contains two diphenylglycoluril and two hydroquinone rings linked through eight methylene bridges. The void in **5** (2.5 × 2.0 Å) is not large enough to hold an organic guest. However, higher homologues of **5**, e.g., those containing additional diphenylglycoluril and hydroquinone rings, do have large enough voids.[10]

Starting from **2**, hosts that have a metal center next to a cavity are readily accessible. As an example, we prepared **6** by reacting **2b** successively with: excess of Tos(OCH$_2$CH$_2$)$_2$Cl and base in Me$_2$SO, excess of benzimidazole (Bz) and NaH in DMF, and 1 equiv of RhCl$_3$ in Me$_2$SO (overall yield 70%). Compound **6** has two trans-coordinated Cl ligands, one being inside the cavity, the other outside. The binding and catalytic properties of hosts **4–6** are currently being investigated and will be published in forthcoming papers.

Acknowledgment. We thank Prof. Wiendelt Drenth for stimulating discussions.

(10) In addition to **5** a compound is isolated which contains three diphenylglycoluril and three hydroquinone rings, linked through 12 methylene bridges (symmetry D_{3h}). The cavity of this cavitand has a diameter of ~5 Å. Sijbesma, R. P.; Smeets, J. W. H.; Nolte, R. J. M., unpublished results.

Observation of a Nonconcerted Double Proton Transfer in the Solid State by 15N CPMAS NMR

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We present here for the first time NMR spectroscopic evidence of a nonconcerted double proton transfer. The double proton motion studied occurs along slightly asymmetric double-minimum potentials in solid TTAA[2] according to Scheme I. For H-chelates of the malonaldehyde type like TTAA, it has been very difficult to establish the double-minimum character of the proton potential using different spectroscopic techniques[3] including NMR.[4] Goedken et al.[5] have performed an X-ray crystallographic analysis of solid TTAA, have postulated the "diagonal" tautomerism **1** ⇌ **3** shown in Scheme I, and have further suggested that the degeneracy of this process is lifted due to a rhombic distortion of the unit cell. However, the X-ray method cannot reveal details such as the nonconcerted character of the double proton motion in TTAA or if the tautomerism is static or dynamic.

Since solid-state proton transfers between nitrogen atoms are most directly probed by 15N CPMAS NMR,[6,7] we have performed

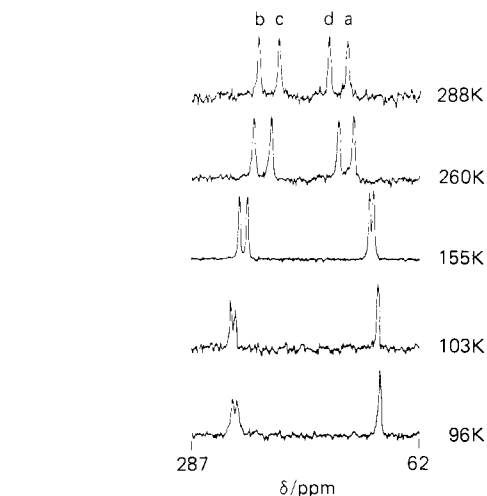(1) (a) IBM Almaden Research Center. Permanent address: Institut für Physikalische Chemie der Universität Freiburg i. Br. (b) Institut für Physikalische Chemie der Universität Freiburg i.Br. (c) Max Planck Institut für Medizinische Forschung, Heidelberg. (d) IBM Almaden Research Center, San Jose, CA.

(2) TTAA = 1,8-dihydro-5,7,12,14-tetramethyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene-15N_4 (tetramethyldibenzotetraaza-(14)annulene).

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Figure 1. 15N CPMAS NMR spectra of 95% 15N-enriched TTAA at 6.082 MHz as a function of temperature: 10-Hz line broadening, 1K–4K zero filling, 25-ms cross-polarization time, 4000-Hz sweep width, 1.5-s repetition time, 9-μs 1H–π/2 pulses, quadrature detection, 1000 scans on the average; reference, external 15NH$_4$NO$_3$.

Scheme I
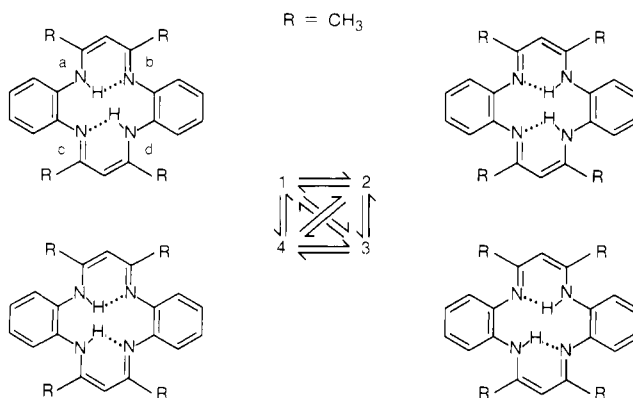
such experiments on 95% 15N-enriched TTAA.[8] Figure 1 shows some of the 15N CPMAS spectra obtained with an apparatus described previously.[9] We observe four lines, a–d, of equal intensity. Between 100 and 80 K, the lowest temperature where experiments were performed, no spectral changes occur, indicating that the chemical shifts are temperature independent within experimental error. Taking into account 15N solution NMR data,[10] we assign the overlapping lines a and d to NH atoms and the two resolved lines b and c to two inequivalent =N— atoms in solid TTAA. As the temperature is increased, lines d and c move toward each other without coalescing, as do lines a and b. The low-field shift of line a from 96 to 288 K matches the high-field shift of line b over the same temperature range. The same is true for lines d and c. Since the intrinsic chemical shifts are temperature independent, these changes can only be explained by fast proton transfer from atom a to b and from atom d to c. In other words, the position of line n depends on the average proton density p_n on atom n. The observed chemical shift difference $\delta_{mn} = \delta_m$

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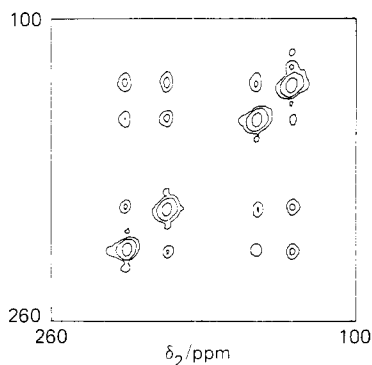(10) Breitmeier, E. *Pharm. Unserer Zeit* **1983**, *6*, 161.

Figure 2. Two-dimensional magnetization transfer ^{15}N CPMAS spectrum (contour plot) of TTAA-$^{15}N_4$ at 300 K with a mixing time of 800 ms. The spectra were obtained at 9.12 MHz by using a Bruker CXP 100 NMR spectrometer. There were 64 by 256 points in the original data, 32 scans per spectrum: 10-ms cross-polarization time, 3-μs ^1H–$\pi/2$ pulses, 2.7-s repetition time; reference, external $^{15}NH_4NO_3$.

– δ_n between the ^{15}N lines m and n, where mn = ab, dc, is given by[6,7]

$$\delta_{mn}/\Delta_{mn} = (1 - K_{mn})/(1 + K_{mn}) \qquad (1)$$

where $K_{mn} = p_n/p_m$. K_{mn} is the equilibrium constant for tautomerism in the ^{15}N pair mn and Δ_{mn} is the intrinsic chemical shift difference. As shown in Figure 1, δ_{dc} decreases more rapidly with increasing temperature than δ_{ab}. Thus, there are two inequivalent proton transfer systems ab and dc present in solid TTAA, with unequal equilibrium constants $K_{ab} < K_{dc} < 1$.[11] Therefore, since $K_{ab} \neq K_{dc}$, the proton motion in system ab cannot take place in concert with the proton motion in system dc.

A central question is whether each TTAA molecule contains both proton transfer systems ab and dc or whether there are two types of molecules in different but equally populated crystallographic sites containing either ab or dc atom pairs. This question was answered by 1D and 2D ^{15}N exchange spectroscopy[12] of solid solutions of TTAA-$^{15}N_4$ in TTAA-$^{14}N_4$. As shown in Figure 2, the 2D spectra contain cross peaks among all four lines, a–d, due to magnetization transfer during the mixing period. These spectra, as well as the magnetization transfer rates obtained by corresponding 1D experiments, did not depend on the TTAA-$^{15}N_4$ mole fraction, which was varied between 0.1 and 1. However, ^1H decoupling during the mixing time resulted in a suppression of magnetization transfer, proof that this effect arises from spin diffusion and not from chemical exchange. Since spin diffusion[13] between nuclei decreases with the third power of the internuclear distance, our observation that the spin diffusion rates are independent of TTAA-$^{15}N_4$ mole fraction confirms that the observed spin diffusion is an intramolecular process.

Thus, the observation of four ^{15}N resonances combined with the proof that all four lines come from atoms within the same molecule shows that there is only one type of nonsymmetric molecule in solid TTAA, in agreement with the crystal structure.[5] Consequently, each TTAA molecule contains both proton transfer systems ab and dc and must therefore be able to exist in four tautomeric states, **1–4**, which interconvert by single proton transfers as shown in Scheme I. It may be that the "diagonal" processes **1** $\rightleftarrows$ **3** and **2** $\rightleftarrows$ **4** involving concerted two-proton transfer occur as a side reaction. Furthermore, our results show that the

rhombic distortion lifts the degeneracy between **2** and **4**, as well as between **1** and **3**.

It is tempting to correlate the nonconcerted proton motion with noncoplanarity[5] of the H-chelate units sterically induced by the methyl groups. This effect could lead to a reduced repulsion of the inner protons of TTAA states **2** and **4** and to reduced electronic interaction of the two H-chelate units. The latter effect is supported by the electronic spectra: the lowest energy transition in the spectrum of the methyl-free compound appears at 452 nm[14] while that of TTAA is at 342 nm.[8]

We have shown here that the protons in the solid malonaldehyde derivative TTAA move rapidly in asymmetric double-minimum potentials between four different tautomeric states which interconvert by single proton transfers according to Scheme I. Further experiments are under way to examine the effect of the removal of the methyl groups on the tautomerism.

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Ab Initio Calculations Predict a Singlet Ground State for Tetramethyleneethane

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Tetramethyleneethane (TME) is the simplest non-Kekulé hydrocarbon whose nonbonding molecular orbitals (NBMOs) can be localized to different regions of space.[1] The localizability of the NBMOs of TME leads to the prediction of a singlet ground state for the planar diradical.[2-4]

In 1970, Dowd reported the first preparation of TME and the observation of a triplet EPR signal for this diradical.[5] Roth and co-workers have also detected a triplet EPR signal[6a] from a TME derivative,[6] but the Curie law studies necessary to establish whether the triplet was the ground state were not reported. Very recently, Dowd and co-workers measured the temperature dependence of the EPR signal intensity for the parent TME, and from the linearity of a Curie–Weiss plot, they concluded that TME has a triplet ground state.[7]

Dowd's finding does not necessarily conflict with the theoretical prediction of a singlet ground state for the *planar* diradical.[3,4] In fact, the results of the ab initio calculations reported here show, in agreement with previous computational studies,[8,9] that both the

(11) We calculate the enthalpy differences $\Delta H_{ab} = 1.01 \pm 0.04$ kcal/mol and $\Delta H_{dc} = 1.09 \pm 0.04$ kcal/mol and the entropy differences $\Delta S_{ab} = 0.6 \pm 0.1$ cal K^{-1} mol^{-1} and $\Delta S_{dc} = 1.1 \pm 0.1$ cal K^{-1} mol^{-1}. The K_{mn} can be expressed in terms of equilibrium constants for the tautomers: $K_{ab} = K_{12}(1 + K_{23})/(1 + K_{14})$ and $K_{dc} = K_{14}(1 + K_{43})/(1 + K_{12})$. $K_{ij} = x_j/x_i$ where x_i is the molefraction of the ith tautomer. We have arbitrarily assigned the lowest energy to tautomer **1**.

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