Marcus relationship for outer-sphere reactions[26] (see, for example, ref 40) that the reactivity ratio R toward a common substrate is expected to be a constant, for example (eq 8), where $k(SO_2/SO_2^-)$

$$R = \frac{k_{SO_2}}{k_{O_2^-}} = \left[\frac{k(SO_2/SO_2^-)}{k(O_2/O_2^-)} 10^{16.9\Delta E}\right]^{1/2} \quad (8)$$

and $k(O_2/O_2^-)$ are the self-exchange rate constants and ΔE is the difference between the reduction potentials of O_2 and SO_2. The reduction potential of the O_2/O_2^- system is -0.16 V[2] and that estimated for SO_2/SO_2^- is -0.26 V.[41] An R value in (8) of 10^3 requires that $k(SO_2/SO_2^-)/k(O_2/O_2^-)$ be $\sim 10^4$. Since the rate constant for the SO_2^-–O_2 reaction is 1.3×10^6 M^{-1} s^{-1} (pH 8.0),[18] that for O_2^-/O_2 self-exchange can be estimated as $\sim 10^3$ M^{-1} s^{-1}. This is slightly larger than that assessed by application of Marcus theory to the $Ru(NH_3)_6^{2+}$–O_2 reaction.[42] This means that the SO_2^-/SO_2 self-exchange is predicted to be $\sim 10^7$ M^{-1} s^{-1}. The reduced reactivity of O_2^- toward H_2O_2[36,37] and ferrioxamine[33] is understandable since reaction of SO_2^- with these substrates is relatively slow. One glaring exception to the enhanced reactivity of SO_2^- is toward horseradish peroxidase. The higher rate constant for O_2^- may reflect an innersphere mechanism not perhaps shown by SO_2^-, since oxyferroperoxidase is the immediate product of the reaction of O_2^- ion.[30]

In summary, we have used a simple source of superoxide ions and demonstrated its value for studying a number of reduction reactions of O_2^- in aqueous solution. Interference from reactions of oxygen and hydrogen peroxide must always be considered and this will be particularly the case with the study of oxidation reactions by O_2^-. Each system will require separate scrutiny. We have shown for seven different types of oxidant a relation between the reactivity of O_2^- and SO_2^- and suggested that this has predictive value.

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Registry No. $Fe(CN)_6^{3-}$, 13408-62-3; $Mn(CyDTA)^-$, 73360-48-2; $Co(terpy)_2^{3+}$, 19137-07-6; O_2^-, 11062-77-4; $S_2O_4^{2-}$, 14844-07-6; Na_2SO_4, 7757-82-6; SO_2^-, 12143-17-8; nitroblue tetrazolium, 298-83-9; 2,6-dichlorophenol, 87-65-0; ferriperoxidase, 9003-99-0.

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The Relaxational Behavior of Self-Associated 6-Methylpurine

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Abstract: Information about the geometry and the thermodynamic parameters of molecular stacks in aqueous solution was obtained from the concentration and temperature dependence of the ^1H chemical shift and the relaxation behavior of ^{13}C and ^1H. All diverging association models and assumptions about the stack shift increments which have been proposed in the literature gave an equally good simulation of the chemical shift data. The obtained range of thermodynamic parameter sets was then analyzed by using a description of the relaxation behavior based on the Woessner formalism yielding the selection of an association model and intermolecular proton–proton distances. The predominantly intermolecular character of the proton relaxation within each stack as well as the existence of two distinct association geometries were proved by the change of the relaxation after partial deuteration. The model compounds used for these investigations are 6-methylpurine and 8-deuterio-6-methylpurine.

While numerous reports exist on the measurement of the stacking behavior of molecules on the basis of chemical shifts,[1-8] only a few investigators have used relaxation behavior for the study of the stacking phenomenon.[9-11] The scope of this study was a careful and critical examination of the application of the relaxation data to obtain information about the geometry and the thermodynamics of molecular stacking systems.

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Measurements

^1H and ^{13}C T_1 relaxation times were measured at various field strengths and molar concentrations. The data obtained together with some T_2 and NOE enhancement values are listed in Table I.

Discussion

A three-step approach was used to obtain information about the stacking phenomenon of 6-methylpurine and its deuterated analogue from the relaxation behavior. First, a model was proposed with use of assumptions about the stack structure and the relaxation channels. Next, the ^1H chemical shifts and the ^{13}C relaxation times were fit by a computer program to a theoretical description of the stacking molecular system. This, in turn, gave theoretical values for the relaxation times of the protons. A comparison of these theoretical values with the observed proton relaxation times at different field strengths allowed the determination of a thermodynamic description of the stacks. Finally, the relaxation times of the undeuterated and deuterated 6-methylpurine were compared to gain information about the molecular structure of the stacks.

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Table I. T_1 Relaxation Times[a]

concn, M	MHz		H(2)	C(2)	H(8)	C(8)	CH_3(H)	CH_3(C)
1.450	200/50.28		6.3	0.38	5.9	0.33	0.8	1.5
	100/25.14		5.2	0.31	5.0	0.29	0.6	
1.000	90.51			0.58		0.55		
	200/50.28		7.9	0.51	7.5	0.45	0.8	1.7
	200/50.28	M	9.2	0.50	7.8	4.60		
	200/50.28	D	9.8	0.50		4.60		
	/50.28	η		1.30		1.20		1.4
	/50.28	T_2		0.49		0.40		
	100/		6.5		6.3		0.6	
0.720	200/50.28		9.0	0.55	8.2	0.51	0.9	1.8
	100/		7.7		7.5		0.7	
0.360	200/50.28		12.5	0.78	11.7	0.76	1.1	2.2
	200/50.28	M	15.3	0.79	14.1	6.40		
	200/	D	16.4					
	/50.28	η		1.90		1.50		1.1
	100/		10.6		10.3		0.9	
0.180	200/		17.1	1.04	14.4	1.02	1.2	2.4
	200/	D	18.2					
	100/		14.3		13.7		1.1	
0.090	200/		23.2		19.2		1.6	
	100/		19.0		16.9		1.4	
0.045	200/		28.3		20.0		2.0	
	100/		22.5		19.5		1.8	

[a] All relaxation times are listed in seconds. D: deuterated product, deuteration degree H(8) = 96%, CH_3 = 39%. M: mixture of 70% deuterated product and 30% undeuterated product. H(2) T_1 extrapolated to infinite dilution: 45 s. C(2) T_1 extrapolated to infinite dilution: 6 s.

Theoretical Description of the Stacks. To describe the stacking equilibria, two models are frequently proposed. In both models the association process is assumed to proceed in steps. Both models are commonly modified by including one independent constant for the first step:[2,12-16]

$$a_0 = a_1 + \frac{K(2)}{K} a_1 \left[\frac{1}{(1 - Ka_1)^2} - 1 \right], \quad a_i = K(2)K^{i-2}a_1{}^i \text{—SEK model}$$

$$a_0 = a_1 + \frac{2K(2)}{K} a_1 [e^{Ka_1} - 1], \quad a_i = \frac{2}{i!} K(2)K^{i-2}a_1{}^i \text{—AK model}$$

The chemical shift defined for the kth nucleus depends on

$$\delta_{calcd}(K) = \delta_1(K) + H_r(K)[\delta_\infty(K) - \delta_1(K)];$$
$$H_r(K) = F(2)/\gamma + F(3)$$

$$F(2) = \frac{2}{a_0} \sum_{i=2}^{n} a_i \qquad F(3) = \frac{1}{a_0} \sum_{i=3}^{n} (i-2)a_i \qquad \gamma = \frac{\delta_3 - \delta_1}{\delta_2 - \delta_1}$$

^{1}H chemical shift values of all protons in 6-methylpurine were measured at different concentrations and temperatures.[17] The concentration-independent values in the region of high dilution were interpreted as monomer shifts δ_1. The chemical shift data were fit by a computer program to the two association models (SEK or AK). The equilibrium constants $K(2)$ and K as well as the optical parameter γ and the stackshift δ_∞ were varied during the computer fit. One constraint was that γ and δ_∞ must remain constant for measurements at different temperatures. The calculated values were allowed to deviate from the measured values at most ±3% of the total shift interval $\delta_\infty - \delta_1$ of the respective proton. As can be seen in Figure 1, no unique set of parameters could be selected.

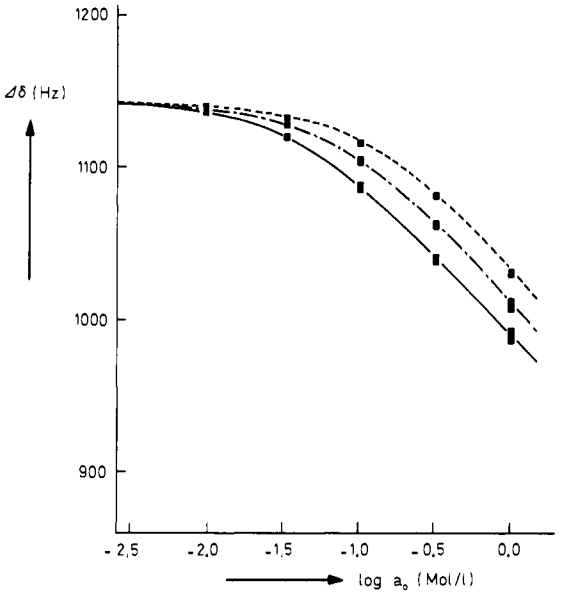

Figure 1. Measured and calculated shifts of 6-methylpurine. H(2) shifts at different temperatures (—, 33 °C; - - -, 55 °C, ···, 79 °C). The squares show the calculated shift values, using six different parameter sets. The parameters used are listed in the order model (optical parameter) K, $K(2)$ at 33 °C/K, $K(2)$ at 55 °C/K, $K(2)$ at 79 °C: SEK (γ = 2) 2.8, 2.5/1.7, 1.7/1.1, 1.1; SEK (γ = 3) 4.0, 4.2/2.7, 2.8/1.8, 1.8; SEK (γ = 5) 6.0, 6.3/3.6, 4.0/2.2, 2.6; AK (γ = 2) 2.4, 7.5/1.7, 4.5/1.0, 3.2; AK (γ = 3) 3.0, 12.0/2.1, 8.0/1.5, 5.0; AK (γ = 5) 4.0, 20.0/2.4, 12.1/1.7, 8.0. The parameters were selected such that the optical parameter and equilibrium constants fit the measured shifts at different temperatures. $\Delta\delta$ + 597.2 Hz is the correction for the shifts to internal Me_4Si.

Calculation of the ^{13}C, ^{1}H Correlation Times. The dipole–dipole mechanism[18] was assumed to be the sole contribution to the relaxation of ^{13}C as well as ^{1}H. We consider this to be reasonable, as no other mechanism can be a significant relaxation channel for the carbon in position 2 and its attached proton.[19] Furthermore, the listed values of the NOE enhancements η indicate that the dipolar mechanism is a major contributor to relaxation.[20] The intramolecular dipole–dipole relaxation of ^{13}C and ^{1}H within the stacks[21] was described by using the well-known Woessner

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(20) The NOE enhancement η = 1.3 for a 1.4 mol solution demonstrates the dependence of the NOE effect on the molecular dynamics.[34]
(21) Due to the fact that the proton relaxation takes place within one individual stack, the term "intramolecular" is used. Also the equations for intramolecular relaxation are employed. Since the lifetime of an individual stack is 8 ns,[12] the definition of one stack as an individual molecule is reasonable.

Table II. Comparison of Calculated T_1 Times and Observed T_1 Times

concn, M		MHz	T_1, m	T_1(calcd) (SEK) $\gamma = 2$	$\gamma = 3$	$\gamma = 5$	T_1(calcd) (AK) $\gamma = 2$	$\gamma = 3$	$\gamma = 5$
1.45	C_2	50.3	0.38	0.39	0.39	0.38	0.38	0.38	0.39
		25.1	0.31	0.33	0.31	0.31	0.35	0.35	0.36
	H_2	200	6.3	8.1	8.0	7.4	7.5	6.9	6.7
		100	5.2	5.4	4.9	4.4	5.6	5.2	4.9
1.00	C_2	90.5	0.58	0.55	0.57	0.57	0.56	0.55	0.53
		50.3	0.51	0.48	0.47	0.48	0.45	0.46	0.48
	H_2	200	7.9	9.6	9.0	8.3	8.9	8.2	7.8
		100	6.5	6.8	6.0	5.3	6.9	6.4	6.2
0.18	C_2	50.3	1.04	1.03	1.02	1.04	1.02	1.02	1.02
	H_2	200	17.1	31.0	24.0	20.0	32.1	27.6	22.0
		100	14.3	29.0	21.0	17.1	28.0	24.1	20.0

[a] The parameter sets used are given in the text.

formalism.[18] The anisotropy of the rotating body was taken into account by using the Perrin integrals.[18,22-24]

$$T_{1i}^{-1} = K(^1\mathrm{H})[J(w_\mathrm{H}) + 4J(2w_\mathrm{H})]$$

$$K(^1\mathrm{H}) = 3/20\gamma_\mathrm{H}^4\hbar^2 r_\mathrm{HH}^{-6}$$

$$T_{1i}^{-1} = K(^{13}\mathrm{C})[J(w_\mathrm{H} - w_\mathrm{C}) + 3J(w_\mathrm{C}) + 6J(w_\mathrm{H} + w_\mathrm{C})]$$

$$J(w) = \sum_1 \frac{C_1\tau_1}{1 + w^2\tau_1^2} \qquad K(^{13}\mathrm{C}) = 1/20\gamma_\mathrm{H}^2\gamma_\mathrm{C}^2\hbar^2 r_\mathrm{CH}^{-6}$$

Calculation of the Average ^{13}C Correlation Time. With respect to the existence of different stack sizes in solution, the association model and the appropriate equilibrium constants, $K(2)$ and K, have been used to calculate the stack distribution.

The geometry of the different stacks was calculated by using 6-methylpurine X-ray data[27] (x,y direction) and a van der Waals radius of each proton valued at 0.12 nm. To allow a small horizontal displacement between adjacent purines within one individual stack which should cause slower rotation diffusion of the associate as compared with a simple vertical stack a variable displacement parameter F was introduced. $r_{x,y}(n) = r_{x,y}(n-1)F$, whereby $r_{x,y}(n)$ represents two radii of the rotational ellipsoid composed of n monomers. F was chosen to be 1.03; this was a necessary adjustment in the simulation of the relaxation data and variations in F did not allow unambiguous fits in combination with thermodynamic parameters. The number of monomers composing the stack of interest was used to determine the third dimension. A value of 0.32 nm was used as the van der Waals thickness of one purine molecule. These three radii of the rotational ellipsoid together with a CH distance of 0.11 nm were used for the calculation of the relaxation rates.

Since relaxation rates add linearly,

$$T_1^{-1} = \sum_i F(i)(a_0)T_{1i}^{-1}(i,a_0)$$

the calculated relaxation rates of the individual stacks, weighted in accordance to their distribution, were summed to give the average relaxation rate. To simplify the calculations, the microviscosity for all different stacks was assumed to be uniform. The value of this microviscosity was obtained by fitting the calculated average T_1 to the measured ^{13}C T_1. Only calculated values which did not deviate from the observed values more than 5% were used. For a few concentrations, T_1 data at three different field strengths were simultaneously used in the fit procedure. In this way the individual correlation times $\tau_{i,1}$ of each associate A_i were obtained.

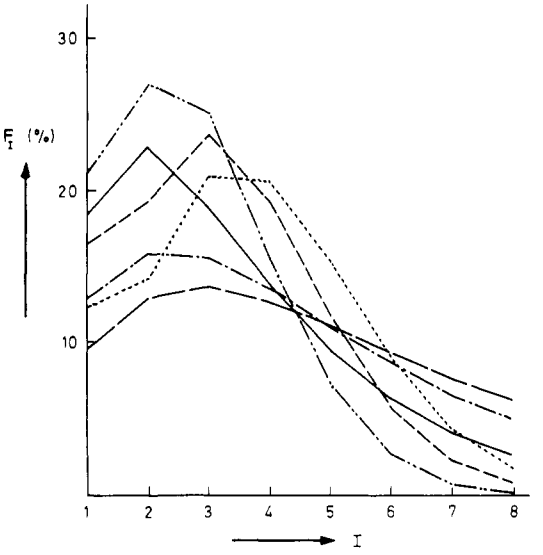

Figure 2. Stack distribution. I = the number of purines/stack; total concentration = 1.00 mol/L; 33 °C; SEK (γ = 2, —); SEK (γ = 3, -·-); SEK (γ = 5, – –); AK (γ = 2, -···-); AK (γ = 3, - - -); AK (γ = 5, ···). The equilibrium constants used for the calculation are listed in the order model (optical parameter) K, $K(2)$: SEK (γ = 2) 2.8, 1.5; SEK (γ = 3) 4.0, 4.2; SEK (γ = 5) 6.0, 6.3; AK (γ = 2) 2.4, 7.5; AK (γ = 3) 3.0, 12.0; AK (γ = 5) 4.0, 20.0 F_i is the percentage of molecules in the different stacks.

Calculation of the Average ^{1}H Relaxation Times. With use of the stack distribution function which depends on the choice of the association model (SEK or AK) and the equilibrium constants ($K(2)$ and K) as well as the correlation times $\tau_{i,1}$, the ^{1}H relaxation times were calculated. From these values we draw the following conclusions: (1) the mean distance between the proton at position 2 and its neighbor must be approximately 0.34 nm, otherwise the deviation between the measured T_1 and calculated T_1 is too large. The results from computer simulations with use of different H–H distances demonstrate that the ^{1}H relaxation can only be explained if a highly ordered structure is present.

MHz	T_1(obsd)		H–H 0.35 nm	0.35 nm	0.39 nm
200	6.3	T_1(calcd)	6.7	8.2	12.2
100	5.2	T_1(calcd)	4.9	6.1	9.2

calculation using the AK model, $\gamma = 5$

(2) The AK model gives the best theoretical fit to the ^{1}H relaxation

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(24) T_{1i}^{-1} is the relaxation rate of the ith stack, $J(w)$ is the spectral density function corresponding to a frequency w, γ is the gyromagnetic ratio, τ_1 are components of the correlation time, and C_1 are components of the orientation of the relaxation vector (C–H or H_2–H_2) within the coordinate system of the rotational ellipsoid formed by the compound of interest. The different τ_1 values are a combination of the main diffusion[18,22,23] constants. τ_1 contains information about the dynamic behavior of the molecule in solution in terms of microviscosity[25,26] and geometry.
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times measured at various concentrations of 6-methylpurine. (3) This procedure for interpreting the relaxation data is very sensitive to the various parameters of association, diffusion geometry, and relaxation vectors which yields very unambiguous fits of parameter sets.

A comparison between measured and calculated values is shown in Table II.

Comparison between Deuterated and Undeuterated 6-Methylpurine. In a mixture composed of 70% 8-deuterio-6-methylpurine and 30% undeuterated 6-methylpurine the relaxation times of H(2) and H(8)[28] are longer than the values in the undeuterated compound (Table I). From these results we conclude that neither head-to-head nor head-to-tail alignment of purine molecules is exclusively formed. With the assumption that the stack is arranged vertically, the number of head-to-head and head-to-tail alignments should be approximately equal. In comparison to the various proposed stack structures of purine, our results for 6-methylpurine are in agreement with those of Jardetzky[1,8] and with the "parallel model" proposed by Cheng.[2] Our results, however, do not support models which assume an intermolecular H_2–H_2 distance greater than 0.35 nm.[2,7]

Summary

We believe that relaxation time measurements of undeuterated self-associating compounds and the mathematical treatment of the relaxation and chemical shift data described in this paper are useful tools in studying stacking phenomena. Use of both relaxation time measurements and chemical shift measurements eliminates uncertainties in the thermodynamic calculations. In addition, from the relaxation behavior of the stacks, the structure of the molecular stacks can be deduced.

Experimental

6-Methylpurine (Sigma M6502) was used without further purification. All measurements were carried out at 33 °C in ^2H_2O (Ega 99,8% 15, 188-2)[29] unless otherwise stated. The 8-deuterio-6-methylpurine was prepared by using the method in reference 13 and twice recrystallized from water. The T_1 relaxation times were measured by using the inversion recovery method;[30] the mean deviation of the T_1 values was 5%. The T_2 relaxation times were measured by the Carr–Purcell–Meiboom–Gill method;[31] the mean deviation of the T_2 values was 10%. Me_2SO was used as an external chemical shift standard, and subsequently the chemical shifts were corrected to internal Me_4Si. The temperature of the sample in the probe was measured by a thermocouple placed in the solution. Most measurements were performed on a Varian XL 200 NMR spectrometer, put to our disposal by the "Fonds zur Föderung der wissenschaftlichen Forschung", which is thankfully appreciated by us. The ^1H and ^{13}C measurements at 100 and 25.1 MHz were performed on a Varian HA 100 D modified for FT mode by Digilab Inc. The ^{13}C measurements at 90.5 MHz were done on a Bruker WH 360 NMR spectrometer by Dr. N. Müller, Institut für Organische Chemie, J.K. Universität Linz, to whom we are indebted.

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Registry No. 6-Methylpurine, 2004-03-7; 8-deuterio-6-methylpurine, 13479-71-5.

(28) The difference in the relaxation times of H(8) and H(2) is due to the fact that proton H(8) can be relaxed by the neighboring N–H group by the scalar coupling relaxation mechanism. The existence of this additional mechanism can be demonstrated by measuring the T_1 of 6-methylpurine dissolved in ^1H_2O (1 M, 33 °C). The relaxation time of H(2) is slightly reduced to 7.1 s, whereas the T_1 of H(8) changes to 5.7 s. Addition of HCl (pH 2 in the solution) leads to a further increase of the H(8) relaxation rate (T_1 = 5.6). There is little effect on the relaxation time of H(2).

(29) The influence of traces of HDO in the solvent and NH–ND exchange was not explicitly taken into account. It certainly leads to a small acceleration of the relaxation rate.

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Photoprocesses in Photosystem I Model Systems†

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Abstract: Photoprocesses in covalently linked bis(pyrochlorophyllide *a*) ethylene glycol diester molecules have been investigated by laser absorption and fluorescence techniques. Solvent interactions significantly alter the photochemical properties of the linked macrocycles. In toluene/ethanol solution the linked pairs fold into a configuration with optical properties that resemble those of the special pair chlorophyll (P700) of photosystem I of green plants. Photoexcitation of the model system results in the formation of an S_1 state. This excited state returns to the ground state primarily by fluorescence and internal conversion. Under appropriate excitation conditions stimulated (laser) emission is observed. Long (30 ns) excitation pulses produce significant triplet populations. The configuration and possible reactions involving this triplet are discussed. In contrast, the folded pairs in methylene chloride/ethanol solution exhibit an unusually short fluorescence lifetime and a correspondingly low quantum yield. Some of the anomalous behavior of the folded pairs photoexcited in methylene chloride are shown to result from differences in ground-state structure and composition. Rapid internal conversion processes prevent the build-up of a significant excited-state population in this solvent system. It is suggested that the internal conversion process responsible for the lifetime shortening involves the formation of charge-transfer states.

The primary light energy conversion events of photosynthesis begin with the absorption of a photon by one of a large assemblage of light-harvesting (antenna) chlorophyll molecules. This is then followed, on a short time scale, by transfer of the light-induced electronic excitation energy through the antenna to a photoreaction center where the excitation energy is trapped by a very few chlorophyll molecules in which charge separation occurs.[1] The photoreaction center and its associated pigment system in green

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(1) Clayton, R. K. "Photosynthesis: Physical Mechanisms and Chemical Patterns"; Cambridge University Press: Cambridge, 1980; Chapter 2, pp 19–50.

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