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THE STRUCTURE OF NAPHTHAZARIN IN SOLUTION.

Molecule with Spectroscopic Properties depending on the Tunneling Rates of Protons in Intramolecular Hydrogen Bonds.

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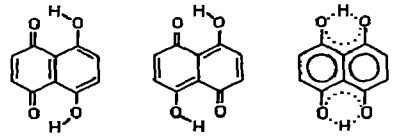
ABSTRACT

IR and NMR spectra of Naphthazarin I and of several methyl and chlorosubstituted Naphthazarins were studied in CCl_4 and $CHCl_3$ solutions. The results indicate that the molecular symmetries of I and its OD analogue, I-d_2, are different on the IR time scale, I belonging to the D_{2h} symmetry group, and I-d_2 to the C_{2h}. The spectral features are interpreted in terms of a centrosymmetrical structure with highly mobile protons in intramolecular hydrogen bonds with double minimum potentials. In the case of I extremely rapid synchronous proton tunnelling between the potential minima results in a structure which is averaged on the IR time scale.

INTRODUCTION

Naphthazarin I has peculiar symmetry properties insofar as its molecular symmetry depends on the positions of two mobile protons in intramolecular hydrogen bonds. The structure of I has been the objective of much spectroscopic (ref.1-8) and crystallographic (ref.9-10) work. Nevertheless, up to now its spectroscopic data in solution had not been fully understood. Josien et al. (ref. 1) proposed the structure Ia (symmetry group D_{2h}) with symmetrical hydrogen bonds. Hadzi and Sheppard (ref. 2) and Blinc et al. (ref. 3) showed that the hydrogen bonds are not



I_a I_b I_c

symmetrical.They assumed that the protons move in a symmetrical double minimum potential characterised by the two equivalent 1,4-quinoid structures Ic (symmetry group C_{2v}). In order to explain the position of the carbonyl absorption at very long wavelength, Merian (ref. 4) proposed the 1,5-quinoid structure Ib (symmetry group C_{2h}). This again was rejected by several authors (ref.3,5,7,8). Using highly purified samples we re-examined the IR and ^{1}H-NMR spectra of Naphthazarin, O-deuterated Naphthazarin (I-d_2), and of methyl- and chlorine-substituted Naphthazarins in CCl_4 and $CHCl_3$ solutions. Our results revealed some features in the spectra which we thought significant enough to warrant a detailed description of the molecular structure and symmetry of I in solution.

EXPERIMENTAL

Naphthazarin and substituted Naphthazarins were obtained by Friedel Crafts condensation of 1,4-Dimethoxybenzene, 2-Methyl-, or 2-Chloro-1,4-dimethoxybenzene with either Maleic-, or Citraconic-, or Chloromaleic-anhydride according to the method in ref. 11, and were purified by fractional crystallization following the procedures in ref. 12. After the fractional crystallization the substances were further purified by sublimation. Fp. and spectroscopic data agreed with the ones given in ref. 12, except for 2,7-Dimethylnaphthazarin, Fp. 137°C (125-27°C, ref. 12).

O-deuterated Naphthazarins were obtained by shaking Chloroform solutions with D_2O and crystallization from the concentrated (not evaporated) $CHCl_3$ phase. The crystals were dried at 10^{-3} Torr. The extent of deuteration was determined by NMR spectroscopy. NMR spectra were recorded on a Varian HA 100 spectrometer. IR spectra were recorded on a Beckman IR 12 spectrometer using pairs of matched cells that allowed complete compensation of solvent absorptions, except for the ranges 840-730 cm^{-1} in CCl_4 and 1250-1200, 840-700 cm^{-1} in $CHCl_3$.

RESULTS AND DISCUSSION

The IR spectrum of I is very rich (fig. 1). In the spectral range 4000-350 cm^{-1} 16 strong and medium bands and at least 10 weak and very weak absorptions are found. Further bands may be obscured by solvent absorption at 840-730 cm^{-1}. The very broad, weak ν_{OH} at 2700-3300 cm^{-1}, centered at about 3030 cm^{-1}, is not shown in fig. 1. According to Hadzi and Sheppard (ref. 2), the ν_{OH} and ν_{OD}, and the in plane deformation vibration, δ_{OD}, can be assigned. A new band appearing at 566 cm^{-1} in I-d_2 is believed to be due to the γ_{OD} (tab. 1).

TABLE 1

IR bands of I and of I-d_2 assigned to vibrations of the OH and OD groups

ν_{OH}	ν_{OD}	δ_{OD}	γ_{OD}	ν_{OH}/ν_{OD}
	cm^{-1}			
3030	2280	1034	566	1.33

In a molecule of 20 atoms with C_{2v} symmetry, 45 of the 54 normal vibrations are IR active. In the case of C_{2h} symmetry there are 27, whereas in the case of D_{2h} symmetry there are 23 IR active vibrations. In addition, overtone and combination bands are expected. Therefore, it is impossible to make a structural assignment on the basis of the number of bands alone. On deuteration significant changes occur, indicating strong coupling between vibrations of the OH-groups and the

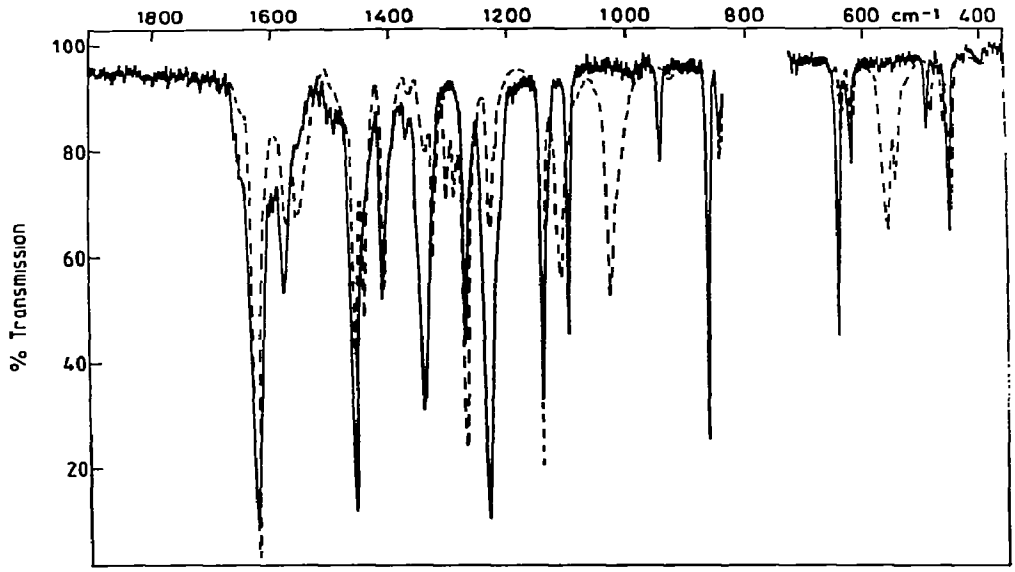
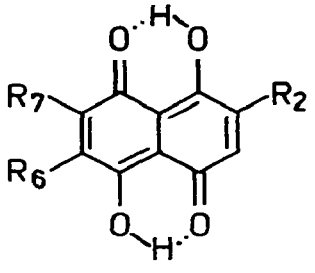


Fig. 1. IR spectrum of I, 2.1×10^{-2}M in CCl_4; dashed line: I-d_2, ca. 80% deuterated, same concentration. Path length 0.5 mm.

skeleton. The spectrum of I-d_2 shows bands split into doublets at 1575 and 1562, 1462 and 1447, 1309 and 1294, 566 and 551, and 470 and 458 cm^{-1}. In I-d_2 the total number of clearly resolved bands is increased by 3 compared with I. The width at half-height $\Delta\nu_{1/2}$ of the carbonyl absorption (ref. 2) at 1627 cm^{-1} decreases significantly on deuteration. The $\nu_{C=O}$ of I and of the substituted compounds has half-widths $\Delta\nu_{1/2}$ between 22 and 34 cm^{-1}, except for 2,6-Dimethylnaphthazarin II and O-deuterated I, where it is only 12 cm^{-1} (Tab. 2). Deuteration does not change $\Delta\nu_{1/2}$ of the $\nu_{C=O}$ in the case of II.

TABLE 2

Position of the $\nu_{C=0}$ and band width at half-height $\Delta\nu_{1/2}$ in Naphthazarins I-VII.



Nr	R_2	R_6	R_7	OH-compound $\nu_{C=0}$ cm^{-1}	OH-compound $\Delta\nu_{1/2}$ cm^{-1}	OD-compound $\nu_{C=0}$ cm^{-1}	OD-compound $\Delta\nu_{1/2}$ cm^{-1}
I	H	H	H	1627	22	1627	12
II	CH_3	CH_3	H	1614	12	1614	12
III	CH_3	H	CH_3	1618	31	1618	20
IV	CH_3	H	H	1617	25		
V	CH_3	Cl	H	1620	23		
VI	Cl	H	H	1620	34		
VII	Cl	H	Cl	1626	30		

The broadened $\nu_{C=0}$ of I and of III-VII may be ascribed to a superposition of two absorptions at almost the same frequency. According to the rules of group theory (ref. 13), if I has D_{2h}, or C_{2v}, or C_s symmetry there are two IR active $\nu_{C=0}$ bands, whereas there is only one IR active $\nu_{C=0}$ in the case of C_{2h} symmetry (tab. 3). The narrow $\nu_{C=0}$ bands of I-d_2 and II, therefore, are indicative of a C_{2h} symmetrical structure. The fact that the number of absorptions of I-d_2 is greater than that of the OH analogue may be taken as evidence of a lowering of the symmetry on deuteration. Therefore, we conclude that the molecule of I takes on a structure with D_{2h}, that of I-d_2 one with C_{2h} symmetry on the IR time scale.

TABLE 3

Symmetry classes of $\nu_{C=0}$ vibrations of I.

molecule	Symmetry of $\nu_{C=0}$	
	IR active	IR inactive
D_{2h}	B_{1u}, B_{2u}	A_g, B_{1g}
C_{2h}	B_u	A_g
C_{2v}	A_1, B_1	-
C_s	2 A'	-

It is quite unusual that replacing OHO by ODO hydrogen bonds changes the structure of a molecule to the extent that its symmetry is altered. Different potential energy curves for the OH and OD stretching motions in the intermolecular hydrogen bonds of α-chromous acid have been discussed by Snyder and Ibers (ref. 14) as an explanation of the anomalous differences between the IR spectra of the OHO and ODO bonds of this acid. An alternative interpretation was given later by Claydon et al. (ref.15). In the case of I, no explanation of the spectral effects of deuteration involving drastic changes in potential energy curves, O..O distances, or bond angles seems acceptable.

As was shown years ago (ref. 2 and 3), there is compelling evidence that the protons in the intramolecular hydrogen bonds of I are not located in the middle between the O atoms. The ν_{OH} at about 3030 cm^{-1} and the isotope frequency shift $^{\nu}OH/^{\nu}OD$ = 1.33 both indicate that the hydrogen bonds are of only moderate strength and have potentials of the double minimum type. The crystal structure data of I, showing an only moderately expanded OH bond length R_{OH} = 1.06 Å and large O..O distance $R_{O..O}$ = 2.55 Å (ref. 10), imply the same type of potential. According to the crystal data, the distance between the two equilibrium positions of the proton in a hydrogen bond of I is shorter than 0.5 Å . For such small distances the tunnelling rate of a proton in a symmetrical double minimum potential is extremely high (ref. 16). We assume that the two equivalent centrosymmetrical structures Ib are interconverted by tunnelling of the two protons at such a high rate that only their average, D_{2h}, symmetry is seen in the IR spectrum. This averaging effect of fast exchange is more common in NMR spectroscopy. This effect has been found before in the IR spectra of complexes with intermolecular hydrogen bonds (ref. 17). The tunnelling rates, decreasing exponentially with increasing mass of the tunnelling particle, are much smaller for the deuterium in I-d_2. Therefore, the apparent symmetry of I-d_2 is that of a molecule with localised OD bonds in the IR spectrum. The D_{2h} symmetry is retained on the much longer time scale of NMR spectroscopy, because only one signal is seen for the ring protons.

Our interpretation of the structure of I implies that the two protons do not move independently. We have checked this point by measuring the IR spectrum of a 1:1 mixture of I and I-d_2, where the compound I-d with one OHO and one ODO bridge should be predominant[§]. Indeed, the δ_{OD} shifts from 1034 cm^{-1} in I-d_2 to 1015 cm^{-1} in the mixture, indicating some coupling between the OH and OD groups in I-d. The same should hold for the two OH groups in I. For a pair of coupled protons in double minimum potentials synchronous motion is the lowest energy pathway of tunnelling (see ref. 18 for a detailed discussion). Therefore, our assumption is justified that the protons move in a concerted manner interchanging two centrosymmetric isomers but avoiding the structure Ic. Accordingly the 1,4-quinoid structure Ic must have a higher energy than the 1,5-quinoid structure Ib.

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[§] The intermolecular proton exchange between different Naphthazarins in CCl_4 solution is too slow to be measured by NMR line broadening techniques, but equilibration occured within the time required to prepare a probe.

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