

Structure and Dynamics of Terephthalic Acid from 2 to 300 K

II. The Temperature Dependence of the Disorder: A Solid-State NMR Study

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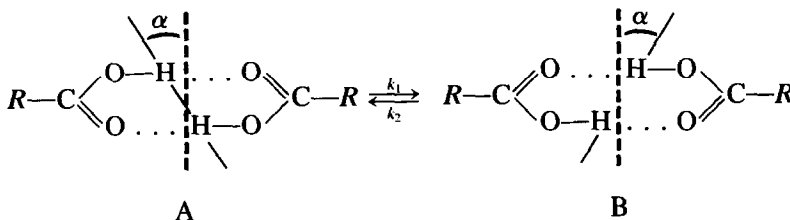
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In the preceding paper the structure of terephthalic acid $C_6D_4(COOD)_2$ has been found to be ordered to a high extent at 2 K, whereas an almost complete disorder of the hydrogen-bond protons was observed at 300 K. In this part, the temperature dependence of the dipolar lineshape of the two hydrogen-bonded protons in ring-deuterated terephthalic acid $C_6D_4(COOH)_2$ is studied. The results are consistent with dynamic disorder in an asymmetric double-minimum potential with a free enthalpy difference of the two tautomeric species of 2 kJ/mole. © 1986 Academic Press, Inc.

Nuclear magnetic resonance is known to be an ideal complement to neutron diffraction because it allows the identification of motional processes in solids. Both relaxation measurements as well as the study of dipolar lineshapes provide access to molecular dynamics. The relevant time scale ranges from a few hertz to some hundred megahertz depending on the observed interaction. The present study attempts to identify the high-temperature disorder of the carboxylic protons observed by neutron

diffraction and described in the preceding paper (5). In a previous NMR investigation of carboxylic acid dimers, it has been possible to study in detail the exchange process which the hydrogen-bond protons are undergoing in *p*-toluic acid (1). Both lineshape studies of a single crystal as well as relaxation measurements are in agreement with an asymmetric double-minimum potential in which the dynamic exchange between the two tautomeric forms A and B proceeds:



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The energetic degeneracy of the forms A and B, as it exists in the free dimer, is broken by lattice effects in the crystalline

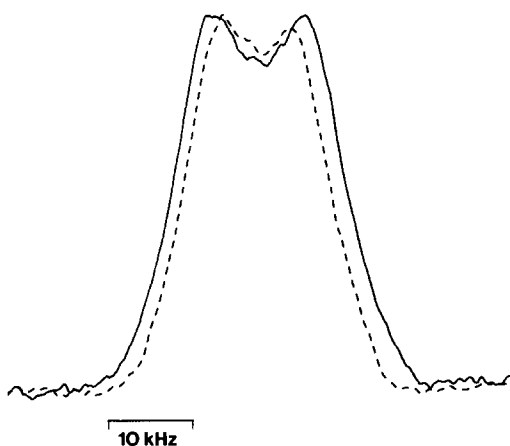


FIG. 1. Observed proton dipolar coupling tensors of a powder sample of ring-deuterated terephthalic acid at 28 K (solid line) and at 300 K (broken line). The measurements have been performed on a carefully dried and sealed powder sample of $C_6D_4(COOH)_2$ at 100-MHz proton frequency using a modified Bruker SXP4-100 high-power pulse spectrometer equipped with a Varian 15-in. magnet, an RSM432 Interface Technology time sequence generator, and a DL402 Data Lab transient recorder. The home-built probe assembly (4) with a Helitran flow cryostat allowed temperature control between 4 and 400 K.

solid. The population of the two tautomeric forms is therefore a function of temperature. Analogous observations have been made by Nagaoka *et al.* (2, 3) for other carboxylic acid dimers.

Relaxation measurements (1) suggested a similar exchange mechanism for terephthalic acid. The smooth temperature dependence of the spin-lattice relaxation time of the protons did not reveal any obvious phase transition between 10 and 300 K. To obtain more information on the underlying dynamics, an analysis of the dipolar lineshape of ring-deuterated terephthalic acid was undertaken. Unfortunately, we did not succeed in growing sufficiently large single crystals for an NMR study. The measurements had to be restricted to a powder investigation. The situation in ring-deuterated terephthalic acid is particularly simple since the lineshape is dominated by the di-

polar interaction within the pairs of hydrogen-bond protons. The additional interpair interaction leads merely to an unstructured broadening of the intrapair "Pake doublet." Two proton resonance spectra of a powder sample of ring-deuterated terephthalic acid recorded at 28 and 300 K are shown in Fig. 1. It is apparent that there is a sizable change of the lineshape as a function of temperature with a narrowing at higher temperatures.

For the analysis of the lineshapes in terms of the proton dynamics, we start with the dipolar interaction between two static protons described by an axially symmetric second rank tensor \mathbf{D} (1):

$$\hbar H = \tilde{\mathbf{I}}^{(i)} \mathbf{D} \mathbf{I}^{(i')} \quad (1)$$

with the spin angular momentum operators $\mathbf{I}^{(i)}$ and $\mathbf{I}^{(i')}$ of the protons i and i' , respectively. The eigenvalues λ of \mathbf{D} are given by

$$\lambda_{1,2} = D \quad \lambda_3 = -D \quad (2)$$

with

$$D = (3\mu_0/(4\pi)^2)\gamma^2\hbar/d_{ii'}^3, \quad (3)$$

where $d_{ii'}$ is the proton-proton distance, γ the gyromagnetic ratio of the proton, and μ_0 the magnetic field constant.

For fast exchange ($k \gg D$), the average dipolar tensor $\bar{\mathbf{D}}$ is given, according to Ref. (1), by a weighted average of the dipolar tensors of the two sites,

$$\bar{\mathbf{D}} = (1-x)\mathbf{D}_A + x\mathbf{D}_B, \quad (4)$$

where x denotes the mole fraction of the tautomer B. The three eigenvalues of $\bar{\mathbf{D}}$ are given by

$$\begin{aligned} \lambda_1 &= D, \\ \lambda_{2,3} &= D\{-\frac{1}{2} \pm \frac{3}{2} \\ &\quad \sqrt{1 - 4 \sin^2 2\alpha [x(1-x)]}\}, \quad (5) \end{aligned}$$

where 2α is the change in angle of the proton proton vector going from structure A to structure B.

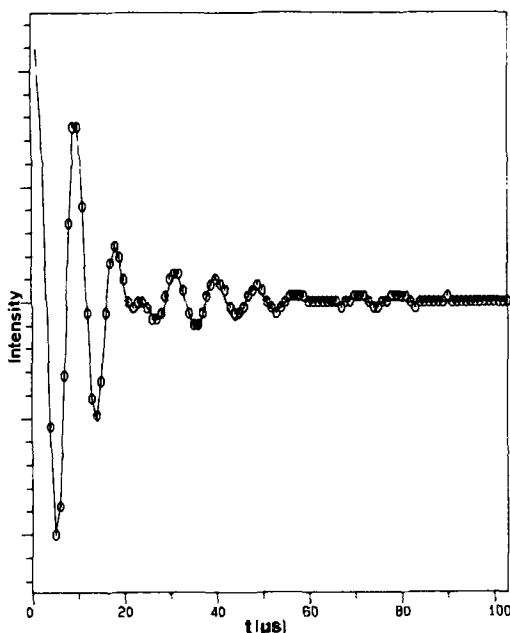


FIG. 2. Proton free induction decay of a powder sample of ring-deuterated terephthalic acid at a temperature of 9 K. The circles denote the experimental points; the solid line is the best fit based on an axially symmetric dipolar coupling tensor.

The dipolar interaction in the fast exchange limit (described by $\bar{\mathbf{D}}$) is partially averaged by the chemical exchange. The eigenvalues of $\bar{\mathbf{D}}$ are therefore smaller than or equal to the ones for the static case (described by \mathbf{D}_A and \mathbf{D}_B). Due to the anisotropic nature of the exchange process, all three eigenvalues are affected differently. Therefore, the resulting tensor is in general no longer axially symmetric (see Eq. (5)).

For an external magnetic field oriented by the angles θ and ϕ with respect to the principal axes frame of the dipolar tensor, the dipolar splitting of the proton resonance is given by

$$\omega_D = \frac{1}{2}[\lambda_1 \sin^2 \theta \cos^2 \phi + \lambda_2 \sin^2 \theta \sin^2 \phi + \lambda_3 \cos^2 \theta]. \quad (6)$$

The theoretical powder spectra have been calculated numerically by summing single-crystal spectra corresponding to

about 10,000 mesh points on the unit sphere approximating an isotropic distribution of the crystalline orientation (θ , ϕ). The resulting spectrum is convoluted with a Gaussian line-broadening function to take into account interpair interactions. A least-squares analysis has been performed to fit the experimental lineshapes by the theoretical ones. It turned out to be of advantage to perform the least-squares fitting on the free induction decay rather than on the spectrum because this avoids baseline problems due to the transmitter deadtime. The mole fraction x , the linewidth of the Gaussian, the phase, and the amplitude of the free induction decay have been selected as free parameters of the fit, whereas the Larmor frequency and the dipolar coupling constant have been treated as constants. Due to the high correlation between the mole fraction and the dipolar constant, it turned out to be impossible to fit them independently.

For fitting the temperature dependence of the lineshape, an ideal two-site jump model has been assumed with identical and temperature-invariant structures of the two tautomers. From the low-temperature lineshape, where the tensor is axially symmetric, a dipolar coupling constant of 15.25 kHz corresponding to a proton-proton distance of 2.28 Å has been determined (Fig. 2). This value is close to the result from neutron diffraction, where 2.34 Å have been found. The flip angle $2\alpha = 37^\circ$ is taken from the preceding neutron diffraction study (5). The same proton-proton distance and flip angle have been used for the fits at all temperatures. The resulting mole fractions of the less stable tautomer are plotted in Fig. 3 against temperature. It is seen that above room temperature an equipartition is approached.

No significant discontinuity can be detected in the temperature dependence of the mole fraction which would indicate a phase transition. This is in agreement with

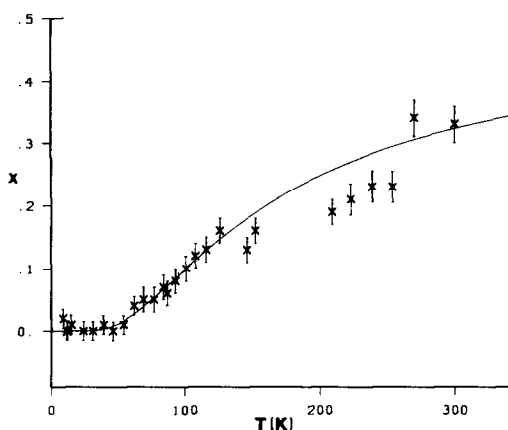


FIG. 3. Population of the less stable tautomeric structure as a function of temperature. The population has been deduced by a least-squares fit of the observed dipolar splitting tensors in a two-site jump model. The dipolar coupling constant was determined to be 15.25 kHz from the low-temperature spectra and kept constant for all fits. The solid line denotes the theoretical population based on a double-minimum potential with $\Delta G^\circ = 1.8$ kJ/mole.

the temperature dependence of the spin-lattice relaxation determined earlier (1).

From the relaxation data, it can be seen that the exchange is fast compared to the dipolar splitting for all temperatures where an asymmetric tensor is found. It appears therefore justified to explain the lineshape data by a fast two-site exchange model. The mole fraction $x(T)$ of the less stable form can then be expressed by the free enthalpy difference ΔG° :

$$x = (1 + \exp[+\Delta G^\circ/RT])^{-1}. \quad (7)$$

If we assume that ΔG° itself is temperature independent, it can be determined

from a plot of $\log[(1-x)/x]$ versus $1/T$. A value of $\Delta G^\circ = 1.8 \pm 0.5$ kJ/mole is found. The error limit is mainly determined by the uncertainty of the dipolar coupling constant.

In conclusion, it has been shown that the temperature-dependent dipolar lineshape as well as the disorder observed by neutron diffraction can be explained by hydrogen-bond dynamics in an asymmetric double-minimum potential with a free enthalpy difference of about 1.8 kJ/mole. Although it does not give as detailed information as a single-crystal study, the dipolar powder pattern is shown to contain valuable information about the proton exchange process.

Acknowledgments

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