amount of energy transfer; CF_4 has a $\langle \Delta E_{down} \rangle$ approximately twice that of CH_4, and CH_2CF_2 is approximately 30% higher than C_2H_4. As has been found previously,[34] the energy transfer seems to be dependent on the vibrational frequencies of the polyatomic bath gases. The enhanced energy transfer may be due to resonance effects. For example, the low-frequency C-F vibrations of CTFCB would transfer energy more efficiently with the C-F vibrations of tetrafluoromethane than with the lowest C-H vibrations of methane, which are of considerably higher frequency.

The $\langle \Delta E_{down} \rangle$ for CO_2 bath gas is of particular interest, as it is considerably less than that obtained for the same bath gas with TFCB.[18] With the only difference between these two reactant molecules being the substitution of a chlorine for a hydrogen atom, one would expect the amount of energy transferred with a particular bath gas to be very similar. This is what is found for C_2H_4 as the bath gas ($\langle \Delta E_{down} \rangle$ = 920 and 965 cm^{-1} for CTFCB and TFCB, respectively) but not for CO_2 (735 and 1740 cm^{-1} for CTFCB and TFCB, respectively). This phenomenon could be explained by resonance effects, although of a nature different from that discussed above. Although the types of vibrations in CO_2 are different from those found in the reactant molecule, both the bath gas and TFCB have identical frequencies of 667 cm^{-1} (bending motion and ring deformation, respectively). This ring deformation mode is expected to be important in interactions with bath gases as it is representative of the whole molecule and therefore should interact in a majority of collisions. The ring deformation mode of the CTFCB molecule is at 738 cm^{-1} and is unlikely to resonate with any of the CO_2 frequencies. The CTFCB molecule does not have any frequencies that coincide with those of the bath gas. The frequency nearest to 667 cm^{-1} is 656 cm^{-1} (CH_2 bend), but this vibration is restricted to a small part of the reactant and therefore the probability of interaction with the CO_2 bath gas is low.

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Liquid- and Solid-State Infrared and Near-Infrared Study of the Proton Dynamics in Azophenine

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The Fourier transform infrared (IR) and near-infrared (near-IR) spectra of crystalline azophenine (AP, 2,5-dianilinobenzoquinone 1,4-dianil), a dye subject to an intramolecular double proton transfer between nitrogen atoms, as well as of AP dissolved in CCl_4, have been measured. The NH stretching bands were assigned via deuteriation of the NH sites. In the solid state these bands were found to be so sharp that evidence for a coupling of the two NH oscillators in AP-H_2 could be obtained. Thus, the quasi-antisymmetric NH stretch ν_-^{HH} and the quasi-symmetric NH stretch ν_+^{HH} in AP-H_2 as well as the NH stretching band ν^{HD} of solid AP-HD were assigned. No evidence of additional splittings of these bands due to anharmonic coupling to a possible hydrogen bond vibration or to a fast proton transfer was found. Only one broad NH stretching band is observed for AP dissolved in liquid CCl_4, and the difference between ν_+^{HH}, ν_-^{HH}, and ν^{HD} is obscured. This observation is interpreted in terms of an inhomogeneous band-broadening mechanism arising from different solvation sites with different NH bond strengths. Previous solid-state NMR experiments on double-proton-transfer systems support this interpretation. In the liquid- and the solid-state near-IR spectra of AP the overtones of the NH stretching vibrations were identified, which are substantially broadened as compared to the fundamental bands. Thus, in spite of this broadening, which is attributed to dynamic processes, the second excited NH stretching states are still discrete states, although they are located well above the barrier for proton transfer. Finally, the C=N stretching and the NH bending vibrations of solid AP were assigned via ^{15}N and ^{2}H labeling. The implications of the IR and near-IR results for the question of intramolecular hydrogen bonding in AP and for the mechanism of proton transfer in AP observed in previous liquid- and solid-state NMR experiments are discussed.

Introduction

Hydrogen bonding and proton transfer are old topics of theoretical and experimental chemistry.[1] Recently, particular interest has been given to neutral multiple proton-transfer reactions,[2] where more than one proton, hydrogen atom, or hydride ion is transferred between heavy atoms according to

$$AH + BH^* \rightleftharpoons \{AH, BH^*\} \rightleftharpoons \{AH^*, BH\} \rightleftharpoons AH^* + BH \quad (1)$$

The fact that ions are not involved in these reactions makes them less sensitive to the environment than usual ionic proton-transfer reactions. Thus, exchange processes according to eq 1 can take place not only in the liquid[3-13] but under certain conditions also in the solid state.[14-25] They can be induced by light even at cryogenic temperatures if the reactants are dyes embedded in solids.[26-28] By contrast, ionic proton transfers are, generally, suppressed in the regime of slow molecular motion.[29] Experi-

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(2) Since neither protons nor other ions are educts or products in these reactions, only the term hydrogen transfer would be correct, which includes the possibility of the transfer of protons, hydrogen atoms, or hydride ions; however, since protons are, generally, transferred in hydrogen-bonded systems, we will use here the term proton transfer.

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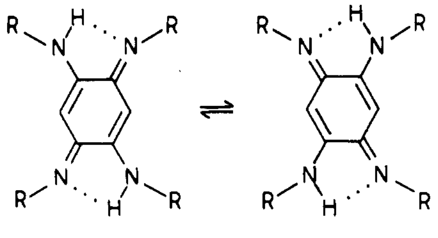

1 2 : R = H

Figure 1. Tautomerism of azophenine (AP); R ≡ phenyl.

mental information on neutral multiple proton-transfer reactions is desirable in view of the fact that they serve as models for the study of the elementary steps of bond breaking and bond formation between atoms and molecules.[1,30–37]

Generally, proton transfer and hydrogen bonding are phenomena that can be conveniently studied by IR and/or NMR spectroscopy.[1,3] Whereas NMR spectroscopy provides rate constants of proton transfer, including kinetic hydrogen/deuterium isotope effects,[3,4,6,7] IR spectroscopy can resolve different molecular environments, e.g. hydrogen-bonded complexes, and give valuable insights into the type of vibrational states of both sides of the barrier for proton transfer.[1,38–43] Unfortunately, so far it has been very difficult to obtain combined IR and NMR information on given proton-transfer systems of the type shown in eq 1. IR studies that complete the dynamic NMR experiments have been reported only for the intramolecular double-proton-transfer system *meso*-tetraphenylporphyrin (TPP),[34] and only vibrational states that lie below the barrier of proton transfer have been observed. To our knowledge overtone IR experiments on double-proton-transfer systems whose kinetics are known have not yet been performed. Such experiments could tell whether vibrational states whose energy is larger than the barrier energy for proton transfer are affected by this process, and whether certain vibrational modes that are assumed to be strongly coupled to the reaction coordinate are more affected than others. This problem is related to the field of vibrational overtone photochemistry.[44–50]

Here, we report liquid- and solid-state IR and near-IR spectra of the double-proton-transfer system azophenine (AP) and of its deuteriated analogue, with special emphasis on the NH stretching bands in the fundamental ($v = 0$) and the overtone ($v = 1$) range. AP is a dye that was first synthesized by Kimich in 1875.[51] The IR spectrum of AP in KBr was reported by Musso et al.[52] A degenerate tautomerism of AP molecules as shown in Figure 1 has been recently established[4] by dynamic liquid-state NMR spectroscopy. The reaction is characterized by kinetic HH/HD/DD isotope effects and takes place also in the solid state, although the degeneracy of the two tautomeric states in Figure 1 is lifted in this environment.[53] From the NMR measurements the activation energy of the AP tautomerism was found to be of the order of 4000 cm^{-1}.[4,53] Energy surface calculations predicted much higher barriers;[37] this discrepancy has been explained by strong contributions of proton tunneling from excited vibrational states to the reaction rates. However, the NMR data support only an over-barrier reaction or tunneling from excited levels just below the top of the barrier.[53] The IR and near-IR experiments on AP reported here were performed in order to explore whether and how the AP tautomerism observed by NMR is also manifested in the IR spectra of AP. Especially, we expected the second excited NH stretching states located above the barrier of proton transfer to be influenced by this process.

After an experimental section the results are reported and then discussed in relation to the problems of hydrogen bonding and proton tautomerism of AP in condensed phases.

Experimental Section

Deuteriation of AP and Preparation of Liquid IR Samples. Deuteriation of AP–H_2 in the NH sites was accomplished according to ref 53 with a biphasic mixture of $D_2O/CHCl_3$ condensed on AP–H_2 and evaporated several times. The same procedure was then repeated with CCl_4 extensively dried over basic alumina (ICN, W2000). Sealed IR samples of AP–H_2 and AP–D_2 in CCl_4 were prepared in a similar way in IR-vacuum cells de-

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TABLE I: Results of the IR and Near-IR Experiments on Azophenine[a]

species	environment	vibration	frequency (line width) $\upsilon = 1$	frequency (line width) $\upsilon = 2$	mechan freq	anharmonicity
AP–H_2	CCl_4	ν^{HH}	3302 (85)	6456 (180)	3376	–74
AP–$^{15}N_4$–H_2	CCl_4	ν^{HH}	3297			
AP–D_2	CCl_4	ν^{DD}	2466 2422			
AP–H_2	CCl_4	ν^{CH}	3065	5590	3135	–70
AP–H_2	solid	ν_-^{HH}	3292 (25)			
AP–H_2	solid	ν_+^{HH}	3338			
AP–HD	solid	ν^{HD}	3315 (12)	6408	3426	–110
AP–H_2	solid	ν^{CH}	3057	5987	3121	–64
AP–H_2	solid	ν^{CN}	1558			
AP–$^{15}N_4$–H_2	CCl_4	ν^{CN}	1544			
AP–H_2	solid	δ^{HH}	1174 1157			

[a] All data are in wavenumbers, cm^{-1}.

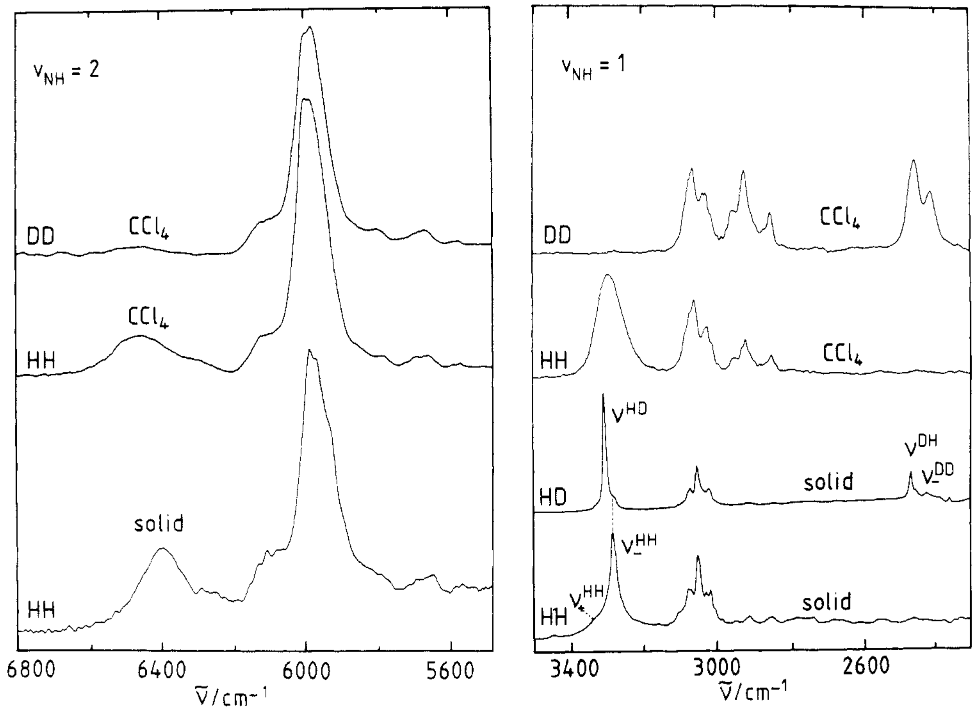

Figure 2. Experimental near-IR and IR spectra of AP in liquid CCl_4 and in a polycrystalline powder.

scribed previously.[34] The preparation of sealed samples was necessary in order to exclude water, which might obscure the NH stretching region and reconvert AP–D_2 into AP–H_2.

IR and Near-IR Measurements. All IR measurements were carried out with a Bruker Fourier transform infrared (FT-IR) spectrometer IFS 113V. The data in the mid-IR range (4000–400 cm^{-1}) were recorded by using a SiC (Globar) source, a Ge-coated KBr beamsplitter, and a room-temperature DTGS detector. For the extension to the near-IR range (10000–4000 cm^{-1}) the remotely controlled selector mirrors were switched to the tungsten lamp and the liquid nitrogen cooled InSb detector. On the automatic beamsplitter changer the position with the Si-coated CaF_2 beamsplitter was selected. During the liquid-state measurements compensation for the solvent bands was accomplished, as described previously,[34] by first condensing the solvent into the cell and taking an IR spectrum. Then the solution was poured into the cell, and the solution spectrum was subtracted from the solvent spectrum. In the IR region cells with silicon windows were used with a cell path length of 0.1 mm. For each spectrum 300 interferograms were taken. In the near-IR region we employed cells with a path length of 100 mm and infrasil windows. This arrangement allowed the measurement of the near-IR and IR spectra of the liquid samples between 2000 and 7000 cm^{-1}. A satisfactory signal to noise ratio was obtained by collecting 500 interferograms per spectrum. By contrast, the IR and near-IR spectra of polycrystalline AP could be measured via diffuse reflection in the region down to 500 cm^{-1}. The principle of this technique has been described by Fuller et al.[54] The IR radiation in the sample compartment is focused onto the powdered sample by an off-axis ellipsoidal mirror. A second symmetrically arranged mirror of the same type collects the diffusely scattered radiation (Praying Mantis Model, Harrick Scientific Corp., Ossining, NY). In order to achieve optimized results in the long-wavelength IR range, the small AP crystallites were mixed with fine powdered KCl. The same pure KCl powder served as reference material. For the measurements in the short-wavelength range—above 2500 cm^{-1}—the pure AP crystallites could be used as sample without dilution. In this case an aluminum mirror surface was taken for reference. Unfortunately, an evacuable sample chamber for the diffuse reflection unit was not available, and therefore, the AP–D_2 sample was slightly dedeuteriated during these measurements.

Results

The results of the liquid- and solid-state IR and near-IR experiments performed on AP and its analogue deuteriated in the NH sites are shown in Figures 2 and 3 and Table I. Let us first comment on the spectra of AP dissolved in CCl_4.

Fundamental and Overtone NH/ND and CH Stretches of AP Dissolved in CCl_4. The fundamental NH stretch, ν^{HH}, of AP–H_2 in CCl_4 gives rise to a band at 3302 cm^{-1} characterized by a width

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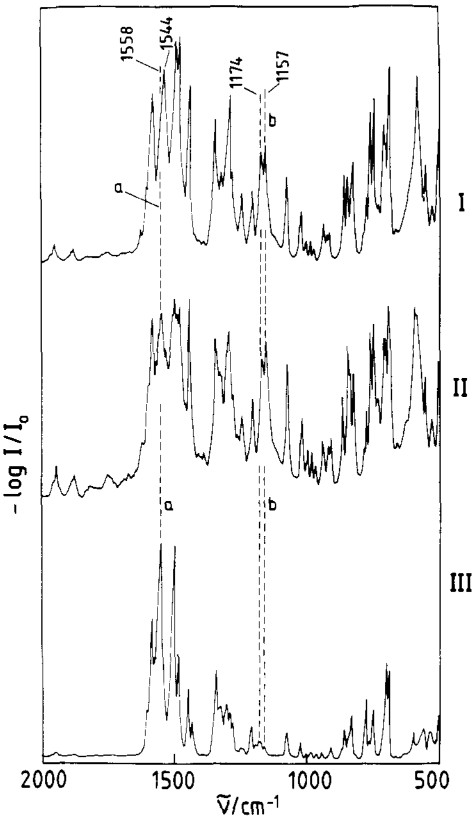


Figure 3. Experimental IR spectra of polycrystalline AP–H_2 and of partly deuteriated polycrystalline AP in the fingerprint region.

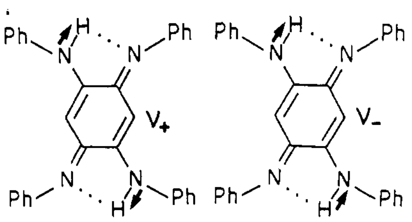
of 85 cm^{-1}. As shown in Figure 2, this band is replaced upon deuteriation by an ND stretching band ν^{DD} split into two components at 2466 and 2422 cm^{-1}. The intensity ratio of the two components does not depend on temperature. Surprisingly, ν^{HH} does not show this splitting, which we tentatively attribute to a Fermi resonance with a combination of the C=N stretching vibration ν^{CN} and the NH bending vibration δ^{DD}. The latter is assigned in the next section. The CH stretches of AP give rise to several peaks around 3000 cm^{-1}, the strongest appearing at 3065 cm^{-1}. We also measured the IR spectra of AP–$^{15}N_4$–H_2, where it was found that ν^{H} is slightly shifted (5 cm^{-1}) to lower wavenumbers, as expected.

In the near-IR region of AP in CCl_4 we find a weak band at 6456 cm^{-1} with a width of about 180 cm^{-1}. The band seems to have a broad shoulder on the low-frequency side. Both the main band and the shoulder disappear upon deuteriation of the sample. We assign this band to the first overtone $v = 2$ of the NH stretch. The anharmonicity B of the latter was calculated according to the Birge–Sponer equation[55] $\nu_v = v(A + vB)$. A is the mechanical frequency. As shown in Table I the anharmonicities of the NH and the CH stretches are not very different. The latter give rise to one broad band at 5990 cm^{-1}.

Fundamental and Overtone NH/ND and CH Stretches of Crystalline AP. As shown further in Figure 2, the frequencies of the fundamental NH and CH stretching bands of crystalline AP, 3292 and 3057 cm^{-1}, are not very different from the liquid solution values. Note that Musso et al.[52] found similar band positions for AP in KBr. In the overtone region the NH stretching vibration $\nu^{HH}(v=2)$ appears at 6408 cm^{-1}.

Whereas the bandwidth of the latter does not differ very much from the width of the corresponding band in liquid CCl_4, an unexpected effect was observed in the fundamental region. As shown in Figure 2, the width of the fundamental NH stretching band of crystalline AP is only 25 cm^{-1}; i.e. the band is much sharper than in the liquid state. When the NH sites are partly deuteriated, a new sharp NH stretching band appears at 3315 cm^{-1} in the crystal spectrum with a bandwidth of only 12 cm^{-1}; we assign this band, which is labeled in Figure 2 as ν^{HD}, to the AP–HD molecule. In view of the substantially larger NH stretching bandwidths, such frequency shifts upon deuteriation of AP could not be observed either in the near-IR spectra of crystalline AP or in the IR or near-IR spectra of AP in CCl_4.

SCHEME I



The observed frequency shift can be explained in terms of a coupling of the two NL oscillators in AP–L_2 (L = H,D). If f_{ii} is the force constant of oscillator i and f_{12} the coupling constant, it follows for the oscillator frequencies that[56,57]

$$4\pi^2\nu_\pm^2 = (2m_1m_2)^{-1}\{\pm[(f_{11}m_2 - f_{22}m_1)^2 + 4f_{12}^2m_1m_2]^{1/2} + f_{11}m_2 + f_{22}m_1\} \quad (2)$$

For the case where $f_{11} = f_{22}$ and $m_1 = m_2 \approx m_H = m_D/2$, it follows that

$$\nu_\pm^{HH} = \frac{1}{2\pi}[(f_{11} \pm f_{12})/m_H]^{1/2}$$
$$\nu_\pm^{DD} = \frac{1}{2\pi}[(f_{11} \pm f_{12})/m_D]^{1/2} \quad (3)$$

ν_+^{LL} is the symmetric, and ν_-^{LL} the antisymmetric, NL stretching vibration (see Scheme I). When $f_{11} \approx f_{22}$ holds only in approximation, we speak of quasi-symmetric and quasi-antisymmetric vibrations. For the case of AP–HD, where $m_1 = m_2/2 \approx m_H = m_D/2$, one obtains

$$\nu_\pm^{HD} = \frac{1}{2\pi}\left\{\frac{f_{11}}{4m_H}\left[3 \pm \left(1 + \frac{8f_{12}^2}{f_{11}^2}\right)^{1/2}\right]\right\}^{1/2} \quad (4)$$

With $f_{12} \ll f_{11}$ it follows in good approximation that

$$\nu_+^{HD} = \nu^{HD} \approx \frac{1}{2\pi}(f_{11}/m_H)^{1/2}$$
$$\nu_-^{HD} = \nu^{DH} \approx \frac{1}{2\pi}(f_{11}/m_D)^{1/2} \quad (5)$$

By comparison of eq 3 and 5 it follows that the coupling constant f_{12} can be calculated from the observed frequency difference between $\nu_\pm^{HH}$ and ν^{HD}. If we assign the peak at 3292 cm^{-1} to the quasi-antisymmetric NH stretching band ν_-^{HH} (Figure 2) and the peak at 3315 cm^{-1} to the NH stretching vibration ν^{HD} of AP–HD, we calculate a frequency of 3338 cm^{-1} for the quasi-symmetric stretching vibration ν_+^{HH}. In fact, the experimental spectra contain a weak band in this region, which appears as a shoulder on the high-frequency side of the NH stretching band. We assign this shoulder to ν_+^{HH} because it disappears, like the ν_-^{HH} band, when only AP–HD molecules are present, as expected. The weakness of the ν_+^{HH} band as compared to the quite high intense ν_-^{HH} band can be explained by a larger change of the dipole moment of AP when the quasi-antisymmetric stretching vibration is excited as compared to the excitation of the quasi-symmetric stretching vibration.

One consequence of the above analysis is that the observed $v = 2$ NH stretching bands in the overtone region may not correspond to an overtone but to a combination of the quasi-symmetric and the quasi-antisymmetric NH stretching band of AP, as expected from the theory of molecular vibrations.[57] On the other

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hand, the concept of normal modes might break down at high degrees of vibrational excitation.[44] For AP this means that the observed NH stretching transition in the near-IR range may also correspond to the excitation of a local NH oscillator. In any event, it seems that the anharmonicity of the NH stretching vibration of AP is slightly larger in the solid state than in the liquid solution, as can be seen in Table I.

NH Bending and C=N Stretching Vibrations of Crystalline AP. In order to assign the NH bending vibration δ^{HH} and the C=N stretching vibration ν^{CN}, the solid-state IR spectra of AP-H_2, AP-$^{15}N_4$-H_2, and of AP partly deuteriated in the NH sites were measured in the fingerprint region between 1500 and 500 cm^{-1}. A comparison of Figure 3a,b shows that band a is shifted from 1558 to 1544 cm^{-1} upon introduction of the ^{15}N label. Therefore, we assign this band to the C=N stretching vibration, which is, however, probably strongly coupled to other heavy-atom vibrations.

When the molecule is partly deuteriated ($D \approx 0.7$) the spectra between 1800 and 500 cm^{-1} change drastically. In particular, a split band at 1174 and 1157 cm^{-1} disappears. Therefore, we tentatively assign this band to the NH bending vibration, although we were not able to observe the expected ND stretching vibration between 1000 and 900 cm^{-1}. The absence of the latter might be a consequence of a strong coupling with other vibrations.

Discussion

The main findings of this IR and near-IR study of polycrystalline AP (Figure 1) and of AP dissolved in CCl_4 are the following: (i) the two NH oscillators in AP are coupled, leading to observable quasi-symmetric and quasi-antisymmetric NH stretching bands in the solid state; (ii) in liquid CCl_4 this coupling is obscured, and only one broad NH stretching band is observed; (iii) both solid AP and AP dissolved in CCl_4 exhibit broad but discrete overtone NH stretching bands in the near-IR spectra. What can these results tell us about the proton-transfer dynamics and hydrogen bonding in AP?

Coupling of the Two NH Oscillators and Its Implication for the Mechanism of AP Tautomerism. The observation that the two NH oscillators in AP are coupled is an important element in the discussion of the mechanism of the AP tautomerism in Figure 1. This coupling is such that when N–H bond 1 is stretched, a force $f_{12} < 0$ arises, which compresses N–H bond 2. A similar coupling of two NH oscillators was previously found for the double-proton-transfer system *meso*-tetraphenylporphine (TPP) as well.[34] In the latter molecule the two NH units are spatially close, and it could not be decided whether this coupling was induced by repulsive van der Waals forces between the two NH protons or whether it was mediated by the electrons. In the case of AP only the latter possibility can be realized because the two protons are located far from each other. Note that the observation of $f_{12} < 0$ is valid only for small displacements of both protons from their equilibrium positions. When NH bond 1 starts to break during the double proton transfer shown in Figure 1, f_{12} will increase and become zero because NH bond 2 cannot be indefinitely compressed. The further behavior of f_{12} can only be guessed as we do not know the potential surface for the reaction. Since the coupling arises from electronic interactions, it is unlikely that it will suddenly disappear as the reaction proceeds; therefore, f_{12} will become positive and eventually cause the breaking of NH bond 2. Whether the protons transfer simultaneously or one after each other cannot be decided here. What can, however, be concluded is that at all stages of the transfer of proton 1, proton 2 experiences this motion of proton 1 via the force f_{12}, for which evidence has been obtained in this IR study. Future calculations of the potential energy surface of AP must be able to reproduce this coupling.

Can Hydrogen Bonding in AP Be Observed by IR Spectroscopy? We come now to the question of whether the IR spectra of AP give evidence for intramolecular hydrogen bonds as shown in Figure 1. Since the NH stretching band of AP, which appears around 3300 cm^{-1}, is not particularly shifted to low frequencies, at first sight the IR spectra do not seem to support the idea of hydrogen bonding in AP. However, this shift criterion for hydrogen bonding does not always apply when the proton donor AH and the acceptor X are held together by covalent bonds and when the A–H bond and the A···X internuclear vector are not parallel,[39,41–43] conditions that are fulfilled in the case of AP. Evidence for at least weak hydrogen bonding in these systems might still be obtained from the observation of strong AH stretching bands.[1,41,42] A look at the spectra in Figure 2 shows that the NH stretching bands of AP are indeed much stronger than the CH stretching bands, by contrast to porphyrins where NH and CH stretching bands were previously found to be of approximately equal intensity.[34] This effect can, therefore, be interpreted with the presence of weak hydrogen bonds involving the NH protons of AP. However, whether inter- or intramolecular hydrogen bonds are formed cannot easily be decided by IR spectroscopy. The intramolecular hydrogen bond network of Figure 1 follows, however, from the temperature and concentration independent NMR chemical shifts of the NH protons and from the observation of the fast intramolecular double proton transfer shown in Figure 1.[1,34]

Differential Width of Fundamental NH Stretching Bands of AP in CCl_4 and in the Crystal. The question arises now of where the differential widths of the fundamental NH stretching bands of AP in the solid state and in liquid CCl_4 come from and what can be learned from this effect. The bandwidth of the overtone NH stretching bands will be discussed in a subsequent section.

There are several reasons why vibrational bands of hydrogen-bonded systems AH···X can be broadened: (i) homogeneous line broadening due to dynamic processes, (ii) inhomogeneous line broadening due to a distribution of different environments, and (iii) band splitting in connection with homogeneous or inhomogeneous line broadening.[1]

Band splitting of the AH stretching band often arises by anharmonic coupling to the low-frequency stretching vibration, which leads to a complicated substructure of the AH stretching band. Generally, this substructure is resolved in the gas phase and in the crystalline state, whereas in liquids only a broad envelope is observed.[1] We can exclude this mechanism here because we find in the solid state only sharp single NH stretching bands, which show no sign of a substructure.

Broad AH stretching bands even in the gas phase are typical for H-chelates like malonaldehyde, where protons move rapidly in strong intramolecular hydrogen bonds along more or less symmetric double minimum potentials with very low lying barriers.[41,43,58] The mechanism of this broadening is still not clear. Probably, it is a combination of the different line-broadening mechanisms mentioned above. Since we know from the solid-state NMR studies that the double proton transfer is not suppressed in crystalline AP, this mechanism cannot account for the differential liquid–solid-state line broadening. This mechanism might, however, be operative in the near-IR region, as discussed below. Any additional dynamic processes solely responsible for the broadening of the NH stretching band in CCl_4 in the liquid then have to fulfill the following conditions: The process must be characterized by a correlation time in the subpicosecond regime, is suppressed in the solid state, has nothing to do with the dynamics of proton transfer, and involves only the NH but not the CH bonds. Although such a process cannot completely be excluded, it is very difficult to imagine such a process at present.

Inhomogeneous Broadening of the Fundamental Stretching Band and Tautomerism of AP. The most natural explanation for the differential liquid–solid NH stretching bandwidth of AP is then a dominant inhomogeneous band-broadening mechanism in the liquid state. Since in the crystalline state all molecules have a similar environment, i.e. similar NH stretching frequencies, sharp NH stretching bands are observed in this environment. In the liquid one then has to assume the existence of different kinds of environments or solvation sites in which the AP molecules experience different NH stretching frequencies. As far as the nature of the environments is concerned, one would first have to discuss

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(58) Redington, R. L.; Redington, T. E. *J. Mol. Spectrosc.* **1979**, *78*, 229.

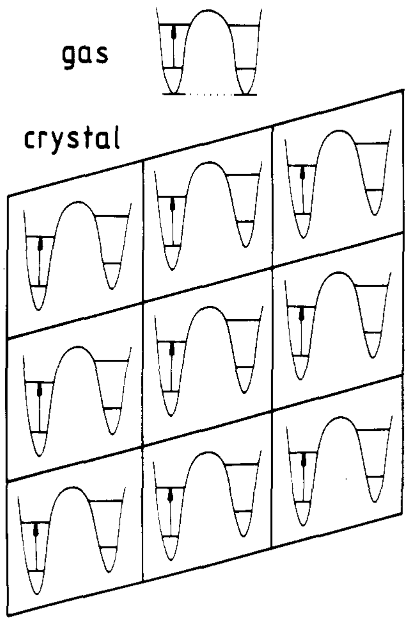

Figure 4. Perturbation of a symmetric gas-phase double minimum potential in the ordered solid state by intermolecular interactions. The arrows indicate the manifold of molecular vibrations.

the presence of different hydrogen-bonded species, e.g. monomers, dimers, etc. This possibility is, however, improbable because the NH stretching frequencies would strongly depend on the hydrogen-bonded state, and one would expect several bands with different concentration-dependent intensities, in contrast to the experimental findings. The assumption of self-association of AP also does not agree with the NMR observation of concentration-independent NH chemical shifts.[53]

The structureless, apparently Gaussian character of the NH band of AP in CCl_4 is more in favor of a broad continuous distribution of AP molecules in different solvation sites with only slightly different force constants of the stretching vibration. One can imagine that in each site the NH···N units are distorted in a different way. This effect might either arise from direct interactions of these units with the solvent molecules or from indirect interactions. For example, the angles between the phenyl rings of AP and the skeleton could easily be influenced by the local environment, leading to the observed distribution of different force constants f_{11} and f_{22}. In principle, even the coupling constant f_{12} may depend on the environment. Note that the lifetimes of the different sites must be large with respect to the inverse width of the NH stretching band of AP in CCl_4. However, these lifetimes are still so small that the different environments cannot be resolved by NMR.[53]

Inhomogeneous Band Broadening and Tautomerism of Symmetric Molecules in Disordered Matrices. In this section we relate the observed features of the NH stretching bands of AP to a microscopic model of tautomerism in ordered and disordered environments, which recently arose from solid-state NMR experiments.[21]

As mentioned above, it was shown by NMR that at room temperature the protons in AP not only move in liquid solution rapidly between the nitrogen atoms according to Figure 1 but also in the crystalline state.[4,53] However, in this state the degeneracy of the two tautomers in Figure 1 was lifted. The energy difference ΔE between the two tautomeric states was found to be 12 kJ mol^{-1}.[53] The situation is schematically illustrated in the model[21] shown in Figure 4. This energy difference arises when the reacting molecules are placed in a nonsymmetric way with respect to an existing preferential axis. In a first approximation, the double minimum potential of one molecule is independent of the molecular state of the neighboring molecules. For an ordered environment such as a crystal lattice it is clear that all molecules will then be characterized by the same energy difference $\Delta E \neq 0$ between the two wells of the double minimum potential. The arrows in Figure 4 indicate the manifold of molecular vibrations whose frequencies depend on the parameters of the double minimum potential; since all molecules are equivalent in the crystal they are all characterized by the same parameters of the double minimum potential, and therefore, by the same IR frequencies, which produce sharp IR bands in the solid.

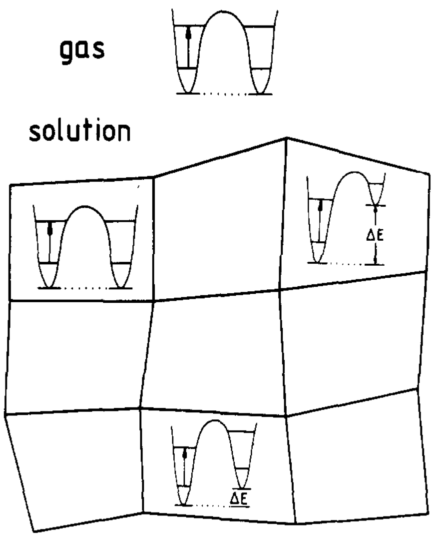

Figure 5. Perturbation of a symmetric gas-phase double minimum potential in the disordered solid state by intermolecular interactions. The arrows indicate the manifold of molecular vibrations.

Now, how is the tautomerism affected when the molecules are placed in a disordered environment in a time scale of slow molecular motion? In view of the fact that in liquids the molecular reorientation times of molecules the size of AP are of the order of pico- to nanoseconds, it is clear that NMR spectroscopy sees only to one averaged molecular environment. However, this drawback of NMR can be overcome by the study of glasses. Recently, the double minimum potential of tautomerism of organic dye molecules embedded in glassy polystyrene was studied by solid-state NMR.[21] The situation differed in a characteristic way from the equivalent process in the crystal and can be represented, schematically, by the molecular model[21] shown in Figure 5. In a disordered condensed medium the periodicity of the unit cells in which the bistable molecules are located has been lost. Depending on the environment, the double minimum potential is distorted in a different way, leading to a continuous distribution of the parameters of the double minimum potential. In particular, the reaction energy ΔE, which is close to the reaction enthalpy ΔG, is site-dependent, as are also the frequencies of those vibrations which are coupled to the reaction coordinate. This is expressed schematically in Figure 5 by different spacings of the vibrational levels in the different sites. For proton-transfer systems AH···B like AP this can be rationalized as follows: ΔE is related to the basicity of the acceptor atom A or B on which the proton is located, i.e. to the strength of the AH bond. Therefore, it is understandable that if intermolecular interactions lead to a distribution of ΔE values of tautomerism, they also lead to a distribution of AH stretching frequencies, i.e. to an inhomogeneously broadened AH stretching band. IR band broadening in the case of such "easy polarizable hydrogen bonds" has been observed previously, although it was established only for very strong hydrogen-bonded systems.[43] It is interesting to note that the width of the distribution of ΔG values of tautomerism of a tetraazaannulene dye, which is a symmetric double-proton-transfer system like AP, was found experimentally to be of the order of 100–200 cm^{-1},[21] which is of the same magnitude as the differential liquid–solid state NH bandwidth of AP found here. When the molecular motions become fast above the glass transition, i.e. in the liquid state, the different sites in Figure 5 interchange fast on the NMR time scale, and only average values of $\overline{\Delta G}$ and $\overline{\Delta E}$ are obtained. In the case of symmetric proton-transfer systems the latter are zero. However, the molecular motions are not fast enough to average out the different IR frequencies of the molecules in the different sites, which leads to one broad NH stretching band in the liquid. Since in the case of AP there is no large difference between the CH stretching bandwidths in the liquid and in the solid, the strength of the CH bonds is much less affected by the environment than the NH···N hydrogen bonds in AP. Therefore, the differential line broadening of the NH stretching bands of AP in the crystalline and the liquid state provides evidence that the NH stretches and the tautomerism of AP are influenced by the same intermolecular interactions. However, we left open the question of whether this observation indicates a strong coupling of the NH stretch to the reaction coordinate of proton transfer, although this is what one would expect by intuition.

Overtone Stretching Bands and Tautomerism of AP. As mentioned above, the second excited NH and CH stretching states are located energetically well above the top of the barrier ($\sim$3900 cm^{-1}) of proton transfer. This does, however, not necessarily mean that these vibrational states are delocalized states between both wells of the double minimum potential. This is only expected within the framework of one-dimensional double-oscillator[40] theory when the normal mode of the vibration excited is equal to the reaction coordinate. In this case, one would expect an unusual anharmonicity and/or additional band splittings. Although the low-frequency shoulder at 6300 cm^{-1} in the near-IR spectra of AP, which disappears on deuteriation (Figure 2), could have something to do with such phenomena, the experimental findings in the overtone region do not support the idea that the $v = 2$ NH stretching state contains significant contributions from both wells of the double minimum potential. To treat a case such as AP a more dimensional double-oscillator theory is needed, in order to study the effects of the proton transfer on the observed vibrational transitions. Such a theory might reveal that the reaction coordinate corresponds to a certain combination of different modes including the NH stretching mode, the NH bending mode, and/or modes involving heavy-atom vibrations.

Note that the $v = 2$ NH stretching states of AP are located above the barrier of proton transfer in a way similar to that of the fundamental $v = 1$ OH stretching states of symmetric proton-transfer systems of the malonaldehyde type. As in the case of AP, these bands neither are particularly shifted to low frequencies nor do they show special band splittings, as expected from one-dimensional double-oscillator theory,[41,42] although ground-state tunneling has been established for such systems.[59] However, as mentioned above, the fundamental OH stretching bands are particularly broad when compared to the CH stretching bandwidths. The same seems to be true for the overtone NH stretching bands of AP (Figure 2). This effect cannot arise from intramolecular interactions, i.e. arise from an inhomogeneous line-broadening mechanism, as in the case of malonaldehyde it has been also observed for the gas phase, and in the case of AP the $\nu^H(v=2)$ NH stretching bands are equally broadened in the liquid and in the crystalline solid. This effect must, therefore, arise either from very short lifetimes of the corresponding vibrational state and/or from additional unresolved band splittings. Shortened lifetimes of highly excited vibrational states as a source for homogeneous line broadening are common and arise from strong anharmonic coupling to other vibrations,[44] which might be especially large when the excited vibrational states have a higher energy than the barrier of proton transfer.

Conclusions

It has been shown that IR and near-IR experiments on intramolecular double-proton-transfer systems such as azophenine (AP, Figure 1) provide interesting dynamic information, especially when combined with kinetic data of the double proton transfer obtained by dynamic NMR spectroscopy. The results of the latter experiments will be reported elsewhere. It is especially fruitful to perform comparative NMR and IR experiments on crystals and glasses, where the regime of slow molecular motion is realized for both methods, in contrast to the liquid state.

In the case of AP, evidence for a coupling of the two NH oscillators was obtained by IR spectroscopy. Evidence has also been obtained for the presence of intermolecular interactions that have an influence on the strength of the NH bonds of AP as well as on the distortion of the symmetric double minimum potential of the proton motion. Whereas in the crystalline state all AP molecules are influenced in the same way, a distribution of different environments in liquid solution can explain the observed line broadening of the NH stretching bands of AP in liquid CCl_4. These different environments interconvert slowly on the IR but fast on the NMR time scale. Near-IR experiments show that the second excited NH stretching states of AP, which lie far above the barrier of proton transfer, are still discrete states, although they seem to be substantially lifetime-broadened. There is no unusual anharmonicity associated with these states, which indicates that the NH stretch is not equal to the reaction coordinate. Probably, this coordinate corresponds to a so far unknown combination of the NH stretching, NH bending, and/or additional vibrational modes.

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Registry No. AP, 4435-12-5; ^{15}N, 14390-96-6; D_2, 7782-39-0.

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