X-Ray crystal structures and NMR solution studies on 2,2′:3′,2″:6″,2‴-quaterpyridine and its *N*-methylated derivative; conformational rigidity in solution arising from an intramolecular electrostatic interaction

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Reaction of 2,2′:3′,2″:6″,2‴-quaterpyridine (QP) with methyl trifluoromethylsulfonate results principally in *N*-methylation on the first-named (non-primed) ring to give [QP-Me][PF_6]. A comparison of the crystal structures of QP and [QP-Me][PF_6] shows that in the solid state, *N*-methylation results in a substantially more folded conformation than occurs for QP, bringing the positive charge of the N–Me group into close proximity with the lone pair of the 2″,6″-disubstituted pyridyl ring (non-bonded N ··· N separation, 3.20 Å). The positive charge is thus, in this conformation, stabilised by an electrostatic interaction with a spatially close pyridyl lone pair. ^{1}H NMR studies (in particular two-dimensional COSY spectra and selective NOE difference spectra) unexpectedly show clearly that the rigid, folded conformation of [QP-Me][PF_6] that is apparent in the crystal structure is retained in both acetonitrile and dimethyl sulfoxide solutions.

Introduction

We have recently been interested in the coordination chemistry of the unsymmetrical bis-bidentate bridging ligand 2,2′:3′,2″:6″,2‴-quaterpyridine (QP; see Fig. 1). Because of its unsymmetrical nature and the consequent inequivalence of its two bidentate metal binding sites, it has proven straightforward to prepare heterobinuclear complexes in a controlled and stepwise manner, by addition of one equivalent of one metal ion at the less hindered 'outer' binding site followed by a second equivalent of a different metal ion at the 'inner' binding site.[1] Two other more symmetrical isomers of quaterpyridine have also received attention for their coordination behaviour; these are the 'linear' 2,2′:6′,2″:6″,2‴-quaterpyridine,[2] and the 'back-to-back' 2,2′:4′,4″:2″,2‴-quaterpyridine.[3] Other isomers of quaterpyridine are of interest for properties as diverse as neurotoxicity[4] and their ability to catalyse photo-reduction of water to H_2,[5] and Zoltewicz and co-workers have synthesised several low-symmetry isomers of quaterpyridine.[6]

In order to modify the electronic properties of our complexes of QP we also recently investigated the effects of *N*-methylation of one binding site whilst the other was occupied by a $[Ru(bipy)_2]^{2+}$ fragment.[7] This has prompted us to investigate the methylation of the free ligand, to determine both the site of methylation and its structural consequences for the conformation of the molecule. Methylated oligopyridine derivatives have been extensively studied because of their electron-accepting properties.[8] In this paper we compare the crystal structures of free QP and its *N*-methylated analogue [QP-Me][PF_6], and describe some detailed NMR studies which shed light on the relationship between the solid-state and solution structures of the two molecules, in particular the conformational consequences of an intramolecular electrostatic interaction in [QP-Me][PF_6].

Experimental

General

QP was available from previous studies.[1] All NMR experiments were performed on JEOL Lambda 300 or GX-400 spectrometers. Electrospray mass spectra were recorded on a VG Quattro instrument using MeCN solutions of the compounds and a cone voltage of 30 V. Electronic spectra were recorded on a Perkin-Elmer Lambda 2 instrument. Electrochemical measurements were made with a PC-controlled EG&G/PAR 273A potentiostat, using platinum bead working and auxiliary electrodes, and an SCE reference electrode. The measurements were performed using acetonitrile distilled over calcium hydride, with 0.1 mol dm^{-3} [NBu^n_4][PF_6] as supporting electrolyte. Ferrocene was added at the end of each experiment as an internal reference, and all redox potentials are quoted *vs.* the ferrocene/ferrocenium couple (Fc/Fc^+).

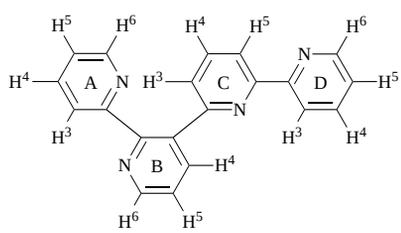

Fig. 1 Structure of QP, showing the NMR labelling scheme

Preparation of [QP-Me][PF_6]

A mixture of QP (0.200 g, 0.65 mmol) and methyl trifluoromethylsulfonate (triflate) (0.095 g, 0.9 equiv.) in dry CH_2Cl_2 (20 cm^3) was refluxed under N_2 for 2 h. After this time the CH_2Cl_2 was removed *in vacuo*. The resultant solid was redissolved in aqueous ethanol (1:1) and excess NH_4PF_6 was added. The mixture was then reduced in volume, and the solid material which precipitated from the aqueous phase was filtered off, washed with water and dried. The crude product was purified by chromatography on alumina using CH_2Cl_2–MeOH (97:3, v/v). Unreacted QP eluted first; the desired [QP-Me][PF_6] eluted more slowly and was isolated in *ca.* 40% yield as a mixture of major and minor isomers in an approximately 10:1 ratio (by ^{1}H NMR spectroscopy; see Results and discussion). Recrystallisation from MeCN–diethyl ether afforded block-like crystals of the pure major isomer. *m/z* (ESMS) 325 (M^+, 100%) (Found: C, 53.5; H, 3.5; N, 11.9. Required for $C_{21}H_{17}F_6N_4P$: C, 53.6; H, 3.6; N, 11.9%).

Table 1 Crystallographic data for QP and [QP-Me][PF_6]

Compound	QP	[QP-Me][PF_6]
Formula	$C_{20}H_{14}N_4$	$C_{21}H_{17}F_6N_4P$
Formula weight	310.35	470.36
System, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$
a/Å	11.277(2)	9.719(2)
b/Å	11.634(3)	20.775(3)
c/Å	11.9160(15)	11.062(2)
β/°	90	112.406(11)
V/Å^3	1563.4(5)	2065.0(5)
Z	4	4
ρ_{calc}/g cm^{-3}	1.319	1.513
μ/mm^{-1}	0.081	0.203
F(000)	648	960
T/K	173	173
Crystal size/mm	0.6 × 0.2 × 0.2	0.5 × 0.5 × 0.6
2θ range for data collection/°	5–55	5–55
Reflections collected (total, independent, R_{int})	9853, 3580, 0.0199	9375, 3626, 0.0167
Data, restraints, parameters	3580, 0, 218	3626, 0. 340
Final R indices: R_1, wR_2 [a,b]	0.0290, 0.0708	0.0449, 0.1267
Weighting factors [b]	0.0414, 0	0.0664, 0.664
Largest peak/hole/e Å^{-3}	+0.17, −0.14	+0.63, −0.51

[a] Structure was refined on F_o^2 using all data; the value of R_1 is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

X-Ray crystallography

Suitable crystals were mounted under a stream of cold N_2 at −100 °C on a Siemens SMART diffractometer fitted with a CCD-type area detector. In both cases data were collected at −100 °C to a 2θ limit of 55° using graphite-monochromatised Mo-Kα radiation. A detailed experimental description of the methods used for data collection and integration using the SMART system has been published.[9] Table 1 contains a summary of the crystal parameters, data collection and refinement.† The structures were solved by conventional direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL 5.03 package on a Silicon Graphics Indy computer.[10] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters. The only significant problem was that in the structure of [QP-Me][PF_6] the hexafluorophosphate anion is disordered over two positions by rotation about the F(5)–P(1)–F(6) axis, such that F(1) to F(4) (all in the same plane) each appear in two sites with fractional site occupancies of 0.60 and 0.40.

Results and discussion

Syntheses and crystal structures

X-Ray quality crystals of QP were grown by slow evaporation from diethyl ether; the crystal structure is shown in Fig. 2. Unlike the well-known 'linear' oligopyridines which are more or less planar in the solid state with adjacent pyridyl rings mutually *transoid*,[11] QP is substantially twisted due to the steric crowding around ring 2 [N(21)–C(26)] which is substituted at both C^2 and C^3. The 'outer' bipyridyl site (rings A and B) has an approximately *transoid* configuration as expected, but there is an angle of 41.7° between the mean planes of these two rings. Between rings B and C there is a twist of 66°, which prevents rings A and C from clashing. (Note that in dinuclear complexes of QP,[1] when the outer site is constrained to be near-planar because it is coordinated to a metal ion, this torsion angle is nearly 90° with the two bipyridyl fragments mutually perpendicular for steric reasons.) Finally, rings C and D are more or less *trans*-coplanar (8.9° between mean planes of these two pyridyl rings) because there is no steric problem to prevent it. Overall, (*i*) the two 2,2′-bipyridyl fragments are as near *trans*-coplanar as possible given steric limitations, and (*ii*) the two fragments have a substantial torsion angle between them (about the bond between rings B and C), again for obvious steric reasons. The structure of QP therefore is interesting but contains no unusual surprises.

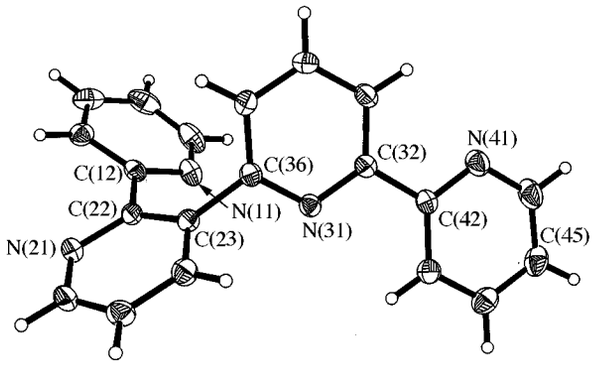

Fig. 2 Crystal structure QP

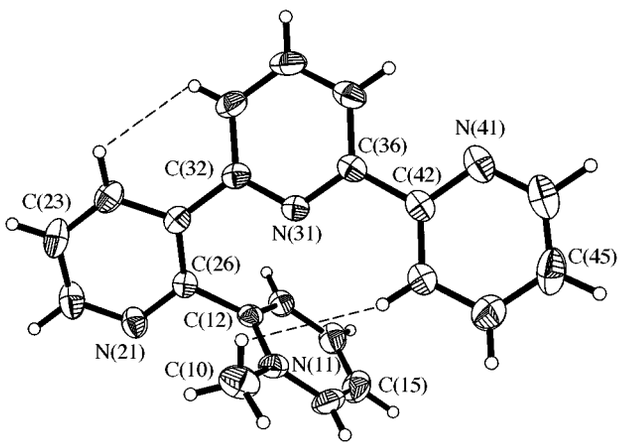

Fig. 3 Crystal structure of the cation of [QP-Me][PF_6]. The significant close contacts that result in the NOE enhancements in solution are shown by dashed lines.

Reaction of QP with one equivalent of methyl triflate in CH_2Cl_2, followed by treatment with NH_4PF_6, afforded a material which was clearly a mono-methylated derivative of QP, *i.e.* [QP-Me][PF_6]; the FAB mass spectrum showed a single peak at *m*/*z* 325. The ^{1}H NMR spectrum showed that the crude product was a mixture of two isomers of [QP-Me][PF_6] in a ratio of *ca.* 10:1, which was evident in particular from the presence of two signals for the *N*-methyl protons near 4.2 ppm. Recrystallisation from MeCN–diethyl ether afforded X-ray quality crystals of a material whose ^{1}H NMR spectrum corresponded exactly to the major isomer in the original reaction product mixture. The crystal structure is shown in Fig. 3.

Methylation has occurred on ring A. It would be expected for methylation to occur at one of the two terminal rings (A or D) for steric reasons; for example, 2,2′:6′,2″-terpyridine (terpy) methylates exclusively on the terminal rings.[12] There is no obvious reason why methylation could not also occur on ring D, and we think it likely that the minor isomer identified by ^{1}H NMR spectroscopy (but not isolated) was this species. Methylation has had a substantial effect on the conformation of the molecule. If Fig. 2 is compared with Fig. 1, it is apparent that the conformation of the 'inner' bipyridyl site (rings C and D) has

† Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/103.

Table 2 ^{1}H NMR data (in ppm *vs.* internal TMS) for QP and [QP-Me][PF_6] (300 MHz, 293 K). Multiplicities and coupling constants in Hz (where resolved) are in parentheses

	QP		[QP-Me][PF_6]		$\Delta\delta$	
	MeCN	DMSO	MeCN	DMSO	MeCN	DMSO
Ring A						
H^6	8.20 (m)	8.22[a]	8.70 (br d; ≈6)	9.20 (br d; ≈6)	+0.50	+0.98
H^5	7.19 (m)	7.26 (ddd; 6.9, 4.9, 1.9)	7.76 (m)	8.00 (ddd; 7.8, 6.1, 1.5)	+0.57	+0.74
H^4	7.84[a]	7.90[a]	8.26 (td; 8.0, 1.0)	8.44 (td; 7.8, 1.1)	+0.42	+0.54
H^3	7.84[a]	7.90[a]	7.67 (dd, 8.0, 1.4)	7.91[a]	−0.17	+0.01
Ring B						
H^6	8.73 (dd; 4.8, 1.7)	8.77 (dd; 4.8, 1.7)	8.89 (dd; 4.8, 1.5)	8.95 (dd; 4.8, 1.5)	+0.16	+0.18
H^5	7.55 (dd; 7.9, 4.8)	7.64 (dd; 7.9; 4.8)	7.82[a]	7.93 (dd; 8.1, 4.8)	+0.27	+0.29
H^4	8.15 (dd; 7.7, 1.7)	8.22[a]	8.46 (dd; 8.1, 1.5)	8.66 (dd; 8.1, 1.7)	+0.31	+0.44
Ring C						
H^5	8.25 (dd; 7.9, 0.9)	8.22[a]	8.26 (dd; 8.0, 1.0)	8.27 (dd; 7.7, 1.3)	+0.01	+0.05
H^4	7.78 (t; 7.8)	7.87 (t; 7.7)	8.05 (t; 7.9)	8.15 (t; 7.8)	+0.26	+0.28
H^3	7.32[a]	7.39[a]	7.91 (dd; 7.8, 1.0)	8.08 (dd; 7.7, 1.3)	+0.59	+0.69
Ring D						
H^6	8.60 (ddd; 4.8, 1.7, 1.0)	8.64 (ddd; 4.7, 1.5, 1.0)	8.62 (ddd; 4.8, 1.8, 1.0)	8.65 (ddd; 4.8, 1.8, 0.9)	+0.02	+0.01
H^5	7.32[a]	7.39[a]	7.38 (ddd; 7.5, 4.9, 1.2)	7.46 (ddd; 7.6, 4.8, 1.1)	+0.06	+0.07
H^4	7.73 (td, 8.1, 1.8)	7.78[a]	7.82[a]	7.89[a]	+0.09	+0.11
H^3	7.84[a]	7.78[a]	7.43 (d, 7.9)	7.40 (d, 7.9)	−0.41	−0.38

[a] Signal wholly or partly overlapping with others, so coupling constant information not available.

not changed significantly, but that a substantial change in the torsion angle about the bond between rings B and C has brought the methylated ring A near to rings C and D. The torsion angles are 97.7° between rings A and B; 29.5° between rings B and C; and 6.6° between rings C and D. The principal consequence of this rearrangement is that the positive charge on N(11) is brought into close contact with the lone pair of N(31), which is directed towards it. The non-bonded N(11)···N(31) distance is 3.20 Å. There is thus an intramolecular stabilisation of the positive charge by the lone pair of N(31), which can only occur because the unusual substitution pattern of the molecule allows N(11) and N(31) to come into close contact. In the more common 'linear' oligopyridines containing only 2-substituted (terminal) or 2,6-disubstituted (inner) pyridyl rings, an intramolecular contact of this type would not be possible; in fact no simple methylated derivatives of such ligands have been crystallographically characterised to our knowledge. Similar electrostatic interactions between the lone pairs of oxygen atoms and the positively charged area of an alkylated pyridine are partly responsible for the efficient binding of diquat and paraquat‡ derivatives by large crown-ether macrocycles.[13,14] The (non-bonded) O···N distances in these complexes typically lie in the range 3.2–3.6 Å,[13] but contacts as short as 2.9 Å can occur.[14] The separation of 3.20 Å between N(11) and N(31) in [QP-Me][PF_6] is clearly a similar interaction.

An additional consequence of the methylation-induced rearrangement is that H^3 of ring D [H(43) according to the crystallographic numbering scheme] is directed approximately towards the methyl group of ring A (Fig. 4), which has significant consequences for its NMR behaviour (see below). It is well known that attractive edge-to-face 'T-stacking' interactions between aromatic rings can play a significant role in controlling molecular conformations.[15] In these cases the proton of one aromatic ring sits approximately above the centre of another ring, due to a weak electrostatic interaction between the proton (δ+) and the charge cloud (δ−). Fig. 4 shows that in [QP-Me][PF_6], the proton H(43) is, however, not directed at the centre of ring A, but rather lies above N(11) with the C(43)–H(43) bond directed towards the methyl group. Atom H(43) lies 2.68 Å from the mean plane of atoms C(10) to C(16); other significant non-bonded distances involving H(43) are 2.81 Å to N(11), 3.05 Å to C(10) and about 2.7 Å to the methyl protons. The mean planes of the two rings shown in Fig. 4 are nearly mutually perpendicular with an angle of 71° between them. There is no steric reason why H(43) could not lie directly above the centre of ring A, but there is a plausible electronic reason: the positive charge, which will be partly delocalised over ring A, will repel the δ+ proton H(43) which is accordingly directed away from the ring centre.

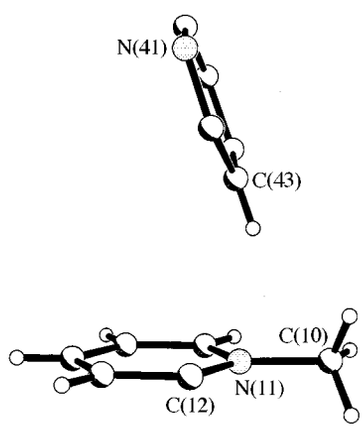

Fig. 4 Part of the crystal structure of [QP-Me][PF_6], showing the intramolecular interaction between H(43) and the methylated ring

Solution NMR studies

The ^{1}H NMR data for QP and [QP-Me][PF_6] in CD_3CN and $(CD_3)_2SO$ are summarised in Table 2. The spectra were assigned with help from two-dimensional ^{1}H–^{1}H COSY spectra and by comparison with the spectra of related oligopyridines. The ^{1}H NMR spectrum of QP has been described before,[1] but in a different solvent ($CDCl_3$); we used CD_3CN and $(CD_3)_2SO$ here because both QP and [QP-Me][PF_6] are soluble in these solvents allowing for a direct comparison of the parent and *N*-methylated molecules.

‡ IUPAC names for diquat and paraquat are: 6,7-dihydrodipyrido-[1,2-*a*:2′,1′-*c*]pyrazinediium and 1,1′-dimethyl-4,4′-bipyridinium, respectively.

For QP, the COSY spectrum allowed easy separation of the 14 signals into two sets of four (the terminal rings A and D) and two sets of three (the inner rings B and C). The signals for rings B and C were readily distinguished since ring B has an H^6 proton (denoted H^{6B}; this naming scheme is used hereafter), identified by its deshielded position and the characteristically small H^{6B}/H^{5B} coupling constant of 4.8 Hz. Assignment of the two sets of four protons to rings A and D was not immediately obvious, but this ambiguity is removed by comparison with the spectrum of [QP-Me][PF_6], since H^{6A} shifts substantially on methylation whereas H^{6D} does not.[12] The shift is much larger in $(CD_3)_2SO$ (+0.98 ppm) than in CD_3CN (+0.50 ppm). This suggests that the change in solvation of QP following methylation is greater in DMSO than in MeCN, consistent with the greater polarity of DMSO. The $\Delta\delta$ values for the other rings are less, and do not vary much between the two solvents, as the positive charge is localised on ring A.

The spectrum of [QP-Me][PF_6] under the same conditions shows some predictable effects and some rather surprising ones. The most obvious effect is that methylation of ring A has resulted in a substantial downfield shift for H^{6A}, H^{5A} and H^{4A} which is a simple charge effect. H^{3A} however is not affected in this way, actually becoming slightly more shielded in CD_3CN. This could be because in QP, H^{3A} is spatially close to the electronegative N atom of ring B as a consequence of the approximately *trans*-coplanar arrangement of rings A and B (*cf.* the crystal structure in Fig. 2); if the relative conformation of rings A and B changes in [QP-Me][PF_6] (*cf.* the crystal structure in Fig. 3) then this deshielding effect will be removed.

On comparing the signals for the other three aromatic rings between QP and [QP-Me][PF_6], there are two signals which show unexpected behavior (Table 2): these are H^{3C} [$\Delta\delta = +0.59$ ppm in CD_3CN and +0.69 ppm in $(CD_3)_2SO$] and H^{3D} [$\Delta\delta = -0.41$ ppm in CD_3CN and −0.38 ppm in $(CD_3)_2SO$]. These observations are both consistent with [QP-Me][PF_6] retaining in solution to a significant extent the 'folded-up' conformation of the crystal structure, in order to retain the electrostatically favourable N(31)···N(11) interaction. Looking at the crystal structure of [QP-Me][PF_6] (Fig. 3), the twist between rings B and C is relatively small (29.5°), and H^{3C} [H(33) according to the crystallographic numbering scheme] is now held close to H^{4B} [H(24)]. This is similar to the behaviour of the H^3 protons of 2,2′-bipyridine when the ligand is forced to change its conformation from *trans*-coplanar to *cis*-coplanar on coordination; the H^3 protons become forced into close contact with one another and their chemical shift increases substantially, by a much larger amount than can be accounted for by the presence of a coordinated metal ion.[15] We would therefore expect H^{4B} to show a similar shift, and it does so, but to a slightly lesser extent [$\Delta\delta = +0.31$ ppm in CD_3CN and +0.44 ppm in $(CD_3)_2SO$]. The second consequence of the 'folded-up' crystal structure is that H^{3D} [H(43) according to the crystallographic numbering scheme] is close to ring A. Although H^{3D} is not directly above the centre of ring A (see Fig. 4), it is directed close enough to it to experience the shielding effect of the ring current, which accounts for its substantial upfield shift. Significantly, the other three protons on ring D are hardly affected at all by methylation of ring A.

Additional proof that the conformation of [QP-Me][PF_6] seen in the crystal structure makes a substantial contribution to the solution structures in both CD_3CN and $(CD_3)_2SO$ was provided by NOE experiments. The NOE difference spectrum produced on irradiation of the methyl signal [4.21 ppm in CD_3CN; 4.26 ppm in $(CD_3)_2SO$] in either solvent showed strong enhancement of just two signals: H^{6A} (adjacent to the irradiated methyl group) as expected, and H^{3D}. Fig. 5 depicts the NOE difference spectrum obtained in this way in $(CD_3)_2SO$, with a 16% enhancement of H^{6A} and a 6% enhancement of H^{3D}; the results in CD_3CN were comparable. The presence of an NOE between the methyl protons on ring A and H^{3D} is exactly consistent with the solid-state structure also being present to a significant extent in solution, in which the separation between H^{3D} and the carbon of the methyl group [C(10)] is 3.05 Å. Of course it does not follow that this is the only solution structure; other conformations may also contribute to the equilibrium population of solution structures. However, examination of the percentage enhancements observed, together with the distances, allows an approximate quantification of this. The separation between H^{6A} and the nearest methyl proton is about 2.25 Å in the crystal structure, and of course this distance is independent of molecular conformation. The separation between H^{3D} and the nearest methyl proton is about 2.72 Å in the folded conformation of the crystal structure; in other conformations it would be much larger. Given the r^{-6} distance dependence of the NOE effect, we would expect that if the folded conformation were retained in solution, the enhancement of H^{3D} would be 0.32 times that of H^{6A}. This is in good agreement with the observed enhancements of 6% and 16%, respectively, and suggests that the folded structure seen in the solid state is also the dominant solution structure.

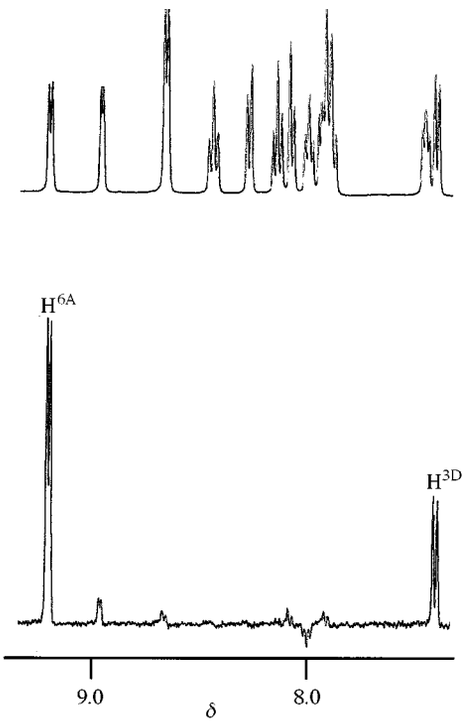

Fig. 5 400 MHz ^1H NMR spectroscopy of [QP-Me][PF_6] in $(CD_3)_2SO$; the upper trace is the aromatic region of the one-dimensional spectrum, and the lower trace is the NOE difference spectrum obtained by irradiation of the methyl group on ring A at 4.26 ppm

Also, irradiation of H^{4B} resulted in strong NOE enhancement (5%) of the signal from H^{3C}, consistent with the approximately *cisoid* conformation of rings B and C which brings these two protons into proximity.[16]

As stated above, the most obvious contribution to the driving force for retention of the folded solid-state conformation of [QP-Me][PF_6] in solution will be the favourable electrostatic interaction between the lone pair of N(31) and the positive charge of the methylated N(11). This must be strong enough to overcome the entropy loss arising from the resulting conformational rigidity of the molecule. In addition, solvation of the molecule will also be an important effect: both the enthalpy of solvation (favourable electrostatic interactions with both the nitrogen lone pairs and the positive charge) and the entropy (loss of freedom of motion of solvent molecules when interacting with the molecule) must be strongly dependent on the conformation of the molecule. Such effects are well known in coordination chemistry where, for example, the difference in the formation constant between complexes of a macrocyclic ligand

and of an open-chain analogue, the macrocyclic effect, is strongly solvent dependent. Generally, it is found that in good donor solvents, ligands adopt the most 'open' conformation possible to maximise solvation enthalpy. It is perhaps surprising therefore that even in DMSO, [QP-Me][PF_6] retains the folded conformation in which solvent interactions are not optimised: the intramolecular interaction between N(31) and the positive charge must be particularly strong.

Conclusions

Methylation of 2,2′:3′,2″:6″,2‴-quaterpyridine (QP) to give [QP-Me][PF_6] occurs principally at the terminal ring A. Comparison of the crystal structures of QP and [QP-Me][PF_6] shows that in the solid state, methylation of QP results in a conformational change to give a more 'folded' structure in which the positive charge of the methylated pyridyl ring is stabilised by intramolecular coordination from the lone pair of another N atom which is brought into proximity. NMR studies show clearly that this folded conformation is retained in MeCN and DMSO solution, and that therefore the intramolecular electrostatic interaction prevents the conformational flexibility that would otherwise have been expected.

Acknowledgements

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References

1 D. A. Bardwell, F. Barigelletti, R. L. Cleary, L. Flamigni, M. Guardigli, J. C. Jeffery and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 2438; V. Balzani, D. A. Bardwell, F. Barigelletti, R. L. Cleary, M. Guardigli, J. C. Jeffery, T. Sovrani and M. D. Ward, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3601; R. L. Cleary, K. J. Byrom, D. A. Bardwell, J. C. Jeffery, M. D. Ward, G. Calogero, N. Armaroli, L. Flamigni and F. Barigelletti, *Inorg. Chem.*, 1997, **36**, 2601.
2 E. C. Constable, S. M. Elder, M. J. Hannon, A. Martin, P. R. Raithby and D. A. Tocher, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2423; C.-M. Che, C.-W. Chan, S.-M. Yang, C.-X. Guo, C.-Y. Lee and S.-M. Peng, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2961.
3 A. J. Downard, G. E. Honey, L. F. Phillips and P. J. Steel, *Inorg. Chem.*, 1991, **30**, 2259; G. E. Honey and P. J. Steel, *Acta Crystallogr.*, *Sect. C*, 1991, **47**, 2247.
4 M. P. Cruskie, Jr., J. A. Zoltewicz and K. A. Abboud, *J. Org. Chem.*, 1995, **60**, 7491.
5 S. Yanagida, T. Ogata, Y. Kuwana, Y. Wada, K. Murakoshi, A. Ishida, S. Takamuku, M. Kusaba and N. Nakashima, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1963.
6 J. A. Zoltewicz and M. P. Cruskie, Jr., *Tetrahedron*, 1995, **51**, 11 393; J. A. Zoltewicz and M. P. Cruskie, Jr., *Tetrahedron*, 1995, **51**, 11 401; J. A. Zoltewicz, M. P. Cruskie, Jr., and C. D. Dill, *Tetrahedron*, 1996, **52**, 4239.
7 M. Guardigli, L. Flamigni, F. Barigelletti, C. S. W. Richards and M. D. Ward, *J. Phys. Chem.*, 1996, **100**, 10 621.
8 See numerous citations in ref. 7.
9 P. L. Jones, A. J. Amoroso, J. C. Jeffery, J. A. McCleverty, E. Psillakis, L. H. Rees and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 10.
10 SHELXTL 5.03 program system; Siemens Analytical X-Ray Instruments, Madison, WI, USA, 1995.
11 E. C. Constable, S. M. Elder, J. V. Walker, P. D. Wood and D. A. Tocher, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 229 and refs. therein; K. T. Potts, K. A. G. Rayford and M. Keshavarz-K, *J. Am. Chem. Soc.*, 1993, **115**, 2793.
12 D. A. Bardwell, A. M. W. Cargill Thompson, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 873.
13 H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, J. B. Wolstenholme and D. J. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, 607.
14 B. L. Allwood, F. H. Kohnke, J. F. Stoddart and D. J. Williams, *Angew. Chem.*, *Int. Ed. Engl.*, 1985, **24**, 581.
15 D. R. Boyd, T. A. Evans, W. B. Jennings, J. F. Malone, W. O'Sullivan and A. Smith, *Chem. Commun.*, 1996, 2269; C. A. Hunter, *Chem. Soc. Rev.*, 1994, 101.
16 E. C. Constable, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 2687; E. C. Constable and J. Lewis, *Inorg. Chim. Acta*, 1983, **70**, 251; E. C. Constable and K. R. Seddon, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 34.

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