Dynamic Liquid State NMR and IR Study of Tautomerism and Conformations of Tetraphenyloxalamidine, a Novel Small Intramolecular Double Hydrogen Transfer System

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Chemical Kinetics / Isotope Effects / Proton Transfer / Spectroscopy, Infrared / Spectroscopy, Nuclear Magnetic Resonance

Using Dynamic NMR spectroscopy we have detected a novel intramolecular double hydrogen transfer in the oxalamidine (OA) system. OA is, therefore, so far the smallest known molecular unit capable of such a transfer. Because of solubility problems, experiments were performed on tetraphenyloxalamidine (TPOA, Ia) and the isotopically labeled compound TPOA-$^{15}N_4$-d_{20} (Ib) dissolved in CD_2Cl_2. At low temperatures TPOA exists in a number of different conformations, of which only one conformation with two intramolecular hydrogen

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bonds is capable of an intramolecular hydrogen transfer which shows up in the ^1H-^{15}N signal of this conformer. At low temperatures a ^1H-^{15}N doublet (88 Hz coupling constant) is observed which changes into a triplet (44 Hz coupling constant) as the temperature is raised. The position of this signal is independent of temperature and concentration. Two further conformations were detected, of which one formed strong intermolecular hydrogen bonds and underwent fast intermolecular proton exchange. Above room temperature all NH signals coalesce into an exchange-broadened singlet. ^{13}C experiments prove that this effect is due to a fast internal conversion of all conformers. IR experiments on TPOA in CCl_4 did not reveal the complicated conformational behavior of TPOA. By lineshape analysis we obtained the rate constants of the HH migration, which are given by $k^{HH} = 10^{10.8} \exp(-43 \text{ kJ mol}^{-1}/RT)$. An upper limit for the HD exchange rates were found for a sample deuterated to 90% in the labile proton sites: $k^{HD} = 10^{12.2} \exp(-53 \text{ kJ mol}^{-1}/RT)$, i.e. $k^{HH}/k^{HD} = 2.1$ at 298 K. The data are compared to previous results on the azophenine rearrangement.

1. Introduction

The study of neutral double hydrogen transfer reactions, including their kinetic hydrogen/deuterium isotope effects, is of considerable experimental and theoretical interest [1–16]. Of special importance are intramolecular transfers because of the possibility of obtaining experimental information on the vibrational states on both sides of the reaction barrier [5]. Unfortunately, intramolecular double hydrogen transfers have been established unequivocally only for porphines (Fig. 1) and related molecules [2–6, 8–10] as well as for azophenine (Fig. 2). The porphine rearrangement was recently shown to take place not only in solution but also in the solid state [8, 9]. Porphines also show phototautomerism at cryogenic temperatures in Shpolskii matrices, an effect which has been discussed in connection with future optical information storage devices [16]. Complete intramolecular kinetic HH/HD/DD isotope effects have been reported for the first time for the porphine and in part for the azophenine rearrangement [3, 9, 11]. Knowledge of such sets of isotope effects is not only important as a help for the interpretation of kinetic isotope effects and transition states of enzymatic reactions [12] but also has theoretical importance. For porphines and for azophenine it was found that k^{HD} is much smaller than the geometric mean value $(k^{HH}k^{HD})^{1/2}$ predicted by transition state theory [3]. In other words, the transition state postulate $k^{HH}/k^{HD} = k^{HD}/k^{DD}$ could not be confirmed in these experiments, i.e. the replacement of the first H atom by D resulted in a greater reduction of the exchange rates than the replacement of the second H by D. These deviations were interpreted in terms of thermally activated hydrogen tunneling [3, 9]. Tunneling of hydrogen atoms through instead of jumping over barriers is an old topic of theoretical and experimental chemistry [13–18]. Ab initio calculations of the porphine rearrangement [13] and semiempirical calculations of the azophenine reaction [15] resulted in theoretical barriers which are between 2 and 4 times larger than the experimental data [3]. This discrepancy has also been interpreted in terms of thermally activated tunneling [13, 15] well below the top of the barrier, resulting in much smaller experimental energies of activation. However, the calculation of theoretical barriers is difficult when many atoms have to be considered. E.g., in the porphine rearrangement one has to take into account in addition to the 4 nitrogen atoms 20 C atoms, and in the azophenine system additional 6 C atoms. Therefore, in order to eliminate uncertainties of the calculations, it is desirable that experimentally smaller double hydrogen transfer systems are studied. If one replaces the six membered central ring of azophenine by a CC bond one obtains an old compound, tetraphenyloxalamidine (TPOA, Fig. 3), which Bauer [19] had already synthesized in 1907 [19]. Although Macovei et al. [20] have postulated from IR data that this compound should form two intramolecular hydrogen bonds, the possibility of a symmetric intramolecular double hydrogen transfer according to Fig. 3 has not been recognized previously.

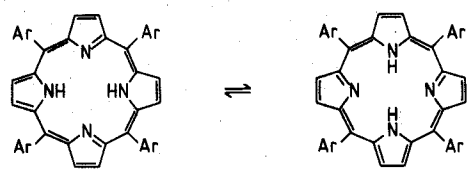

Fig. 1
The porphine tautomerism

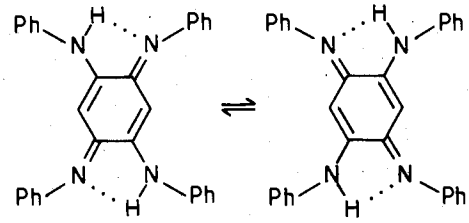

Fig. 2
The azophenine tautomerism

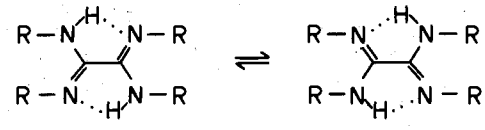

Fig. 3
The intramolecular oxalamamidine tautomerism. Oxalamidine: R = H. Tetraphenyloxalamidine (TPOA, Ia): R = Ph. TPOA-$^{15}N_4$-d_{20}: Ib

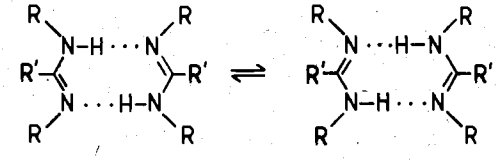

Fig. 4
The intermolecular amidine tautomerism. Formamidine: R = R′ = H. Diphenylformamidine: R = Ph, R′ = H. Oxalamidine and derivates: R′ = RNCNHR

In this kinetic study of TPOA we establish, therefore, for the first time experimentally the reaction shown in Fig. 3. Thus, TPOA is the smallest double hydrogen transfer system

known up to date. Also, a comparison of the exchange rates of the oxalamidine rearrangement with those of the azophenine rearrangement as well as with those of the intermolecular double proton transfer in diphenylformamidine (Fig. 4), studied at present in our laboratory, was expected to give valuable insights in the dynamics of these processes. We also report here IR spectra of TPOA in CCl_4, but it turns out that NMR is the only reliable method to monitor the reaction and structure of the reactants shown in Fig. 3. However, because of the quadrupole relaxation of the ^{14}N nucleus, labeling of TPOA with ^{15}N was required. In order to avoid the interference of the aromatic protons of TPOA with the $^1H^{15}N$ proton signals, we have also deuterated the phenylgroups and performed the dynamic ^1H NMR measurements on TPOA-$^{15}N_4$-d_{20}. In section 2 we describe the synthesis of this compound, the sample preparation and the spectroscopic techniques. The NMR spectra described in section 3 show a complex tautomeric and conformational behavior of TPOA in solution. Kinetic results, including some preliminary kinetic HH/HD isotope effects for the reaction in Fig. 3, will be given and discussed in section 4.

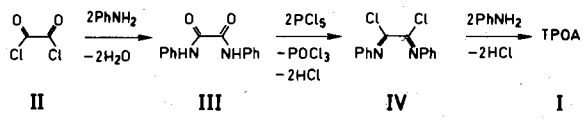

Fig. 5
Synthesis of TPOA

2. Experimental

2.1. Synthesis of TPOA

The synthesis of TPOA from oxalylchloride and aniline is shown in Fig. 5. The first step was described by Bornwater [21], the second by Bauer [19], the last by Bauer [19] and Heeramaneck [22]. Whereas Bauer uses aniline as solvent for the last step, the latter proposed N,N-diethylaniline, which is an important improvement especially for the synthesis of the isotopically labeled TPOA. However, aniline was still added in excess, which had to be avoided here because C_6D_5-$^{15}NH_2$ (VI) was available only in small quantities. In addition, since no NMR experiments have been performed so far on TPOA, it has not yet been recognized that the synthesis of pure TPOA is difficult, a fact we learnt only during the course of this study of TPOA-$^{15}N_4$-d_{20}. Therefore, we describe in the following an improved synthesis of isotopically labeled chemically pure TPOA.

2.1.3. Diphenyloxalimidchloride (IV)

$C_6D_5{}^{15}NH_2$ (VI) was prepared by reduction [23] of $C_6D_5{}^{15}NO_2$ (V), in turn obtained by nitration of C_6D_6 (Merck, Darmstadt) with $NH_4{}^{15}NO_3$ (Rohstoff-Einfuhr, Düsseldorf) according to the method of Crivello [24]. 0.0065 mol II and 0.013 mol VI were suspended according to Bornwater [21] in toluene. As proposed by Bauer [19], an equimolar quantity (0.014 mol) PCl_5 was added and the mixture refluxed for 3 hours during which HCl gas evolved. After removal of the solvent the solid yellow residue was pressed on filter paper and cut up in order to hydrolyze residual PCl_5. The powder was then treated in the heat with 50 ml of a hydrocarbon mixture (Fp. 50°C) and filtrated. After evaporation of the solvent IV was obtained as a yellow powder which was not further purified.

2.1.4. Tetraphenyloxalamidine (I)

As proposed by Heeramaneck et al. [22], IV (0.065 mol) was dissolved in N,N-diethylaniline which was previously dried over sodium and freshly distilled. However, not an excess but only 0.013 mole VI was added to the mixture, which was then heated to 100°C for 1 hour after which the solvent was evaporated in vacuo. The following purification of the raw product obtained in this way was developed using low temperature ^1H NMR of TPOA-$^{15}N_4$-d_{20} as a diagnostic for impurities. Raw TPOA was treated with 40 ml benzene in the heat to which 5 ml triethylamine was added in order to remove excess HCl as triethylammonium chloride. The latter precipitated and the mixture was filtered and washed with benzene. After evaporation of the solvent a HCl free TPOA was obtained. It still contained, however, minor amounts of IV which could hydrolyze to III and undesired HCl. Therefore, IV was removed by chromatography under dry N_2 gas over excessively dried silica (24 h at 180°C at 10^{-2} bar) using absolute toluene/ether (9:1) as solvent. IV was the fastest running fraction. The main fraction of I still contained small quantities of III which was removed in a second chromatography over non-dried silica with CH_2Cl_2 as solvent. During this step I was still partly hydrolyzed, however, not to III but only to oxanilic acid-N,N'-diphenylamidine (VII), where one aniline subunit of I is replaced by oxygen. VII could easily be removed by four repeated recrystallisations. For this purpose I was dissolved under gentle heating in benzene to which a fourfold excess of hydrocarbon mixture (Kp. 50°C) was added rapidly. After several hours I crystallized in large yellow-green crystals which were filtered and washed (Fp. 156°C, Lit: 153°C [19] and 156–158°C [22], 19.5% yield with respect to VI, i.e. 522 mg). The mass spectrum showed peaks at 390, 296, 195, 169, 119, 104, 93, 77, 65, and 51. The ^1H and the ^{13}C spectra of I in CD_2Cl_2 did not show signals of III or VII after this purification.

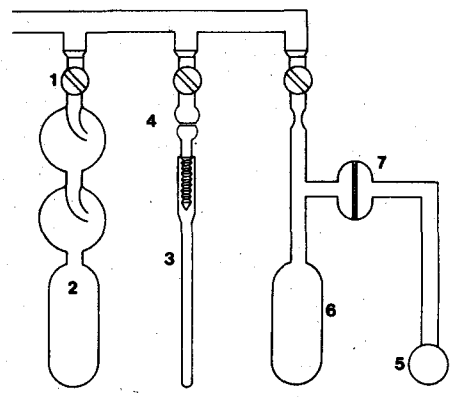

Fig. 6
Preparation of NMR and IR samples. A: Vacuum line; 1: teflon valves; 2: solvent container; 3: NMR tube with valve according to [24]; 4: teflon-glass seal with o-ring (Rotulex); 5: IR cell with silicon or infrasil windows (path length 1 mm to 10 cm) as described in [5], including solvent container (6) and glass frit (7)

2.2. Sample Preparation

NMR samples were prepared in vacuo using an apparatus shown in Fig. 6. Solvents were kept in container 2 over a drying agent (basic alumina, W200, ICN for chlorinated hydrocarbons and sodium/potassium alloy/anthracene for tetrahydrofuran). Weighted amounts of I were placed in the NMR tube 3 or in the solvent container 6 of the IR cell, after which dry solvent was condensed on I. I was excessively dried by repeated evaporation and recondensation of the solvent. Since impurities were produced by thermal decomposition of residual CD_2Cl_2 in the gas phase or on the glass walls during the sealing of the NMR tubes, even though the solutions were kept at 77 K, we employed here NMR tubes with a needle valve 4 proposed by Mohanty et al. [25]. The vacuum IR assembly for liquids has been described previously [5]. The solution is stored in container 6 and the cell is first filled with pure solvent by condensation, after which the IR spectrum of the cell and the solvent is taken. After pouring the solution into the cell the solution IR spectrum is taken and subtracted from the solvent spectrum.

2.3. Spectroscopic Measurements

NMR measurements were performed on a Bruker CXP-100 FT NMR spectrometer working at 90.02 MHz for ^1H. For simulation the spectra were transfered by means of a data line to the Univac 1108 computer of the Rechenzentrum der Universität Freiburg. IR measurements were performed on a Bruker FT IR spectrometer IFS 113v.

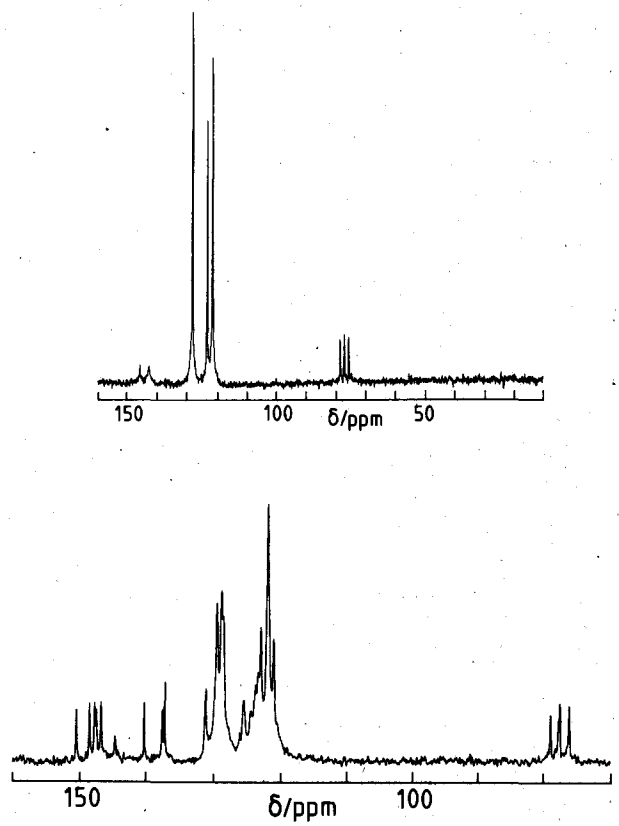

Fig. 7
22.64 MHz ^{13}C NMR spectra of TPOA (Ia) in $CDCl_3$ at 61 °C (above) and at −55 °C (below)

3. Results

3.1. ^{13}C NMR Spectra of TPOA

Fig. 7 shows the ^{13}C NMR spectra of TPOA in $CDCl_3$ at high and low temperatures. At −55 °C at least 20 lines of different intensities are resolved, which we did not attempt to assign. As shown later, these signals arise from a superposition of different conformers formed by I. The lines do not stem from impurities because at 61 °C only very few dyamically averaged signals are observed. The three high field lines are typical for the o-, m-, and p-position of a phenylgroup. The remaining two small low field signals stem from the tertiary olefinic and aromatic carbons. All phenylgroups and the two C atoms of the central bond have become chemically equivalent by the dynamic averaging processes going on in TPOA. In the intermediate temperature range extreme linebroadening is observed which was not further analyzed. The recording of the high temperature ^{13}C NMR spectrum was, however, important to establish the purity of the compound and to establish the fast interconversion of the different conformers of TPOA at high temperatures.

3.2. ^1H NMR Spectra of TPOA-$^{15}N_4$-d_{20}

Since the residual solvent protons of chloroform-d interfered with the ^1H-^{15}N signals we chose CD_2Cl_2 as solvent for the kinetic ^1H NMR measurements. In order to demonstrate the possible impurities III and VII in TPOA Fig. 8 shows some ^1H NMR spectra

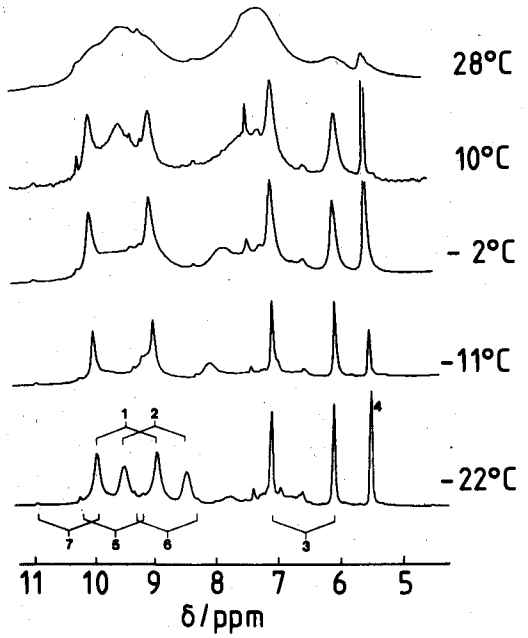

Fig. 8
90.02 ^1H NMR spectra of TPOA-$^{15}N_4$-d_{20} (Ib) in CD_2Cl_2 (concentrated solution) as a function of temperature. For further details see text

of unpurified TPOA-$^{15}N_4$-d_{20} (Ib) in CD_2Cl_2 as function of temperature. At low temperatures we observe for Ib three different ^1H-^{15}N doublets, with coupling constants of the order of 90 Hz, i.e. signal 1 at 9.4 ppm, signal 2 at 8.8 ppm, and signal 3 at 6.4 ppm. The position of signal 1 is independent of temperature and changes its structure from a pure doublet ($J_{^1H\text{-}^{15}N}$ = 88 Hz) to a triplet as the temperature is increased, with an apparent coupling constant of 44 Hz. This observation proves that the protons which give rise to signal 1 migrate at room temperature fast between always the same two ^{15}N atoms, i.e. it proves an intramolecular HH transfer. The same effect has been found previously for azophenine-$^{15}N_4$, where the reaction according to Fig. 2 could be established in this way [4, 11]. The position of signal 3 is also quite independent of temperature, but the signal retains its doublet structure as temperature is raised. By contrast, the position of signal 2 is extremeley dependent on concentration and temperature, and the doublet lines of this signal broaden and coalesce as concentration and temperature are raised, due to intermolecular proton exchange. In addition, the relative signal intensities were found to depend on concentration, higher concentrations favoring the intensity of signal 2. Above 10 °C all NH signals broaden and coalesce eventually. If the coalescence would be due to simple intermolecular proton exchange between the three signals the complexity of the ^{13}C NMR spectra should be retained at high temperature which is not the case. Therefore, the main source of coalescence of the three NH signals is the interconversion of the conformers. Above room temperature, the lineshapes of the three signals depend then mainly on these interconversion rates.

Additional features in the spectra of Fig. 8 are signal 4 at 5.3 ppm arising from the proton in $CHDCl_2$, residual aromatic proton signals which give an underground of small peaks in the region between 6.5 to 8 ppm, a very weak ^1H-^{15}N doublet (signal 5) at 9.4 ppm arising from an III impurity, and two ^1H-^{15}N doublets (signals 6 and 7) at 8.5 and 10.1 ppm, which stem from a small quantity of VII. In the final NMR samples signals 5 to 7 were absent. If we use THF as solvent, we find only one ^1H-^{15}N doublet at 9.2 ppm which proves that there is only one conformer present in THF at room temperature – probably hydrogen bonded to the solvent – with no signs of exchange broadening due to intra- or intermolecular proton exchange.

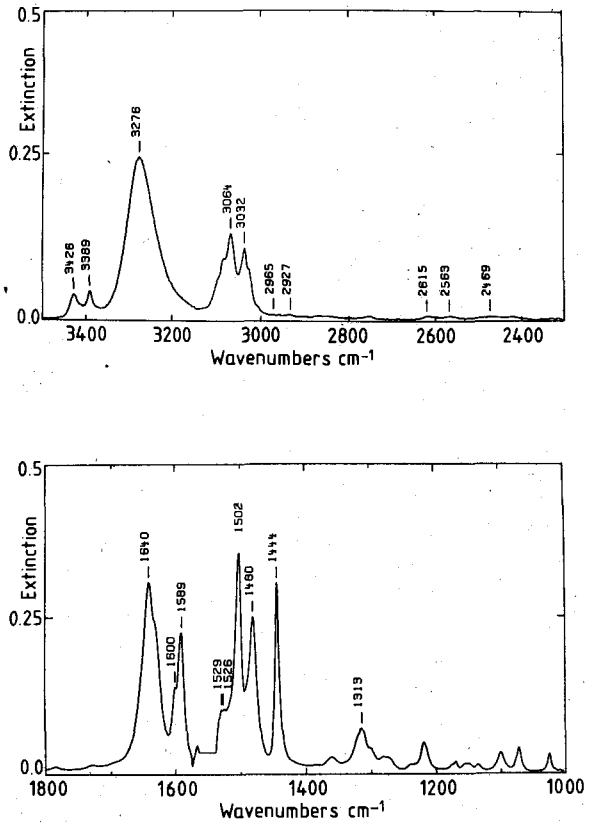

Fig. 9
IR spectra of TPOA in CCl_4 at room temperature. In the range from 1530 to 1580 cm^{-1} the solvent absorption renders the data unreliable

3.3. IR-Spectra of TPOA in CCl_4

The water and oxygen free IR spectrum of TPOA in CCl_4 at room temperature is shown in Fig. 9. The main feature is, as was reported previously [20], a broad NH stretching band of moderate strength. The band at 1640 cm^{-1} was assigned to the CN double bond by Macovei et al. [20]. These authors found additional bands at 3378 cm^{-1} and 1681 cm^{-1} which are absent in our spectra. Like Macovei et al. [20] we did not find significant changes with concentration, although two samples at 10^{-2} M and 10^{-4} M were studied. As shown in Fig. 9, we find, however, additional bands in the 3400 cm^{-1} region which are either combination bands or NH groups in a non hydrogen bonded environment.

3.4. ^1H NMR Lineshape Analysis of Signal 1 of TPOA-$^{15}N_4$-d_{20} in CD_2Cl_2

The lineshapes of ^1H-^{15}N signals in the presence of proton exchange depend on whether the exchange takes place along an intramolecular pathway between always the same two ^{15}N atoms or along an intermolecular pathway where the exchange occurs between different ^{15}N atoms in different molecules. In the case of intermolecular exchange the ^1H-^{15}N doublet broadens and collapses into a singlet because every other exchange a jumping proton experiences a spin flip of the neighboring ^{15}N atom from spin state α and β or vice versa. This spin flip is associated with a change in Larmor frequency of the proton from $\nu - J_{^1H\text{-}^{15}N}/2$ to $\nu + J_{^1H\text{-}^{15}N}/2$, where ν is the chemical shift in Hz of the exchanging proton, leading to a collapse of the ^1H-^{15}N doublet. In the intramolecular case we find completely different behavior [3]. The protons always migrate between the same ^{15}N atoms, and four different reactions take place:

$$N(\alpha)-H\cdots N(\alpha) = N(\alpha)\cdots H-N(\alpha)\,, \quad (1)$$

$$N(\alpha)-H\cdots N(\beta) = N(\alpha)\cdots H-N(\beta)\,, \quad (2)$$

$$N(\beta)-H\cdots N(\alpha) = N(\beta)\cdots H-N(\alpha)\,, \quad (3)$$

$$N(\beta)-H\cdots N(\beta) = N(\beta)\cdots H-N(\beta)\,. \quad (4)$$

Protons reacting according to Eqs. (1) or (4) do not change their Larmorfrequency and contribute, therefore, always sharp line components at $\nu \pm J_{^1H\text{-}^{15}N}/2$. Protons switching between ^{15}N atoms in the spin states α and β according to Eqs. (2) and (3) also give in the slow exchange regime sharp contributions at $\nu \pm J_{^1H\text{-}^{15}N}/2$, but when the exchange becomes faster these linecomponents broaden, coalesce, and eventually give rise to one sharp line in the center of the signal, i.e. a triplet appears.

The lineshape is given as a superposition of a symmetrical two-site exchange and two non-exchanging one-site systems, which can be easily calculated. We used a computerprogram similar to the one described previously [3]. Input parameters for the program were the chemical shifts of signal 1, the coupling constants $J_{^1H\text{-}^{15}N}$, the rate constant k, and the transverse Redfield relaxation matrix, which contains off diagonal cross terms [26]. These terms were, however, calculated to be smaller than 1 s^{-1} and were neglected. Thus, the relaxation matrix was taken as diagonal, and all diagonal elements were set equal to $R = -1/T_{2\text{eff}} = -W_0/\pi$, where W_0 is the linewidth in absence of exchange.

Fig. 10 shows an excellent fit of the experimental and the calculated lineshapes of signal 1 of a $5 \cdot 10^{-3}$ M solution of TPOA-$^{15}N_4$-d_{20} in CD_2Cl_2 as a function of temperature. The

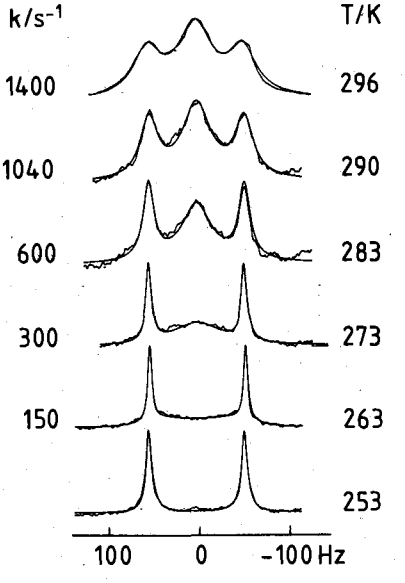

Fig. 10
Superposed experimental and calculated 90.02 MHz ^1H NMR lineshapes of signal 1 of Ib in CD_2Cl_2 as function of temperature. k is the intramolecular HH rate constant. Concentration: $5 \cdot 10^{-3}$ M, 5 mm NMR tube, 45° pulses, 1500 Hz sweep width, 8 K spectra, 3s repetition time. The spectrum at 296 K was recorded at 250 MHz

low concentration was chosen at the expense of the signal to noise ratio in order to shift signal 2 out of the range of signal 1 over the whole temperature range. Note that the parameters $J_{^1H\text{-}^{15}N}$ and W_0 could be obtained even in the fast exchange range by simulation of the outer lines of the triplet which are not affected by the exchange. W_0 depends on the inhomogeneity of the magnetic field, unresolved coupling constants, and transverse relaxation times. The last contribution can become important at low temperatures [6]. At higher temperatures each line of signal 1 is additionally broadened due to the finite lifetime τ_1 of the conformer leading to signal 1. The parameter W_0 used in the calculations is then given by

$$W_0 = W_{0LT} + (\pi\tau_1)^{-1}, \quad (5)$$

where W_{0LT} is the low temperature value. Eq. (5) is valid only well below the coalescence point of the three ^1H-^{15}N signals. The results of the calculations are shown in Table 1. The rate constants follow an Arrhenius law given by

$$k^{HH} = 10^{10.8}\exp(-43\,\text{kJ mol}^{-1}/RT)\,\text{s}^{-1}. \quad (6)$$

These rate constants did not depend on concentration.

Table 1
Parameters for the simulation of signal 1 shown in Fig. 10

T/K	k/s^{-1}	δ/ppm	$J_{^1H\text{-}^{15}N}$/Hz	W_0/Hz	τ_1^{-1}/s^{-1}
296	1400	9.24	88.0	30.0	80
290	1040	9.26	87.5	20.0	50
283	600	9.26	87.9	12.5	–
273	300	9.25	87.6	6.7	–
263	150	9.25	88.0	4.7	–
253	70	9.27	87.9	5.4	–

T: temperature, k: intramolecular HH exchange rate constants, W_0: see text, τ_1: life-time of the conformer leading to signal 1.

In order to obtain an idea of kinetic isotope effects of the hydrogen migration in oxalamidine we prepared a sample of 90% TPOA-$^{15}N_4$-d_{22} + 10% TPOA-$^{15}N_4$-d_{20} in CD_2Cl_2, i.e. with a deuterium fraction of 90% in the NH sites. The deuteration was carried out in a 10 mm NMR tube on the vacuum line according to Fig. 6 using a mixture of 2 ml CH_2Cl_2 + 1.8 ml D_2O + 0.2 ml H_2O, which was condensed on 28 mg of TPOA-$^{15}N_4$-d_{20}. After evaporation of the mixture, adding dry CH_2Cl_2 and evaporation, and finally adding 2 ml CD_2Cl_2, we obtained a $3.4\cdot10^{-2}$ M solution. Some superposed experimental and calculated spectra of this "HD" sample are shown in Fig. 11. 90% of the lineintensity shown stem from the HD molecules, where the migrating H atom is monitored and the second migrating atom is deuterium. The 10% contribution of the HH molecules to the signal were neglected. Therefore, the rate constants obtained by simulation of these spectra are upper limits for the rate constants k^{HD} of the HD reaction. From the data in Table 2 we obtain

$$k^{HD} = 10^{12.2}\exp(-53\,\text{kJ mol}^{-1}/RT)\,\text{s}^{-1}, \quad (7)$$

i.e. a kinetic isotope effect of $k^{HH}/k^{HD} = 2.1$ at 298 K.

Table 2
Parameters for the simulation of signal 1 shown in Fig. 11

T/K	k/s^{-1}	δ/ppm	$J_{^1H\text{-}^{15}N}$/Hz	W_0/Hz	τ_1^{-1}/s^{-1}
293	400	9.23	87.5	32.0	80
288	370	9.23	88.5	18.0	40
284	250	9.22	88.5	16.0	–
283	210	9.24	88.5	23.0	–
280	180	9.23	87.7	12.5	–
276	140	9.23	87.7	9.2	–
273	95	9.26	88.5	14.7	–
267	60	9.25	88.6	7.5	–

k: upper limit for the HD rate constants.

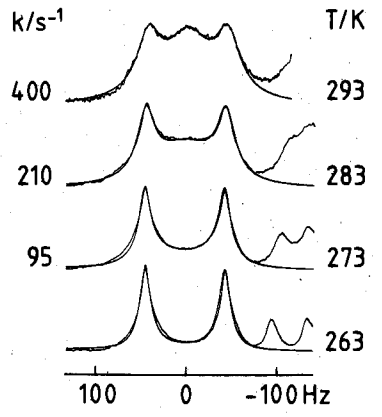

Fig. 11
Superposed experimental and calculated 90.02 MHz ^1H NMR lineshapes of signal 1 of Ib in CD_2Cl_2 as function of temperature after 90% deuteration of the NH sites. Concentration: $3.4\cdot10^{-2}$ M, 10 mm NMR tube. No sample spinning was employed for the recording of these spectra which leads to larger W_0 values as compared to the spectra of Fig. 10, which were recorded with sample spinning

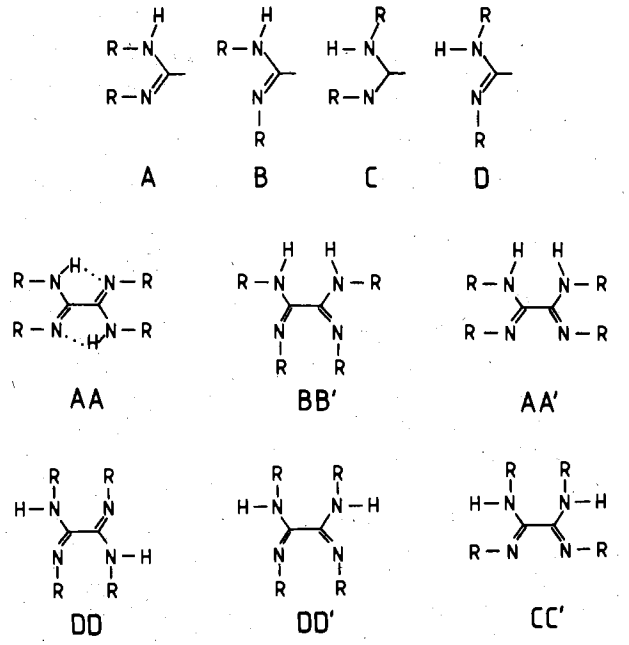

Fig. 12
Possible conformational amidine subunits and possible symmetrical conformers of TPOA

4. Discussion

The ^1H NMR spectra of TPOA-$^{15}N_4$-d_{20} (Ib) in CD_2Cl_2 show at least three different types of amidine groups leading to signals 1, 2, and 3 in Fig. 8. These three environments could not be resolved by IR experiments, neither here nor previously [20]. In principle, we have to discuss the presence of four different amidine subunits A to D as shown in Fig. 12, which can lead to 20 different conformers of which only some are shown below in Fig. 12. We can here assign unequivocally only signal 1 to conformer AA, whose existence has been postulated from the concentration independent IR spectra [20]. Signal 1 appears at quite low field, at frequencies found previously for azophenine (Fig. 2), indicating moderately strong hydrogen bonding, as expected for the AA structure. The most convincing argument for assigning signal 1 to this conformer with two intramolecular hydrogen bonds is, however, the observation of the change of the ^1H-^{15}N doublet to a triplet as temperature is increased. This change proves an intramolecular proton transfer between always the same two N atoms. From the spectral analysis we know that the HH transfer is faster than the interconversion rates of the different conformers. Therefore, the observed rate constants do not contain any term arising from the interconversion between the conformers and the HH transfer must take place within the AA conformer. The fact that a H atom exchanges more slowly when the second H atom is replaced by deuterium confirms this assignment to the process shown in Fig. 3.

Signal 2 must come from an amidine subunit capable of strong intermolecular hydrogen bonding and fast intermolecular proton exchange as shown in Fig. 4. Therefore, we have to assign signal 2 to substructure D in Fig. 12. Whether this would lead to symmetrical conformers DD or DD′ or to unsymmetrical structures cannot be decided at present. The increase of the relative intensity of signal 2 as concentration is increased and temperature decreases is easily explained by the intermolecular association of the amidine substructure D, shifting the conformational equilibrium to the side of this conformer. The position of signal 2 is an average of the associated and the non-associated form of subunit D. At high concentrations and low temperatures signal 2 absorbs at lower fields than signal 1, indicating the greater strength of the intermolecular as compared to intramolecular H bonding of amidine subunits.

From signal 3 we know only that it stems from an amidine subunit which is not or only weakly hydrogen bonded, and which does not exchange its NH protons along an intermolecular pathway. Eventually, the protons are exchanged along an intermolecular pathway, but only via the conformer leading to signal 2, i.e. at temperatures where the interconversion between the different conformers is fast. The same is true also for the AA conformer. We can speculate that signal 3 stems from conformers like BB′ or AA′ or corresponding unsymmetrical structures. It might even be possible that the 3426 and 3389 cm^{-1} bands in the IR spectrum of TPOA are the IR counterparts of signal 3.

Furthermore, it is interesting to note that in tetrahydrofurane only one sharp doublet is observed which shows no sign of proton exchange. Probably only one conformer like DD′ or DD is present in this solvent. A similar effect of THF on the rates of intermolecular HH transfer between acetic acid and methanol has been found previously [4, 7]. Note that THF does not decrease the proton transfer rates in well shielded systems like porphines (Fig. 1) [4].

There is a surprising coincidence between the rate constants found here for the intramolecular HH migration in TPOA of about 1500 s^{-1} at 298 K and the solvent independent rate constant of about 900 s^{-1} found for the azophenine rearrangement (Fig. 2) [3, 9]. Apparently, the presence of four more C atoms in azophenine as compared to TPOA is of no major importance. Note that one would expect that these heavy atoms have to rearrange slightly when the protons jump, since double bonds have to become single bonds and vice versa. More important seems to be the geometry of the non linear intramolecular hydrogen bond in the five-membered ring, which is similar in both compounds. Also, the NH stretching bands are in the region between 3200 and 3300 cm^{-1} and seem to be quite similar. The kinetic HH/HD isotope effect of about 2 at 298 K found here is smaller than the corresponding effect of about 4 for azophenine [3, 9], and of about 10 for the porphine rearrangement [3]. However, the k^{HH}/k^{HD} values of TPOA derived here are at present lower limits, and it is difficult to obtain exact values because of the complexity of the conformer equilibria. Nevertheless, a smaller kinetic isotope effect indicates a substantial heavy atom motion during the reaction, and this could perhaps be a rearrangement of the phenylgroups. It is interesting to note the rate constant of the intermolecular exchange in diphenylformamidine (Fig. 4) is of the order of 10^6 s^{-1} at 298 K [27], i.e. about 10^3 times faster than the value for the intramolecular HH transfer in TPOA. Thus, the barrier of the HH transfer along the intermolecular H bonds in Fig. 4 is much smaller than along the intramolecular H bonds in Fig. 3.

The smaller frequency factor of the HH reaction in TPOA as compared to the HD reaction (Eqs. (6), (7)) could be taken as evidence for a thermally activated HH tunneling process [3, 17]. However, rate constants could not be obtained in a temperature range wide enough to substantiate this conclusion. In order to know whether tunneling is important in the intramolecular TPOA HH transfer the knowledge of the full kinetic HH/HD/DD isotope effects is necessary.

In conclusion, we have demonstrated experimentally for the first time the existence of an intramolecular double hydrogen transfer in tetraphenyloxalamidine, using dynamic NMR spectroscopy. Oxalamidine is, therefore, the smallest known system capable of such a process. However, the observation of a complex conformer equilibrium complicated the evaluation of the multiple HH/HD/DD isotope effects of the reaction, which should be known for a better comparison of experiment and theory. Although the conformer equilibrium itself is very interesting because of its solvent and concentration dependence, it is advisable to perform kinetic studies of the intramolecular oxalamidine tautomerism on other derivates where only the interesting conformer is present. Such studies are necessary also in order to be able to assign the bands in the IR spectrum of oxalamidines. Further studies along these lines, which require a considerable synthetic effort because of the isotopic labeling, are in progress in our laboratory. However, this effort is worth-

wile now that the possibility of the rearrangement in the oxalamidine system according to Fig. 3 has been established. It is hoped that the study of the rearrangement in this small hydrogen transfer system might lead to better agreement between theory and experiment.

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