

An infrared study on matrix-isolated benzoic acid

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The infrared spectra of benzoic acid and deuterobenzoic acid embedded in Ar matrices were obtained. The only benzoic acid conformer with *syn* position of O-H and C=O groups was found to fix in the matrices. We have demonstrated that both a raise of benzoic acid concentration and a matrix annealing lead to formation of H-bonded benzoic acid dimers. The results of semiempirical AM1 calculations allowed us to determine probable structures of the dimers observed. The interpretation of the experimental IR spectra was carried out by normal-coordinate analysis for benzoic acid monomer and dimer.

1. INTRODUCTION

Benzoic acid (BA) is a simplest aromatic carboxylic acid and its IR spectra and structure are the object of numerous studies. Most of them have been carried out for BA in condensed phase (See, e.g., Refs. [1,2]). However up to now, the investigations of BA trapped in low temperature inert matrices have not been performed. We have undertaken the present work to determine the structure of isolated BA monomers and dimers by combined use of the matrix isolation IR spectroscopy and computational techniques.

2. METHODS

Commercial BA was evaporated from the Knudsen cell at 45°C. The matrix gas was 99.99% Ar. The optic substrate for matrix was a CsI plate and its temperature during the matrix deposition was maintained at 17 K. The samples destined to annealing were protected by Kr film, deposited over the matrix. To prepare the samples of the required matrix-to-sample ratio (M/S) a low temperature quartz microbalance was used. Deuterated BA (DBA) was obtained by double recrystallization of BA from the D₂O solution. The experimental setup used for the matrix IR spectroscopy is described elsewhere [3]. The IR spectra were recorded with an updated Specord IR-75 grating spectrometer, purged with dry nitrogen.

The semiempirical AM1 method [4] was employed to determine the BA monomer and dimer structures. The molecular geometries were fully optimized by the use of MOPAC 6 computational package [5]. The option "PRECISE" was invoked in each computation. The spectroscopic program [6] was employed to perform normal-coordinate analysis. The following strategy was used to interpret the experimental spectra. Firstly, the force constants of phenyl group and acetic acid were transferred to BA. Later, this test force matrix was defined more accurately to decrease difference between observed and calculated frequencies. The same force constants were used for both BA and DBA. In the case of BA dimers, the force constants of carbonyl group were changed to achieve a reasonable agreement between the observed and calculated spectra.

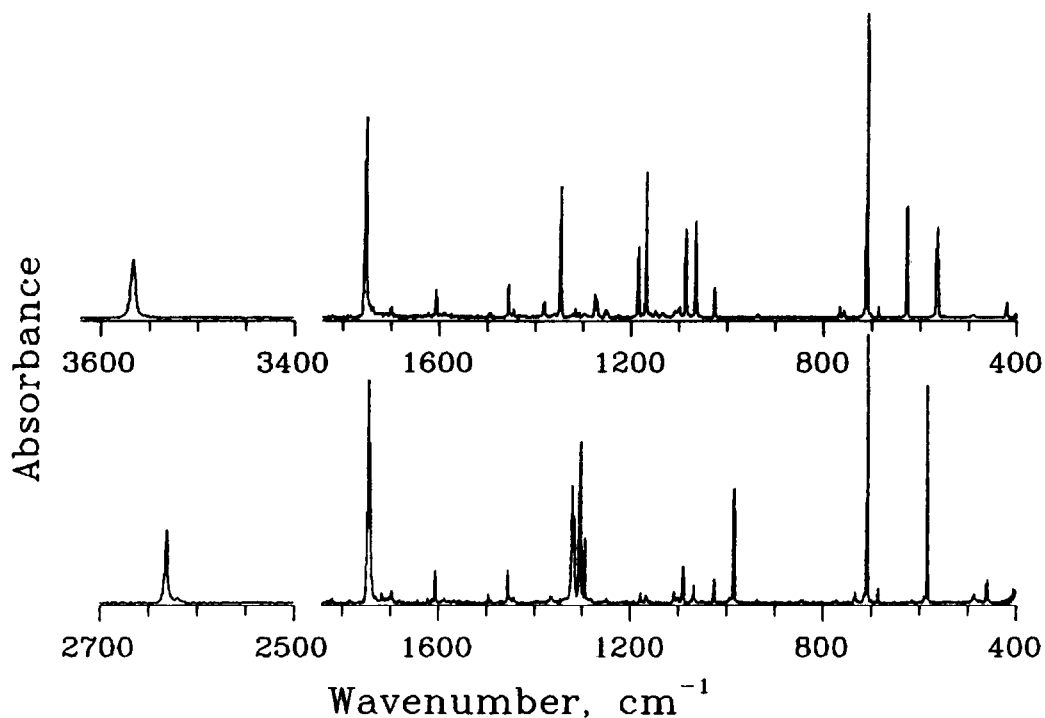


Figure 1. The IR spectra of BA (upper) and DBA (lower) isolated in Ar matrices. $M/S=750$. The sets of observed and calculated frequencies are available from the authors on request.

3. RESULTS AND DISCUSSION

3.1. Spectra and structure of monomeric benzoic acid.

Observed IR spectra of BA and DBA isolated in Ar matrices are shown in Fig. 1. Let us analyze these spectra in terms of conformations. It should be noted that the occurrence of different conformations manifests itself experimentally in the band splitting. It was demon-

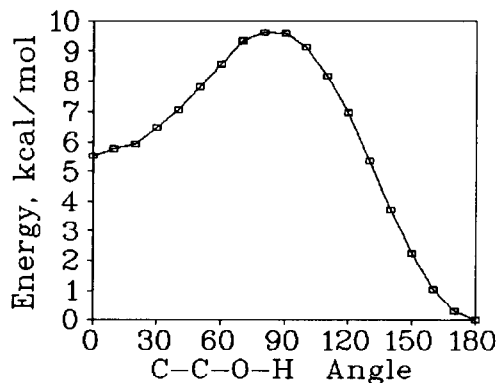


Figure 2. AM1 calculated conformational energy of benzoic acid as a function of dihedral angle C-C-O-H.

strated that most conformationally sensitive vibration for the carbonyl contained compounds is the C=O stretching [7-9]. Conformational splitting of the carbonyl stretching vibration measures 23 cm^{-1} for proline [7], 22 cm^{-1} for glycine [8], and amounts up to 32 cm^{-1} for fluoroacetic acid [9]. As seen from the spectra (Fig. 1), the C=O stretching bands 1752 cm^{-1} (BA) and 1745 cm^{-1} (DBA) have the non-splitting structure. This result suggests that the only BA conformer fixed in the matrices.

The semiempirical AM1 method was used to study the potential energy surface of BA. The possibility of rotation around the C-O and C-C bonds of carboxyl group was taken into account in calculation. As a result the two minima were found (Fig. 2). The global minimum corres-

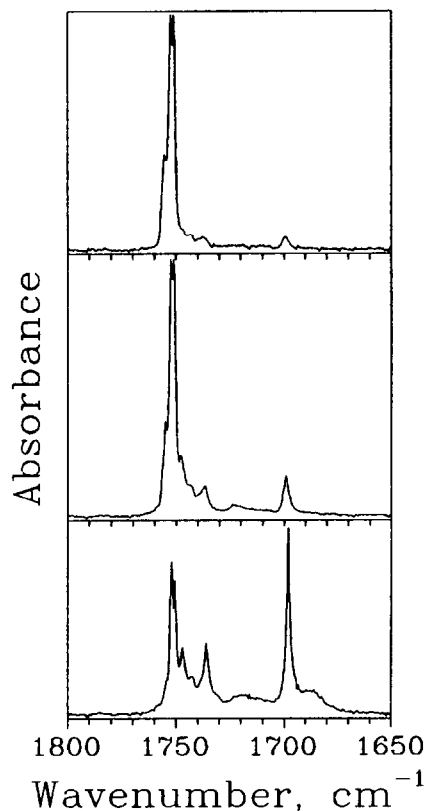


Figure 3. C=O stretching region of benzoic acid isolated in Ar matrix. (upper) M/S=750; (middle) M/S=250, spectrum after matrix deposition at 17 K; (lower) M/S=250, spectrum after matrix annealing at 33 K during 30 min.

The normal-coordinate analysis was carried out for BA and DBA and allowed us to determine the force constant matrix based on the experimental spectra.

3.2. Structure of hydrogen bonded BA dimers

We have used two ways to study the associative ability of BA. Firstly, the spectra of BA under various concentrations were investigated. Secondly, the matrix samples were annealed. As it is evident from the Fig. 3, both raise of M/S and matrix annealing give birth to the new bands 1737 and 1699 cm^{-1} (1730 and 1697 cm^{-1} for DBA, respectively). We assign these bands to vibrations of the H-bonded BA dimers. The development of two shifted C=O stretching bands generates the assumption that two types of H-bonded dimers may be formed in matrices.

The geometries of BA dimers were evaluated by gradient optimization using the AM1 method. The result of calculation is in agreement with experiment: two possible types of H-bonded dimers has been revealed. Their optimal structures are depicted in Fig. 4. The dimers

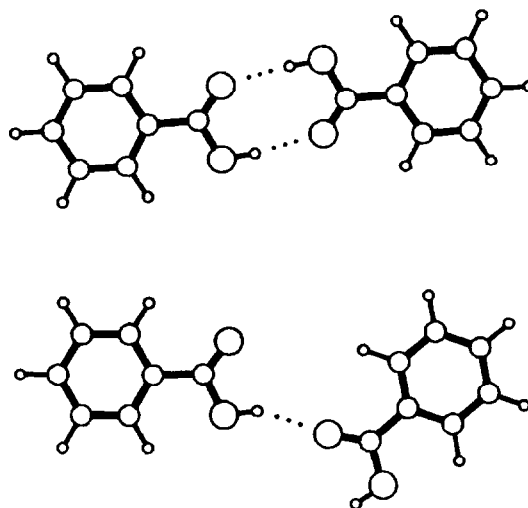


Figure 4. AM1 calculated structures of H-bonded benzoic acid dimers. The equilibrium geometries are available from the authors on request.

ponds to the planar conformation of BA which is characterized by the *syn* disposition of C=O and O-H bonds. The local minimum was found for *anti* conformation, which has slightly turned carboxylic group as to phenyl ring. The difference in the heats of formation of the BA conformations is 5.5 kcal/mol and the barrier between the conformations is 9.6 kcal/mol . This result confirms that the only BA conformer can be observed in IR spectra under the present experimental conditions.

of the first type (C_{2h} structure) are stabilized by the two equivalent intermolecular hydrogen bonds. The second type of dimers (C_s structure) includes only one H-bond. It was determined that AM1 method underestimates the energies of hydrogen bonds in BA dimers in comparison with *ab initio* 4-31G results. The latter predicts the energy difference between the equilibrium cyclic dimer and the two isolated monomers to be 21.2 kcal/mol [10]. The energies of H-bonds in the dimers are estimated from the frequency shifts to be 5-7 kcal/mol [11].

4. CONCLUSIONS

The IR spectra of benzoic acid and deuterobenzoic acid isolated in Ar matrices were obtained for the first time. It is shown, that the only benzoic acid conformer is observed in matrices. This conformer is characterized by the *syn* disposition of C=O and O-H bonds. This fact is in agreement with the results of AM1 calculations which predict the *syn* conformer to be ca. 5.5 kcal/mol more stable than *anti* one.

The analysis of the IR spectra of samples with various concentration of the BA, as well the spectra of annealed samples was carried out to determine the vibrational frequencies of H-bonded BA dimers isolated in Ar matrices. The AM1 calculation leaves room for the existence of two types of BA dimers which are formed owing to two and one intermolecular hydrogen bonds respectively. The analysis of the spectra showed that both types of the BA dimers are formed in matrices. The energies of hydrogen bonds in the dimers are estimated to be 5-7 kcal/mol.

The normal-coordinate analysis was employed to interpret the experimental spectra. As a result, the set of fundamental frequencies of BA monomers and dimers was determined.

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