Investigation of the Structure of an Insoluble Pigment by Means of Nuclear Magnetic Resonance

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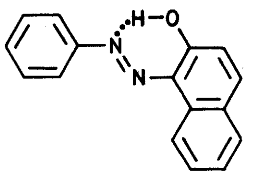
The structure of the insoluble pigment, CIPR 57:1, the monohydrated calcium salt of 1-(2-sulpho-4-methylphenylazo)-2-hydroxynaphthalene-3-carboxylic acid, has been investigated by high-resolution n.m.r. techniques appropriate to solids. The ^{13}C spectra of the pigment and a range of structurally related compounds support the view that these compounds exist as the keto-hydrazo tautomers in the solid state. The selective enrichment of the α- and β-nitrogens with ^{15}N and the observation of the ^{15}N high-resolution n.m.r. spectra confirm directly the existence of the keto-hydrazo structure. ^{113}Cd N.m.r. spectra of pigments obtained by the use of Cd^{2+} in place of Ca^{2+} are used in conjunction with the other n.m.r. results to infer a polymeric sheet-like structure for the pigments in which the divalent ion is co-ordinated by carboxy and sulphonate groups from different pigment molecules.

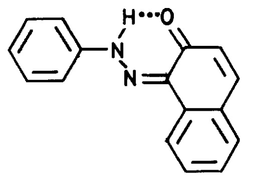
Azo Pigments.—Pigments have a diversity of applications in, for example, paints, inks, and plastics. One of the properties required of a good pigment is insolubility and this characteristic makes them difficult to study by traditional crystallographic structure determination methods.

Yellow and red pigments are usually based on the diazo bond, and the pigment which is the subject of this study is the monohydrated calcium salt of 1-(2-sulpho-4-methylphenylazo)-2-hydroxynaphthalene-3-carboxylic acid, otherwise known as Colour Index Pigment Red 57:1 (CIPR 57:1). This pigment is an important commercial product and, owing to its extreme insolubility and the consequent failure of attempts at growing a crystal large enough for an *X*-ray crystallographic investigation, its crystal structure has not been determined. It is in this context that the n.m.r. investigation reported here has been undertaken as, for this technique, the sample is not required to be crystalline or specially prepared and it can be studied in the form in which it is used commercially. The results obtained and reported below demonstrate the use of high-resolution n.m.r. of the solid state in deducing the main features of the molecular structure of solid CIPR 57:1. The nuclei used as probes were ^{13}C, ^{15}N, and ^{113}Cd. Principal amongst the questions to be answered were: (a) whether the pigment exists as the enol-azo or keto-hydrazo tautomer and (b) the nature of the interaction of the calcium ion with the organic molecule.

Keto-hydrazo tautomerism.—Keto-hydrazo–enol-azo tautomerism (Figure 1) has been investigated in phenylazo-2-naphthols, phenylazo pigments, and phenylhydrazones.[1–12] The keto-hydrazo tautomer represents an increase in conjugation over the enol-azo form and provides the stabilization of approximately coplanar naphthalene and hydrazo groups. This tautomerism is distinguishable by both ^{13}C and ^{15}N n.m.r. of solutions.



enol-azo



keto-hydrazo

Figure 1. Keto-hydrazo–enol-azo tautomerism in the phenylazo-2-hydroxynaphthalene unit

(a) ^{13}C *N.m.r.* A series of investigations into the solid-state structures of some phenylazo-2-naphthols, closely related to the molecules of concern here, has demonstrated the presence of a carbonyl resonance at δ *ca.* 182 p.p.m. (from Me$_4$Si) rather than a hydroxy-substituted aromatic carbon which would be expected to give rise to a resonance at δ *ca.* 152 p.p.m.[11] Other chemical shift information helped to assign the phenyl ring ^{13}C resonances as arising from the keto-hydrazo tautomer,[1,2,11,12] in complete agreement with the *X*-ray-determined structures of these materials.[4–9] A series of Substituent Chemical Shift parameters (SCS) was generated for the hydrazo substituent using the solution-state ^{13}C n.m.r. results of Compernoller *et al.*[2] A series of solid-state SCS parameters for the azo substituent has previously been derived and exhibits a difference for aromatic carbons *ortho* to the azo group in *cis* or *trans* configurations.[13] The mean of these two solid-state *ortho*-SCS parameters is found to be similar to the solution-state *ortho*-SCS parameter.[12,13] Gelbcke *et al.*[3] did not consider keto-hydrazo–enol-azo tautomerism in their investigation of some food dyes based on the phenylazonaphthol unit, even though there were large anomalies between their calculated enol-azo chemical shifts and the experimentally measured resonance positions, which proved to be of the keto-hydrazo tautomer.[2]

(b) ^{15}N *N.m.r.* ^{15}N N.m.r. has proved to be useful in the investigations of the azo and hydrazo groups *via* solution-state studies.[14–20] These include: (a) azo-^{15}N;[14,15,18,19] (b) pro-

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tonated azo-^{15}N;[15] (c) metal-complexed azo-^{15}N;[16,17] (d) hydrazo-^{15}N;[18–20] and (e) hydrazo–azo equilibria.[19] The two ^{15}N nuclei in an azo group have similar chemical shifts. Upon complexation of an azo nitrogen to a metal ion however, large changes in chemical shift are observed. Pregosin and Steiner[16] and Gehrig *et al.*[17] observed that the change in chemical shift of the ^{15}N nucleus involved in complex formation, relative to the free azo ^{15}N nucleus, was in the range $\Delta\delta$ -150 to -196 p.p.m. and that the chemical shift change of the other ^{15}N nucleus in the azo link, relative to the same nucleus in the uncomplexed molecule, was in the range $\Delta\delta$ -50 to -64 p.p.m. The chemical shift changes are large and are a valuable indicator for complexation of azo-nitrogens. The difference in the chemical shifts of the two nitrogens in the hydrazo link, $\delta_\beta - \delta_\alpha = \Delta$, is *ca.* $\Delta = 200$ p.p.m.[18–20] This chemical shift separation is very large and cannot be confused with the azo-^{15}N or complexed azo-^{15}N. ^{15}N N.m.r. was expected, therefore, to prove a valuable probe of the nature of the (N,N) link in CIPR 57:1.

Model Compounds.—To aid the interpretation of the n.m.r. measurements on CIPR 57:1, **I**(i) from this point, a series of model compounds were synthesized, the details of which are summarized in Figure 2 and Table 1. These include: (a) molecules with specific isotopic labelling of the nitrogens in the hydrazo–azo link; (b) molecules with the Ca^{2+} ion replaced with Cd^{2+} allowing ^{113}Cd n.m.r. investigations; (c) sodium salts of the acid dyestuff **I**; (d) chemically modified pigments, *e.g.* with the sulpho or carboxy groups removed. The parent structure of these model compounds and **I**(i) is drawn as the keto-hydrazo tautomer in Figure 2, which also illustrates the atomic numbering employed for chemical shift assignment purposes. Table 1 also contains information on the stoicheiometry and, in some cases, the degree of hydration of the metal salts formed under various conditions.

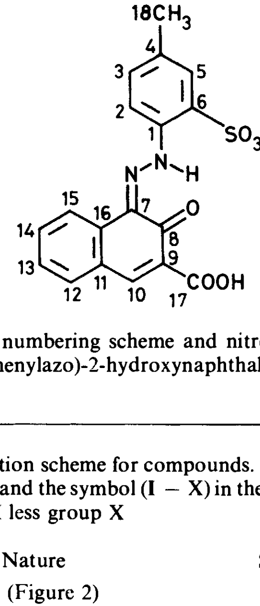


Figure 2. Carbon numbering scheme and nitrogen labelling for 1-(2-sulpho-4-methylphenylazo)-2-hydroxynaphthalene-3-carboxylic acid **I**

Table 1. Identification scheme for compounds. All structures are based on **I** (see Figure 2) and the symbol (**I** − X) in the stoicheiometry column implies structure **I** less group X

Compd.	Nature	Stoicheiometry
I	Free acid (Figure 2)	
I(i)	Ca^{2+} of **I**, monohydrate	Ca^{2+}(**I** − 2H$^+$)$^{2-}$·H$_2$O
I(ii)	β-^{15}N enriched **I**(i)	Ca^{2+}(**I** − 2H$^+$; β-^{15}N)$^{2-}$·H$_2$O
I(iii)	α- and β-^{15}N enriched **I**(i)	Ca^{2+}(**I** − 2H$^+$; α- and β-^{15}N)$^{2-}$·H$_2$O
I(iv)	Ca^{2+} salt of **I**, dihydrate	Ca^{2+}(**I** − 2H$^+$)$^{2-}$·2H$_2$O
II(i)	Na$^+$ salt of **I**	(Na$^+$)$_2$(**I** − 2H$^+$)$^{2-}$
II(ii)	50% α- and β-^{15}N enriched **II**(i)	(Na$^+$)$_2$(**I** − 2H$^+$; α- and β-^{15}N)$^{2-}$
III(i)	Na$^+$ salt of **I** without COOH group	Na$^+$(**I** − COOH, −H$^+$)$^-$·H$_2$O
III(ii)	Ca^{2+} salt of **I** without COOH group	Ca^{2+}(**I** − COOH, −H$^+$)$_2^-$·4H$_2$O
IV	Ca^{2+} salt of **I** without SO$_3$H group	Ca^{2+}(**I** − SO$_3$H, −H$^+$)$_2^-$·2H$_2$O
V(i)	Cd^{2+} salt of **I**	Cd^{2+}(**I** − 2H$^+$)$^{2-}$·4.5H$_2$O
V(ii)	Cd^{2+} salt of **I**	Cd^{2+}(**I** − 2H$^+$)$^{2-}$·H$_2$O
VI	2-Hydroxynaphthalene-3-carboxylic acid	

Experimental

Preparation of the Pigments.—The pigments were prepared by standard methods of which the following is illustrative.

(a) *Calcium salt monohydrate* **I**(i). 5-Methyl-2-aminobenzenesulphonic acid (27.3 g) was dissolved in 0.5M-KOH solution (300 ml) and cooled to 5 °C. Sodium nitrate (10.2 g) in water (50 ml) was added, followed by concentrated hydrochloric acid (37 ml), keeping the temperature below 5 °C with ice. The diazonium salt precipitated from solution.

2-Hydroxynaphthalene-3-carboxylic acid (**VI**) (27.5 g) was dissolved in 1.6M-KOH solution (300 ml) and the volume made up to 800 ml at 15 °C. The diazonium salt slurry was added over 40 min and the final pH adjusted to 8.5.

Calcium chloride dihydrate (30 g) in water (300 ml) was added to the dyestuff, the pH adjusted to 7, and the mixture heated to 80 °C. The pigment was filtered off, washed with water until the filtrate was chloride-ion free, and dried in air at 90 °C. The yield was 95—100%. The calcium salt dihydrate **I**(iv) was obtained by drying the pigment obtained above at 20 °C.

(b) β-^{15}N *Calcium salt monohydrate* **I**(ii). A similar procedure to (a) using Na^{15}NO$_2$ (95%; Amersham International) afforded **I**(ii).

(c) α- *and* β-^{15}N *calcium salt monohydrate* **I**(iii). 4-Toluoyl chloride was converted into ^{15}N-enriched 5-methyl-2-aminobenzenesulphonic acid *via* the amide (using ^{15}NH$_4$OH), Hofmann reaction to the amine, and sulphonation. Diazotization using Na^{15}NO$_2$ gave the doubly labelled diazonium salt. The pigment was prepared as in (a).

(d) 50% α- *and* β-^{15}N *bis-sodium salt* **II**(ii). Coupling equimolar mixtures of the unlabelled [from (a)] and doubly labelled [from (c)] diazonium salts to **VI**, salting out the dyestuff, and drying gave **II**(ii).

(e) *Metal-free pigment* **I**. The coupling was carried out with ammonia replacing KOH and the dyestuff acidified and dried under high vacuum to remove ammonium salts.

(f) SO$_3$H-*free pigment* (**IV**). *p*-Toluidine was diazotized and coupled to **VI**. The calcium salt was prepared as in (a).

(g) *Cadmium salts* **V**(i) *and* **V**(ii). Method (a) was used except cadmium chloride replaced calcium chloride. **V**(i) was not heated in the slurry whereas it was heated to 80 °C to obtain **V**(ii); a marked phase change occurred during this heat treatment. The final products showed different Cd^{2+}–H$_2$O ratios and distinctly different powder *X*-ray diffraction patterns.

N.m.r. Measurements.—The combined techniques of cross-polarization (CP), dipolar-decoupling, and magic-angle rotation (MAS) were used to obtain the high-resolution n.m.r. spectra of the low-abundance nuclei (^{13}C, ^{15}N, ^{113}Cd). These and related techniques have been discussed in detail previously.[21–30]

The ^{13}C n.m.r. measurements were carried out on two home-built spectrometer systems, each using Nicolet 1180 data systems and 293A pulse programmers. The first is based on a 2.1 T Bruker BE38M electromagnet, the second on an Oxford Instruments 4.7 T superconducting magnet, giving ^{13}C observation frequencies of 22.63 and 50.3 MHz, respectively. The superconducting system uses standard Bruker CXP CPMAS probes.

The ^{113}Cd n.m.r. spectra were measured on the 4.7T spectrometer (44.4 MHz) whilst the ^{15}N n.m.r. spectra were obtained by courtesy of Bruker Spectrospin, Karlsruhe, West Germany at an observation frequency of 30.4 MHz.

Samples were contained in either cylindrical glass rotors (^{13}C at 22.63 MHz) or in Andrew-Beams mushroom-shaped rotors (all measurements at 4.7 T) constructed with bases of Delrin (polyoxymethylene) and bodies of Macor (Corning). Sample spinning rates were 2 and 3.5 kHz at 2.14 and 4.7 T respectively with sample volumes *ca.* 0.3 cm^3. The temperature for all measurements was ambient, the samples being isolated from any indirect heating effects arising from the high-power radio frequency irradiation by the flow of air used for spinning. All chemical shifts are quoted relative to Me_4Si (liquid) and were determined by use of an adamantane secondary standard by sample replacement. The high-frequency-positive convention is used.

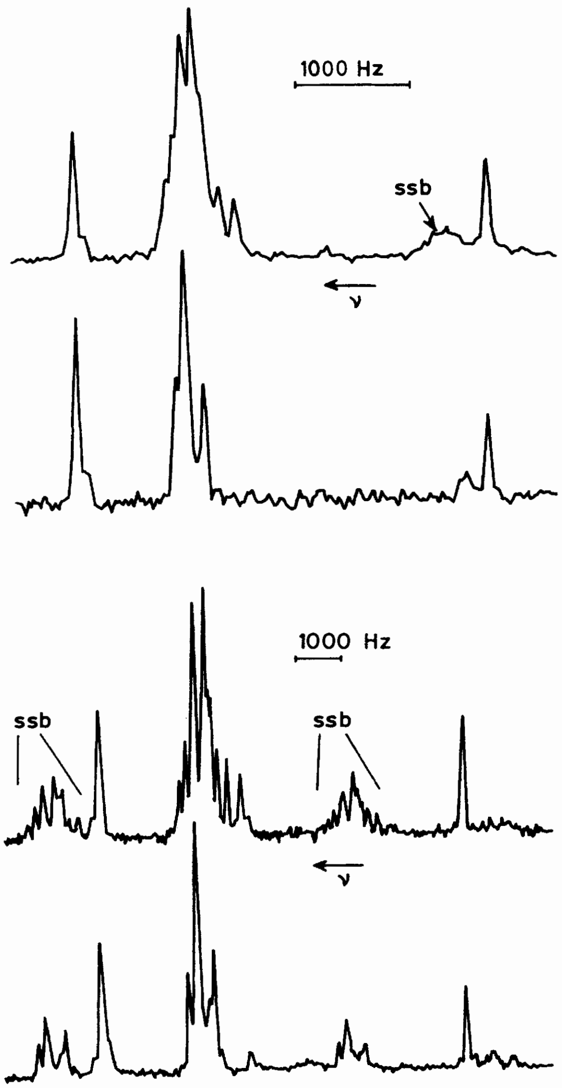


Figure 3. Typical 22.6 and 50.3 MHz ^{13}C n.m.r. spectra of the Ca^{2+} salt I(i). The top two spectra were measured at 22.6 MHz and the lower at 50.3 MHz. The spectral conditions were: (starting at the top) 16 kHz spectral width, 0.8 s recycle delay, 5 ms contact, 3 contacts per cycle, 6 500 cycles; dipolar-dephased, 16 kHz spectral width, 1 s recycle delay, 10 ms contact, 20 000 cycles, 40 μs dephasing delay; 20 kHz spectral width, 1 s recycle delay, 5 ms contact, 3 contacts per cycle, 7 000 cycles; dipolar-dephased, 20 kHz spectral width, 1 s recycle, 5 ms contact, 21 000 cycles, 40 μs dephasing delay

Results and Discussion

Stoicheiometry of the Salts.—From Table 1 it can be seen that the salts of **I** with divalent (Ca^{2+},Cd^{2+}) and monovalent (Na^+) cations indicate the removal of two protons from **I**. Possible sources of these protons are the sulpho and carboxy groups and the hydroxy and/or hydrazo group, depending on the tautomeric form. The stoicheiometry of the series of salts **III** and **IV** in which **I** has had either the sulpho or carboxy group removed suggest strongly that it is the protons of these groups which are involved. The Cd^{2+} salts of **I** conform with the Ca^{2+} salt in that **I** behaves as a dibasic acid, losing two protons giving salts with a metal:ligand ratio of 1:1.

^{13}C *Chemical Shifts.*—The ^{13}C n.m.r. spectra of the materials investigated are complex and crowded. Examples are given in Figures 3 and 4. Whilst, in general, complete and unambiguous spectral assignments were not possible, use of both normal CP and dipolar-dephased (NQS) spectra[31,32] and relative intensities, together with substituent chemical shift (SCS) parameters, allowed tentative assignments to be made which, in the main, are self-consistent. Table 2 contains the ^{13}C chemical shifts for 2-hydroxynaphthalene-3-carboxylic acid **VI** and the corresponding SCS parameters based on the naphthalene group after subtraction of the hydroxy solution-state SCS values.[33] The high-resolution spectrum of solid β-naphthol has no measureable ^{13}C chemical shift differences compared with the solution-state spectrum ($CDCl_3$). These SCS parameters are intended as an aid to the calculation of the chemical shifts of the ten-carbon ring system for the enol-azo tautomer. They do not, of course, apply to the keto-hydrazo tautomer. Table 3 summarizes the empirically calculated ^{13}C chemical shifts using SCS parameters[1–3,10–13] and Table 4 lists the observed resolvable resonance lines for all compounds studied (except for the ^{15}N-enriched materials which showed no differences from the normal compounds) together with the provisional assignments to the carbon sites identified by the numbering scheme in Figure 2. It should be noted that SCS parameters are

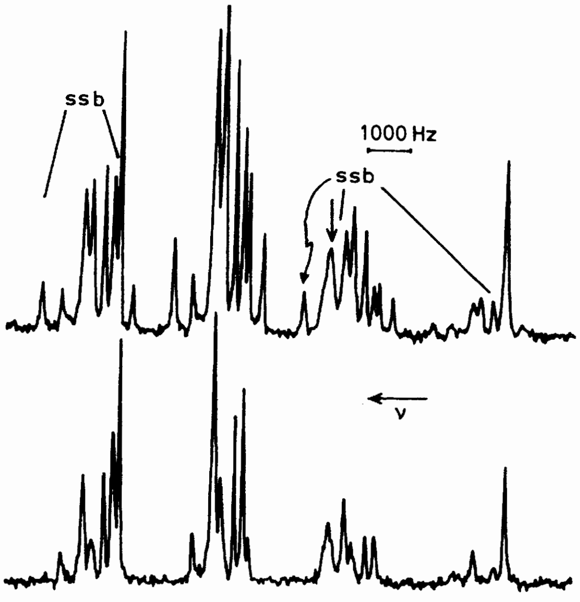
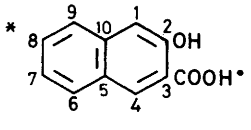


Figure 4. 50.3 MHz ^{13}C n.m.r. spectra of the Cd^{2+} salt V(ii): (upper spectrum) 20 kHz spectral width, 0.78 s recycle delay, 5 ms contact, 20 000 cycles; (lower spectrum) dipolar-dephased, same conditions as for the upper spectrum with a 40 μs dephasing delay. The peaks marked 'ssb' are spinning sidebands and the peak marked with a vertical arrow arises from the delrin base of the sample rotor

available only for the phenyl ring for the keto-hydrazo tautomer whereas, for the azo tautomer, use of the values in Table 2 allows the prediction of the resonance positions of all carbons. For the compounds **III**(i) and (ii), previous solution-state work allows the prediction of the chemical shifts of the naphthalene ring.[10] The experimental chemical shifts for the phenyl ring carbons agree well with the values predicted for the keto-hydrazo tautomer. For example, C-1, -4, and -6 are quaternary and, for the azo tautomer, are predicted to occur at δ *ca.* 140—146 p.p.m. However, no such quaternary resonances are observed in this range, the only such resonance generally being assigned to C-10 of the naphthalene ring. On the other hand, signals having quaternary character (as revealed by the n.q.s. spectra) were found in regions corresponding to those predicted for C-1, -4, and -6 on the basis of the keto-hydrazo tautomer SCS parameters. In the case of the naphthalene ring, whilst the SCS parameter approach must be regarded as no more than a guide, the observed shifts show some disagreement with those predicted on the basis of the azo tautomer. In particular, there is no resonance in the n.q.s. spectra corresponding to a hydroxy-substituted aromatic carbon which would be predicted to be in

Table 2. The 22.63 MHz ^{13}C chemical shifts of 2-hydroxynaphthalene-3-carboxylic acid **VI** from Me_4Si liquid together with the substituent chemical shifts (SCS) for the 3-carboxy group. The latter were obtained by subtracting the effects of the hydroxy group from the corresponding naphthalene chemical shifts[31]

Carbon no.*	Chemical shift (p.p.m.)	SCS (p.p.m.)
1	110.0	+0.6
2	155.9	+2.7
3	112.5	−5.1
4	133.3	+3.5
5	125.0	−3.9
6	131.3	+3.6
7	122.4	−1.1
8	126.9	+0.5
9	126.9	+0.6
10	137.2	+2.7
COOH	175.4	



non-systematic

Table 3. Calculated ^{13}C chemical shifts based on available substituent chemical shift (SCS) parameters*

(a) Phenyl ring

	Compounds			
	I, II, III, V		IV	
Carbon no.	Azo	Hydrazo	Azo	Hydrazo
1	145.6	138.0	148.3	140.7
2	115.8	115.4	115.0	114.6
3	132.3	133.7	129.4	130.4
4	140.2	133.0	139.4	132.3
5	126.7	127.7	129.4	130.4
6	145.0	129.1	130.5	114.6

(b) Naphthalene ring

	I, II, IV, V	III	
	Azo	Azo	Hydrazo
7	133.8	133.2	133.2
8	149.9	147.2	187.7
9	114.2	119.3	122.6
10	136.2	132.7	143.3
11	125.9	129.8	131.6
12	131.3	127.7	127.5
13	121.9	123.0	126.3
14	126.9	126.4	129.1
15	126.9	126.3	129.8
16	131.3	128.6	129.8

* Refs. 1—3, 10—13.

Table 4. Observed ^{13}C chemical shifts* of the solid compounds listed (see Table 1). The assignments given in brackets (see Figure 2) are, in general, tentative (see text)

I[a]	I(i)	I(iv)	II(i)	III(i)	III(ii)	IV[a]	V(i)	V(ii)
18.7 21.1 }(18)	21.0(18)	19.5(18)	19.2(18)	20.5(18)	20.1(18)	20.8(18)	19.4(18)	18.6(18)
114.2(2)	114.4(6)	113.7(6)	114.0(6)	114.1(6)	114.2(6)	114.4(6)	116.8(6)	114.7(6)
119.6(13,14)	119.9(13)	120.3(13)	120.3(9)	121.0(9)	120.0(9)	120.7(13)	121.3(13)	120.1(13)
126.5(9)	124.0(14)	123.0(14)	123.6(14)	123.5(13)	123.1(13)	127.1(2,9,14)	124.7(9)	122.6(9)
128.3(3,5,12,15)	126.6(9)	125.4(9)	128.2(9)	128.2(2)	127.6(2)	128.6(3,5,11,12,15)	125.9(14)	126.1(2)
129.2(6)	128.5(5,12)	127.9(2)	129.3(3,5,12,15)	129.4(3,5,12,14,15,16)	129.0(12,15,16)	132.5(16)	126.1(2)	130.9(3,5,12,14,15)
131.3(16)	129.9(3,12,15)	133.2(3,4,5,7,11,12,15,16)	131.5(2)	131.3(11)	130.3(3,5)	135.1(4,7)	127.6(3,5,12,15)	131.5(7)
133.5(4,11)	134.2(4,7,11,16)	136.8(1)	134.8(7,11,16)	134.4(4,7)	132.2(11)	138.5(1)	130.2(11,16)	134.3(4,11,16)
136.5(1,7)	137.6(1)	141.9(10)	136.1(4)	137.4(1)	134.1(4,7)	170.5(8)	133.4 135.1 }(7,14)	142.9(1)
169.1 171.7 }(8)	140.6(10)	170.2(8)	139.3 141.5 }(1,10)	141.8(10)	136.7(1)	176.2(17)	149.4(10)	149.9(10)
174.1(17)	174.0(8,17)	173.2(17)	172.6(8)	175.2(8)	142.1(10)		174.5(8,17)	171.8(8,17)
			175.5 177.6 }(17)		175.3(8)			

* p.p.m. from Me_4Si at 50 MHz; obtained by sample substitution with solid adamantane.
[a] Resonance not assigned to C-10.

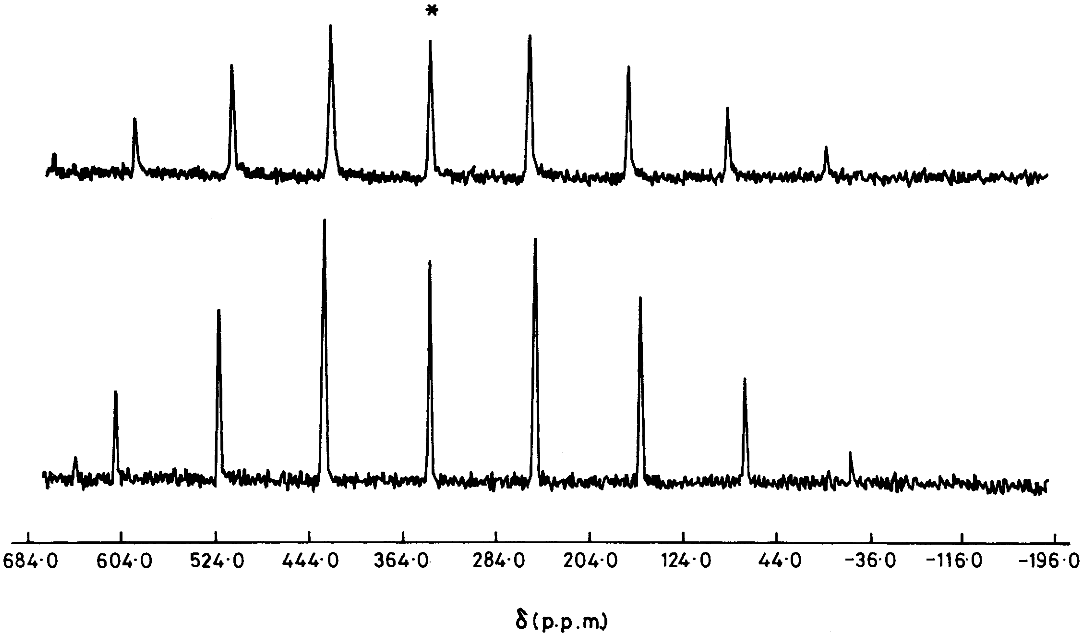


Figure 5. 30.4 MHz ^{15}N CPMAS N.m.r. spectra of the β-^{15}N enriched Ca^{2+} salt **I(ii)**. Both spectra were obtained with a 29 412 kHz spectral width, 3 s recycle delay, 5 ms contact, and 83 cycles. The spectra differ only in sample spinning rate and the asterisk identifies the isotropic chemical shift centreband

Table 5. 30.4 MHz ^{15}N N.m.r. chemical shifts of **II(ii)**, **I(ii)**, and **I(iii)**, in p.p.m. from $^{15}NH_4NO_3(S)$[a]

Compound	α-^{15}N	β-^{15}N	Δ
I(ii)		347.6	
I(iii)	178	345.8	168
II(ii)	172	334.9[b]	163[b]
		331.5	160

[a] Using the high-frequency-positive convention. [b] Crystallographic splitting present for the β-^{15}N.

the δ 145—155 range. On the other hand, the intensity of resonances in the carbonyl region and, for some of the compounds, resolved separate carbonyl peaks [**I**, **I(iv)**, **II(i)**, **II(ii)**, **IV**] clearly establish the dominance of the keto-hydrazo form. It is interesting to note that in the Cd^{2+} salts **V(i)** and **V(ii)**, the carbonyl resonances assigned to C-8 and C-17 are near-degenerate and unresolvable, as with the Ca^{2+} salts **I(i)**—(iv) for which they are models. C-2 and -6 of **IV** are assigned different chemical shifts arising from a different environment of the *ortho*-carbons, *i.e. cis* and *trans* to the NN link. Similar situations have been observed for solid azobenzenes.[13]

Overall, the clear conclusion from the ^{13}C data is that all of these species exist as the keto-hydrazo form to within the level of detection of the n.m.r. technique.

^{15}N *N.m.r. Spectra.*—As indicated in the Introduction, it was expected that ^{15}N n.m.r. was likely to prove of considerable utility in investigation of both the tautomeric form and the nature of the bonding in the salts of **I**. The strategy behind choosing to prepare the ^{15}N-enriched samples **I(ii)**, (iii), and **II(ii)** was that **II(ii)** would provide a compound in which it was likely that the N-N link was not involved in direct interaction with a metal ion and which was in the keto-hydrazo form as shown by the ^{13}C n.m.r. results. **I(ii)** on the other hand, being singly labelled, would provide the ^{15}N chemical shift for the β-^{15}N site in the Ca^{2+} salt whilst **I(iii)** would allow the characterization of both sites. In particular, it was expected that the isotropic chemical shifts should provide definitive information concerning both the tautomeric structure and on whether the Ca^{2+} ion was chelated by either of the azo nitrogens. In this context the dipolar dephasing (n.q.s.) experiment was expected to be decisive since, in such an experiment, any ^{15}N bonded directly to a proton should be lost from the spectrum much more rapidly than one without such a direct proton bond.

The ^{15}N n.m.r. spectra of all three compounds are shown in Figures 5—7 and the isotropic chemical shifts are summarized in Table 5.

The β-^{15}N site has a large shielding anisotropy as evidenced by the many spinning sidebands present in the spectra of **I(ii)**. Figure 5 illustrates ^{15}N spectra of **I(ii)** measured at two different spinning speeds in order to identify the isotropic chemical shift of the β-^{15}N. This is assigned a value of δ 347.6 p.p.m. from solid $^{15}NH_4NO_3$. This shift, and the substantial shielding anisotropy, was essential in the identification of the signals arising from the β-^{15}N site in the doubly enriched compounds **I(iii)** and **II(ii)**.

Figure 6(a) shows the ^{15}N n.m.r. spectrum of the doubly enriched calcium salt **I(iii)**. The resonance arising from the β-site is readily assigned. The resonance of the α-nitrogen is seen to have an isotropic chemical shift of δ 178 p.p.m. relative to solid $^{15}NH_4NO_3$ and to have a considerably smaller anisotropy as evidenced by the smaller number of spinning sidebands. Figure 6(b) is the ^{15}N spectrum observed for **I(iii)** using the n.q.s. or dipolar-dephasing experiment with a dephasing time of 70 μs. It is clear that the amplitude of the resonance from the α-nitrogen is a strong function of the dephasing time and this identifies it as having one or more protons in close proximity to it. Whilst it is not possible to be certain that this proton (or protons) is directly bonded to the α-nitrogen the rate of change of the signal with dephasing time makes it almost sure that it is. It is very unlikely that an intermolecular N • • • H distance could be short enough to produce such a dipolar coupling and the nearest intramolecular non-bonded distance is too large.

Figure 7 illustrates the ^{15}N spectra for **II(ii)**. It is clear that

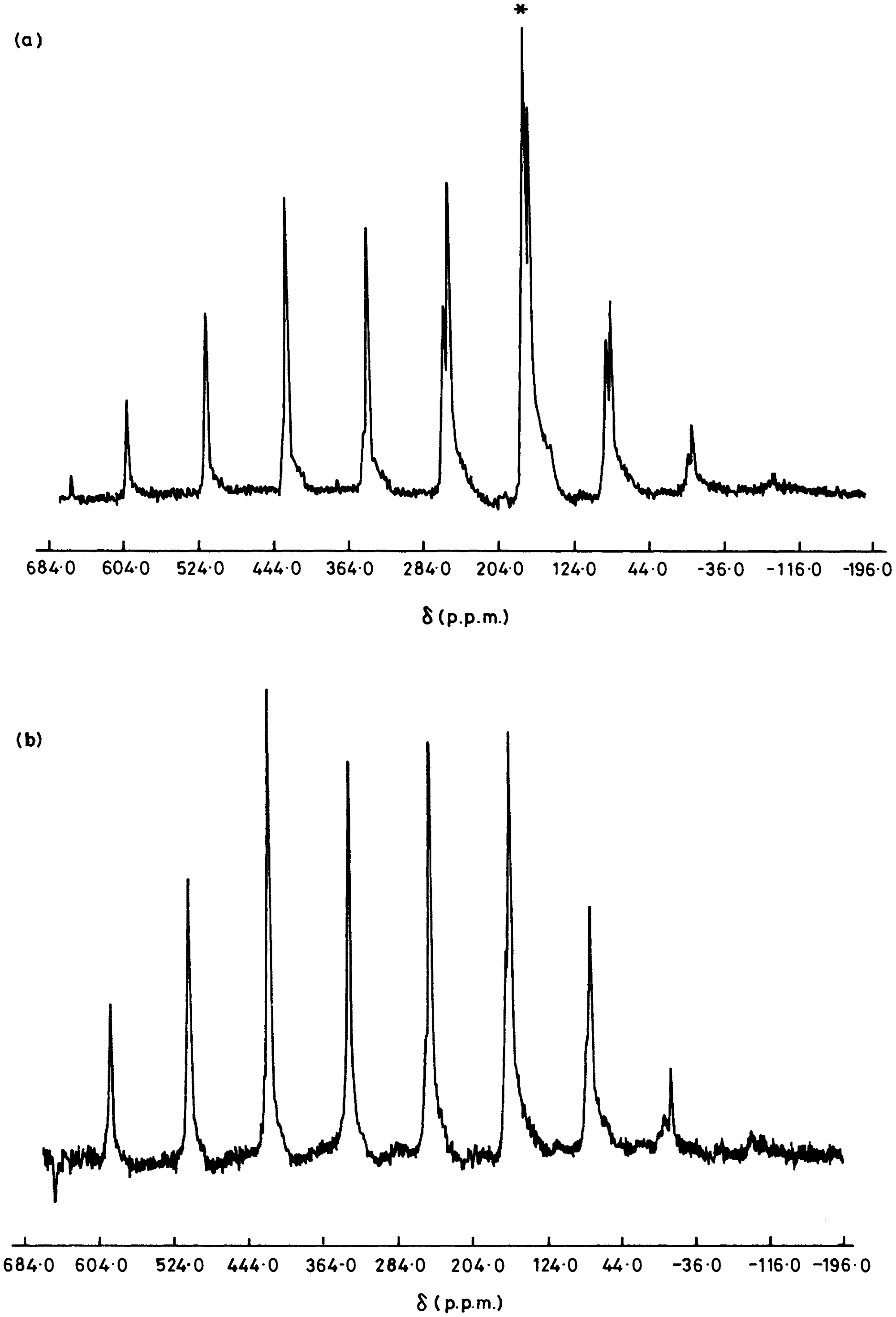


Figure 6. 30.4 MHz ^{15}N CPMAS N.m.r. spectra of the doubly ^{15}N enriched Ca^{2+} salt I(iii). The conditions were generally as for Figure 5 except that for (a) 1 132 cycles were acquired. The α-^{15}N site is readily apparent by comparison with Figure 5 which gives the β-^{15}N spectrum. (b) Dipolar-dephased spectrum with a dephasing delay of 70 μs; obtained with 393 cycles. The peak marked with an asterisk in (a) is the isotropic centreband for the α-^{15}N site

these are closely similar to those for **I(iii)**, the only additional feature being that the β-nitrogen resonance shows a 1:1 splitting of *ca.* 3.4 p.p.m. which is likely to be due to a crystallographic inequivalence. Such a 1:1 splitting was also observed for the ^{13}C resonance assigned to the carboxy carbonyl. The isotropic chemical shifts for the sodium salt are between 6 and 10 p.p.m. to low frequency of those for the calcium salt, but these are very small effects in comparison with the total shift range and the results strongly support the view that the organic molecule is in a very similar state in both salts and that the ionization of two protons occurs from the sulpho and carboxy groups, with the azo-hydrazo nitrogens not being

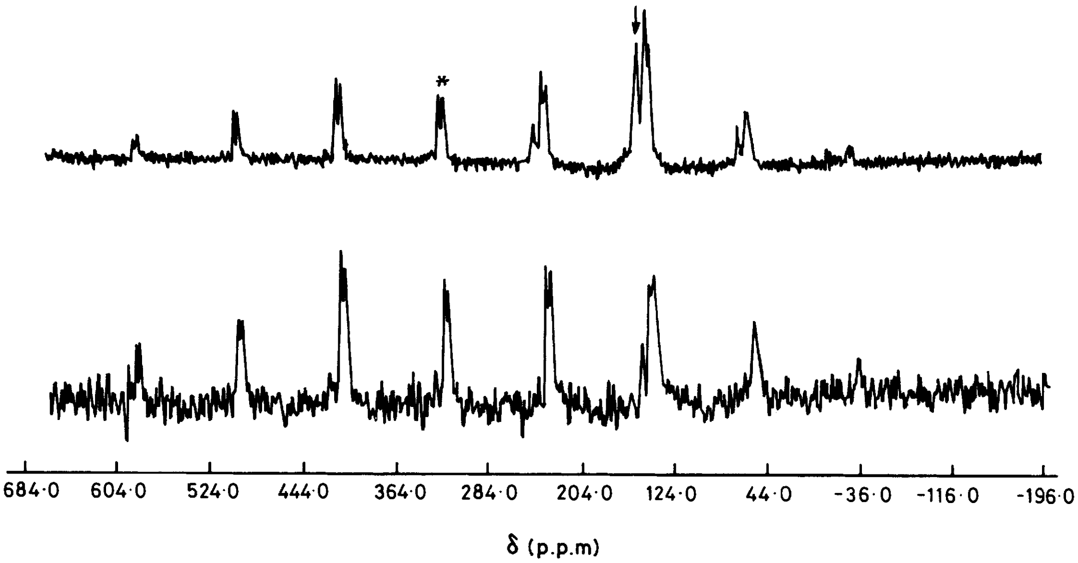


Figure 7. 30.4 MHz ^{15}N N.m.r. spectra of the bis-sodium salt **II**(ii). (a) 29 412 kHz spectral width, 3 s recycle delay, 5 ms contact, and 400 cycles. (b) Is a dipolar-dephased spectrum (70 μs dephasing time) corresponding to 140 cycles with other conditions as for (a). The asterisk and vertical arrow identify the β-^{15}N and α-^{15}N chemical shifts, respectively

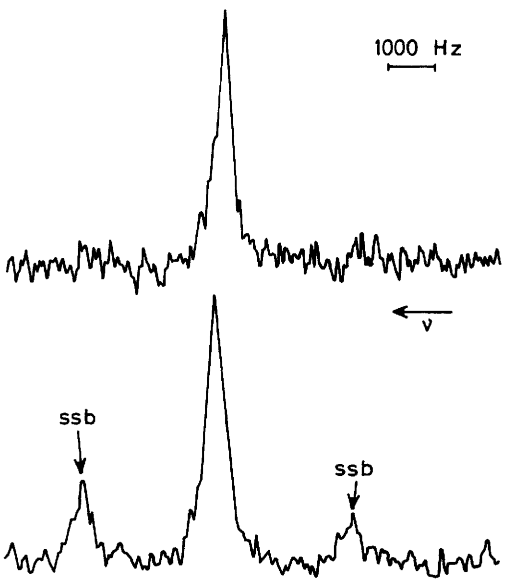


Figure 8. 44.4 MHz ^{113}Cd N.m.r. spectra of the Cd^{2+} salts **V**(i) and (ii). (a) **V**(i), 20 kHz spectral width, 1.5 s recycle delay, 5 ms contact, 10 000 cycles. (b) **V**(ii), conditions as for (a)

involved in bonding to the metal ion. This is further supported by both the values of the chemical shifts and their differences, as discussed in the introduction.

It has been suggested that a shift difference of 200 p.p.m. is associated with a system which is completely in the hydrazo tautomeric form.[18—20] The shift differences observed for the calcium and sodium pigments, **I**(iii) and **II**(ii), are 168 and 163—160 p.p.m., respectively. These values could be interpreted as indicating that the electronic structure is not completely in the hydrazo form. This might reflect either a dynamic equilibrium in which the proton jumps between two unequal potential wells, spending more time in that corresponding to the fully hydrazo structure, or a static six-membered-ring structure with the appropriate electron distribution. Low-temperature n.m.r. studies might allow investigation of these possibilities.

^{113}Cd *N.m.r. Spectra.*—Whilst calcium has a magnetic isotope it is both of low abundance and quadrupolar in nature, giving rise to severe difficulties in observing it in n.m.r. experiments, particularly those in solids where chemical information is the objective. In such a situation it has been common practice in studies of calcium-containing proteins, for example, to use substitution by cadmium and observation of ^{113}Cd n.m.r. as an approach to studying the structures from the viewpoint of the metal ion.[34—36]

The ^{113}Cd n.m.r. spectra of compounds **V**(i) and (ii) are shown in Figure 8. For both compounds the spectra consist of a single isotropic chemical shift, with that for **V**(ii) showing a larger anisotropy as evidenced by the presence of spinning sidebands. The isotropic chemical shifts, relative to the higher intensity resonance in solid tricadmium sulphate, are **V**(i), δ 19 p.p.m., and **V**(ii), δ 28 p.p.m. The difference in shift between the two compounds is negligible in the context of the very large chemical shift range for ^{113}Cd. The absolute values are consistent with Cd^{2+} in a largely ionic oxygen environment. The most significant observation, however, is that there is only a single site for the ^{113}Cd in these molecules and, assuming that the cadmium pigment is a model for the calcium material, that there is, by implication, only a single site for the Ca^{2+} ion.

A Proposed Structure for the Pigment.—The ^{13}C and ^{15}N n.m.r. evidence presented above establishes beyond any doubt that the predominant form of (**I**) and its salts in the solid state is the keto-hydrazo tautomer. Together with the stoicheiometry of the various compounds listed in Table 1, the n.m.r. evidence is also conclusive in establishing that it is the sulpho and carboxy groups which lose protons on formation of salts with both mono- and di-valent cations.

Assuming isomorphous replacement of Ca^{2+} by Cd^{2+}, the evidence of the ^{113}Cd n.m.r. spectra is that there is a unique site for the divalent metal ion within the pigment structure with oxygen co-ordination. Since both the sulphonate and carboxylate groups must be in close proximity to the $Ca^{2+}:Cd^{2+}$ ions this last observation suggests strongly that each cation is co-

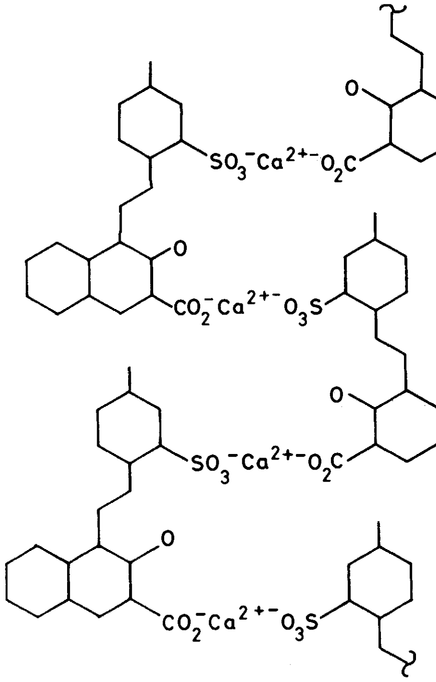


Figure 9. A possible polymeric structure for the Ca^{2+} pigment suggested by the n.m.r. results

ordinated by a sulphonate and a carboxylate group. If this were not so then there should be at least two distinct sites for the metal ion, corresponding to co-ordination with two sulphonates and two carboxylates, respectively. The possibility that this is so and that the ^{113}Cd n.m.r. chemical shifts of the two sites are too similar to be resolved is unlikely, given the large range of ^{113}Cd shifts.

The above evidence can be combined to suggest a structure for **I**(i) and this is illustrated in Figure 9. Each divalent metal ion is co-ordinated by oxygen atoms from single sulphonate and carboxylate groups on *separate* organic molecules. The water molecules in the structure will satisfy any residual co-ordination sites at the metal ion or form part of the general lattice. In this context it is significant that the ^{113}Cd n.m.r. spectrum of **V**(ii) has a larger chemical shift anisotropy than **V**(i). This suggests that removal of water molecules has led to an increase in the electronic asymmetry at the ionic site, implying an involvement of these water molecules with that site.

The most important conclusion from this model is that, because of the necessary involvement of two molecules of the organic compound in the co-ordination to the metal ion, together with the highly planar nature of these molecules, the overall structure is likely to be of sheet-like polymeric chains which could account for its highly insoluble nature. There is also the possibility that water molecules could provide for O–H ··· O hydrogen bonds to produce substantial inter-chain interactions which would further stabilize the structure and add to the insolubility.

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