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Structural Study of the Methylnaphthazarins. X-Ray Structure of the Tetramethylnaphthazarin, a Charge Transfer Complex

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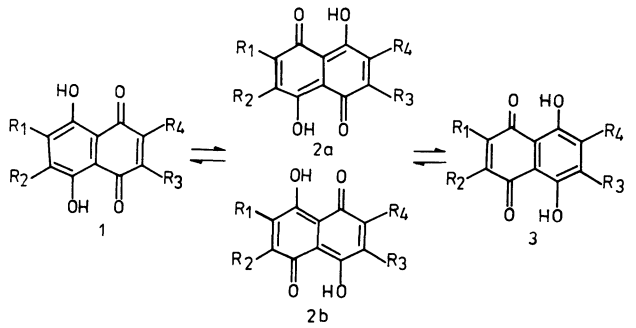
The synthesis and analysis by ^{1}H NMR of the methyl substituted naphthazarins were attempted. The chemical shifts of the substituents and of the ring protons were compared with those in their diacetates and were then correlated with the quinonoid or benzenoid nature of the rings. X-Ray diffraction analysis of tetramethylnaphthazarin, 2,3,6,7-tetramethyl-5,8-dihydroxy-1,4-naphthoquinone, has shown that this exists, in solid state, as a centrosymmetric charge-transfer complex with itself. The compound crystallizes in the *Ibam* space group, with an orthorhombic cell of dimensions a=17.479(1), b=9.983(1), c=6.752(1) Å, and four molecules in the unit cell. The crystal is built from molecules stacked up the c-axis and the interplanar distance between two overlapping molecules is 3.38 Å.

The naphthazarin nucleus 5,8-dihydroxy-1,4-naphthoquinone exists in nature in the spinochromes of the echinoderms,[1] and some derivatives can be used as the starting products in the synthesis of the tetracyclic antibiotics.[2]

Various investigations in the solid state of each of the three naphthazarin crystalline forms,[3] designated A, B, and C, have led to the conclusion that the molecule is centrosymmetric.

"Magic angle" spinning techniques, in ^{13}C NMR analysis, have provided evidence for dynamic disordered structures of naphthazarin (B form) in the solid state at −160 °C.[4]

On the other hand, NMR studies in solutions[5] indicates that a fast tautomeric equilibrium among **1⇄2a⇄2b⇄3** (Scheme 1) is present until −75 °C. From IR analysis,[6] it is observed that naphthazarin exists as 5,8-dihydroxy-1,4-naphthoquinone.

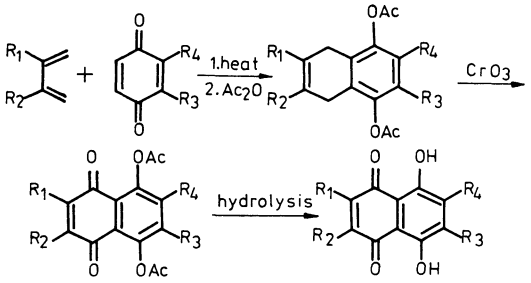


Scheme 1.

In a previous paper[7] we reported a structural study of dimethylnaphthazarin as a charge-transfer complex. This compound is present in the solid state as 2,3-dimethyl-1,5-dihydroxynaphthoquinone whilst a tautomeric equilibrium is observed in chloroform solution. The molecular structure of the tetramethylnaphthazarin in solid state has now been investigated and compared with that in chloroform solution. In a continuing study of the tautomerism of the naphthazarin system, the structural behavior in solution of the methylnaphthazarins with the substitution has now been analyzed. This structural elucidation can be applicable to the polyhydroxyanthraquinones and other related systems.

Synthesis

According to the known procedures,[8] methyl substituted naphthazarins were obtained by Diels–Alder cycloaddition of appropriate 1,3-butadiene and *p*-benzoquinone, followed by acetylation and chromium trioxide oxidation of the adducts and hydrolysis of the corresponding diacetate of naphthazarin (Scheme 2).



Scheme 2.

Experimental

For the preparation of unknown compounds, the synthesis of the methyl substituted naphthazarins which were not reported in the previous paper,[8] are now described in this section.

All melting points were taken in a hot plate microscope and are uncorrected. ^{1}H NMR spectra were obtained in $CDCl_3$, with TMS as an internal reference, at 60 MHz with a Hitachi Perkin Elmer R 24 A or at 100 MHz with a Varian XL 100 spectrometers. The elemental analysis were made in a Perkin Elmer Model 240 Elemental Analyzer. X-Ray analysis were carried out with an automatic Philips 1100 diffractometer. IR spectra were obtained with a Pye Unicam SP-1100 spectrophotometer.

Dimethylnaphthazarin (General Procedure). 2,3-Dimethyl-*p*-benzoquinone. 2,3-Dimethyl-*p*-benzoquinone was obtained by oxidation of 2,3-dimethylphenol (6 g) with Fremy's salt (1440 ml aqueous solution composed by 30 g of Fremy's salt and 3 g of sodium acetate); ethereal extraction was washed with aqueous sodium hydroxide, dried with sodium

sulfate and finally recrystallized from heptane, yielding 75% of pure quinone, mp 54—55 °C. Found: C, 70.51; H, 5.82%. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92%.

2,3-Dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone. A benzene solution of 2,3-dimethyl-*p*-benzoquinone (5 g) and 1,3-butadiene (3.5 g) was heated at 100 °C in a glass sealed tube for 4 h. The adduct was recrystallized from heptane, yielding 81% of the title compound, mp 74—75 °C. IR 1685 cm^{-1} (C=O). ^1H NMR (60 MHz) δ=5.6 (s, 2H), 3.2 (m, 2H), 2.3 (m, 4H), 2.0 (s, 6H). Found: C, 75.58; H, 7.36%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

Diacetate of the 2,3-Dimethyl-5,8-dihydro-1,4-naphthalenediol. A solution of 2,3-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (3 g) in 20 ml of acetic anhydride and 2 ml of acetic acid were refluxed for 3 h. The mixture was added over 500 ml of ice-water. Precipitate was filtered off and the white crystalline product recrystallized from ethanol, yielding 80% of the diol, mp 186 °C. IR 1750 cm^{-1} (C=O). ^1H NMR (60 MHz) δ=5.7 (s, 2H), 3.1 (s, 4H), 2.3 (s, 6H), 2.1 (s, 6H). Found: C, 70.12; H, 6.56%. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%.

Diacetate of the 2,3-Dimethylnaphthazarin. To a saturated solution of chromium trioxide (4.5 g) in acetic acid (80%), was added a solution of the diacetate of the adduct (3 g) in glacial acetic acid, while the reaction temperature was kept at 0—5 °C. The mixture was stirred at room temperature overnight and finally added on 500 ml of ice-water with continuous stirring. By filtration was obtained a yellow solid which was recrystallized from ethanol, yielding 35% of the diacetate, mp 184—186 °C. ^1H NMR at 100 MHz of this solid indicates that it was a mixture of the diacetates of 2,3- and 6,7-dimethylnaphthazarin. Integration of the ^1H NMR signals shows that the ratio of 2,3- to 6,7-dimethyl compounds is 97:3. Found: C, 63.39; H, 4.58%. Calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67%.

Dimethylnaphthazarin. An aqueous solution of sodium hydroxide (10%) was stirred with the diacetate of 2,3-dimethylnaphthazarin for 2 h until a dark blue homogeneous solution was formed. Neutralization was carried out with aqueous hydrochloric acid (10%) and a red precipitate was formed. Then, it was extracted with chloroform and purified by silica-gel column chromatography eluting with chloroform, to give the dimethylnaphthazarin, in nearly quantitative yield, as the sole product, mp 165 °C (subl.). Found: C, 66.20; H, 4.53%. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62%.

Trimethylnaphthazarin. 2,3,6-Trimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone. This compound was obtained according to the method described above for 2,3-dimethylnaphthazarin.

2,3-Dimethyl-*p*-benzoquinone (5 g) and isoprene (3 g) in benzene, were refluxed for 4 h. The adduct was recrystallized from heptane, yielding 83% of the title compound, mp 71—72 °C. IR 1680 cm^{-1} (C=O). ^1H NMR (60 MHz) δ=5.3 (s, 1H), 3.2 (m, 2H), 2.3 (m, 4H), 2.0 (two s, 6H), 1.7 (s, 3H). Found: C, 76.47; H, 7.72%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

Diacetate of 2,3,6-Trimethyl-5,8-dihydro-1,4-naphthalenediol. 2,3,6-Trimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone was acetylated in a similar manner as described above, yielding 82% of the title compound, mp 137—138 °C. IR 1750 cm^{-1} (C=O). ^1H NMR (60 MHz) δ=5.5 (m, 1H), 3.0 (s, 4H), 2.3 (two s, 6H), 2.1 (s, 6H), 1.8 (s, 3H). Found: C, 70.91; H, 6.84%. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%.

Diacetate of 2,3,6-Trimethylnaphthazarin. Oxidation of the diacetate of the adduct with chromium trioxide provides a yellow solid, in 35% yield, mp 164—167 °C. ^1H NMR at 100 MHz of this solid, indicates that it was a mixture of the diacetates of 2,3,6- and 2,6,7-trimethylnaphthazarins. Integration of the ^1H NMR signals indicates the ratio of 2,3,6- to 2,6,7-trimethyl compounds is 88:12. Found: C, 64.47; H, 5.29%. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10%.

Trimethylnaphthazarin. Hydrolysis of the diacetates of 2,3,6- and 2,6,7-trimethylnaphthazarin gave the trimethylnaphthazarin in quantitative yield, as the sole product, mp 165 °C (subl.). Found: C, 67.20; H, 5.27%. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21%.

Tetramethylnaphthazarin. 2,3,6,7-Tetramethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone. 2,3-Dimethyl-*p*-benzoquinone (12 g) and 2,3-dimethyl-1,3-butadiene (7.2 g), in benzene, were refluxed for 4 h. The adduct was recrystallized from heptane, yielding 80% of the title compound, 100—101 °C. IR 1680 cm^{-1} (C=O). ^1H NMR (60 MHz) δ=3.2 (m, 2H), 2.2 (m, 4H), 2.0 (s, 6H), 1.6 (s, 6H). Found: C, 76.87,; H, 8.26%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

Diacetate of the 2,3,6,7-Tetramethyl-5,8-dihydro-1,4-naphthalenediol. 2,3,6,7-Tetramethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone was acetylated in a similar manner as described above, yielding 75% of the title compound, mp 205—207 °C. IR 1760 cm^{-1} (C=O). ^1H MNR (60 MHz) δ=3.0 (s, 4H), 2.3 (s, 6H), 2.0 (s, 6H), 1.7 (s, 6H). Found: C, 71.36; H, 7.19%. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33%.

Diacetate of 2,3,6,7-Tetramethylnaphthazarin. Oxidation of the diacetate of the adduct with chromium trioxide provided 50% of a yellow solid, mp 219—220 °C. Found: C, 65.46,; H, 5.38%. Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49%.

2,3,6,7-Tetramethylnaphthazarin. Hydrolysis of the diacetate of 2,3,6,7-tetramethylnaphthazarin gave 2,3,6,7-tetramethylnaphthazarin in nearly quantitative yield, mp 186—187 °C (subl.). Found: C, 68.19; H, 5.79%. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73%.

X-Ray Structure Determination

Good crystals of 2,3,6,7-tetramethylnaphthazarin for X-ray study were formed by evaporation from an ethyl acetate solution at low temperature.

Space group and preliminary cell dimensions were determined from oscillation and Weissenberg photographs. Accurate lattice constants and intensities were measured on an automatic Philips 1100 diffractometer with Mo $K\alpha$ radiation (0.71069 Å) monochromatized by a graphite crystal. Refined cell parameters were calculated by a least-squares fit of the θ angles of 25 reflections.

The crystal data are: $C_{14}H_{14}O_4$, M=246.3, space group *Ibam* with a=17.479(1), b=9.983(1), c=6.752(1) Å, V=1178.2 Å^3, Z=4, density (calcd)=1.388 g cm^{-3}, absorption coefficient μ=0.9507 cm^{-1}.

The intensities were collected within the range $2<2\theta<60°$ by the $\omega/2\theta$ scan technique. Of the 1386 reflections measured, 1023 were considered observed, $I>2\sigma(I)$. Two standard reflections monitored every 61, remained essentially constants, showing no X-ray damage. Lorentz and polarization factors but no

Table 1. ^{1}H NMR (100 MHz) of the Methyl-Substituted Naphthazarins

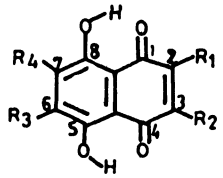
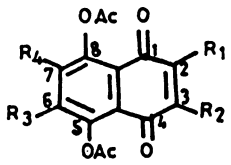
	OH	H_2 H_3	H_6 H_7	Me_2 Me_3	Me_6 Me_7
R_1=R_2=R_3=R_4=H	12.40	7.15	7.15	—	—
R_1=Me, R_2=R_3=R_4=H	12.86	—			
	12.54	6.99 (q)	7.30	2.34 (d)	—
		J=1.38 Hz		J=1.38 Hz	
R_1=R_2=Me, R_3=R_4=H	12.60		7.18	2.18	
R_1=R_3=R_4=Me, R_2=H	12.97	—	—	2.23 (d)	2.12
	12.64	6.89 (q)	—	J=1.02 Hz	
		J=1.02 Hz		—	
R_1=R_2=R_3=R_4=Me	13.37	—	—	2.23	2.23

Table 2. ^{1}H NMR (100 MHz) of the Diacetates of the Methyl-Substituted Naphthazarins

	OAc	H_2 H_3	H_6 H_7	Me_2 Me_3	Me_6 Me_7
R_1=R_2=R_3=R_4=H	2.40	6.86	7.31	—	—
R_1=Me, R_2=R_3=R_4=H	2.43	—		2.09 (d)	
	2.41	6.66 (q)	7.35	J=1.6 Hz	—
		J=1.6 Hz		—	
R_1=R_2=Me, R_3=R_4=H	2.43	—	7.30	2.07	—
R_1=R_2=H, R_3=R_4=Me	2.43	6.66	—	—	2.36
R_1=R_2=R_3=Me, R_4=H	2.46	—	—	2.07	2.27
	2.42		7.19		
R_1=R_3=R_4=Me, R_2=H	2.46	6.56	—	—	2.22
	2.42	—		2.07	
R_1=R_2=R_3=R_4=Me	2.47	—	—	2.20	2.39

absorption corrections were applied.

Results and Discussion

^{1}H NMR analysis of the methyl substituted naphthazarins (see Tables 1 and 2).

Naphthazarin. The 100 MHz ^{1}H NMR spectrum of the naphthazarin in solution of $CDCl_3$ shows only one signal for both, the benzenoid and the quinonoid protons, at δ 7.15. This averaged chemical shift of the signals for the benzenoid and the quinonoid protons of the naphthazarin, can be observed as a fast prototropic tautomerism among **1**⇄**2**⇄**3** forms (Scheme 1). This equilibrium is blocked by acetylation of the hydroxyl groups of the naphthazarin and thus, their diacetate shows two different signals for the benzenoid and the quinonoid protons at δ 7.31 and 6.86 respectively (7.09 as averaged value for both protons).

Methylnaphthazarin. ^{1}H NMR spectrum of the methylnaphthazarin shows a quartet signal centered at δ 6.99 (J= 1.38 Hz) for a quinonoid proton, a doublet signal at δ 2.34 (J=1.38 Hz) for a quinonoid methyl and two benzenoid protons at δ 7.30 vs. 6.66 q (J=1.6 Hz), 2.09 d (J=1.6 Hz), and δ=7.35 for their diacetate.

From those spectral data it can be deduced that methylnaphthazarin in $CDCl_3$ solution is mainly as 2-methyl-5,8-dihydroxy-1,4-naphthoquinone (Scheme 1).

Dimethylnaphthazarin. ^{1}H NMR spectrum of the dimethylnaphthazarin shows two protons at δ 7.18 and two methyl groups at 2.18 as singlet signals (vs. 7.30 and 2.07 for their diacetate). Those averaged chemical shift of the signals for annular and methyl protons can be rationalized by the above referred prototropic tautomerism (Scheme 1). In solid state this molecule is mainly present as the tautomer 2,3-dimethyl-5,8-dihydroxy-1,4-naphthoquinone.[7]

Trimethylnaphthazarin. ^{1}H NMR spectrum of the trimethylnaphthazarin shows a quartet signal centered at δ 6.89 (J=1.02 Hz) for a quinonoid type proton, a doublet signal at 2.23 (J=1.02 Hz) for a quinonoid methyl and a singlet signal at δ 2.12 for two methyl

groups (vs. 6.56 q (J=1.4 Hz), 2.07 d (J=1.4 Hz), and 2.22 for the diacetate of 2,6,7-trimethylnaphthazarin). The quadruplet signal indicates that this proton have an appreciable quinonoid character and the averaged chemical shift of the signals can be rationalized by the above referred prototropic tautomerism (Scheme 1) for this compound.

Tetramethylnaphthazarin. ^{1}H NMR spectrum of the tetramethylnaphthazarin shows a singlet at δ=2.23 for all the methyl groups, while their diacetate shows two different signals at δ 2.39 and 2.20 for the methyl groups attached to the benzenoid or to the quinonoid ring respectively (δ 2.30 as averaged value for both methyl groups type). This spectral data indicates that a tautomeric equilibrium among **1**⇄**2**⇄**3** is present, in solution, at room temperature.

Hydroxyl Groups. Hydroxyl groups in these methyl substituted naphthazarins show an important intramolecular chelation of the hydroxyl group in ^{1}H NMR as a bridge hydrogen bonding between phenolic and quinonoid oxygens. The effect of the methyl substituents on the chemical shift of the peri-hydroxyl protons is summarized in Table 1. The signal of the hydroxyl protons in the ^{1}H NMR spectrum is shifted further to downfield when the methyl substituent is nearer to this hydroxyl group. Of the steric and electrical substituent effect, the former is predominant.

X-Ray Analysis of the Tetramethylnaphthazarin

Structure Solution and Refinement. Assuming the centrosymmetric space group *Ibam* (vs. *Iba*2) as it was evidenced by refinement techniques and suggested by the normalized structure factor statistics, the molecule must occupy a special position at the intersection of a twofold axis with a mirror plane or at the intersection of three twofold axes. The first position is the only possible accordingly to the symmetry of the molecule. From an analysis of the Patterson function, it was deduced the position of the molecule. The atomic positions were refined by full-matrix least-square methods, first isotropically and finally anisotropically. The minimized function was $\sum\omega(|F_o|-|F_c|)^2$ with ω=1.00.

A difference synthesis showed all the hydrogen atoms. These were included in the refinement with an isotropic B value equal to that of the carried carbon atoms and they were allowed to vary. Refinement was stopped when the parameter shifts were $<0.1\sigma$. The adequacy of the weight was checked by inspection of the mean of $\omega|F_o^2|$ as a function of the F_o and sin δ/λ ranges. In both cases the function was nearly constant. The final R and R_ω are 0.087 and 0.068 respectively for all observed reflections. Scattering factors were taken from International Tables for X-Ray Crystallography.[9] Positional and thermal parameters are in Table 3.

The X-ray diffraction study in the solid state of the tetramethylnaphthazarin showed that the molecule is completely planar and centrosymmetric since it is situated in the intersection of a symmetry mirror plane and a twofold axis. Both, the bond distances C(2)–O(1)=1.293(3) and C(4)–O(2)=1.304(4) Å (Fig. 1) and the important intramolecular chelation of the hydroxyl group observed in solution, indicates that the H(O2) should occupy a mid-way position between the two oxygen atoms. A peak was experimentally observed in this position by difference synthesis (Fig. 2); bond distances O(2)–H(O2)=1.24(5) and O(1)···H(O2)=1.37(5) Å. When the H(O2) was refined, however, its position moved closer to the O(2) atom which may indicate a double-minimum potential energy surface. What should be taken into account is that the temperature factor value of the H(O2) atom was perceptibly decreased. The refined bond length resulted to be O(2)–H(O2)=1.01(5) and the nonbonded intramolecular distance was O(1)···H(O2)=1.63(5) Å.

In addition, the bond lengths C(1)–C(2)=1.444(4) and C(4)–C(5)=1.451(5) indicates a considerable single bond character.

Moreover, C(1)–C(5′)=C(5)–C(1′) has a value of 1.357(4) slightly larger than the corresponding double bond of diacetate of naphthazarin,[10] whilst the corresponding double bond of 2,3-dimethylnaphthazarin[7] and diacetate of tetramethylnaphthazarin[11] reach a similar value. Then, it is assumed that this lengthening is due to the steric hindrance between the two methyl groups bearing in those carbon atoms (see also bond angles in Fig. 1).

Final position and thermal parameters for the tetramethylnaphthazarin are listed in Table 3.

The structural molecular disorder can be considered as a frequent fact in the crystalline solid state of the compounds forming CT complexes. Molecular disorder was analyzed around C_6–C_7, which are more affected by thermal vibrations, in tetramethylnaphthazarin but all the attempts in this way does result unsuccessful and thus molecular disorder was not detected.

Table 3. Tetramethylnaphthazarin Atomic Cordinates and B_{eq}

Atom	x/a	y/b	z/c	B_{eq}
C_1	0.6315(2)	0.6165(3)	0.0000	3.2899
C_2	0.6064(1)	0.4787(3)	0.0000	3.3688
C_3	0.5271(1)	0.4474(2)	0.0000	2.6056
C_4	0.5014(2)	0.3131(3)	0.0000	3.3425
C_5	0.4204(2)	0.2821(3)	0.0000	3.3951
C_6	0.7170(2)	0.6384(5)	0.0000	5.1322
C_7	0.3986(3)	0.1365(4)	0.0000	5.7112
O_1	0.6574(1)	0.3847(3)	0.0000	5.0532
O_2	0.5496(2)	0.2135(3)	0.0000	5.1585
H_{02}	0.6030(3)	0.2560(5)	0.0000	8.5273
H_{61}	0.7420(2)	0.5970(3)	0.1120(5)	7.8117
H_{63}	0.7310(3)	0.7260(6)	0.0000	8.5273
H_{71}	0.3730(2)	0.1090(3)	0.0990(6)	8.5273
H_{73}	0.4420(3)	0.0750(5)	0.0000	8.5273

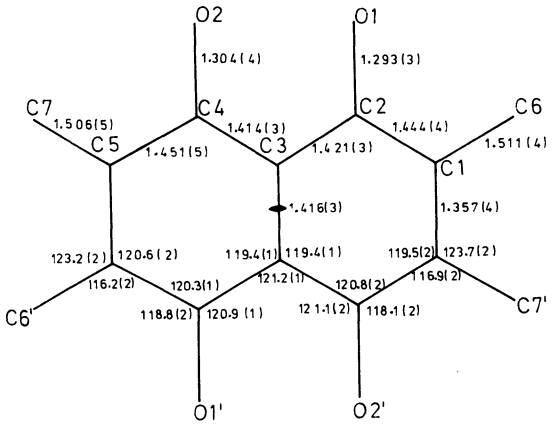


Fig. 1. Bond distances and angles of tetramethylnaphthazarin.

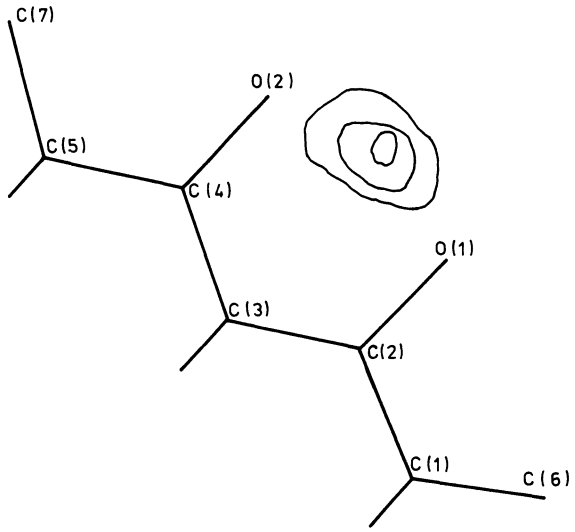


Fig. 2. Density map showing the hydroxyl hydrogen position before refinement.

There could be distortion in the bond distances of the naphthazarin nucleus (Fig. 1) arising from the fact that a molecular charge-transfer complex is formed between two molecules of the tetramethylnaphthazarin. The molecular overlap is shown in Fig. 3 and the interplanar distance, C/2, is 3.38 Å.

Finally, according to bond distances in tetramethylnaphthazarin, the molecular structure of this compound, in solid state, could be represented as a resonance hybrid between molecular forms of the type **2a**. **2b** and **1** and **3** contributing in minor extent, Scheme 1, better than a tautomerism because of the absence of molecular disorder.

Ring substitution seems to affect the tautomerism of the naphthazarin system in chloroform solution. Thus, while methylnaphthazarin is present as the tautomer

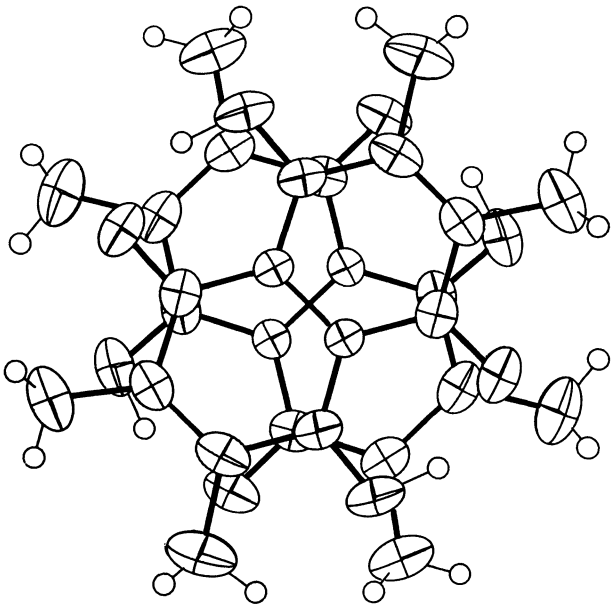


Fig. 3. Molecular overlapping of tetramethylnaphthazarin being 3.38 Å the interplanar distance.

with the substituent on the quinonoid ring, dimethyl-, trimethyl-, and tetramethylnaphthazarins, which have two methyl groups attached on the same ring show averaged structures according to the prototropic equilibrium pointed out in Scheme 1. This effect agrees with the observed increase of the C_2–C_3 bond length in solid state.

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