

# Structures of the Azo Dyes Sudan Red G [1-(2-Methoxyphenylazo)-2-naphthol], $C_{17}H_{14}N_2O_2$ , and Sudan Yellow (1-Phenylazo-2-naphthol), $C_{16}H_{12}N_2O$

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Sudan Red G:  $C_{17}H_{14}N_2O_2$ , MW = 278.31, orthorhombic, *Pbca*,  $a = 5.885(1)$ ,  $b = 14.591(3)$ ,  $c = 30.902(5)$  Å,  $V = 2653.5(8)$  Å<sup>3</sup>,  $T = 138$  K,  $Z = 8$ ,  $D_x = 1.392$  Mgm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71069$  Å,  $F(000) = 1168$ ,  $R = 0.0432$  for 1577 unique reflections; Sudan Yellow:  $C_{16}H_{12}N_2O$ , MW = 248.29, monoclinic, *C2/c*,  $a = 27.832(4)$ ,  $b = 6.028(2)$ ,  $c = 14.870(3)$  Å,  $\beta = 103.79(01)^\circ$ ,  $V = 2422.8(8)$  Å<sup>3</sup>,  $T = 138$  K,  $Z = 8$ ,  $D_x = 1.360$  Mgm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71069$  Å,  $F(000) = 1040$ ,  $R = 0.0423$  for 1593 unique reflections.

Both substances crystallize in the hydrazo form. The intramolecular hydrogen bond in Sudan Red G does not seem to influence the planarity, as both compounds are nearly planar and crystallize in an anti-parallel herringbone fashion.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The powdered root of *Curcuma longa* L., turmeric, is used as a spice throughout the world. It has a strong yellow hue due to the presence of curcumin and related compounds. In order to enhance this hue, other coloring agents have been added from time to time. In a sample of turmeric purchased in Tanzania in 1981, a strong reddish color, different from the yellow one usually seen, was observed. In order to determine whether this color was due to addition of natural or synthetic pigments, or metal complexes of the curcuminoids, the red pigment was isolated and analyzed by UV, IR, NMR, mass spectroscopy<sup>1</sup> and X-ray diffraction, resulting in its identification as the azo dye Sudan Red G (SRG). The X-ray study of Sudan Red G and the closely related Sudan Yellow (SY) is reported here.

## Experimental

Crystals of the title compounds were grown from toluene. The symmetry of the crystals of Sudan Red G was orthorhombic with systematic absences:  $0kl$  for  $k$  odd,  $h0l$  for  $l$  odd and  $hk0$  for  $h$  odd, indicating space group *Pcba*, No. 61.<sup>2</sup> For Sudan Yellow, the symmetry was monoclinic with systematic absences:  $hkl$  for  $h+k$  odd and  $h0l$  for  $l$  odd, indicating space group *C2/c*, No. 9.<sup>2</sup> Unit cell parameters were determined from 25 specially selected reflections for both compounds. The values determined were  $a = 5.885(2)$ ,  $b = 14.591(3)$ ,  $c = 30.902(5)$  Å,  $V = 2653.5(8)$  Å<sup>3</sup>,  $T = 138$  K,  $Z = 8$ ,  $D_x = 1.3932(4)$  Mgm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71069$  Å,  $F(000) = 1168$  (for SRG), and  $a = 27.832(4)$ ,  $b = 6.028(2)$ ,  $c = 14.879(3)$  Å,  $\beta = 103.79(01)^\circ$ ,  $V = 2422.8(8)$  Å<sup>3</sup>,  $T = 138$  K,  $Z = 8$ ,  $D_x = 1.360$  Mgm<sup>-3</sup>,  $\lambda = 0.71069$  Å,  $F(000) = 1040$  (for SY). Crystals of  $0.3 \times 0.1 \times 0.05$  mm for SRG and of  $0.4 \times 0.1 \times 0.2$  mm for SY were used for data collection on an Nicolet P3 automatic diffractometer at a temper-

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Table 1. Atomic and thermal parameters for Sudan Red G (SRG).

Atom	x	y	z	$U_{eq}^a$
O1	0.69208(37)	0.44875(11)	0.63201(6)	0.0311
O2	0.18914(36)	0.41727(11)	0.69476(5)	0.0281
H1	0.57021(41)	0.26025(14)	0.62107(6)	0.0228
H2	0.44041(41)	0.31033(15)	0.64622(7)	0.0225
C1	0.74919(51)	0.29974(17)	0.60250(7)	0.0214
C2	0.81295(56)	0.39603(17)	0.60871(8)	0.0257
C3	1.01814(57)	0.42787(19)	0.58780(9)	0.0286
C4	1.14847(58)	0.37148(19)	0.56438(9)	0.0285
C5	1.09379(49)	0.27648(17)	0.55795(8)	0.0221
C6	1.23843(56)	0.21853(20)	0.53426(8)	0.0279
C7	1.18565(60)	0.12807(19)	0.52790(9)	0.0298
C8	0.98542(57)	0.09303(19)	0.54531(9)	0.0281
C9	0.84075(57)	0.14778(15)	0.56905(8)	0.0258
C10	0.89235(49)	0.24037(17)	0.57601(7)	0.0206
C11	0.25013(50)	0.27050(17)	0.66617(7)	0.0212
C12	0.11350(50)	0.32823(17)	0.69174(8)	0.0223
C13	-0.07602(56)	0.29388(19)	0.71188(8)	0.0255
C14	-0.13254(56)	0.20139(19)	0.70673(8)	0.0266
C15	0.00011(55)	0.14421(18)	0.68121(9)	0.0272
C16	0.19132(56)	0.17910(18)	0.66119(8)	0.0249
C17	0.04479(62)	0.48858(20)	0.71739(10)	0.0303

$$^a U_{eq} = 1/3 (U_{11} + U_{22} + U_{33}).$$

Table 2. Atomic and thermal parameters for Sudan Yellow (SY).

Atom	x	y	z	$U_{eq}^a$
O1	0.23137(5)	0.36832(26)	0.09090(10)	0.0334
H1	0.12797(6)	0.26482(28)	0.03766(11)	0.0242
H2	0.15807(7)	0.13296(30)	0.00681(11)	0.0252
C1	0.14724(8)	0.43848(33)	0.09026(13)	0.0223
C2	0.19973(8)	0.48992(36)	0.11577(14)	0.0263
C3	0.21472(8)	0.68862(37)	0.17036(15)	0.0284
C4	0.18132(8)	0.82343(39)	0.19431(15)	0.0280
C5	0.12883(8)	0.77960(36)	0.16868(13)	0.0241
C6	0.09531(8)	0.92891(37)	0.19252(15)	0.0283
C7	0.04527(8)	0.88665(39)	0.16852(15)	0.0295
C8	0.02794(8)	0.69171(38)	0.12080(15)	0.0288
C9	0.06045(8)	0.54215(38)	0.09665(15)	0.0264
C10	0.11155(7)	0.58405(34)	0.11864(13)	0.0225
C11	0.13822(8)	-0.05157(35)	-0.04851(13)	0.0236
C12	0.17165(8)	-0.19473(37)	-0.07550(14)	0.0281
C13	0.15418(9)	-0.38116(39)	-0.12790(15)	0.0307
C14	0.10396(9)	-0.42529(38)	-0.15326(15)	0.0301
C15	0.07115(9)	-0.28081(37)	-0.12636(15)	0.0283
C16	0.08777(8)	-0.09357(38)	-0.07399(14)	0.0271

$$^a U_{eq} = 1/3 (U_{11} + U_{22} + U_{33}).$$

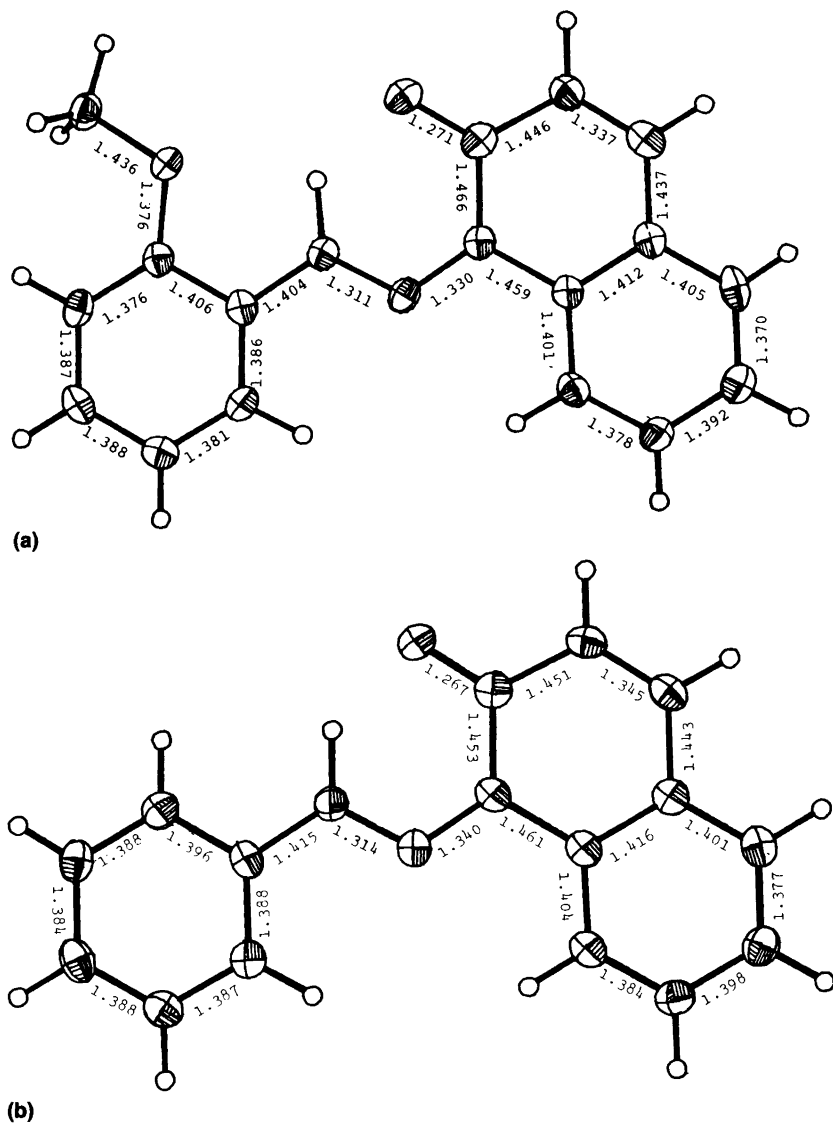


Fig. 1. Bond distances in (a) Sudan Red G (SRG) and (b) Sudan Yellow (SY). Standard deviations in bond distances are from 0.004 to 0.007 Å in SRG and from 0.002 to 0.003 Å in SY.

ature of 138 K, using monochromated MoK $\alpha$  radiation,  $\omega$ - $2\theta$  scan, scan speed =  $1.5^\circ \text{ min}^{-1}$ ,  $2\theta$  max =  $50^\circ$  and three test reflections for every 60 reflections (211, 239, 0112) for SRG and (2010, 72 -2, 411) for SY. The total number of measured reflections for SRG was 2742, out of which 1577 had  $I > 2.5\sigma(I)$ . For SY, the total number of measured reflections was 2854, and 1593 had  $I > 2.5\sigma(I)$ . The absorption coefficients are  $\mu = 9.88 \text{ mm}^{-1}$  (SRG) and  $\mu = 9.25 \text{ mm}^{-1}$  (SY). The intensities were corrected for

Lorentz and polarization effects, but not for absorption and extinction. The structure of the compound isolated from turmeric (SRG) was solved by direct methods using MULTAN 80<sup>3</sup> and Fourier syntheses combined with spectroscopic information from analyses of the compound. The structure of Sudan Yellow (SY), included for comparison, was solved similarly, but here structural information gained for SRG was used in the structure determination instead of spectroscopic data. Both structures were subsequently refined

Table 3. Bond angles for Sudan Red G (SRG) (left) and for Sudan Yellow (SY) (right). Standard deviations in parentheses.

Angle	SRG	SY	Angle	SRG	SY
N1 -N2 -C11	119.6(4)	119.0(2)	N2 -N1 -C1	118.3(4)	118.5(2)
N1 -C1 -C10	116.2(4)	115.6(2)	N1 -C1 -C2	124.1(3)	123.8(2)
O1 -C2 -C1	120.7(3)	121.7(2)	C2 -C1 -C10	119.6(3)	120.5(2)
C1 -C2 -C3	117.6(4)	117.4(2)	O1 -C2 -C3	121.7(5)	120.9(2)
C3 -C4 -C5	122.7(3)	122.6(2)	C2 -C3 -C4	121.5(5)	121.5(2)
C4 -C5 -C10	119.6(4)	119.1(2)	C4 -C5 -C6	121.1(3)	120.6(2)
C5 -C6 -C7	121.1(3)	120.6(2)	C6 -C5 -C10	119.3(5)	120.3(2)
C7 -C8 -C9	121.0(5)	120.8(2)	C6 -C7 -C8	119.4(4)	119.5(2)
C1 -C10 -C5	119.0(4)	118.9(2)	C8 -C9 -C10	120.4(3)	120.7(2)
C5 -C10 -C9	118.8(4)	118.1(2)	C1 -C10 -C9	122.2(3)	123.1(2)
N2 -C11 -C16	123.3(3)	122.1(2)	N2 -C11 -C12	117.0(4)	117.3(2)
C11 -C12 -C13	119.6(5)	119.6(2)	C12 -C11 -C16	119.7(4)	120.6(2)
C13 -C14 -C15	120.6(3)	119.5(2)	C12 -C13 -C14	120.1(4)	120.3(2)
C11 -C16 -C15	120.6(4)	118.8(2)	C14 -C15 -C16	119.4(4)	121.2(2)
C12 -O2 -C17	116.7(4)				
O2 -C12 -C11	114.7(3)				
O2 -C12 -C13	125.7(4)				

by full-matrix least-squares techniques.<sup>4</sup> The function minimized was:  $\sum w(|F_o| - |F_c|)^2$ ,  $w$  being the reciprocal of the variance. The scattering factors used were taken from Doyle and Turner<sup>5</sup> except for those for hydrogen, which were taken from Stewart, Davidson and Simpson.<sup>6</sup> The hydrogen atom positions were calculated from hybridization considerations. The most interesting hydrogen position is associated with the azo/hy-

drazo form of Sudan Red G (Fig. 2). To distinguish between the two forms, hydrogen atoms with weight factors,  $g$ , of 0.5 were attached both to nitrogen N2 and oxygen O1, and, everything else kept constant, these weight factors were allowed to vary. The result, i.e.  $g = 0.86$  for H on N2 versus  $g = 0.14$  for H on O1, as well as the distances determined, gives support for placing hydrogen on nitrogen. The predominant tau-

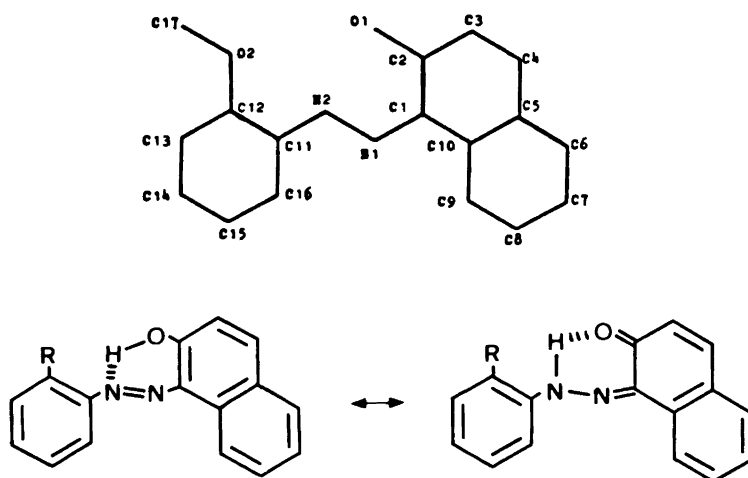


Fig. 2 Azo/hydrazo tautomerism for Sudan Red G ( $R = \text{OCH}_3$ ) and Sudan Yellow ( $R = \text{H}$ ). Azo form shown left, hydrazo form right. Also included is the atomic numbering.

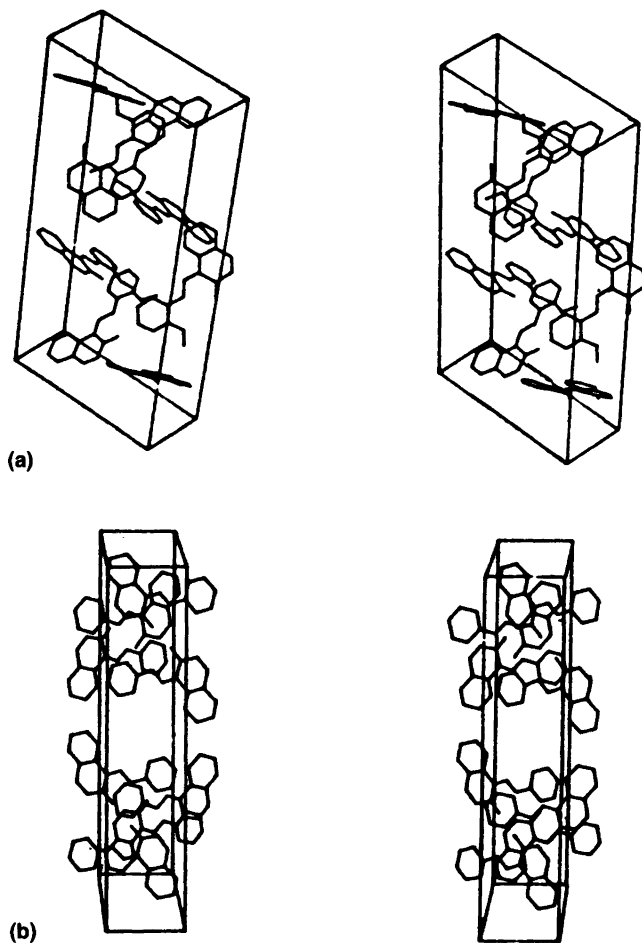


Fig. 3. Packing diagrams (a) of Sudan Red G, origin upper left, and (b) of Sudan Yellow, viewed along *c*.

toomer is therefore the hydrazo form of the molecule. Anisotropic temperature factors were introduced and refined for the non-hydrogen atoms.

The final  $R [\Sigma(F_o - F_c)/\Sigma F_o]$  values were 0.0432 and 0.0423, respectively. Final atomic coordinates and standard deviations are given in Tables 1 and 2. Lists of observed and calculated structure factors, anisotropic temperature factors and calculated H-atom positions are available from one of the authors (B.F.P.).

### Discussion

Bond distance and angles are given in Fig. 1 and Tables 3 and 4, all with corresponding standard deviations. Fig. 1 also shows the molecules with

the thermal ellipsoids for the non-hydrogen atoms at 50% probability.

The principal thermal vibration ellipsoids for non-hydrogen atoms correspond to maximum r.m.s. amplitudes of between 0.12 and 0.22 Å, the largest ones at the ends of the molecules. It is evident from the structure that the compound isolated from Tanzanian turmeric, which appears to be the azo dye Sudan Red G,  $C_{17}H_{14}N_2O_2$ , is added artificially and is not a natural constituent. In Norway this compound is illegal as a food additive. All bond lengths agree well with corresponding values in related molecules. The interatomic distances and angles in Sudan Red G and Sudan Yellow are equal within the experimental uncertainty. The methoxy substituent on C12 does not seem to have a major influence on

Table 4. Dihedral angles for Sudan Red G (SRG) (left) and Sudan Yellow (SY) (right). Standard deviations in parentheses.

Angle	SRG	SY
N2 -N1 -C1 -C2	0.7(5)	-0.2(3)
N2 -N1 -C1 -C10	178.0(3)	177.3(2)
C1 -N1 -N1 -C11	179.9(3)	179.8(2)
N1 -N2 -C11 -C12	-178.1(3)	-176.4(2)
N1 -N2 -C11 -C16	0.8(6)	2.3(3)
N1 -C1 -C2 -O1	-2.0(6)	-1.5(3)
N1 -C1 -C2 -C3	177.3(4)	177.8(2)
N1 -C1 -C10 -C5	-175.5(3)	-175.5(2)
N1 -C1 -C10 -C9	2.3(5)	2.9(3)
C2 -C1 -C10 -C5	1.9(5)	2.1(3)
C2 -C1 -C10 -C9	179.7(3)	-179.5(2)
C10 -C1 -C2 -O1	-179.3(4)	-178.9(2)
C10 -C1 -C2 -C3	0.1(5)	0.4(3)
O1 -C2 -C3 -C4	178.0(4)	177.5(2)
C1 -C2 -C3 -C4	-1.4(6)	-1.8(3)
C2 -C3 -C4 -C5	0.7(6)	0.7(3)
C3 -C4 -C5 -C6	-178.0(4)	-177.8(2)
C3 -C4 -C5 -C10	1.5(6)	1.9(3)
C4 -C5 -C6 -C7	-179.6(4)	-178.7(2)
C4 -C5 -C10 -C1	-2.7(6)	-3.2(3)
C4 -C5 -C10 -C9	179.4(4)	178.3(2)
C6 -C5 -C10 -C1	176.8(4)	176.5(2)
C6 -C5 -C10 -C9	-1.1(6)	-2.0(3)
C10 -C5 -C6 -C7	0.9(6)	0.7(3)
C5 -C6 -C7 -C8	-0.1(6)	0.7(3)
C6 -C7 -C8 -C9	-0.5(6)	-0.7(3)
C7 -C8 -C9 -C10	0.3(6)	-0.7(3)
C8 -C9 -C10 -C1	-177.3(4)	-176.4(2)
C8 -C9 -C10 -C5	0.6(6)	2.0(3)
N2 -C11 -C12 -C13	179.6(4)	178.(2)
N2 -C11 -C16 -C15	-179.1(4)	-178.(2)
C12 -C11 -C16 -C15	-0.2(7)	0.3(3)
C16 -C11 -C12 -C13	0.6(6)	-0.3(3)
C11 -C12 -C13 -C14	-0.4(6)	-0.1(3)
C12 -C13 -C14 -C15	-0.2(6)	0.4(3)
C13 -C14 -C15 -C16	0.7(6)	-0.4(3)
C14 -C15 -C16 -C11	-0.5(6)	0.1(3)
C17 -O2 -C12 -C11	174.8(5)	
C17 -O2 -C12 -C13	-6.6(4)	
N2 -C11 -C12 -O2	-1.6(5)	
C16 -C11 -C12 -O2	179.4(5)	
O2 -C12 -C13 -C14	-179.0(4)	

distances and angles. The hydrogen bonding scheme O...H-N is similar in the two compounds, but the possibility of a bifurcated hydrogen bond is only present in Sudan Red G. However, this only seems to influence the free rota-

tion about N2-C11 in Sudan Red G, and probably is responsible for the Z configuration found for this bond. The aromatic character of both the benzene and naphthol moieties is evident, as is the partial double-bond character of the N-N bond, resulting in almost planar molecules.

Several authors have studied the azo/hydrazo equilibrium of Sudan Red G and related substances. Burawoy *et al.*<sup>7</sup> found from electronic spectroscopy that Sudan Red G occurs almost exclusively in the hydrazo form in all solvents studied, while Sudan Yellow occurs as the azo form in the non-polar solvent hexane, but as the hydrazo form in more polar solvents. The predominance of the hydrazo forms has been suggested also by Millefiori and Fasone<sup>8</sup> (on the basis of electronic spectroscopy of benzene and dioxane solutions and of solids in KCl pellets), by Dehari *et al.*<sup>9</sup> (using diffuse reflectance spectroscopy of the solids) and a Yoshida<sup>10</sup> (using X-ray photoelectron spectroscopy of the solids). However, Matsunaga,<sup>11</sup> on the basis of studies on diamagnetic susceptibilities of the solids, reported that the azo form was predominant for Sudan Red G, while for Sudan Yellow the hydrazo form was the more important one. Millefiori *et al.*<sup>12</sup> concluded from dipole moment analyses of benzene solutions that the azo form predominated for both substances. Finally, Connor *et al.*<sup>13</sup> concluded from NMR, IR and electronic spectroscopy that in the solid and in ethanol solutions of Sudan Red G the hydrazo form predominated slightly, but that in less polar solvents such as chloroform, the azo form was the main one.

Thus, the question of azo/hydrazo equilibrium in these substances, both as solids and in solutions, seems as yet an unresolved one. X-ray studies by Whitaker on 1-(4-chloro-2-nitrophenylazo)-2-naphthol<sup>14</sup> and on 1-(4-methyl-2-nitrophenylazo)-2-naphthol<sup>15</sup> showed, however, that these pigments occur as the hydrazo form in the crystals. This is in accordance with our findings for Sudan Red G and Sudan Yellow. Whitaker gave bond lengths and angles comparable to the ones we have found, with one exception, viz. C2-O1 which was found to be about 0.04 Å shorter in his compounds.

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