63,104] necessitate a re-examination of these views.



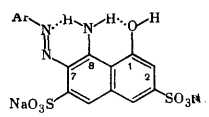
(XXXII)

Thus, it follows from the results obtained[55–58] that dyes of the form of monosubstituted derivatives of chromotropic acid have one and the same quinone hydrazone structure (XXXII). This applies not only to the simplest dye in the series—Chromotrope 2R (Ar = C_6H_5)—but also to any of the more complex structures—Victoria Violet BS, Acid Blue 3, Chromotrope 6B, etc. The main spectral feature of all the dyes is the presence of a signal with chemical shift 179–182 p.p.m. corresponding to C(1) in the naphthalene region of their ^{13}C NMR spectra. Signals from the carbonyl group of quinonoid compounds (in 1,2-naphthoquinone, for example, $\delta_{C(1)}$ = 180.9 p.p.m.[109]) are known to occur in this region of the spectrum.

Thus, in none of the dyes does the corresponding tautomeric equilibrium actually occur since it is displaced towards the quinone hydrazone form (XXXII). In this case the keto group of the dyes participates in the formation of two intramolecular hydrogen bonds to give six-membered rings—a particularly strong keto–enol O–H...O=C bond and an additional keto–amine O...H–N bond. For the alternative azo structure, the intramolecular hydrogen bond in which the C(1)–OH naphthol group would be expected to participate is noticeably weaker.



(XXXIII)

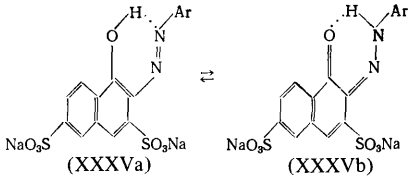


(XXXIV)

In monosubstituted derivatives of H-acid obtained in alkaline media (that is, synthesised under conditions where the site of addition of the arylazo group can only be the C(2) atom of the initial H-acid), for all the dyes investigated, either without (Acid Strong Fuchsin 2B) or containing a given substituent in the side chain, there is a ^{13}C NMR signal in the region 181–182 p.p.m.[61,104] This result is consistent only with the quinone hydrazone structure (XXXIII) and does not support the traditionally held view. For monosubstituted derivatives of H-acid that are synthesised under acid conditions where there is attack on the C(7) atom, it follows from the NMR data[61] that in this case the dyes formed exist in solution only in the azo form (XXXIV) similar to that observed in other azo derivatives of naphthylamine.

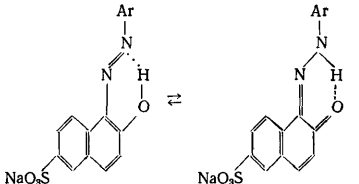
In one study[63] ^{13}C NMR data are reported on dyes of type (XXXV) (monosubstituted derivatives of violet acid), which do not contain a functional group at C(8) to participate in the formation of an intramolecular hydrogen bond. As a result, tautomers (XXXVa) and (XXXVb) exist at the same time in solution, although equilibrium (22) is displaced to the right to a considerable degree. Thus, while in monoazo derivatives of chromotropic and H-acids (XXXII) and (XXXIII)/(XXXIV) the respective tautomeric equilibria are only

theoretically possible, in derivatives of Violet acid (XXXV) the absence of additional six-membered rings involving keto–enol O–H...O=C or keto–amine N–H...O=C hydrogen bonding makes tautomeric equilibrium (22) quite real, observable, and it can be displaced by the effect of particular factors, structural or solvation.



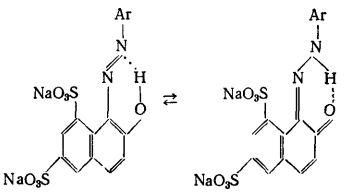
(XXXVa) (XXXVb) (22)

The ^{13}C NMR data which relates to several monoazo derivatives of Schaeffer's acid that are substituted in the aryl ring (Acid Brilliant Orange G) clearly suggest that azo–quinone hydrazone equilibrium (23) occurs in these dyes.[52,53] In this hypothesis the substantial differences in the experimental ^{13}C NMR chemical shifts from those calculated by the authors[52,53] for the traditional hypothesis of only the azo structure (XXXVIa) can readily be explained. The use of the method of calculation proposed in recent studies[63,72] in assessing the ^{13}C NMR data[52,53] leads to the conclusion that in system (23) when Ar = *m*-$NaO_3SC_6H_4$ the compound occurs to about 90% in the quinone hydrazone form (XXXVIb).

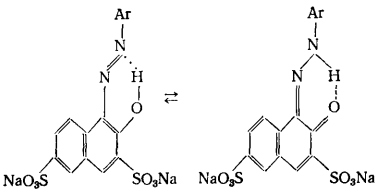


(XXXVIa) (XXXVIb) (23)

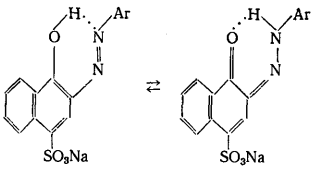
In some studies[52,53,104] ^{13}C NMR was used for the first time to study individual examples of dyes that actually (if the chemical shifts of the $\delta_{13_{CO}}$ nuclei obtained by the authors are analysed objectively) exist as equilibrium mixtures (23)–(26) as well as a number of other systems. Since the assessment of the ^{13}C NMR data in two studies[52,53] was made, in contrast to the other study,[104] from the traditional standpoint of the azo structure without including ideas about the possible occurrence of azo–quinone hydrazone tautomerism in these compounds, a reinterpretation of these findings and a possible reassignment of some signals is inevitable.



(24)



(25)

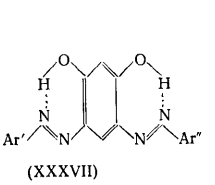


(26)

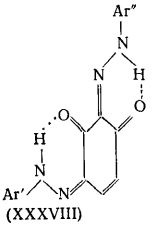
It is well known that azo-substituted derivatives of chromotropic acid as well as many other dyes are used over a very wide region of variation in the acidic and basic properties of the medium. In this connection, studies on the changes in the ^{13}C NMR spectra of azo dyes (XXXII) with the pH of the medium[57,58] are important. Although this aspect of the problem can include several different situations, there are two that are the most important. The first case occurs when there is a proton-donor group R (R = COOH, OH, AsO_3H_2, etc.) at the *ortho* position of Ar. In this case a corresponding structural complexity is possible in the compounds as a result of the formation of additional intramolecular hydrogen bonds. The second case occurs when the *o*-R group in Ar is a fairly "inert" group in relation to the formation of an additional hydrogen bond (R = Cl, CH_3, etc.). The first case has been examined[57] for R = AsO_3H_2. It transpired that in aqueous media the region for the compound existing in the azo form (more precisely, as the corresponding azo–quinone hydrazone equilibrium) is quite narrow—only in a weakly alkaline medium when the hydroxyl proton at C(8) still remains sufficiently strongly bonded to the oxygen atom. The second case was analysed[58] using a series of compounds with an "inert" *ortho*-group R. Here the changes in chemical shifts of the C(5)–C(9) nuclei, situated near the C(8)–OH hydroxy group, are in qualitative agreement with the successive change in pH observed in 1-naphthol and phenol up to complete removal of the hydroxy proton. In this case both tautomeric forms coexist in alkaline media to an approximately equal extent.

VII. POLYAZO DYES

Bis- and poly-azo aromatic derivatives are among the most important compounds industrially, but their previous study by means of NMR spectroscopy has been particularly brief[9,15,18,53,56,61,109]



(XXXVII)

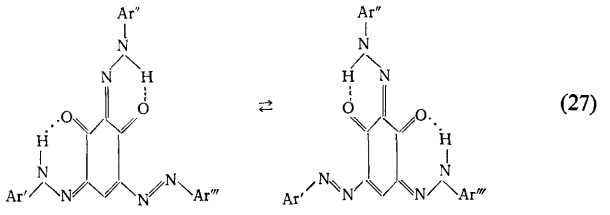


(XXXVIII)

It follows from the respective ^1H NMR data[18] that both *bis*-azo compounds synthesised from the monofunctional azo component phenol, have the azo structure in solution, as do the monoazo compounds.

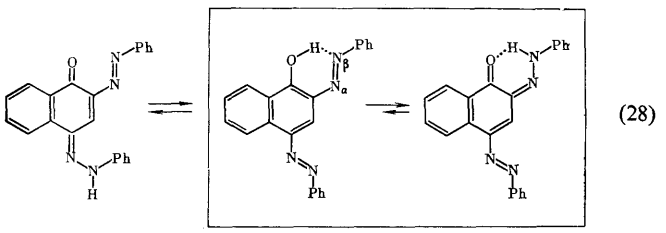
The NMR data on *bis*-azo derivatives of difunctional azo components such as resorcinol reveal a more complex picture. According to ^1H[9,18] and ^{13}C NMR[109] data, out of two structures the 4,6-isomer has the traditional *bis*-azo form (XXXVII). On the other hand, the 2,4-isomer occurs in a quite unexpected *bis*-quinone hydrazone form (XXXVIII). The shielding of the protons that participate in the two slightly nonequivalent NH...O hydrogen bonds does not leave open the possibility in the latter compound (δ_{NH} = 15.7 and

16.6 p.p.m. in $CDCl_3$ [9] and in DMSO;[18] $Ar' = Ar'' = C_6H_5$) of proposing any small amount of the corresponding mixed azo–quinone hydrazone forms. The ^{13}C NMR spectroscopic data is completely consistent with these results.[109] The conclusion about the structure of the 2,4- and 4,6-isomers as (XXXVIII) and (XXXVII) is consequently extremely important for understanding the structure in solution of dyes such as Acid Leather Brown 3K (XXXVIII), Acid Leather Light Brown (XXXVII), etc.



(27)

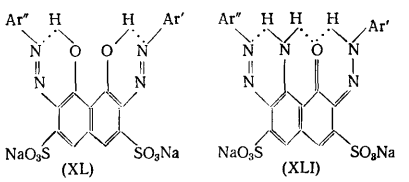
The *bis*-quinone hydrazone form of the *tris*-azo derivative of resorcinol ($Ar' = Ar'' = Ar''' = C_6H_5$) is sufficiently stable only at fairly low temperatures.[109] With an increase in temperature changes occur in the ^1H and ^{13}C NMR spectra that correspond to interconversion (27) of two *bis*-quinone hydrazone forms (when $Ar' = Ar'' = C_6H_5$ are equivalent). These findings are important for understanding the properties of the dye Acid Leather Brown K.



(28)

(XXXIXb) (XXXIXa) (XXXIXc)

NMR data that relates to the *bis*-azo derivative of 1-naphthol [system (11), R = H, X = N=N–C_6H_5] have been reported.[15,103] In this dye, which traditionally could have been represented as (XXXIXa), there are two possibilities for formation of a quinone hydrazone form—(XXXIXb) and (XXXIXc). By introducing a $^{15}N_\beta$ isotope label the authors of one study[15] ruled out the 1,4-quinone hydrazone form (XXXIXb). A positive indication of the 1,2-quinone hydrazone form (XXXIXc) is given not only by the doublet splitting of the labile NH proton in the ^1H NMR spectrum of the labelled compound but also by the magnitude of shielding of this proton (δ_{NH} = 15–16 p.p.m.). From the change in the value of the $^1J_{^{15}N-^1H}$ constant as the temperature was decreased it was possible to establish that equilibrium (28) is displaced almost completely to the right under these conditions.

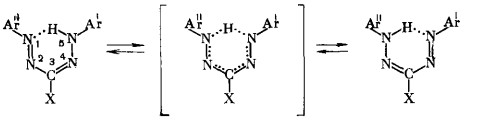


(XL) (XLI)

When we consider the 2,7-*bis*-azo derivatives of chromotropic acid and also H-acid, we can observe a basic difference in them. According to the ^{13}C NMR data,[56] the derivatives of chromotropic acid have the *bis*-azo structure (XL) in solution, which is quite distinct from quinone hydrazone structure (XXXII) that is typical for the corresponding monazo derivatives. On the other hand, the NMR spectroscopy data[61] for *bis*-azo derivatives of H-acid are consistent with structure (XLI), combining, as it were, both types of monoazo derivative obtained in alkaline and acid media [quinone hydrazone structure (XXXIII) and azo structure (XXXIV) respectively]. This applies, for example, to some well-known dyes such as Acid Blue Black ($Ar' = C_6H_5$, $Ar'' = p\text{-}O_2NC_6H_4$) and Acilan Dark Green B ($Ar' = C_6H_5$, $Ar'' = p\text{-}H_2NC_6H_4$).

VIII. FORMAZAN DYES

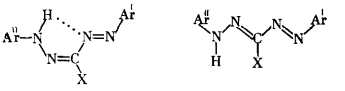
Formazan dyes have already been fairly widely accepted for solving practical problems.[5] They exist in two forms, "red" and "yellow", depending on the properties of the substituent X at the *meso*-carbon atom. There has until now been comparatively little NMR data[116–124] relating to formazans and their complexes with metal ions. In solution the "red" 3-X-1,5-diarylformazans (X = NO_2, Ar, and certain other groups that prevent the compounds being classified as dithizone derivatives, that is, when X ≠ SR) exist as equilibrium mixtures (29) of two cyclic *syn-s-cis* forms (XLIIa) and (XLIIc) with N(1)...H–N(5) and N(1)–H...N(5) intramolecular hydrogen bonds. When metal-complex dyes are formed the metal ion is introduced into the centre of the formazyl group with displacement of the hydrogen atom.



(29)

(XLIIa) (XLIIb) (XLIIc)

In 1,5-diarylformazans the N...H–N hydrogen bond is fairly strong (energetically favourable six-membered ring) but not so much as to exclude when there are certain forms of X (for example, when X = Cl, CH_3, etc.) the possibility of these compounds existing in solution in the "yellow" form, where the formazyl group acquires the *syn-s-trans* configuration (XLIII) with a weaker hydrogen bond as part of a five-membered ring or even the *anti-s-trans* structure (XLIV) completely without intramolecular hydrogen bonds (stabilised by intermolecular hydrogen bonding).



(XLIII) (XLIV)

It follows from ^1H [116–121] and ^{13}C [122–124] NMR data on compounds in which group X does not participate in the formation of strong hydrogen bonds that in relation to the NMR parameters these compounds can be separated into two groups that are chemically distinct. In the "red" formazans the signals from the NH protons occur in a region characteristic for compounds with strong intramolecular hydrogen bonds [δ_{NH} = 13.7–15.7 p.p.m. in $CDCl_3$);[117,119,121] structures (XLIIa) and (XLIIc)], and their chemical shift is only slightly dependent on the properties of the medium.[118] In the "yellow" formazans the chemical shift of the NH protons varies considerably (δ_{NH} = 8.7–8.8 p.p.m. in $CDCl_3$ for X = Cl,[12] and 10.2 p.p.m. in DMSO for X = CH_3 [119]), which

indicates the absence of strong hydrogen bonding [structures (XLIII) and (XLIV) with a weaker intramolecular hydrogen bond or with an intermolecular hydrogen bond].

The participation of the NH proton in rapid intramolecular tautomeric conversions (29) in "red" formazans was demonstrated by means of ^{1}H NMR with isotopically enriched samples.[117,118,121] When N(1) = ^{15}N the NH proton appears as a double with $^1J_{^{15}N-^1H}$ = 46–47 Hz, and when N(1) = N(5) = ^{15}N it appears as a triplet with the same magnitude of spin-spin coupling constant. Since the coupling constant observed has half the magnitude of that typical for structures of a similar kind, the only reason for its decrease could be the participation of the NH proton in alternate formation of an N–H valence bond first with N(1) then with N(5) as part of the tautomeric intrachelation process (29) (a spin-spin interaction does not occur in an N...H hydrogen bond).

Our view has been expressed that the halving in value of $^1J_{^{15}N-^1H}$ can, in principle, be caused not only by process (29) but also by the formation of the mesomeric structure (XLIIb) instead of the limiting tautomeric forms (XLIIa) and (XLIIc).[118] This proposal can be rejected when taking into account the findings of one study,[117] in which the structural factors causing a displacement of equilibrium (29) in either direction were investigated on triarylformazans as a model. When X = C_6H_5 and N(1) = ^{15}N, introduction of a substituent into the *para* position of one of the aromatic rings (Ar′) (the other ring Ar″ = C_6H_5) has a marked effect on the constant $^1J_{^{15}N-^1H}$; when Ar′ = p-$CH_3OC_6H_4$, it amounts to 86.5 Hz, while when Ar′ = p-$O_2NC_6H_4$ it becomes equal to zero. Thus, electron-donor substituents at the *para* position of one of the aromatic rings promote such a displacement of equilibrium (29) that the azo group is stabilised next to this ring. Electron-withdrawing substituents have the opposite effect. In proposing mesomeric structure (XLIIb) these results would have no rational explanation. The tautomeric process (29) is a low-energy one since it is not possible to slow it down noticeably even on cooling the solutions.[118,119,121] This fact indicates the importance of establishing the position of this and similar equilibria by means of NMR spectroscopy. Apart from the one study,[117] related to this are two reports,[123,124] in which appropriate ^{13}C NMR data is presented.

IX. COMPLEX COMPOUNDS OF AZO DYES WITH METAL IONS

Metallated and metal-containing hydroxyazo dyes constitute a fairly large and essentially important group of dyes. The NMR data relating to their complexes with metal ions[28–32,74–76,105,124] are still sparse, very incomplete, and provide only a few answers to certain structural problems.

In particular, data relating to the ^{1}H NMR spectra of complexes of 1-(2-hydroxybenzeneazo)-2-naphthol (XXIXa) with certain metal ions have been reported.[32] The absence of details in the interpretation of the spectra makes it difficult to discuss these data, but the conclusion of the authors[32] about the quinone hydrazone form of the ligand in the complex with Zr(IV) of composition 1 : 2 was not confirmed by the subsequent application of ^{13}C NMR spectroscopy.[75] It was established that the azo form of the ligand is preserved on complex formation with these ions.

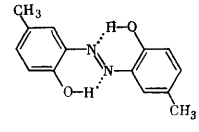
By means of ^{1}H,[28–31,76] ^{15}N,[105] and ^{13}C[76] NMR spectroscopy it was possible to study the isomerism for two types of complex based on 2,2′-dihydroxyazobenzene compounds with a wide variety of structure in which the dye is a tridentate O,N,O ligand—octahedral Co(III) complexes of the type (O N O)$_2$Co,[28–31,76] and square planar Pt(II) and Pd(II) complexes of the form (O N O)MB (B is pyridine or another additional ligand that has basic properties).[31,76,105]

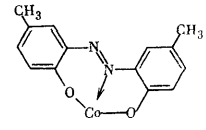

(XLVa)


(XLVb)

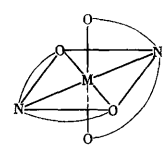
Some authors[31,76,105] used NMR spectroscopy methods to study, in particular, the differences between the isomers (XLVa) and (XLVb) of square planar Pt(II) and Pd(II) complexes when the left- and right-hand sides of the 2,2′-dihydroxyazobenzene dye molecule are nonequivalent.

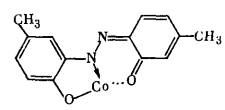
A series of studies[28–31,76,105] constitutes the start of an extensive and technically important trend in NMR investigations that would be simply impossible without polynuclear NMR spectroscopy. Possibly because of the difficulties in interpreting ^{1}H and ^{13}C NMR spectra for complex structures, the authors limited themselves to discussion of only isolated NMR signals. The contemporary state of NMR spectroscopy permits the study of complex compounds—metal-containing dyes or compounds that are metallated in the dyeing process—with complete interpretation of the spectra.


(XLVI)


(XLVIIa)

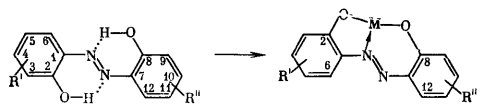
To what extent this step is important can readily be seen from the studies[28,29,76] in which NMR spectroscopy was used to study octahedral Co(III) complexes with two ligands attached to one metal ion. The complex with substituted 2,2′-dihydroxyazobenzene (XLVI)[28] was studied by ^{1}H NMR. On replacement of two protons by metal the initial symmetrical dye (XLVI) becomes asymmetric in the coordination unit (XLVIIa), and in the spectrum of the complex instead of one there are two methyl signals ($\Delta\delta_{CH_3}$ = 0.1 p.p.m.) and two H(6) signals (Δd_H = 0.08 p.p.m.). Since only one set of ^{1}H NMR occurs in the spectrum of the complex, the solution to the problem concerning the configuration process of two coordination units of (XLVIIa) is considerably simplified—there are two planar (XLVIIa) fragments arranged perpendicular to each other in the octahedron [structure (XLVIII)].


(XLVIII)


(XLVIIb)

Thus the nonequivalence of the left- and right-hand sides of coordination unit (XLVIIa) for the symmetrical initial ligand (XLVI) follows from the very fact that coordinated and uncoordinated nitrogen atoms exist in it. In two studies,[28,29] where the discussion concerns complexes of Co(III) with an asymmetric 2,2′-dihydroxyazobenzene ligand, namely, with the possible formation of isomers and a more complex NMR pattern, the authors attribute the quinonoid structure (XLVIIb) to one of the sides of the ligand in the

coordination unit instead of the azoid structure (XLVIIa). Although this is not essential for the construction of the octahedral complex (XLVIII), this hypothesis in itself was not supported by the ^1H NMR spectra. The results of subsequent study of ^{13}C NMR spectra led the authors to the conclusion that coordination unit (XLVIIa) containing an azo structure was occurring.[76]



(XLIX)

A method for identifying the signal that corresponds to the C(6) carbon atom was proposed.[76] When coordination unit (XLIX) is formed, out of the two atoms C(6) and C(12) only atom C(6) changes its spatial position relative to the N=N bond, occupying a *cis* position relative to the N=N double bond after rotation about the C–N bond. Consequently, after rotation and subsequent complex formation (OH → OM), the signal corresponding to C(6) must be shifted upfield by an order of magnitude of 9 p.p.m. (plus or minus an addition shift due strictly to the effect of complex formation). The actual values of the upfield shift depending on the metal amount to: 13–14 p.p.m. for Pd(II) and Pt(II); 14–15 p.p.m. for Co(III). Thus, the upfield shift due to complex formation (as a result of replacing H^+ by M^{n+} and the change in angle values when going from a six-membered ring involving hydrogen bonding to a five-membered ring with M^{n+}) for C(6) amounts to 4–5 p.p.m. for Pd(II) and Pt(II) and 5–6 p.p.m. for Co(III). However, it may be assumed that this additional upfield shift is mainly due to transformation of the six-membered hydrogen bonded ring to the five-membered coordination ring since when complex formation occurs with preservation of a six-membered ring the C(6) signal is shifted downfield only by ~2.5 p.p.m.

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