contains two diphenylglycoluril and two hydroquinone rings linked through eight methylene bridges. The void in \(5 \ (2.5 \times 2.0 \text{ Å})\) is not large enough to hold an organic guest. However, higher homologues of \(5\), e.g., those containing additional diphenyl-

glycoluril and hydroquinone rings, do have large enough voids.\(^9\)

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 \(\text{Tos(OCH}_{3}\text{CH})_{3}\text{Cl}\) and base in \(\text{Me}_2\text{SO}\), excess of benzimidazole (\(\text{Bz}\)) and \(\text{NaH}\) in \(\text{DMF}\), and \(1\) equiv of \(\text{RhCl}\) in \(\text{Me}_2\text{SO}\) (overall yield \(70\%\)). Compound \(6\) has two trans-coordinated \(\text{Cl}\) 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.

\(1\) 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 \(\sim 5\ \text{Å}\).

\\(2\) \(\text{Sjibesma}, \ R. \ P.; \text{Smeets}, \ J. \ W. \text{H.}; \text{Noite}, \ R. \ J. \ M.; \text{unpublished results.}\)

### Observation of a Nonconcerted Double Proton Transfer in the Solid State by \(\text{\(^{15}\text{N}\)} 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 1. For \(\text{H}-\text{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}\(^1\) including NMR.\(^4\)

Goedken et al.\(^c\) have performed an X-ray crystallographic analysis of solid TTAA, they have postulated the "diagonal" tautomeration \(I \rightleftharpoons 3\) shown in Scheme 1, 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 tautomeration is static or dynamic.

Since solid-state proton transfers between nitrogen atoms are most directly probed by \(\text{\(^{15}\text{N}\)} CPMAS NMR,\(^c\) \(we\) have performed

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\(10\) 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 \(\sim 5\ \text{Å}\).

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### Scheme 1

![Scheme 1](image-url)

\(\text{\(^{15}\text{N}\)} CPMAS NMR spectra of \(\text{\(^{15}\text{N}\)}\)-enriched TTAA at 6.082 MHz as a function of temperature: 10-Hz line broadening, 1K-4K zero filling, 25-ps cross-polarization time, 4000-Hz sweep width, 1.5-s repetition time, 9-\(\mu\)s H-\(\tau/2\) pulses, quadrature detection, 1000 scans on the average; reference, external \(\text{\(^{15}\text{NH}_3\)}\)NO\(_3\).

\(5\) \(\text{H. H. Limbach; Gerritsen, D.; Rumpel, H.; Wehrle, B.; Otting, G.;}

Zimmermann, H.; Kendrick, R.; Yannoni, C. S. In \text{Photochrome Fotokörper,}


\(7\) Limbach, H. H.; Gerritsen, D.; Rumpel, H.; Wehrle, B.; Otting, G.;

Zimmermann, H.; Kendrick, R.; Yannoni, C. S. In \text{Photochrome Fotokörper,}


tautomeric states, processes expressed in terms of equilibrium constants for the tautomers:

\[ K_{ab} = \frac{[A]}{[B]} = 1.09 \pm 0.04 \text{ kcal/mol} \]

where \( K_{ab} \) is the equilibrium constant for tautomers in the 15N pair and \( \Delta H_\text{ab} \) is the intrinsic chemical shift difference. As shown in Figure 1, \( \delta_g \) decreases more rapidly with increasing temperature than \( \delta_b \). Thus, there are two inequivalent proton transfer systems ab and dc present in solid TTA, with unequal equilibrium constants \( K_{ab} < K_{dc} \). 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 TTA 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 2D and 15N exchange spectroscopy \(^\text{12}\) of solid solutions of TTA \(-^{15}\text{N} \) in TTA \(-^{14}\text{N} \). 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 TTA \(-^{15}\text{N} \) mole fraction, which was varied between 0.1 and 1. However, the 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 \(^\text{13}\) between nuclei decreases with the third power of the internuclear distance, our observation confirms that the observed spin diffusion is an intramolecular process.

Thus, the observation of four 15N 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 TTA, in agreement with the crystal structure. Consequently, each TTA molecule contains both proton transfer systems ab and dc and must therefore be able to exist in four tautomeric states I-I4, which interconvert by single proton transfers as shown in Scheme I. It may be that the "diagonal" processes 1 \( \rightarrow \) 3 and 2 \( \rightarrow \) 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 \(^\text{14}\) of the H-chelate units sterically induced by the methyl groups. This effect could lead to a reduced repulsion of the inner protons of TTA states 2 and 4 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 \(^\text{15}\) while that of TTA is at 342 nm.8

We have shown here that the protons in the solid malonaldehyde derivative TTA 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 Tetramethylethene

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Tetramethylethene (TME) is the simplest non-Kekulé hydrocarbon whose nonbonding molecular orbitals (NBOs) can be localized to different regions of space.1 The localization of the NBOs 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.3,2,4 Roth and co-workers have also detected a triplet EPR signal6 from a TME derivative 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.6,7

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 that both the

(1) The simplest conjugated hydrocarbon whose NBOs have this property is cyclobutadiene, which is an antiaromatic annulene.


(9) Dowd, P.; Chang, W.; Paik, Y. H. J. Am. Chem. Soc. 1986, 108, 7416. We are indebted to Professor Dowd for sending us a preprint of his manuscript.

