Structural Studies of the Bisimidazole 5,5-Dimethyl-1,3,2-Dioxaphosphorinane-2-Thioxo-2-Hydroxy Complex

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The molecular complex of imidazole (Im) with 5,5-dimethyl-1,3,2-dioxaphosphorinane-2-thioxo-2-hydroxy acid (DPTHA) involves strong (O−H···H and N·H⁺···N) and weak (C−H···O and C−H···S) hydrogen bonds and has an unusual molecular packing. The crystals are monoclinic, space group $I2/m$, with $a = 10.609(5)$ Å, $b = 11.1739(2)$ Å, $c = 14.069(7)$ Å, $\beta = 95.47(2)°$, $V = 1660.1(11)$ Å^3, $Z = 8$, $D_c = 1.274$ g/cm^3, $F(000) = 672$, and $\mu = 2.760$ mm^{-1}. A comparison of ^{13}C CP/MAS NMR data for imidazole and the Im···H⁺···Im cation shows that the ^{13}C isotropic chemical shifts of the C4 and C5 carbons, and of the δ_{22} and κ parameters for C2 carbons for each compound are different. GIAO calculations at the HF/6-311⁺G(2d,p)//B3LYP/6-31G* level reveal correlations between the differences in the ^{13}C chemical shift between the C4 and C5 atoms, the values of δ_{22} and κ for the C2 carbon, and the N···H⁺ distance. An analysis of ^{13}C chemical shift parameters provides information about the strength of the hydrogen bonds and the localization of the proton in the N···H⁺···N linkage.

Introduction

Through their unique catalytic properties, imidazole and the imidazolium ion play an important role in many biological processes.[1] As imidazole is a strong base and the imidazolium ion a strong acid, the two species can act as base or acid catalysts.[2] Since the imidazole ring is present in its side chain, histidine, imidazole and its derivatives are often used to model the mechanism of enzymatic catalysis and the nature of hydrogen bonding.[3] There is also much interest in the interactions of imidazole with organophosphorus compounds. Imidazole is responsible for the cleavage of RNA.[4] Holmes et al. studied complexes of imidazole with phosphoric acid to examine the ability of the compound to form hydrogen bonds.[5] The structure of thiophosphoric acid derivatives with imidazole in terms of hydrogen bonding[6] and the influence of P=O···H−N intermolecular contacts on the molecular packing[7] have also been considered. The discovery of an unusually small intermolecular nitrogen−nitrogen distance in the N(3)···H⁺···N(3) linkage in the imidazole···H⁺···imidazole cation prompted us to examine the relationship between the strength of intermolecular hydrogen bonds and the chemical shift parameters of imidazole and bisimidazole DPTHA complex **1** using X-ray diffraction, solid-state NMR, and quantum mechanical computational techniques.

Methods for computing magnetic shielding are continuing to improve. IGLO (individual gauge for localized orbitals) and LORG (local orbitals-local origins) give satisfactory magnetic shielding even with modest basis sets,[8,9] and GIAO (gauge including atomic orbitals) is now efficiently implemented.[10] The introduction of the density functional theory (DFT) for calculating magnetic shieldings greatly extended the size of molecules which could be studied with the inclusion of electron correlation effects.[11] The application of these methods to NMR studies of nitrogenous heterocyclic compounds has recently been discussed.[12] Comparing experimental results with the results of GIAO calculations, we show that GIAO can identify changes in ^{13}C shielding parameters in the Im···H⁺···Im complex with sufficient accuracy. The ^{13}C chemical shift parameters can be used to estimate the distance between the N3 and H⁺ centers.

Experimental Section

X-ray Diffraction. Single-crystal diffraction data (Table 1) were collected using an Enraf-Nonius CAD-4 diffractometer.[13] Atomic coordinates, thermal factors, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.[14]

Solid-state NMR. ^{13}C magic-angle-spinning (MAS) NMR spectra with ^{1}H−^{13}C cross-polarization (CP) were recorded on a Bruker MSL-300 spectrometer at 75.46 MHz with high-power proton decoupling. Powdered samples of complex **1** and imidazole were spun in MAS rotors at 2.5−10 kHz. The field strength for ^{1}H decoupling was 1.05 mT, contact time 5 ms, repetition 10 s, and spectral width 25 kHz. We acquired 8K data points with 2K scans to achieve a reasonable signal-to-noise ratio. ^{13}C chemical shifts were measured indirectly by reference to the carbonyl glycine line set at 176.34 ppm. The

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TABLE 1: Crystal and Structure Refinement for Bisimidazole 2-Hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-sulfide 1

chemical formula	$0.5\ [(C_5H_{10}O_3PS)^-(2x\ C_3H_{4.5}N_2)^+]$
formula weight	2×159.17
temperature	293(2) K
crystal system	monoclinic
space group	*I* 2/*m*
unit cell dimensions	
a	10.609(5) Å
b	11.173(2) Å
c	14.069(7) Å
α	90.00°
β	95.47(2)°
γ	90.00°
volume	1660.1(11) Å^3
Z	8
crystal size	$0.6 \times 0.5 \times 0.45$ mm
density (calculated)	1.274 Mg/m^3
absorption coefficient	2.760 mm^{-1}
F (000)	672
Θ range for data collection	5.00−77.48°
index range	$0 \le h \le 13,\ -14 \le k \le 0,$ $-17 \le l \le 17$
reflections collected	1931
independent reflections	1835 [*R*(int)= 0.0335]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1832/0/107
goodness-of-fit on F^2	1.161
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0525, wR2 = 0.01104
R indices (all data)	R1 = 0.0910. wR2 = 0.1563
extinction coefficient	0.0084 (4)
largest diffraction peak and hole	0.441 and −0.462 eÅ^{-3}

TABLE 2: Bond Lengths [Å] and Bond Angles [deg] for Complex 1

P1−O1	1.492(3)	C1−C2−C3	110.5(5)
P1−O2	1.592(3)	C1−C2−C4	108.5(5)
P1−S1	1.953(2)	C3−C2−C4	108.9(7)
O2−C1	1.441(4)	C2−C3−H3A	110.4(2)
C1−C2	1.508(5)	C2−C3−H3B	107.9(4)
C1−H1A	0.96	H3A−C3−H3B	110.7
C1−H1B	0.96	C2−C4−H4A	106.7(6)
C2−C1	1.508(5)	C2−C4−H4B	110.7(3)
C2−C3	1.519(11)	H4A−C4−H4B	107.4
C2−C4	1.530(10)	C2I−N1I−C5I	108.1(3)
C3−H3A	0.96	C2I−N1I−H1IN	125.9(2)
C3−H3B	0.95	C5I−N1I−H1IN	126.0(2)
C4−H4A	0.96	C2I−N3I−C4I	106.7(3)
C4−H4B	0.96	C2I−N3I−H3IN	125.4(4)
N1I−C2I	1.324(5)	C4I−N3I−H3IN	127.9(4)
N1I−C5I	1.353(5)	C5I−C4I−N3I	108.7(4)
N1I−H1IN	0.90	C5I−C4I−H4I	126.1(3)
N3I−C2I	1.309(6)	N3I−C4I−H4I	125.2(2)
N3I−C4I	1.364(6)	C4I−C5I−N1I	106.5(4)
N3I−H3IN	1.337(3)	C4I−C5I−H5I	127.6(3)
C4I−C5I	1.335(5)	N1I−C5I−H5I	125.9(2)
C4I−H4I	0.96	N3I−C2I−N1I	110.0(4)
C5I−H5I	0.96	N3I−C2I−H2I	124.6(2)
C2I−H2I	0.96	N1I−C2I−H2I	125.4(2)
O1−P1−O2	106.04(13)	C4I−N3I−H3IN	127.9(4)
O2−P1−O2	102.0(2)	C5I−C4I−N3I	108.7(4)
O1−P1−S1	118.0(2)	C5I−C4I−H4I	126.1(3)
O2−P1−S1	111.70(10)	N3I−C4I−H4I	125.2(2)
C1−O2−P1	117.4(2)	C4I−C5I−N1I	106.5(4)
O2−C1−C2	111.1(4)	C4I−C5I−H5I	127.6(3)
O2−C1−H1A	109.1(2)	N1I−C5I−H5I	125.9(2)
C2−C1−H1A	110.4(3)	N3I−C2I−N1I	110.0(4)
O2−C1−H1B	110.1(2)	N3I−C2I−H2I	124.6(2)
C2−C1−H1B	107.6(4)	N1I−C2I−H2I	125.4(2)
H1A−C1−H1B	108.5		
C1−C2−C1	109.8(5)		

principal elements of the ^{13}C chemical shift tensor and shielding parameters were calculated with the WIN-MAS program.[15] Details of the method and calculation accuracy are discussed elsewhere.[16,17] The principal components δ_{ii} of the shielding tensor were used to calculate the shielding parameters: span Ω and skew κ.[18]

Computational Methods. Ab initio calculations for imidazole, protonated imidazole and the complexes were performed using standard techniques[19] as implemented in the Gaussian 94 package[20] running on a Silicon Graphics Power Challenge computer. Geometries were optimized using the B3LYP hybrid density functional method[21] with the 6-31G*-polarized basis set. All structures were identified by frequency calculations as corresponding to true local minima on the potential energy surface.

Results and Discussion

X-ray Crystallography of the Bisimidazole DPTHA Complex. Crystallographic data for bisimidazole/DPTHA complex **1** are given in Table 1. Selected geometric parameters are given in Table 2, Figure 1 shows a perspective drawing with the atom numbering scheme, and Figure 2 shows the molecular packing. Two imidazole rings are located very close to each other in the face-to-face orientation and the proton is disordered between the center of symmetry. The distance between the N3 and N3i atoms is 2.673(6) Å. The simultaneous presence of three different types of intermolecular hydrogen bonds is an interesting feature of the structure. The P−O···H−N1i bond (2.866(4) Å, 167°) between the thiophosphoryl group and imidazole, as well as the weak P−O···H−C2 bond (3.313(5) Å, 135°) between the thiophosphoryl group and imidazole, are accompanied by a highly unusual very weak P=S···H−C4 bond (3.856(5) Å, 159°). Because of these intermolecular interactions, the thiophosphoric acid is enclosed in a cage formed by the imidazole molecules. A search of the Cambridge Structural Data Centre, and a comparison of the molecular packing of **1** with that of other organophosphorus-imidazole complexes revealed that the
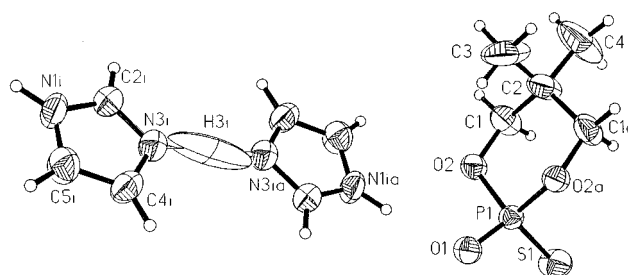

Figure 1. Thermal ellipsoidal view (50% probability) and atom numbering scheme for complex **1** in the asymmetric part of the unit cell.

structure is unique. We note that the structure of an imidazole···H$^+$···imidazole complex obtained by treating imidazole with perchloric acid has been reported.[22]

Solid-state NMR. The aliphatic part of the ^{13}C CP/MAS spectrum of **1** recorded at room temperature with MAS at 10 kHz (Figure 3(a)) contains lines from methyl groups (at 18.9 and 20.5 ppm), quarternary carbon (32.0 ppm) and methylene carbons (73.0 and 75.1 ppm). The aromatic region contains three imidazole resonances at 136.2 ppm (C2), 122.2 ppm (C4), and 118.8 ppm (C5).

At slow (2.5 kHz) MAS the isotropic lines of C2, C4, and C5 carbons are flanked by spinning sidebands caused by the large chemical shift anisotropy (Figure 3b). The principal components of the ^{13}C chemical shift tensor were calculated from sideband intensities using the Berger−Herzfeld method.[15−17] All carbons in imidazole are directly bonded to ^{14}N ($I = 1$), and the usual MAS line shape for the isotropic line of a spin $I = 1/2$ nucleus bonded to a $I = 1$ nucleus with a large electric
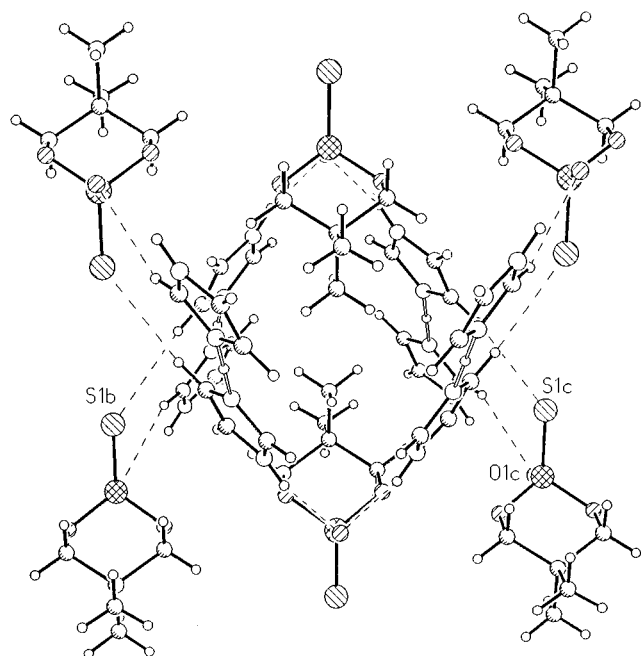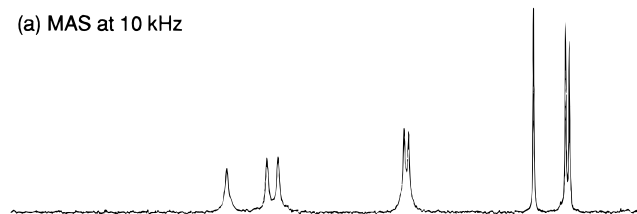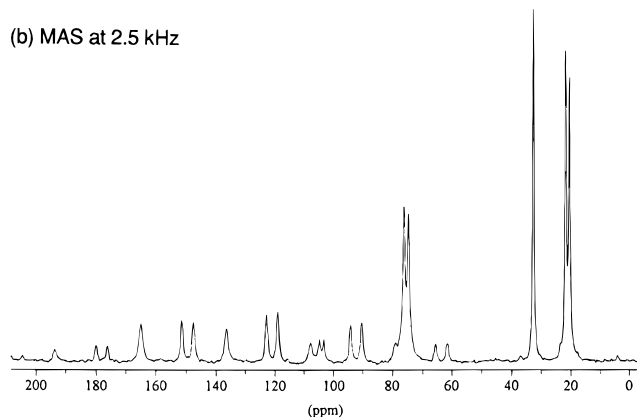
Figure 2. Molecular packing of complex **1**.

$^1H - ^{13}C$ CP/MAS NMR

(a) MAS at 10 kHz

(b) MAS at 2.5 kHz

Figure 3. $^1H-^{13}C$ CP/MAS NMR spectra of complex **1** recorded with spinning at (a) 10 kHz and (b) 2.5 kHz. Line broadening of 10 Hz was used.

field gradient (EFG) is an asymmetric doublet.[23,24] The effect is magnetic field dependent. The line shape strongly depends on the orientation of the EFG with respect to the molecular frame.[25] In our case, the line width at half-height of the ^{13}C CP/MAS NMR spectrum is 100 Hz. We thus conjecture that the quadrupolar interaction only broadens the ^{13}C resonances and the splitting is in the range 100–150 Hz. The influence of the neighboring ^{14}N nuclei on the ^{13}C lines in the solid-state spectra of imidazole and its derivatives has been discussed in detail.[26] The conclusion was that at 7.05 T the role of both the dipolar and quadrupolar interactions on the ^{13}C resonance is negligible. With this proviso, the calculated values of the

TABLE 3: ^{13}C NMR Chemical Shift Tensor Parameters for Imidazole[a] and Complex 1[b] and ^{31}P NMR Parameters for Complex 1

nucleus	carbon	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	Ω (ppm)	κ
^{13}C	C2[a]	136.2	210	142	56	154	0.11
	C4[a]	126.7	208	122	51	157	−0.09
	C5[a]	115.2	193	118	34	159	0.05
^{13}C	C2[b]	136.7	200	160	50	150	0.47
	C4[b]	122.7	190	127	50	140	0.09
	C5[b]	118.8	188	123	46	142	0.09
^{31}P		40.8	121	88	−87	208	0.68

[a] The error in δ_{11}, δ_{22}, and δ_{33} is estimated at ±2 ppm and the error in δ_{iso} at ±0.2 ppm. [b] Principal components of the chemical shift tensor are defined as $\delta_{11} > \delta_{22} > \delta_{33}$. Isotropic chemical shift is $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, span is $\Omega = \delta_{11} - \delta_{33}$, and skew is $\kappa = 3(\delta_{11} - \delta_{iso})/\Omega$.

$^1H - ^{13}C$ CP/MAS NMR
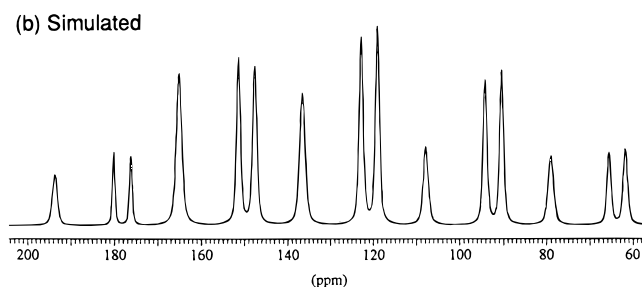
(a) Experimental
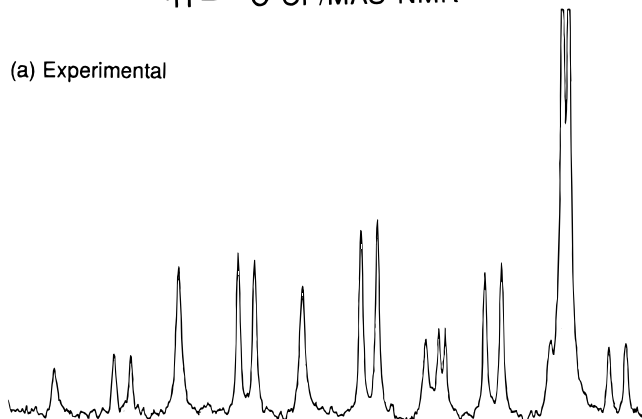
(b) Simulated

Figure 4. (a) Aromatic part of the spectrum in Figure 3b. (b) Spectral simulation using WIN-MAS.

principal tensor elements δ_{ii}, as well as chemical shift parameters for **1**, are given in Table 3. Figure 4 shows the experimental and calculated spectra of **1** in the aromatic region.

The comparison of ^{13}C NMR data for the imidazole-H^+–imidazole cation and imidazole (Table 3) reveals that (i) the difference in ^{13}C isotropic values between C4 and C5 atoms for the former compound is only 3.7 ppm compared with 11.5 ppm for imidazole; (ii) in complex **1** the skew κ for C2 carbon is over four times larger than in imidazole whereas it is similar for other carbons; (iii) the protonation of imidazole causes a significant increase of δ_{22} for C2, while the values for other carbons are similar.

The ^{31}P solid-state NMR spectrum for **1** may be examined in terms of the influence of the strong P−O···H−N1 hydrogen bond and the weak hydrogen bonds (P−O···H−C4− and P=S···H−C5−) on the local environment of phosphorus. The values of δ_{ii} for ^{31}P are given in Table 3. However, a comparison of ^{31}P data for **1** with other salts of DPTHA does not reveal significant differences.[27] The electronic environment of the phosphorus center is presumably dominated by the

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SCHEME 1: B3LYP/6-31g*-Optimized Structures of Imidazole, Protonated Imidazole, and Their Complexes with Ammonia

SCHEME 2

A. Lowest energy structure

B. Transition state structure
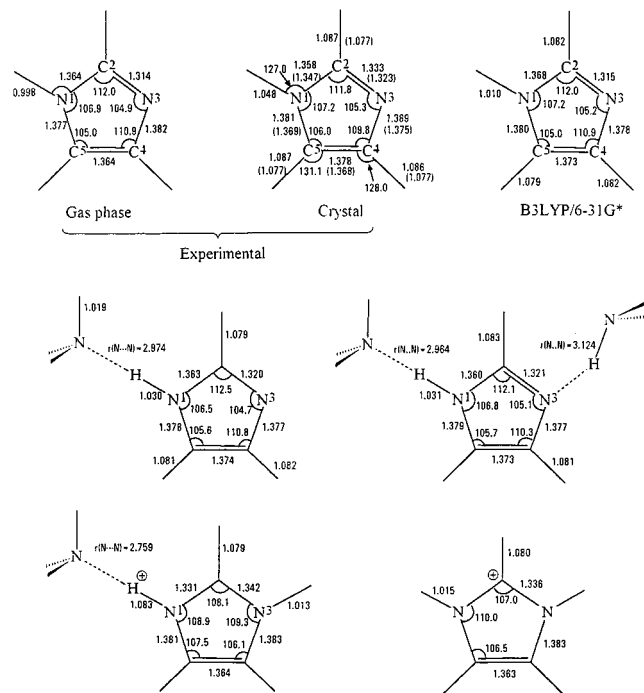
presence of the six-membered ring and by the ionic character of the P(S)O$^-$ residue. Hence, the influence of intermolecular interaction on δ_{ii} is not observed for ^{31}P.

GIAO Calculations. The geometry of imidazole and its derivatives has been extensively studied by different computational methods.[28,29] The chemical shift parameters were studied by IGLO[30] and GIAO.[31,32] The influence of intermolecular interactions on NMR chemical shift parameters in complex imidazole 2(H$_2$O) has also been considered. The purpose of our calculations was to answer two questions: (i) Is it possible to correlate the ^{13}C chemical shift difference between the C4 and C5 atoms ($\Delta\delta$C4C5) with the N$\cdots$H$^+$ distance? (ii) Are the different values of δ_{22} and κ for the C2 carbon in complex **1** and imidazole casual or do they represent a general tendency? If there is a positive answer to these questions, a simple analysis of ^{13}C chemical shift parameters could provide insights into the strength of hydrogen bonding and localization of the proton in the N$\cdots$H$^+\cdots$N unit. Such information is normally not easily available. Geometries of model species shown in Scheme 1 were optimized by means of the B3LYP/6-31G* method,[20,33] and the calculated equilibrium geometry of imidazole is in excellent agreement with the experimental results.

The neutron diffraction structure of imidazole differs slightly from that in the gas phase,[34,35] due to intermolecular interactions (mainly hydrogen bonding) in the crystal network. Imidazole crystallizes in the space group *P*2$_1$/*c* with four molecules in the unit cell and one molecule as an asymmetric unit. The N$-$H$\cdots$N intermolecular bonds of 2.86 Å form a chain of molecules along the *c* axis.[36] Since magnetic shielding is sensitive to even very subtle changes in molecular geometry, we have optimized the structures of model hydrogen complexes of imidazole, Im(NH$_3$), and Im(NH$_3$)$_2$, hoping that the binding parameters of the imidazole ring in these species would be similar to those in solid imidazole. Indeed, the calculated geometries of these complexes reflect the geometry of imidazole in the solid-state better than the calculated geometry of the isolated molecule. The ^{13}C shieldings were calculated with
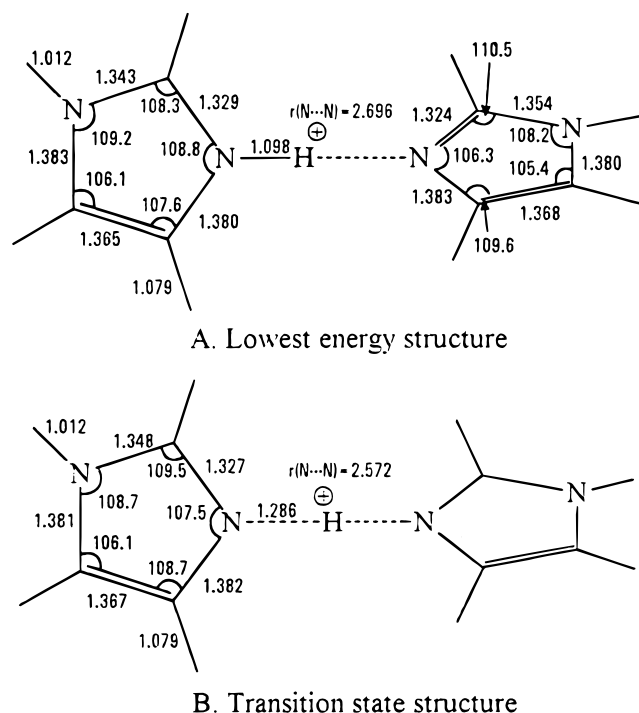
GIAO at the HF/6 311$^+$G(2d,p) level using B3LYP/6-31G* geometries.[37] The use of the B3LYP/6-311$^+$G(2d,p) method was also considered,[38] but the ^{13}C GIAO magnetic shielding tensors for imidazole obtained by this method were inferior compared to those obtained at the Hartree$-$Fock level. Using B3LYP/6-311$^+$G(2d,p), the absolute isotropic shielding σ_{iso} for C2, C4, and C5 is 44.5, 46.3, and 65.3 ppm, respectively, while HF/6-311$^+$G(2d,p) gives 46.5, 55.9, and 73.4 ppm, respectively. The difference of 1.8 ppm between σ_{iso} for C2 and C4 with B3LYP/6-311$^+$G(2d,p) is not consistent with the experimental results.

The HF GIAO method gives σ_{iso} values higher by ca. 10 ppm than those found experimentally in the liquid and solid phases. However, our results are consistent with the values of Schindler,[30] obtained using IGLO with two different basis sets, DZ and II. We have chosen the HF/6-311$^+$G(2d,p) method, as we are interested in the *relative* values of the NMR parameters. The relationship between the magnetic properties of the hydrogen complexes of imidazole and the strength of the hydrogen bond was determined by calculations performed on B3LYP-optimized geometries of the Im$\cdots$H$^+\cdots$Im and Im-H$^+$$-NH_3$ complexes. In a series of calculations performed for each complex, the skeleton of the molecule remained unchanged, and only the length of the N$-$H hydrogen bond was varied. We have assumed that the N$\cdots$H$^+\cdots$N bridge is linear. The N$-$H bond length was taken as an approximate measure of hydrogen bond strength. For the Im$\cdots$H$^+\cdots$Im complex the transition state structure was calculated using the TS option implemented in Gaussian 94 (Scheme 2).

Calculations reveal minor changes in the geometry of the transition state compared to that based on the ground-state structure, where the proton is moved to the central position between the two rings. These changes are also reflected in the NMR calculations. For the molecule optimized in the transition state the carbons C2 and C2′, C4 and C4′, and C5 and C5′ in both imidazole rings are magnetically equivalent, while in the modified "ground-state" molecule they are slightly inequivalent. However, the differences in the calculated ^{13}C chemical shifts

TABLE 4: ^{13}C NMR Chemical Shift Tensor Parameters Calculated by GIAO for Im···H$^+$···Im with Different N···H$^+$ Distances^a

carbon	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	Ω	κ	$\Delta\delta_{(C4-C5)}$ (ppm)	$d_{(N-H)}$ (Å)
C2	146.55	216.06	176.57	48.18	167.88	0.54		
C4	127.72	219.23	128.13	35.79	183.44	0.01	2.13	1.098
C5	125.59	216.84	122.51	37.36	179.48	−0.05		
C2′	147.45	231.06	156.34	54.91	176.15	0.15		
C4′	132.33	223.26	131.06	42.61	180.65	−0.02	7.37	1.598
C5′	124.96	218.21	120.35	36.33	181.88	−0.08		
C2	146.40	218.60	172.73	47.86	170.74	0.46		
C4	128.37	219.57	129.15	36.40	183.17	0.01	3.00	1.190
C5	125.37	216.58	122.11	37.42	179.16	−0.05		
C2′	147.44	228.20	160.21	53.90	174.30	0.22		
C4′	131.67	222.06	131.50	41.45	180.61	0.00	6.46	1.506
C5′	125.21	218.52	120.74	36.15	182.61	−0.07		
C2	146.30	220.24	170.32	48.36	171.88	0.42		
C4	128.80	219.99	129.66	36.74	183.25	0.01	3.53	1.240
C5	125.27	216.50	121.83	37.48	179.02	−0.06		
C2′	147.20	226.51	162.66	53.32	173.19	0.27		
C4′	131.27	221.34	131.40	41.06	180.28	0.02	5.98	1.456
C5′	125.29	218.52	121.26	36.08	182.44	−0.07		
C2	146.12	224.20	164.63	49.50	174.70	0.32		
C4	129.83	221.42	130.54	37.55	183.87	0.01	4.73	1.348
C5	125.10	216.48	121.15	37.70	178.78	−0.07		
C2′	147.72	222.64	168.50	52.02	172.62	0.36		
C4′	130.33	219.84	131.02	40.15	179.69	0.01	4.97	1.348
C5′	125.36	218.23	121.86	35.99	182.24	−0.06		
C2	146.86	223.67	166.54	50.37	173.30	0.34		
C4	129.77	220.60	130.53	38.19	182.41	0.01		
C5	125.37	217.31	121.66	37.14	180.17	−0.06	4.40	1.286
C2′	146.86	223.59	166.57	50.36	173.29	0.34		
C4′	129.77	220.59	130.52	38.14	182.45.	0.01		
C5′	125.37	217.31	121.66	37.14	180.17	−0.06		

^{a} The N···H$^+$···N distance was assumed to be constant at 2.696 Å. Data are converted from the absolute shielding values σ_{ii} to the relative chemical shift δ_{ii} (see text).

TABLE 5: ^{13}C NMR Chemical Shift Tensor Parameters Calculated by GIAO

carbon	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	Ω	κ	$\Delta\delta_{(C4-C5)}$ (ppm)	$d_{(N-H)}$ (Å)
C2^a	146.34	237.87	140.62	60.52	177.35	−0.10	17.45	
C4^a	136.29	227.14	133.98	47.77	179.37	−0.04		
C5^a	118.84	211.17	110.64	34.71	176.46	−0.14		
C2^b	149.83	238.73	151.06	59.68	179.05	0.02	16.42	
C4^b	135.37	226.67	132.17	47.26	179.41	−0.05		
C5^b	118.97	210.64	109.83	36.44	174.20	−0.16		
C2^c	145.52	231.58	152.69	52.29	179.29	0.12	5.92	1.67
C4^c	131.42	224.38	130.16	39.73	184.65	−0.02		
C5^c	125.50	217.53	121.16	37.81	179.72	−0.07		
C2^c	146.13	216.02	174.89	47.47	168.55	0.51	1.36	1.18
C4^c	127.28	217.92	127.67	36.25	181.67	0.01		
C5^c	125.92	217.24	123.46	37.09	180.15	−0.04		
C2^d	147.67	210.14	186.80	46.07	164.07	0.72	0	
C4^d	127.01	219.41	124.97	36.66	182.75	−0.03		
C5^d	127.01	219.41	124.97	36.66	182.75	−0.03		

^{a} Imidazole−NH$_3$ complex. ^{b} Imidazole−2NH$_3$ complex. ^{c} Imidazole−H$^+$−NH$_3$ for different N···H$^+$ distances. ^{d} Imidazole cation.

for both molecular geometries are less than 1 ppm: 0.8 ppm for C2, C2′ and less than 0.5 ppm for C4, C4′, C5, and C5′ (Table 4). The results of the calculations are thus sufficiently precise to confirm a correlation between the magnetic properties and the strength of the hydrogen bond.

The results for the Im···H$^+$···Im complex are listed in Table 4. The data have been converted from the absolute shielding values σ_{ii} to the relative chemical shift δ_{ii} (from TMS) using the relationship $\delta_{ii} = 192.7 - \sigma_{ii}$, to make the changes of experimental values (192.7 ppm−^{13}C shielding of TMS carbons at HF/6-311$^+$G(2d,p)//B3LYP/6-31G*) easy to follow.

Figure 5a shows a linear correlation between the N···H$^+$ distance and the difference in isotropic chemical shifts among C4 and C5 ($\Delta\delta$C4C5). $\Delta\delta$C4C5 decreases with the decreasing length of the N···H$^+$ intermolecular contact (stronger hydrogen bond). This is understandable given that $\Delta\delta$C4C5 = 0 for the

imidazolium cation. Figure 5(b) also shows a linear relationship between the N···H$^+$ distance and δ_{22} for the C2 carbon. This can be explained by the orientation of the principal elements of the chemical shift tensor with respect to the molecular frame of imidazole: δ_{22} is aligned in the plane of the C−N bond and the most significant changes of geometric parameters during protonation are related only to the C2 center. In consequence, we observe distinct values of δ_{22} in a series of calculated structures. The third relationship, between the N···H$^+$ distance and κ (Figure 5c), is obvious given that $\kappa = 3(\delta_{22} - \delta_{iso})\Omega_{34}$.

Table 5 shows the results of GIAO calculations for imidazole···H$^+$···NH$_3$ complexes for different distances. The results are consistent with those reported for **1** and follow the same trend. We conclude, therefore, that the correlation between the ^{13}C NMR parameters of imidazole and the position of the proton are likely to be applicable to other systems. A search
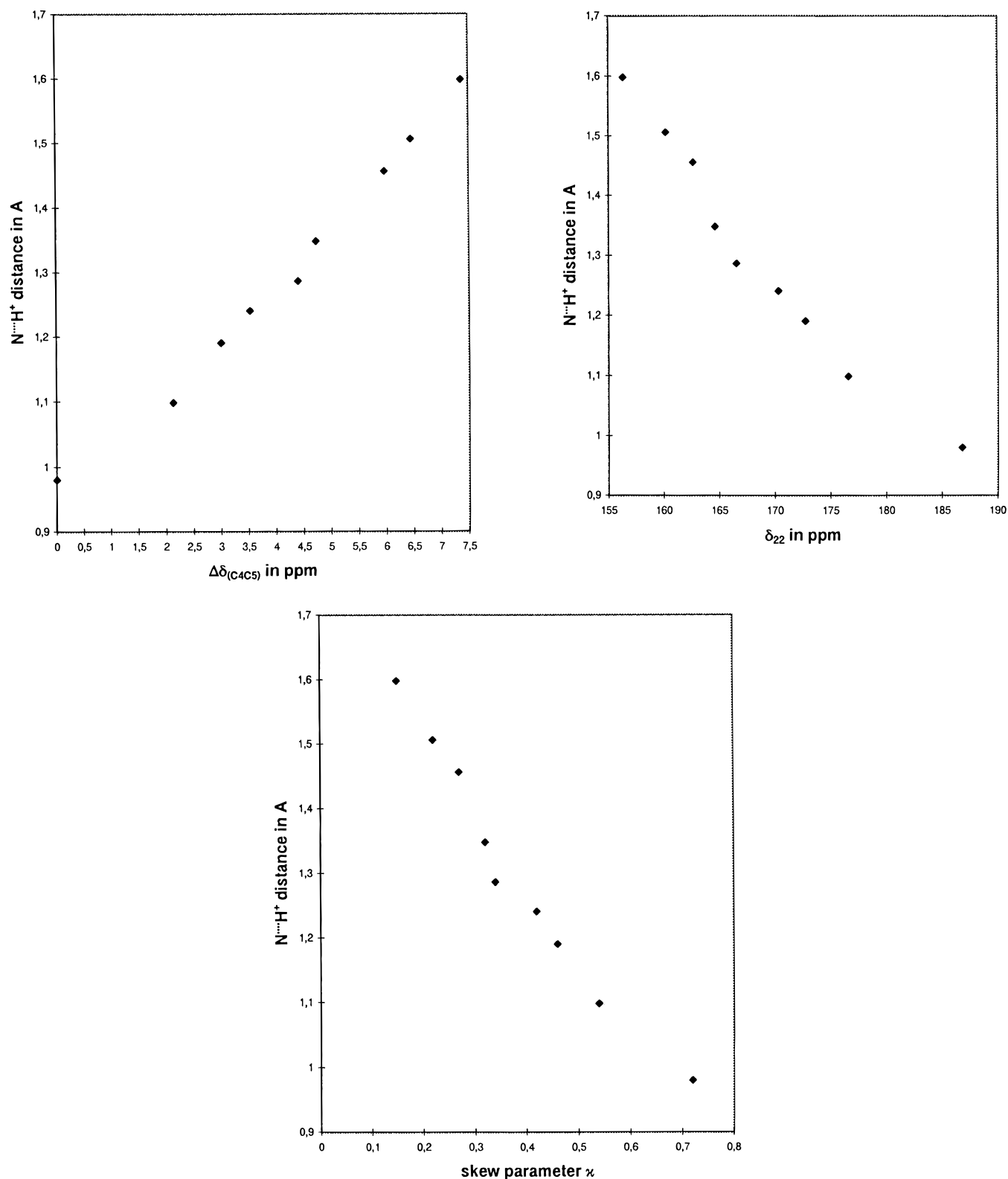
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Figure 5. Correlations between the N···H$^+$ distance and (a) $\Delta\delta$C4C5, (b) δ_{22}, and (c) κ for Im···H$^+$···Im complexes with different geometries, established from the data in Table 4.

for possible correlations between ^{15}N NMR parameters and the structure of the Im···H$^+$···Im complex is in progress.

Conclusions

Imidazole forms a molecular complex with DPTHA with strong (O−H···H, N···H$^+$···N) and weak (C−H···O, C−H···S) hydrogen bonds and unusual molecular packing. The com-

plex has been used to model molecular interactions in the solid state related to changes in the ^{13}C NMR parameters of the Im···H$^+$···Im fragment. A comparison of ^{13}C CP/MAS NMR results for complex **1** and imidazole shows different isotropic chemical shifts for the C4 and C5 carbons, and the δ_{22} and κ parameters for the C2 carbon for the two compounds. The results were rationalized by GIAO calculations to establish

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a general correlation between N···H⁺···N geometry and ^{13}C shielding parameters. The measured values of δ_{22} and κ for **1** are consistent with the calculated values. Although the relationship between the N···H⁺ distance and $\Delta\delta$C4C5 was slightly different, the GIAO calculations neglect the hydrogen bonds between thiophosphoric acid and imidazole. A combination of the experimental and computational approach allows us to establish relationships between the geometry of the molecular complex and ^{13}C NMR parameters.

Supporting Information Available: Tables of atomic coordinates, isotropic, and anisotropic temperature factors, bond lengths and bond angles and torsional angles for complex **1** (3 pages). Ordering information is given on any current masthead page. Tables of atomic coordinates, thermal parameters, results of geometry calculations and GIAO calculations of NMR parameters have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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