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# Solid-state $^{13}C$ NMR CP MAS High-resolution Spectroscopy of Chromogens: Structural Aspect of Problem

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*ABSTRACT*

*Chromogens of different classes, viz., arylazo derivatives of resorcinol, naphthols, naphthylamines, chromotropic acid and its cyclic modification, and also some formazans, are investigated using high-resolution solid-state NMR $^{13}C$ CP MAS. The technique revealed spectral data pertinent to the similarity and difference of the compounds in the solid state and in solution.*

## 1 INTRODUCTION

NMR spectroscopy has given a new impetus to structural research in the chemistry of chromogens, especially of dyes and analytical chemicals.[1–4] The technique has been applied to many classes of compounds containing chromophoric groups, and especially to azo compounds, and contributes half the compounds referred to in this present paper. Informative data has been obtained using $^{13}C$ NMR,[2–8] but interesting data has also been obtained on other nuclei, such as $^{15}N$. Nonetheless, technical progress in

NMR spectroscopy and especially NMR methodology over the last 10 years[4-9] has stimulated and broadened this area of research.

This present review exemplifies this using the technique of high-resolution solid-state $^{13}C$ NMR spectroscopy.[9] Some applications of this have been reported for investigations of azo compounds.[10-16] We have attempted to evaluate, as far as possible, the use of these methods for solving problems such as the identification of spectral and structural changes during the change of phase. This enables comparison to be made of these spectra with those recorded in dye solutions.

## 2 EXPERIMENTAL

Solid-state $^{13}C$ CP MAS spectra were recorded at 75·47 and 100·4 MHz using MSL-300 and MSL-400 Bruker spectrometers. Samples were packed in ceramic rotors and spun using MAS 4–5 frequencies of kHz, respectively. The combined techniques of high-power proton decoupling and single-contact cross polarization (CP) were employed. As this spinning rate was not enough to suppress side bands, the TOSS technique was employed. The reference was external adamantan and hexamethylbenzene.

Spectral conditions were as follows: spectral width, 29·4 kHz; cross-polarization time, 1–3 ms; proton 90° pulse, 5 ms; recycle delay, 3–5 s; number acquisition, 100–1000. Dipolar dephasing spectra were obtained by turning off the high-power $^{1}H$ decoupling 0·5–0·7 ms prior to acquisition.

## 3 RESULTS AND DISCUSSION

The general positions of high-resolution solid-state $^{13}C$ NMR application to chemical problems have been considered in detail.[9] Two problems are especially important, viz., the elimination of rotational side bands from NMR spectra (routine TOSS), and dipolar dephasing method for observing signals of quaternary carbon atoms only.

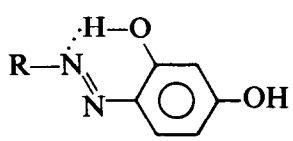
### 3.1 Arylazo derivatives of resorcinol

Many reports have been made on the $^{13}C$ NMR spectra of azo derivatives of hydroxy- and aminobenzene compounds in solution,[3,17-24] including phenols,[3,18] pyrocatechols[3] and resorcinols.[3,17-19] Of special interest is the structural solid state $^{13}C$ NMR of resorcinol arylazo derivatives. These compounds are typical in respect of structural variations and in the diversity of the interpretation of azo–quinonehydrazonic tautomerism which has been reported by different authors.

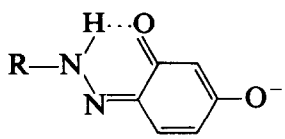
**TABLE 1**
$^{13}C$ Chemical Shifts of Arylazo Derivatives of Resorcinols I and III

| | *Compound* | *Conditions* | *Carbon* | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *1* | *2* | *3* | *4* | *5* | *6* |
| I | R = $C_6H_5$ | Acetone-$d_6$ | 132·6 | 156·1 | 103·1 | 162·7 | 108·9 | 134·6 |
| | *p*-$NO_2C_6H_4$ | Acetone-$d_6$ | 133·9 | 158·1 | 103·7 | 165·0 | 110·7 | 135·4 |
| | *m*-$SO_3NaC_6H_4$ | Methanol-$d_4$ | 133·2 | 157·4 | 103·0 | 164·0 | 109·8 | 134·4 |
| | Py | DMSO | 132·7 | 159·5 | 103·4 | 165·4 | 111·6 | 132·2 |
| III | R = $C_6H_5$ | $D_2O$ (pH 10·0) | 134·5 | 175·7 | 106·5 | 184·4 | 123·1 | 135·5 |
| | *p*-$NO_2C_6H_4$ | $D_2O$ (pH 10·7) | 137·0 | 177·0 | 106·5 | 186·1 | 126·1 | 135·7 |
| | *m*-$SO_3NaC_6H_4$ | $D_2O$ (pH 10·6) | 135·1 | 177·6 | 106·6 | 185·1 | 124·0 | 135·9 |
| | Py (Na-form) | DMSO | 136·5 | 175·2 | 105·1 | 183·5 | 127·8 | 133·4 |
| | | Solid | 136·5 | 177·8 | 108·2 | 184·1 | 126·3 | 133·3 |

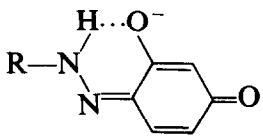
It is doubtful whether the structure of resorcinol-based chromogens (e.g. CI Solvent Orange 1 and CI Acid Orange 6) has been fully investigated, because of the current conception about their azo-modification in solution. It is apparent from Table 1, which lists $^{13}C$ NMR chemical shifts for azo resorcinol derivatives containing aromatic and heterocyclic diazosubstituents, that in solution these compounds exist only in the azo configuration **I**. This follows, for example, from chemical shifts C(2) and C(4).[17] However this data pertains only to acid media and the problem of the structure of resorcinol derivatives in alkaline media has not been discussed, although salts of azo resorcinol derivatives are present in a number of chromogens.




**I**




**II**




**III**

It has been established by $^{13}C$ NMR,[17,21] that the monosodium salts of azo resorcinols derived from any diazo component (aromatic or heterocyclic) in organic solvents, and azo resorcinols in alkaline media, exist only in the quinone–hydrazone configuration (bottom of Table 1). It was also shown, that the *ortho*-quinoidic structure **II** is not actually realised but that the compounds exist in the *para*-quinoidic **III**. However, the structure of these compounds in the solid state has not been discussed.

$^{13}C$ NMR data show (Table 1) that a transition from solution to solid state is not accompanied by any structural changes. Comparison between

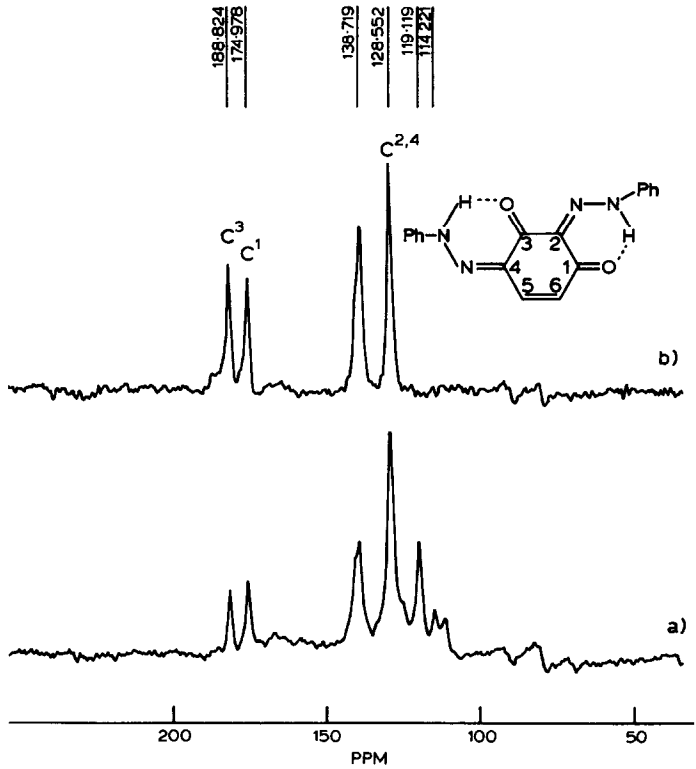
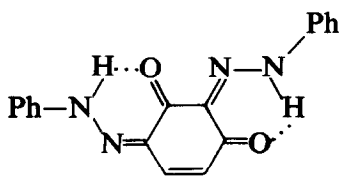


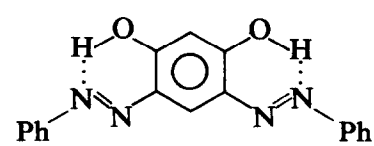

**Fig. 1.** High-resolution solid-state $^{13}C$ NMR spectra of unsymmetrical bisarylazo derivative of resorcinol **IVa**. (a) normal spectrum; (b) dipolar dephasing spectrum.

the solution and solid-state data confirms the preservation of the quinone–hydrazone structure, and the *para*-quinoidic structure **III** is again realised, as is typical for solutions.[3] Direct evidence of this is the C(5) chemical shift, which is identical in both solid and solution, and which corresponds to the presence of $O^-$ at C(2).

With respect to resorcinol bisarylazo derivatives, it has been shown by $^{13}C$ NMR,[3,21] that the unsymmetrical bisarylazo derivatives exist in solution in the bisquinoidic form **IVa**, but the symmetrical derivatives exist in the bisazo form **IVb**. Furthermore, study of the unsymmetrical compound **IVa** in the solid state showed some unusual features. Thus it was found that the transition from solution to solid is accompanied with some high-field




**IVa**



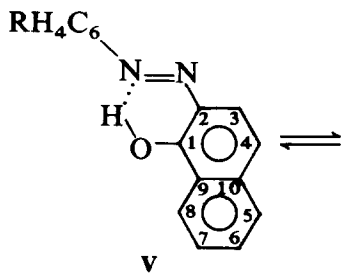

**IVb**

displacement of both of the carbonyl signals ($\delta = 183{\cdot}0$ and $178{\cdot}1$ ppm in solution, and $180{\cdot}8$ and $175{\cdot}0$ ppm in the solid state; Fig. 1). This effect is similar to the chemical shift change after introduction into the molecule of structural strain by the bridging of two aromatic groupings with some fragments.[23] So, in the case under consideration, we can attribute the spectral changes to a packing effect in the solid state.

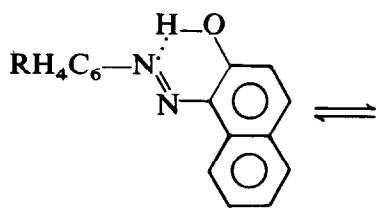
### 3.2 Arylazonaphthols

Arylazo derivatives of α- and β-naphthols are an important group of compounds, not only in dye chemistry,[25] but also with respect to theoretical organic chemistry, since two fundamental concepts were initially formulated from them, viz., tautomerism[26] and hydrogen bonding.[27] $^{13}C$ and $^{15}N$ NMR has therefore been applied to the study of such compounds and especially to 1-arylazo derivatives of β-naphthols,[28–36] 2-arylazo derivatives of α-naphthol[35–37] and to 4-arylazo derivatives of α-naphthol.[35,38–48] Some $^{13}C$ NMR data for arylazo derivatives of β-naphthylamine have also been reported.[41]

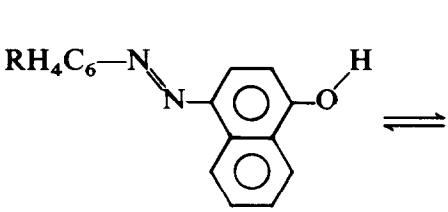
In general, arylazo naphthols have been described[3,4,25,42] with respect to the azo–quinone–hydrazone tautomeric equilibria (1)–(3):




V VI (1)




VII VIII (2)




IX X (3)

**TABLE 2**
$^{13}C$ Chemical Shifts of Arylazo Derivatives of Naphthol-1 and Naphthol-2

| *Compound* | | *Conditions* | *Carbon* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* |
| **V/VI** | *p*-$CH_3$ | $CDCl_3$ | 170·9 | 132·4 | 128·2 | 120·3 | 127·4 | 131·5 | 125·9 | 126·3 | 129·7 | 137·4 |
| | | Solid | 170·0 | 134·5 | 129·4 | 120·2 | 128·0 | 129·4 | 125·3 | 125·3 | 129·4 | 138·8 |
| **VII/VIII** | *p*-$NH_2$ | $CDCl_3$ | 129·2 | 157·7 | 121·3 | 135·0 | 128·0 | 124·3 | 127·6 | 121·5 | 133·0 | 128·6 |
| | *p*-$NMe_2$ | $CD_2Cl_2$ | 129·4 | 156·1 | 121·0 | 134·0 | 127·4 | 124·1 | 128·1 | 121·7 | 133·3 | |
| | | Solid | 128·6 | 154·7 | 121·6 | 131·3 | 128·6 | 123·1 | 128·6 | 123·1 | 132·8 | 128·6 |
| | H | $CDCl_3$ | 129·9 | 171·5 | 124·6 | 139·8 | 128·6 | 125·5 | 128·4 | 121·6 | 133·4 | 127·9 |
| | | Solid | 126·1 | 172·7 | 126·1 | 140·0 | 126·1 | 126·1 | 126·1 | 120·5 | 131·9 | 126·1 |
| | *p*-$NO_2$ | $CDCl_3$ | 131·9 | 180·0 | 126·3 | 143·4 | 129·7 | 127·5 | 129·1 | 122·4 | 133·0 | 128·5 |
| | | Solid | 128·9 | 179·5 | 126·4 | 144·4 | 129·2 | 129·2 | 129·2 | 123·1 | | 128·9 |
| **IX/X** | *p*-$SO_3Na$ | $D_2O$ (pH 2·4) | 136·0 | 125·8 | 123·3 | 186·4 | 125·3 | 132·9 | 128·1 | 126·6 | 128·9 | 132·1 |
| | *p*-$NO_2$ | Solid | 135·4 | 126·0 | 123·0 | 186·4 | 126·0 | 132·0 | 128·3 | 126·0 | 128·5 | 133·2 |

The tautomeric equilibria (1) and (2) in solution of *ortho*-azo derivatives of α-naphthol and β-naphthol[25,42] are realised in the framework of intramolecular hydrogen bonds.[3,43] From the results of $^{13}C$ NMR studies, these equilibria are characterised by a smaller dependence on solvent properties,[32,43] and by a significant dependence on the nature of substituents.[3,43] It is not clear, however, whether these equilibria occur in the solid state or are transformed to give mixtures of stable isomers.

Table 2 contains results for some individual azo derivatives of α-naphthol and β-naphthol.[3,36] For azo derivative of α-naphthol, studies were made on **V/VI**, in which $R$ = *para*-Me. As the $^{13}C$ NMR data show,[37] this compound exists in solution in the form of a tautomeric equilibrium (1). Present data demonstrate that this is so in the solid state: two different sets of signals for the mixture of tautomers **V** and **VI** are absent in the spectrum, which show an intermediate picture which is characteristic for the equilibrium (1). Despite this, in the solid state, the ratio of the tautomeric forms **V** and **VI** is maintained. Thus, in the solid state, there is observed a slight change of the shielding of the indicator nucleus C(1): $\delta = 170{\cdot}9$ ppm in $CDCl_3$ and 170·0 ppm (an average value, since two signals with $\delta = 168{\cdot}8$ and 171·1 ppm are actually observed). Thus for the dye where $R$ = *para*-Me, in the solid state, the equilibrium (1) remains and is only slightly displaced to the left.

It must be noted, however, that in the solid state, the signal of the side chain C(12,16) is split (112·9 and 118·2 ppm). This can be interpreted in two ways, viz: it may indicate some residual slowing of rotation around the C—N bond and the plane of the compound,[15] but more preferably, it is relatable to the influence of residual dipolar splitting.[12,13]

Results of the solid-state $^{13}C$ NMR of 1-arylazo-2-naphthols are similar (Table 2). In the solid state, the equilibrium is maintained, this equilibrium existing in solution and being displaced to one side or the other depending on the substituent $R$. This is also in agreement with available $^{13}C$ and $^{15}N$ data.[12,14,15]

Our results of the NMR-analysis of compound **VII/VIII**, where $R$ = *para*-$NO_2$ (CI Pigment Red 1), entirely coincide with known data,[12] but with a reassignment of some signals. It can thus be concluded that the compound in which $R$ = *para*-$NO_2$ has, in the solid state, only the quinone–hydrazonic form **VIII**, i.e., the equilibrium is completely moved to the right. During the preparation of this present work, data has been published[15] on some solid-state $^{13}C$ NMR for compound **VII/VIII** in which $R = H$ (CI Solvent Yellow 14). These data are in accord with our results, except, again, for some signal reassignments. As follows from Table 2, the equilibrium (2) in solution and in the solid state is rather displaced to the left, i.e., to the azo form **VII**. According to our data the content of the quinone–hydrazone form **VIII** increases in the solid state compared to in solution (in the transition from

solution to solid, the C(2) signal is displaced to low field from 171·5 ppm to 172·7 ppm).

Two further aspects require consideration. Signal assignments for C(3, 5, 7, 8) have been previously reported,[15] and also for C(6).[3,36] Further data in respect of these is assigned in this present work, and also for the compound in which $R = para\text{-}NMe_2$ investigated in the report,[15] and this is shown in Table 2.

The second problem concerns the position of the signal for C(2) in the spectrum in the case of complete displacement of the equilibrium 2 to the left. The authors of Ref. 15 were influenced by the value 147 ppm[44] but, in our opinion, the more correct assignments are their measurement for the compound with $R = para\text{-}NMe_2$ (155–156 ppm), and our[37] value for the compound with $R = para\text{-}NH_2$ (157·7 ppm). This is in accord with investigations of the equilibrium (2) by optical methods,[45] which revealed the simultaneous existence of two tautomers in solution, in contrast to the single structure in the case where $R = para\text{-}NH_2$ or $R = para\text{-}NO_2$.[37] NMR $^{13}C$ data for the compounds where $R = para\text{-}NH_2$,[37] $R = para\text{-}NMe_2$[15] and $para\text{-}NO_2$[32] also confirm this conclusion. Thus the value offered in Ref. 44 and quoted by other authors,[15] is not correct. Using the new chemical shift value of 155–157 ppm, some changes are necessary in calculating the constants[15] of the tautomeric equilibrium.

Solid-state $^{13}C$ NMR data for 4-arylazo-1-naphthol with $R = para\text{-}NO_2$ (Fig. 2, Table 2) show that, in the solid state, this compound exists only in a quinone–hydrazone form, in accord with the prediction based on solution

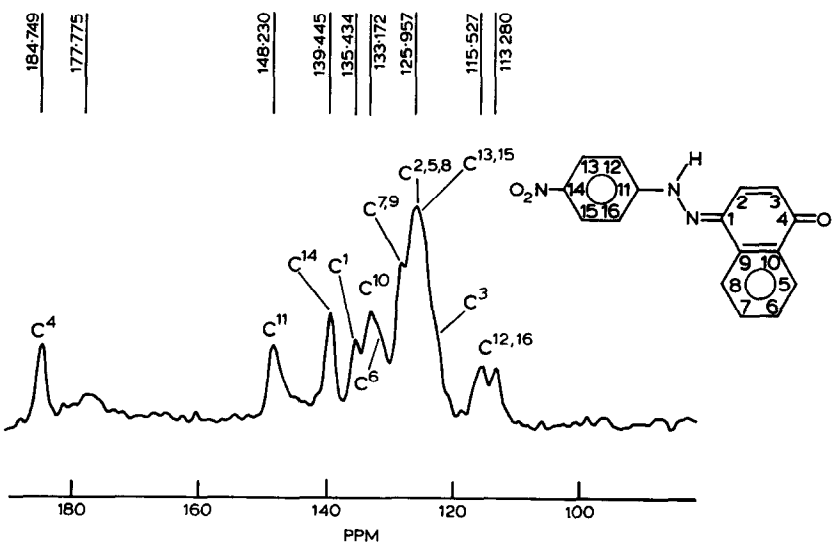
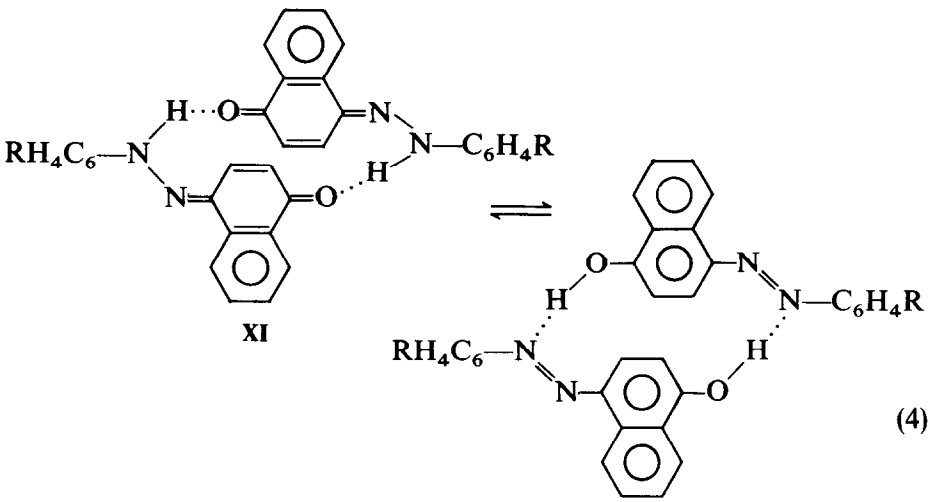



**Fig. 2.** High-resolution solid-state $^{13}C$ NMR spectrum of 4-arylazo-1-naphthol **X** ($R = p\text{-}NO_2$).

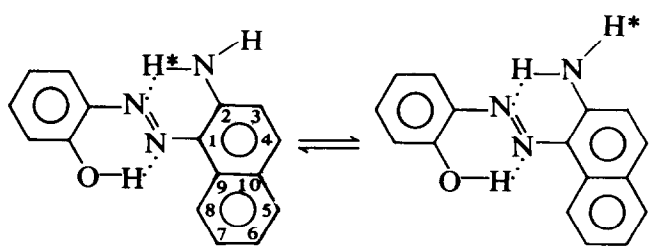
$^{13}C$ NMR data.[40] However, the feature of compounds of type **IX/X** is their existence in the solid state, not in the monomeric form **X**, but in some associated form, for instance, the dimeric form **XI/XII**.[40] This is important in understanding the tautomeric mechanism (3) in 4-arylazo-1-naphthols. In the configuration **XI/XII**, this process is readily interpreted as an intermolecular mechanism (4), in contrast to intramolecular tautomerism (1) and (2) for 2-arylazo-1-naphthols and 1-arylazo-2-naphthols.




(4)

**XII**

In conclusion, it is necessary to point out the peculiarity of naphthylamine arylazo derivatives. $^{13}C$ NMR data for these compounds in solution[3,41] shows the absence of tautomerism, in contrast to naphthol derivatives. Figure 4 shows a solid-state $^{13}C$ NMR CP MAS spectrum of one of compounds **XIII**, which is quite in accord with results for solution data. The signal positions for **XIII** (Fig. 3, Table 2) in solution and in the solid state are practically the same. However, there are some differences observed in the positions of the signals for C(1), C(2) and C(11). This may be due to a change in the strength of the intramolecular hydrogen bonding N—H...N in the solid state, because in this case there is an inhibition of the dynamics, concerning the interexchange of the amine hydrogen atoms:




**XIII**

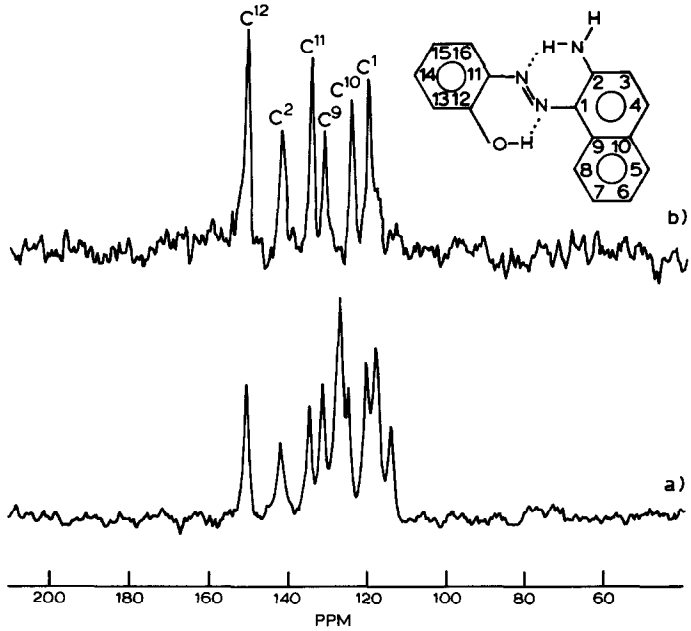
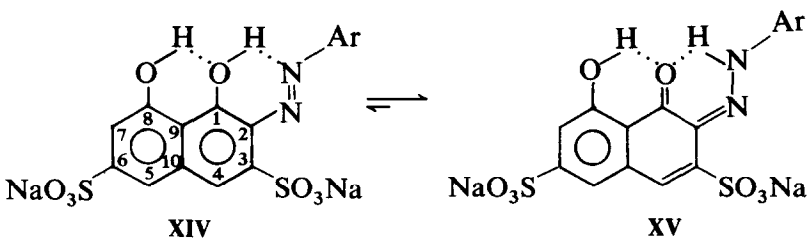



**Fig. 3.** High-resolution solid-state $^{13}C$ NMR spectra of compound **XIII**. (a) normal spectrum; (b) dipolar dephasing spectrum.

### 3.3 Aryazo derivatives of chromotropic acid

Sulphonaphthol arylazo derivatives contribute significantly to azo chromogens.[25,42] There are available detailed $^{13}C$ and $^{15}N$ NMR spectroscopy data concerning structural investigations of sulphonaphthol arylazo derivatives in solution,[3,18,44,46-57] including derivatives of chromotropic acid,[3,48,53-57] H-acid,[47-49] gamma- and J-acids[48-50] and S-acid.[51] This present paper restricts its considerations to only one class of these compounds, viz., mono- and bis-arylazo derivatives of chromotropic acid, which permit structural variations which have not been previously investigated fully by spectroscopic methods.

In research on chromogens forming the class of monoazo derivatives of chromotropic acids (e.g., CI Acid Red 29, CI Acid Red 176, CI Acid Violet 13), the main accent has been given to an azo form **XIV** for these compounds,[42] including quantum chemical calculations.[58] The quinone–hydrazone form **XV** has not been seriously considered, but solution $^{13}C$ NMR for many such compounds[3,53-56] give results at variance with this hypothesis. Conventional $^{13}C$ NMR data show that in any media (water or organic solvents) and for any type of side chain, these compounds have the same quinone–hydrazone structure **XV**.[3] This result has been confirmed using two-dimensional NMR spectroscopy and $^{15}N$ NMR.[57]




(5)

The solid-state $^{13}C$ NMR spectrum of the compound in which Ar = *ortho*-$AsO_3H_2C_6H_4$ is shown in Fig. 4. Comparison with the NMR data for some similar compounds (Table 3) shows, that in the solid state, the structure found in solution is also repeated. The most important evidence is the position of the C(1)-signal in the solid state $^{13}C$ NMR spectrum, since this can only result from a quinoidic form of the naphthalene ring, **XV**. So, in the solid state, as in solution, there is no reason to postulate the equilibrium 5, which is entirely moved to the right.

In contrast to monoarylazo chromotropic acid derivatives, the case of bisazo substituted derivatives is quite different. According to $^{13}C$ NMR data[56] the bisazo structure **XVI** is realised in solution, as is indicated, e.g., from the C(1) chemical shift. It was important, however, to check this in the solid state, as in compounds **XVI** with different *ortho*- and *para*-substituents in the Ar ring, and for cyclic compounds **XVII** which include fragments of chromotropic acid. The summary of $^{13}C$ NMR data (Table 4) demonstrates,

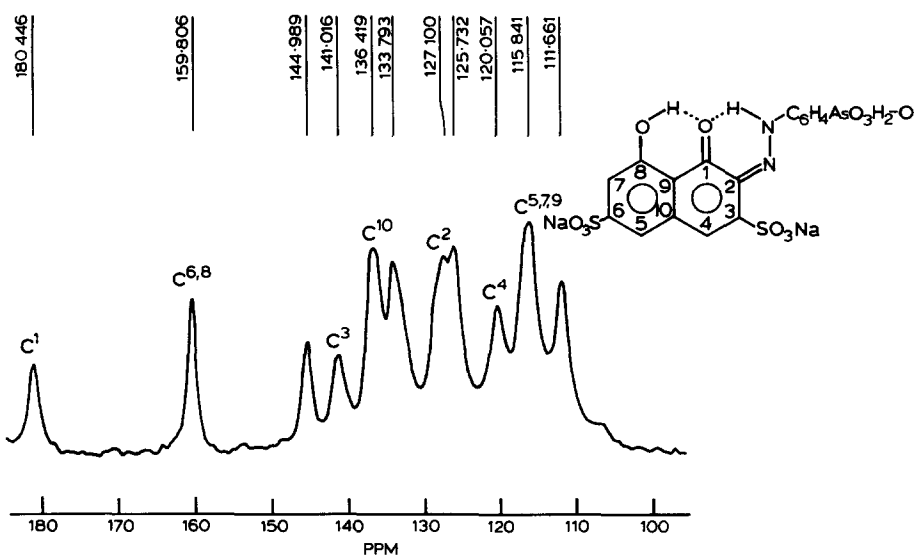



**Fig. 4.** High-resolution solid-state $^{13}C$ NMR spectrum of compound **XV** (Ar = *o*-$AsO_3H_2C_6H_4$).

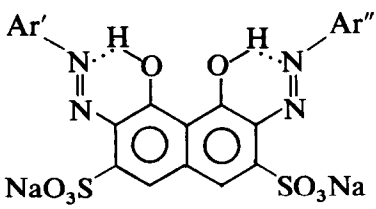
**TABLE 3**
$^{13}C$ Chemical Shifts of Arylazo Derivatives of Chromotropic Acid XV

| *Ar* | *Conditions* | *Carbon* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* |
| $C_6H_5$ | $D_2O$ (pH 1·5) | 180·3 | 127·5 | 139·8 | 123·4 | 118·4 | 149·6 | 112·7 | 162·4 | 119·1 | 137·1 |
| | Methanol-$d_4$ | 181·5 | 128·4 | 142·7 | 122·9 | 117·7 | 152·5 | 113·0 | 163·7 | 117·7 | 137·3 |
| | DMSO-$d_4$ | 180·2 | 127·9 | 143·3 | 121·1 | 116·9 | 154·4 | 111·9 | 162·6 | 115·8 | 136·6 |
| *o*-$SO_3NaC_6H_4$ | Methanol-$d_4$ | 181·5 | 128·9 | 141·8 | 123·3 | 117·6 | 152·4 | 113·3 | 164·2 | 117·5 | 137·2 |
| | $D_2O$ (pH 2·5) | 182·4 | 129·2 | 139·7 | 125·1 | 118·7 | 150·1 | 113·8 | 163·1 | 118·7 | 137·4 |
| *o*-$AsO_3H_2C_6H_4$ | DMSO-$d_6$ | 180·7 | 129·9 | 141·7 | 122·3 | 116·9 | 155·1 | 114·1 | 163·8 | 116·9 | 136·4 |
| | Methanol-$d_4$ | 181·7 | 129·7 | 139·7 | 120·1 | 118·0 | 152·5 | 114·3 | 163·1 | 118·3 | 137·2 |
| | Solid | 180·5 | 127·1 | 141·0 | 120·1 | 115·8 | 159·8 | 115·8 | 159·8 | 115·8 | 136·4 |
| | $D_2O$ (pH 2) | 182·6 | 127·2 | 140·2 | 126·1 | 118·0 | 150·5 | 111·9 | 162·1 | 118·8 | 137·3 |
| *o*-$MeC_6H_4$ | $D_2O$ (pH 2·4) | 180·1 | 128·1 | 139·9 | 123·2 | 118·3 | 149·7 | 112·7 | 162·4 | 118·6 | 137·1 |
| *m*-$SO_3NaC_6H_4$ | $D_2O$ (pH 3) | 181·5 | 128·3 | 139·8 | 124·3 | 118·5 | 150·1 | 113·4 | 162·9 | 118·6 | 137·1 |
| *p*-$OHC_6H_4$ | Methanol-$d_4$ | 179·6 | 127·4 | 141·5 | 121·8 | 117·3 | 151·5 | 112·1 | 163·4 | 117·9 | 137·1 |
| *p*-$NO_2C_6H_4$ | DMSO-$d_6$ | 181·9 | 129·8 | 143·3 | 123·2 | — | 155·7 | 112·7 | 163·0 | 115·1 | 136·6 |
| | $D_2O$ (pH 3) | 182·0 | 129·4 | 139·9 | 125·8 | 118·7 | 151·0 | 114·2 | 162·6 | 117·5 | 136·8 |
| *p*-$SO_3NaC_6H_4$ | $D_2O$ (pH 0·8) | 181·7 | 128·6 | 139·6 | 124·8 | 118·7 | 150·1 | 113·7 | 163·0 | 118·2 | 137·2 |

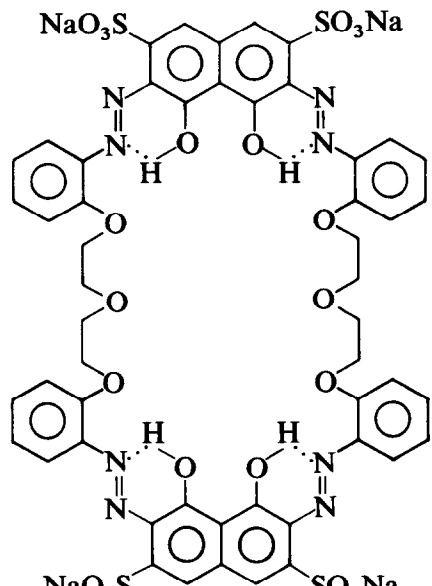
**TABLE 4**
$^{13}C$ Chemical Shifts of Bisarylazo Derivatives of Chromotropic Acid XVI–XVII in Solid and in Solution

| *Compound* | *Conditions* | *Carbon* | | | | | |
|---|---|---|---|---|---|---|---|
| | | *1* | *2* | *3* | *4* | *5* | *6* |
| **XVII** | DMSO-$d_6$ | 170·1 | 131·9 | 135·2 | 122·4 | 149·8 | 117·7 |
| | Solid | 166·2 | 130·0 | 134·0 | 123·7 | 149·7 | 118·5 |
| **XVI** | | | | | | | |
| Ar′ = Ar′ = $C_6H_5$ | DMSO-$d_6$ | 167·3 | 132·8 | — | 120·4 | 147·4 | 118·1 |
| *p*-$MeC_6H_4$ | DMSO-$d_6$ | 167·2 | 132·5 | 137·2 | 120·2 | 147·4 | 118·2 |
| | Solid | 166·1 | 130·0 | 138·6 | 119·5 | 144·1 | 118·0 |
| *o*-$OHC_6H_4$ | DMSO-$d_6$ | 167·1 | 131·0 | 138·1 | 120·0 | 147·7 | 118·8 |
| | Solid | 170·0 | 132·0 | 138·0 | 120·7 | 149·0 | 118·0 |
| *p*-$COOHC_6H_4$ | DMSO-$d_6$ | 167·3 | 130·0 | 136·7 | 120·3 | 146·7 | 117·0 |

that in contrast to monoazo derivatives, bisazo derivatives of chromotropic acid have only the bisazo structure **XVI** both in the solid state and in solution.




**XVI**

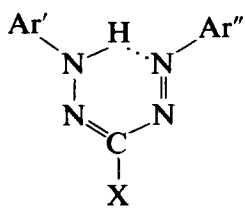



**XVII**

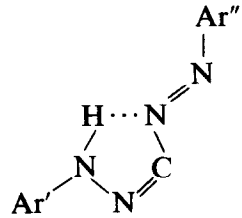
### 3.4 Formazans

Chromogens whose skeleton contains two conjugated azo groupings, e.g., formazans, are widely used as photochromic materials. It is known[42] that

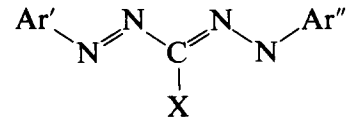
the presence of two azo groups in formazan derivatives (including dithizons) contributes to their deep color and structural variety. $^{1}H$, $^{15}N$ and $^{13}C$ NMR spectroscopy in solution provides an effective technique for a firm grasp of this variety.



**XVIII**

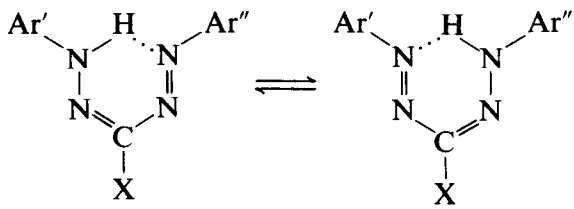


**XIX**



**XX**

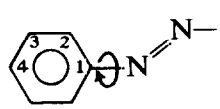
There are two problems in structural investigations of formazans. One pertains to the rationisation of the spectroscopic features of isomers with different types of intramolecular hydrogen bonds N... H—N (e.g., red **XVIII** and yellow **XIX** isomers) and of formazan **XX**, which has no such isomers. The other problem concerns the determination of the position of the tautomeric equilibrium (6) in red formazans **XVIII**:



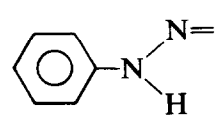
(6)

Some $^{1}H$, $^{15}N$[59–62] and $^{13}C$[63,64] NMR data for formazans in solution have been reported. Figures 5–7 show some new $^{13}C$ NMR solid-state spectra of several formazans and Table 5 gives some NMR data for these compounds in solution.

The $^{13}C$ NMR spectra of the yellow formazan **XIX** (e.g. for $X = Cl$) confirm the fixed structure of this compound without any dynamics. It is significant that dynamics of type **XVIII** $\rightleftharpoons$ **XIX** are observed not only in the solid state but also in $CDCl_3$ solution. The two aromatic rings at the ends of the chromotropic chain —NH—N=C—N=N— are accompanied by different and clearly distinct sets of signals in the $^{13}C$ NMR spectra, both in the solid state are in solution (Table 5, Fig. 5). The positions of C(1)-N carbon signals (chemical shifts, 152 ppm for **XXI** and 142–143 ppm for **XXII**[3]) confirm that these sets correspond to structures **XXI** and **XXII**.



**XXI**



**XXII**

**TABLE 5**
$^{13}C$ Chemical Shifts of Formazans

| *Compound* | *Conditions* | *Carbon* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Ar'* | | | | | | *Ar''* | | | | *C—X* |
| | | *1* | *2* | *3* | *4* | *5* | *6* | *1* | *2* | *3* | *4* | |
| **XVIII** | | | | | | | | | | | | |
| $Ar' = X = C_6H_5$, $Ar'' = p\text{-}MeC_6H_4$ | $CDCl_3$ | 147·7 | 117·2 | 129·3 | 125·6 | 129·3 | 117·6 | 146·0 | 120·1 | 129·9 | 139·3 | 140·9 |
| | Solid | 145·4 | 112·6 | 128·6 | 125·2 | 128·6 | 112·6 | 145·4 | 121·2 | 128·6 | 137·6 | 138·0 |
| $Ar' = Ar'' = o\text{-}MeC_6H_4$, $X = NO_2$ | $CDCl_3$ | 145·4 | 130·9 | 129·8 | 131·4 | 127·6 | 117·6 | 145·4 | 130·9 | 129·8 | 131·4 | 146·5 |
| | Solid | 144·7 | 131·2 | 128·1 | 131·2 | 128·1 | 113·5<br>115·9 | 144·7 | 131·2 | 128·1 | 131·2 | 146·5 |
| **XIX** | | | | | | | | | | | | |
| $Ar' = Ar'' = C_6H_5$, $X = Cl$ | $CDCl_3$ | 141·7 | 114·9 | 129·6 | 129·2 | 129·6 | 114·9 | 152·3 | 123·5 | 129·2 | 131·5 | 134·9 |
| | Solid | 143·0 | 116·0 | 128·7 | 128·7 | 128·7 | 116·0 | 151·7 | 121·3 | 128·7 | 133·0 | 133·0 |
| **XXV** | | | | | | | | | | | | |
| $Ar' = Ar'' = C_6H_5$ | $CDCl_3$ | 140·0 | 119·1 | 130·1 | 130·4 | 130·1 | 119·1 | 140·9 | 119·1 | 130·1 | 130·4 | 169·5 |
| | Solid | 139·5 | 119·0 | 128·3 | 129·6 | 128·3 | 119·0 | 139·5 | 119·0 | 128·3 | 129·6 | 169·1 |

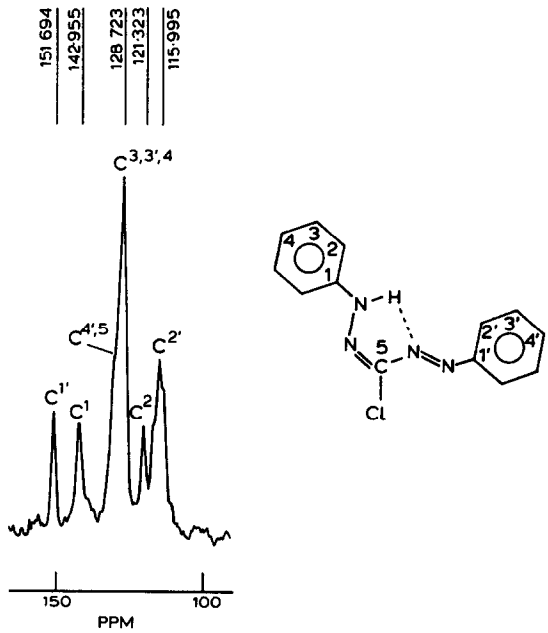



**Fig. 5.** High-resolution solid-state $^{13}C$ NMR spectrum of yellow formazan **XIX** (Ar′ = Ar″ = Ph, $X$ = Cl).

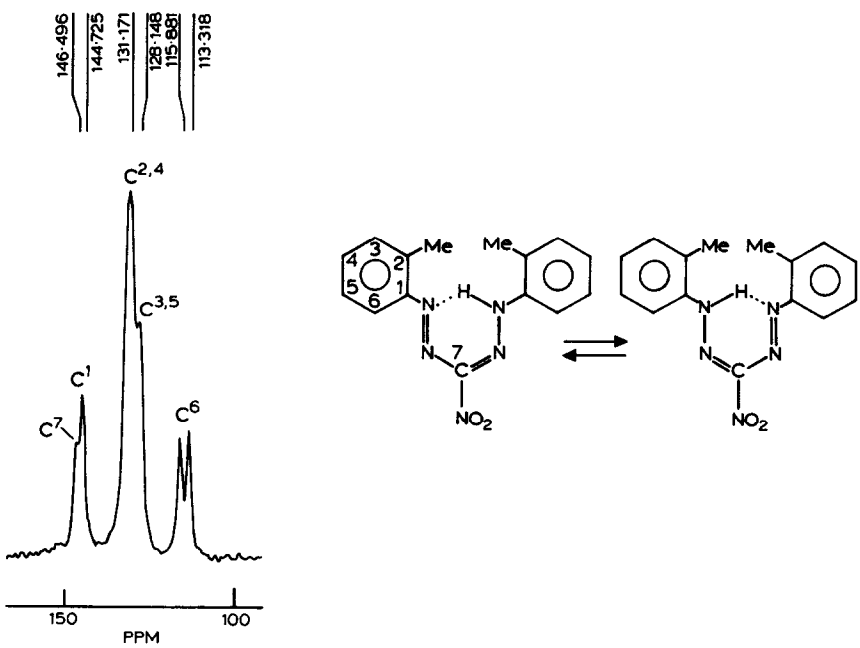



**Fig. 6.** High-resolution solid-state $^{13}C$ NMR spectrum of symmetrical red formazan **XVIII** (Ar′ = Ar″ = $o$-$MeC_6H_4$, $X = NO_2$).

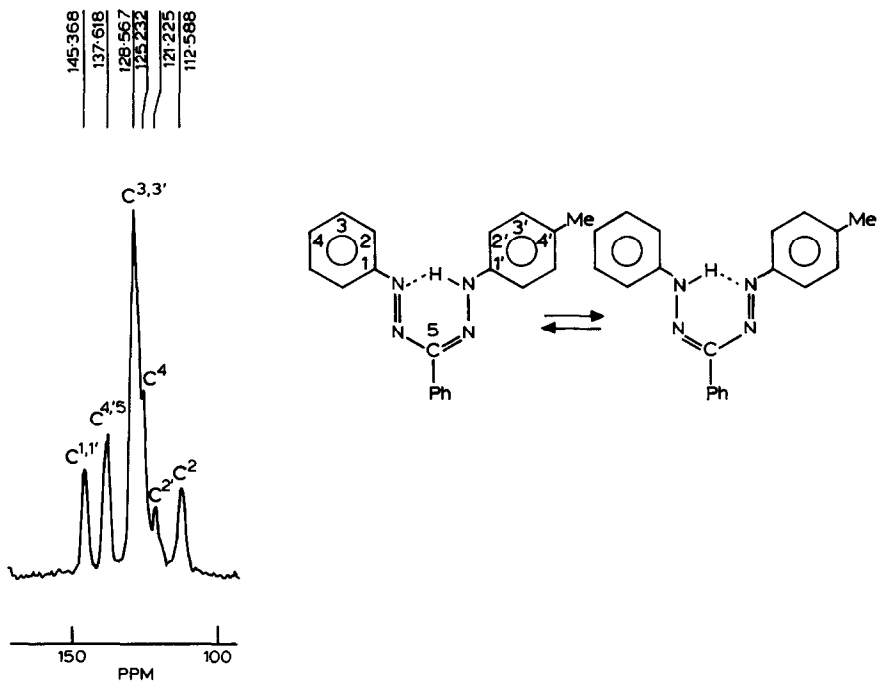
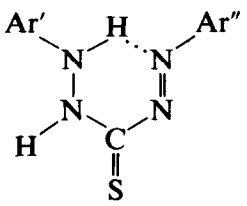



**Fig. 7.** High-resolution solid-state $^{13}C$ NMR spectrum of unsymmetrical red formazan **XVIII** (Ar′ = *X* = Ph, Ar″ = *p*-$MeC_6H_4$).

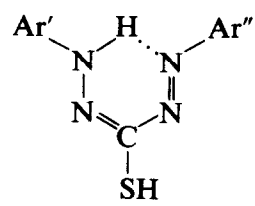
The solid-state NMR spectra of two red formazans are shown in Figs 6 and 7, i.e. a symmetrical formazan with Ar′ = Ar″ = *ortho*-$MeC_6H_4$ and X = $NO_2$, and an unsymmetrical formazan with Ar′ = X = Ph and Ar″ = *para*-$MeC_6H_4$. These spectra correspond to dynamic equilibrium (6) which is retained going from solution to solid.

It has been shown[64] that for red formazans the chemical shift for C(1) in the left-hand side aromatic ring (with Ar′ = X = Ph) is sufficient evidence for the equilibrium 6, displacement to one or other side depending on the substituent in the Ar″ ring (and similarly for the signal C(2)). In the case where Ar″ = *para*-$MeC_6H_4$,[64] the equilibrium is somewhat removed from its centre, because of the slight electron-donating influence of the *para*-Me-group, but in solid state (Fig. 7, Table 5) the position of the equilibrium (6) for this compound is only generally similar to that in solution, and the C(1) chemical shift in the solid state indicates some new displacement of the equilibrium to the left side, compared to solution data. This is also indicated by the C(2) and C(11) chemical shifts.

Formazans in which X = SH (together with SR) (dithizones) have been investigated by NMR.[65,66] Structural features of dithizones are due to types of intramolecular hydrogen bonds which arise in formazans where X = SH,



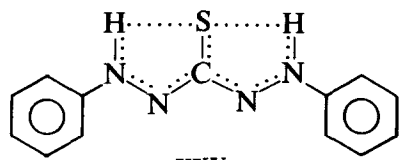
XXIII



XXIV

although it was originally proposed[67] that dithizone represents an equilibrium between two tautomers (**XXIII** and **XXIV**).

The solid-state $^{13}C$ NMR spectrum of the simplest dithizone (Ar′ = Ar″ = Ph) is totally in contradiction to structures **XXIII** and **XXIV**. The spectrum in the solid state as in solution, is mainly in accord with structure **XXV** (Table 5), as has also been recently concluded from X-ray crystal diffraction data.[68] The $^{13}C$ NMR chemical shifts of these compounds (Table 5) indicate the absence of any differences between NMR signals for solid and for solution.



XXV

It should be noted also that, in contrast to yellow formazans **XIX**, in the dithizon **XXV**, both aromatic rings are of the same structural type **XXII**.

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