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## HYDROGEN BONDING INTERACTIONS OF A BENZYLIDENE TYPE SCHIFF BASE IN THE SOLID STATE

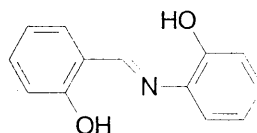
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Schiff bases of the benzylidene type are widely studied molecules, however, those containing OH groups in the ring(s) are out of the focus of researchers. It is somewhat surprising, since the presence of OH groups provides the possibility of H-bonding interactions, which may greatly influence the physical and spectroscopic properties of the compounds [1]. If the OH groups are in appropriate positions relative to the C=N functionality, both intramolecular and intermolecular H-bonds may appear. In this work 2-hydroxybenzylidene 2-hydroxy-aniline was chosen as possible model for detecting both kinds of interaction in the solid state.

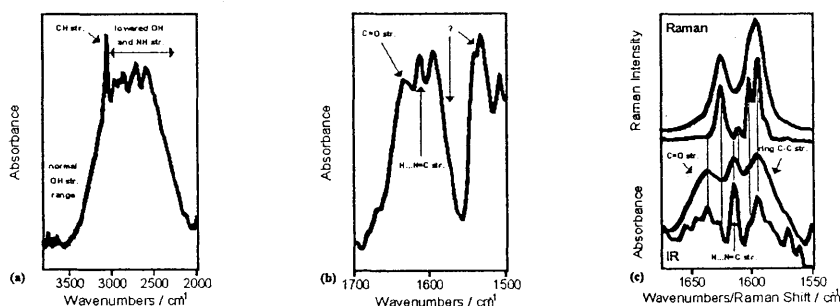


Photoacoustic spectroscopy (PAS) and Raman spectroscopy were used as primary experimental tools. Molecular modeling was also applied to help visualising and rationalising experimental results obtained.

Photoacoustic IR spectra (PAS) of solid samples were recorded using an MTEC-200 detector on a Bio-Rad Digilab Division FTS-65A/896 Fourier Transform Infrared (FTIR) spectrometer. Raman spectra were taken on a Bio-Rad Digilab Division Fourier Transform Raman spectrometer using the 1064 nm line of a T-10-106c type Nd:YVO4 laser from Spectra Physics. The laser power at the sample position was 500 mW. Molecular modeling of the possible dimers were performed by the PM3 [2] semiempirical quantum chemical code implemented in the Hyperchem package [3].

There are two types of functionalities in the molecules to take into consideration when association properties are concerned. One of them is the OH group. In the photoacoustic spectra taken in the range of the  $\nu_{\text{OH}}$  vibrations, a broad band shifted enormously to low wavenumbers relative to the position of the isolated OH group, was observed (Figure 1/a). It indicates strong hydrogen bond involving the OH group. The

other important functionality is the C=N part of the molecule. This part of the spectrum displayed unexpected features (Figure 1/b). The band observed at  $1636\text{ cm}^{-1}$  is too high to be acceptable as C=N stretching mode, rather, it can be assigned to C=O stretching mode. Further intriguing observation was the missing of a band in the  $1580\text{--}1560\text{ cm}^{-1}$  range, which could have been assigned to the skeletal mode of the aromatic ring connected to the C atom of the C=N group [4, 5]. Its lack may indicate the possible destruction of the benzoic structure of the ring. The comparison of the Raman and IR-PAS spectra for the molecules confirmed this assumption, since higher symmetry element was found for our compound. The double bond region, displayed in Figure 1/c, indicated the presence of inversion centre in the structure. The pair of the band at  $1636\text{ cm}^{-1}$  in the PAS-IR spectrum was found at  $1625\text{ cm}^{-1}$  in the Raman spectrum. Deconvolution of both spectra revealed another pair of bands, which showed the exclusion rule at  $1614\text{ cm}^{-1}$  in the PAS-IR and at  $1610\text{ cm}^{-1}$  in the Raman spectrum. Three pairs of bands in the aromatic C-C skeletal region appeared at the same wavenumbers showing that the interaction between the rings was too small.



**Figure 1.** PAS-IR spectrum of 2-hydroxybenzylidene 2-hydroxy-aniline (a) in the  $3600\text{--}2000\text{ cm}^{-1}$  range, (b) in the  $1700\text{--}1500\text{ cm}^{-1}$  range and (c) deconvoluted PAS-IR and Raman spectra in the  $1700\text{--}1550\text{ cm}^{-1}$  range

Molecular modeling, in complete accordance with experimental results, revealed that both intra- and intermolecular hydrogen bonding interactions are viable when the benzylidene ring loses its aromaticity and a quinoidal structure is assumed. Then, intermolecular hydrogen bond is formed between the oxygen of the quinoidal carbonyl group of one molecule with the proton of the OH group of the other. Two such interactions can be observed. Intramolecular hydrogen bond is formed between the carbonyl oxygen and proton of the C-H bond in the bridge connecting the two rings. Once again two such interactions can be identified.

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