1.547 Å, B-O-B 120.3°, O-B-O 119.3° (mean values); shortest intermolecular B···O distance 4.441 Å [10].

[7] During the phase transformation of 2,6-diorgano-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalynediones, a similar effect was observed in the transition from the 2,6-diethyl to the 2,6-diphenyl compound, and was interpreted in the same way. M. Yalpani, R. Boese, D. Bläser, *Chem. Ber. 116* (1983) 3338.

[8] Space group *Pnma*. Cell data (-70°C, m.p. $= -65.3$°C) [Å]: $a = 8.325(2)$, $b = 15.772(6)$, $c = 8.432(3)$; $Z = 4$, ρ_{calc} [g cm^{-3}] $= 0.96$; $\mu(\mathrm{Mo}_{K\alpha})$ [cm^{-1}] $= 0.50$; $2\theta_{max}$[°] $= 60$; 529 observed reflections $F_0 \geq 5.5\sigma(F)$); R, $R_w = 0.086$, 0.099; C_s symmetry of the molecule, two ethyl groups arranged *cis*, one *trans*. Torsion angles C(phenyl)-C(phenyl)-C(ethyl)-C(ethyl) [°] $= -90$, $+97$, $+88$; smallest intermolecular C-C distances are C(ethyl)-C(phenyl) 3.579 Å [10].

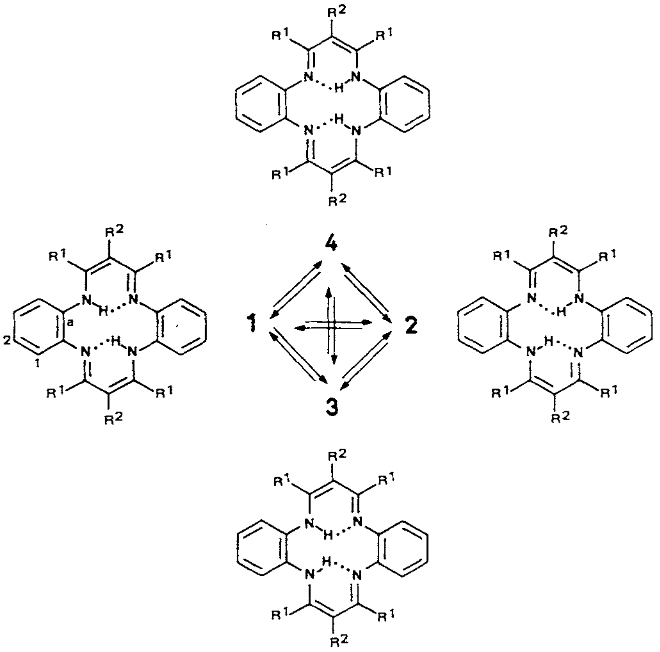
[9] Space group $Pna2_1$. $Z = 4$; angle of twist of the phenyl groups [°] $= 40.7$, -37.2, 36.1; smallest intermolecular C-C distance is C(central benzene ring)-C(phenyl) 3.441 Å: Y. C. Lin, D. E. Williams, *Acta Crystallogr. B31* (1975) 318.

[10] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-52244, the names of the authors, and the journal citation.

Kinetic ^{15}N-CPMAS-NMR Study of a Double Proton Transfer in a Crystalline Malonaldehyde Diimine Derivative[**]

By *Hans-Heinrich Limbach,* Bernd Wehrle, Herbert Zimmermann, Ray D. Kendrick,* and *Costantino S. Yannoni**

We report here the rate constants of proton transfer in a strong intramolecularly hydrogen bonded six-membered ring H-chelate of the malonaldehyde type. The data were obtained by dynamic ^{15}N-CPMAS-NMR spectroscopy[1] of crystalline DTAA[2] (Scheme 1). The problem of proton motion in malonaldehyde and its derivatives is a matter of continuing experimental[3-10] and theoretical interest.[11] Evidence for motion along a double minimum potential in these compounds has been obtained using different spectroscopic techniques[3-7] including NMR spectroscopy. Microwave studies[4] indicate a coherent proton tunnel process in gaseous malonaldehyde. So far, these proton transfer processes were found to be so fast that rate constants could not be obtained by NMR or any other method. Using solid state NMR techniques,[12] proton localization was observed for naphthazarine (5,8-dihydroxy-1,4-naphthoquinone)[8,9] and for tropolone[10] at low temperatures, an effect which was, however, caused by intermolecular H-bond formation. This complication does not arise in DTAA. On the other hand, double proton transfers have also been observed in solid porphines.[13,14] However, these compounds are not able to form strong intramolecular H-bonds as do malonaldehyde and its derivatives.



Scheme 1. DTAA: $R^1 = H$, $R^2 = CH_3$; TTAA: $R^1 = CH_3$, $R^2 = H$. N 95% for ^{15}N.

Since solid state proton transfers between nitrogen atoms can be conveniently studied by ^{15}N-CPMAS-NMR spectroscopy of ^{15}N-enriched compounds[13] we have synthesized DTAA-$^{15}N_4$ by slight modifications of the procedures published for the unlabeled compound.[15] The ^{15}N-CPMAS-NMR spectra of DTAA consist of two lines at all temperatures as shown in Figure 1. At low temperature, both the high-field line (which we signify as a), characteristic for an NH environment, and the low-field line (b), characteristic for an sp^2 nitrogen,[16] are sharp. As the temperature is increased, the lines broaden, sharpen again, and move towards each other, but never coalesce. Such line-shape changes are typical for the presence of two un-

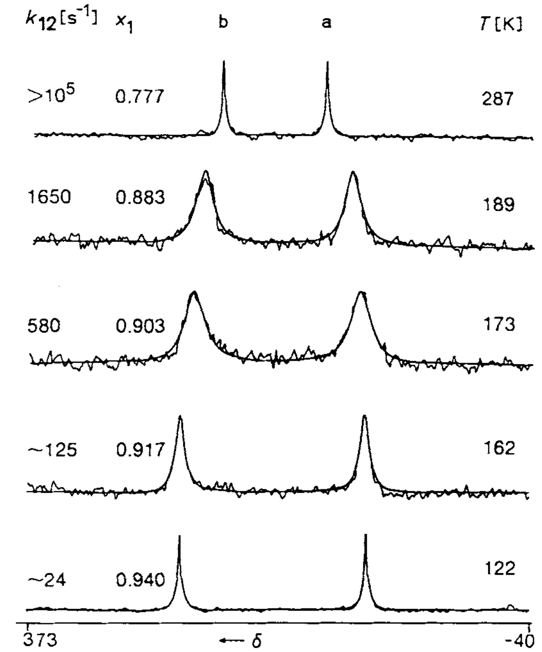


Fig. 1. Superposed experimental and calculated ^{15}N-CPMAS-NMR spectra of enriched DTAA (95% ^{15}N) at 6.082 MHz as a function of temperature. 5 ms cross polarization time, 4 kHz sweep width, 1 s repetition time. Number of scans from 122 to 287 K: 1640, 1770, 6048, 10464, 10464. Reference: external $^{15}NH_4NO_3$. x_1 is the probability of the dominant tautomer **1**, k_{12} the forward rate constant. The linewidth in the absence of exchange was taken from the spectra at 122 and 287 K.

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equally populated interconverting tautomeric states $\mathbf{1} \rightleftharpoons \mathbf{2}$ of the structure $N_aH\cdots N_b \rightleftharpoons N_a\cdots HN_b$.[13, 14] The lineshapes were simulated in terms of two superposed single-spin systems each of which exchanges between the states **1** and **2** shown in Scheme 1. In addition, it was assumed that for the chemical shifts

$$\delta_a(\mathbf{1}) = \delta_b(\mathbf{2}) \quad \text{and} \quad \delta_b(\mathbf{1}) = \delta_a(\mathbf{2}).$$

In the fast exchange limit, the equilibrium constant K_{12} of the tautomeric process can be calculated according to equation (a), where δ is the line separation at temperature

$$\delta/\Delta = (1 - K_{12})/(1 + K_{12}), \tag{a}$$

T and $\Delta = \delta_a(\mathbf{1}) - \delta_b(\mathbf{1})$ is the intrinsic chemical shift difference obtained at low temperatures.[14] The observation of two ^{15}N lines in the fast exchange regime indicates that the degeneracy of the two tautomers **1** and **2** is lifted due to a solid state effect. Approximatively 20% of the minor tautomer **2** is found at room temperature. A reaction enthalpy of $\Delta H_{12} = 3.8 \pm 0.4$ kJ mol^{-1}, a reaction entropy of $\Delta S_{12} = 2 \pm 0.4$ J K^{-1} mol^{-1} and, as rate constant for the forward reaction

$$k_{12}(T) = 10^7 \exp(-14.7 \pm 4.2 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$

were found by spectral simulation.

In view of the small temperature range between 160 K and 220 K, over which rate constants could be obtained so far, the temperature dependence of k_{12} given above is tentative and might be subject to a large error. Deuteration of the molecule in the NH sites resulted in dramatic spectral changes. At 210 K, the deuteron transfer is about 10 times slower than the proton transfer. Whereas the entropy difference between the two tautomeric states **1** and **2** found here for crystalline DTAA is negligible, the energy difference is considerable. This inequivalence is absent in solution and arises, therefore, from a solid state effect. Unfortunately, a crystal structure of DTAA, which might suggest the reason for this inequivalence, has not yet been obtained. In accordance with the literature[15, 18, 19] we assign the structures shown in Scheme 1 to the interconverting states **1** and **2**, where a possible van der Waals interaction between the inner protons is minimized. The fact that we find only two ^{15}N lines in the fast exchange regime indicates that the four nitrogen atoms in solid DTAA are pairwise equivalent, i.e. that the two proton transfer units are characterized by the same equilibrium constants (K_{12}) of tautomerism. In other words, both protons jump in concert or one immediately after the other, i.e. the tautomeric states **3** and **4** in Scheme 1 are not significantly populated. This result is in contrast to solid TTAA (Scheme 1), where all four tautomers **1** to **4** were observed.[17] These tautomers interconvert rapidly on the NMR time scale and are characterized by different energies i.e. different temperature dependent populations.

Our working hypothesis as to why the proton transfer in DTAA is much slower than in TTAA is that in TTAA the protons move independently from each other,[17] whereas in DTAA the two proton transfer units are more or less coupled together. Independent support for this idea comes from the observation that tetraaza[14]annulenes such as DTAA are dark red due to an electronic absorption band in the 450-nm region.[19] This band is absent in the yellow TTAA,[18] which correlates with the fact that the four methyl groups of TTAA sterically hinder a coplanar arrangement of the two chelate subunits in the crystal.[20] Thus, the two H-chelate subunits in TTAA are, to a crude approximation, decoupled electronically leading to independent proton motion, in contrast to DTAA. Since malonaldehyde derivatives also show phototautomerism,[21] we would expect a different behavior of DTAA and TTAA when exposed to light.

In summary, we have found evidence not only for a double minimum potential in solid DTAA for the proton motion $\mathbf{1} \rightleftharpoons \mathbf{2}$, but also for a measurable rate process which involves a kinetic isotope effect.

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[1] CP = cross polarization, MAS = magic angle spinning. Recent review of ^{15}N-NMR spectroscopy: W. von Philipsborn, R. Müller, *Angew. Chem. 98* (1986) 381; *Angew. Chem. Int. Ed. Engl. 25* (1986) 383.

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A Novel Route to Azaalkenylidene-Metal Complexes[**]

By *Helmut Werner*,[*] *Wolfgang Knaup*, and *Michael Dziallas*

In contrast to the well-documented alkenylidenemetal complexes [$L_nM{=}C{=}CRR'$], which have been the subject

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