Structures and cationic complexes of 18[(2,6)pyridino-6-corand-6] ('sexipyridine')

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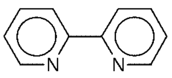
The conformers of the title compound and its (gas phase) complexes with alkali metal cations and some molecular cations have been structurally optimized at HF/3-21G and HF/6-31G* levels of theory, with extended basis set single-point DFT calculations to include some of the effects of electron correlation. The only stable conformer found for the free macrocycle has D_3 symmetry, and stable complexes of the same symmetry are demonstrated for Na^+ and K^+. Stable complexes of lower (C_3) symmetry are also found for the possible template cations H_3O^+ and NH_4^+. Binding energies for the alkali metal cations ions are significantly larger than those found in comparable computational studies on structurally-related macrocycles. Finally, the complex with another potential template cation, $C(NH_2)_3^+$, is also explored.

Introduction

Macrocycles consisting of coupled 2,2′-bipyridines (**1**) have proved to be far from straightforward to synthesize (and can have low solubilities), so relatively little is known about their properties. Given the extensive coordination chemistry of 2,2′-bipyridine itself, it seems likely that such macrocycles would have a similarly wide range of applications. Quantum chemical methods are now sufficiently 'mature' to provide useful, quantitative measures of the relative stability of conformers and binding energies of macrocyclic complexes, and might therefore be used to explore more appropriate template cations for their synthesis. However, suitably high-level *ab initio* studies have only been carried out for 2,2′-bipyridine (at the MP2/6-31G** level[1]); and recently a dicyano-dibutyl-tetrapyridyl macrocycle **2** has been studied at the HF/3-21G* level.[2] There is therefore a large gap in our understanding of the conformational, electronic and binding properties of this family of macrocycles.



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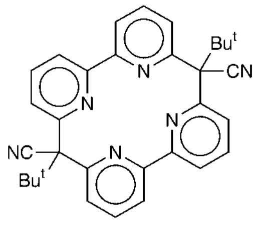

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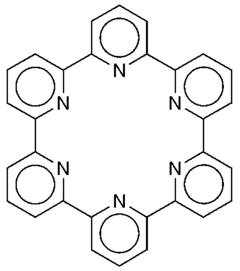

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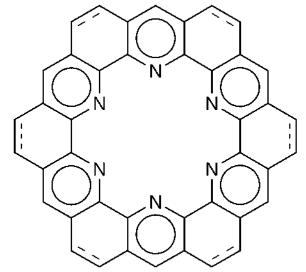

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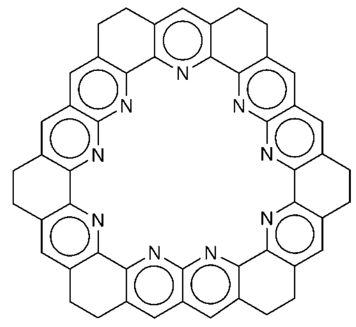

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The first example of a sexipyridine (hereafter SPy, **3**) was reported by Toner,[3] with the first successful preparation of the parent macrocycle by Newkome and Lee,[4] although the macrocycle was not structurally characterised. In a wider context, it could be considered that SPy belongs to a class of aromatic conjugated macrocyclic ligands which includes torands[5] and hexaazakekulenes **4** (although the latter will of course have markedly different electronic properties). Arguably, the synthesis of SPy has proven difficult due to the lack of an appropriate template cation. The only complexes of torands so far studied in detail have been alkali metal ion complexes. In these studies, the torands displayed almost no selectivity between different cations. This is very probably due to the inflexible sexipyridine core in torands—the ligand cavity cannot adjust to accomodate ions of different radii—and it is further compounded by annulation of the 3,3′ positions *via* ethylene linkages. Newkome has proposed the ammonium cation as a potential templating agent.[3] Consequently, the complex of SPy with NH_4^+ will be explored in this paper.

SPy itself has some flexibility in its N–C–C–N dihedral angles. Interestingly, an expanded torand structure with ligating 1,8-diazanapthalene units (**5**) has been prepared using guanidinium as a template.[6] While the 'normal' torand cavity is certainly too small to complex ions the size of guanadinium, $C(NH_2)_3^+$, it remains an open question whether SPy may be flexible enough to achieve this. This is another question addressed in this work.

Several possible conformers of SPy and its cationic complexes must be considered. A staggered D_3 conformer, in which the pyridine rings are alternantly 'up' and 'down', was considered the most likely candidate for the ground state minimum energy conformation, since it mimics the conform-

Table 1a HF/3-21G electronic and vibrational data for complexes of atomic cations[a]

	Electronic energy[b]/kJ mol^{-1}			Vibrational energy at 298 K/kJ mol^{-1}			Number of imaginary frequencies		
	C_{2v}	D_3	D_{6h}	C_{2v}	D_3	D_{6h}	C_{2v}	D_3	D_{6h}
SPy[b]	+5.7	0.0	+76.4	1230.8	1232.1	1231.4	1	0	3
$[SPy{\cdot}Li]^{+}$[c]	−3.1	0.0	+64.4	1240.6	1242.5	1241.7	3	2	5
$[SPy{\cdot}Na]^{+}$[d]	+1.8	0.0	+63.4	1244.8	1246.6	1245.6	1	0	3
$[SPy{\cdot}K]^{+}$[e]	+10.2	0.0	+58.8	1243.0	1244.4	1243.2	1	0	3

[a] HF/3-21G electronic energies for cations (in au): $Li^+ = -7.18709$; $Na^+ = -160.67375$; $K^+ = -596.00659$. [b] Relative to the D_3 structure with $E = -1464.96206$ au. [c] Relative to the D_3 structure with $E = -1472.37635$ au. [d] Relative to the D_3 structure with $E = -1625.85855$ au. [e] Relative to the D_3 structure with $E = -2061.15009$ au.

Table 1b HF/3-21G electronic and vibrational data for complexes of molecular cations[a]

	Electronic energy (au)	Vibrational energy at 298 K/kJ mol^{-1}	Number of imaginary frequencies
SPy	−1464.96206	1232.1	0
$[SPy{\cdot}H_3O]^{+}$[b]	−1541.06527	1346.5[c]	3
$[SPy{\cdot}H_3O]^{+}$[d]	−1541.07529	1349.8[c]	0
$[SPy{\cdot}NH_4]^{+}$	−1521.36635	1392.5[c]	0
$[SPy{\cdot}C(NH_2)_3]^{+}$[d]	−1668.44775	—	—

[a] HF/3-21G energies of cations (in au): $H_3O^+ = -75.89123$; $NH_4^+ = -56.23386$; $C(NH_2)_3^+ = -203.40112$. [b] D_3 conformer, with hydrogens of the (planar) H_3O^+ moiety pointing *at* SPy nitrogens. [c] HF/3-21G vibrational energies of cations (in kJ mol^{-1}) at 298 K are $H_3O^+ = 99.9$; $NH_4^+ = 145.5$. [d] C_3 conformer.

ation of three fused *cis*-bipyridines. Planar D_{6h} structures, although unlikely to be the lowest-energy conformers, are of interest as potential transition states for inversion. Other possible symmetries considered include C_{2v} (a saddle-shaped conformer), C_2 and C_1.

Computational method

The Hartree–Fock (HF) geometry optimizations employed direct SCF techniques within the July 1995 release of GAMESS[7] running on a Silicon Graphics multiprocessor Origin 2000 at the Chemistry Department, Cardiff. The 3-21G basis sets due to Pople and Hariharan[8] were employed in the conformational study of SPy and its complexes, since harmonic frequency calculations (to check for a stable structure and provide estimates of thermal energies) were feasible at this level. Complexes of Li^+, Na^+ and K^+ were optimized using D_{6h}, D_3 and C_{2v} symmetry constraints. The free macrocycle was additionally optimized with C_2 and C_1 symmetry constraints at this level. Optimizations of the complexes of SPy with the cations H_3O^+ (hydronium), NH_4^+ (ammonium) and $C(NH_2)_3^+$ (guanidinium) were subsequently performed, checking stability using frequency calculations, where possible.

Having established the (stable) lowest energy conformers of SPy and various complexes, optimization was repeated using 6-31G* basis sets (consistently employing sets of 6 cartesian *d*-type gaussians).[9] This was followed by single point calculations at HF and B3-LYP levels with extended basis sets which we shall denote generically as 'Basis1': a diffuse sp shell was added to the nitrogen atoms of the macrocycle and all non-hydrogen atoms of the complexed cations (*i.e.* 6-31+G* on Li, N, O, Na, K). The basis set on the macrocycle carbon atoms and all hydrogen atoms remained at 6-31G*. Counterpoise corrections to the binding energies were computed with the usual Boys–Bernardi method[10] at the highest level of theory only, *i.e.* B3-LYP/Basis 1.

The electrostatic potential at the centre (intersection of rotation axes) of the free macrocycle has also been computed for the HF/6-31G* D_3 conformer, with the result −0.1398 au, equivalent to a binding energy of 362.1 kJ mol^{-1}. This simple electrostatic estimate for a point positive charge may be compared with the actual binding energies of the atomic ions. The SPy→cation charge transfers for the complexes, computed from Mulliken population analyses, will also be reported.

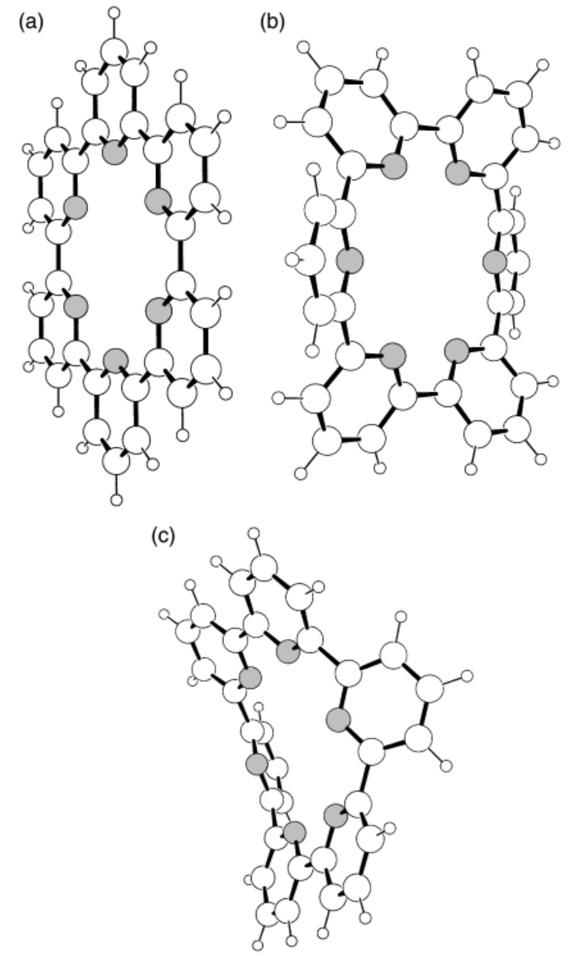

Fig. 1 HF/6-31G* conformers of SPy (macrocycle nitrogen atoms are shaded). (a) D_{6h} saddle-point conformer, (b) D_3 stable conformer, (c) C_{2v} saddle-point conformer.

Results

Free macrocycle conformations

(a) HF/3-21G level (Table 1). Optimization was first carried out for a high-symmetry, flat D_{6h} structure (Fig. 1a) with nonbonded contacts $r(\mathrm{N}\cdots\mathrm{N}) = 2.847$, 4.930 and 5.693 Å. A harmonic frequency calculation gave 3 imaginary frequencies, verifying that it is an unstable (third-order saddle point) conformer on the SPy potential energy surface. Optimization in the D_3 point group leads to a structure with alternate 'up' and 'down' pyridines (Fig. 1b) with torsion angles N–C–C–N = 40.3° and N···N nonbonded distances of 2.843, 4.912 and 5.676 Å. A harmonic frequency calculation verified that this is a stable conformer (no imaginary frequencies), and gave an estimate of its vibrational energy. This D_3 conformer is 75.8 kJ mol^{-1} lower in energy (electronic + scaled vibrational energy difference at 298 K) than the flat D_{6h} saddle-point. Convincing evidence that this D_3 structure has the lowest energy came from an optimization following a C_2-distortion of the (flat) D_{6h} structure. This optimized successfully to the higher-symmetry D_3 structure, despite having only the constraint of a single symmetry element (*i.e.* a C_2 axis).

A distortion of the D_{6h} structure into C_{2v} symmetry, which could not recover the D_3 structure (since C_{2v} is not a subgroup of D_3) gave the saddle-shaped structure of Fig. 1c. This consists of two completely flat *cis* bipyridines (as demanded by the point group) and two pyridine units strongly twisted away from the bipyridines (N–C–C–N = 43.2°). Despite this twisting, all six nitrogen heteroatoms are within ±0.03 Å of the mean plane. This C_{2v} structure was only 5.8 kJ mol^{-1} higher in energy than the D_3 conformer. However, a harmonic frequency calculation found one imaginary frequency, so this is a saddle-point rather than another minimum energy conformer at this level of theory.

Three cases of optimization at this level were also carried out in C_1, using as the starting structures relatively large (±40°) random perturbations of the N–C–C–N (inter-pyridine ring) torsion angles away from the D_{6h} planar structure. In two cases, the C_{2v} saddle point structure was recovered, and in one other case the D_3 minimum energy structure was obtained. Thus it did not prove possible to find any new stationary point by relaxing all symmetry constraints, and the D_3 structure remains the only verified local minimum energy conformer. Since it is also the lowest in energy, it seems most likely that this is indeed the *global* minimum energy ground state conformer of SPy.

(b) HF/6-31G* structures and relative energies. The D_{6h}, C_{2v} and D_3 optimized structures obtained at the HF/3-21G level were then re-optimized with HF/6-31G*(6d) basis sets on all atoms. The electronic energy differences between the structures are: $(D_3) < 13.6$ kJ mol^{-1} $(C_{2v}) < 88.3$ kJ mol^{-1} (D_{6h}), *i.e.* the energy-ordering is unchanged from the HF/3-21G level. Including vibrational energy at the (scaled) 3-21G level has very little effect on the relative energies: $(D_3) < 12.4$ kJ mol^{-1} $(C_{2v}) < 88.8$ kJ mol^{-1} (D_{6h}). The interplanar angle betweeen pyridines for the D_3 conformer is 44.2°, almost identical to that found in gas phase *cis* 2,2′-bipyridine at the HF/6-31G** level (44.9°[1]). The N···N non-bonded distances in Å for the non-planar D_3 (planar D_{6h} in parentheses) structures are: 2.833 (2.831); 4.892 (4.904); and 5.653 (5.662), respectively. The very small differences between D_3 and D_{6h} values can be explained by a small, compensatory expansion of the planar structure (relative to a staggered D_3 structure) due to increased N···N electrostatic repulsion.

The high-symmetry D_{6h} structure would seem the most likely candidate for the inversion transition state. However, the 3-21G level frequency calculation finds three imaginary frequencies for this conformer. (A single imaginary frequency ought to be associated with the (single) internal coordinate, with respect to which nuclear motion is unstable at the transition state.) The C_{2v} conformer, on the other hand, does have a single imaginary frequency at this level of theory, which identifies it as a transition state between two stable structures. However, C_{2v} is the wrong symmetry for the transition state connecting the two inversion-related D_3 lowest energy conformers (it is not a subgroup of D_3). The symmetry-allowed possibilities are C_2 and C_3 (as subgroups of D_3) or D_{6h} (D_3 is a subgroup of D_{6h}). Since we were unable to find any additional structures with C_2 or C_3 symmetry in our conformational searching, we are led to two possible conclusions regarding the transition state structure (and its energy barrier): (i) the transition state *is* the planar D_{6h} structure, implying a substantial (≈102 kJ mol^{-1}) barrier to inversion; or (ii) the transition state has C_2 (or possibly even C_3) symmetry, with a very low barrier to inversion (≈14 kJ mol^{-1}), but the conformer with this energy has the 'wrong' symmetry at the HF/3-21G level. In either case, it indicates that the potential energy surface topology is not correctly represented at the HF/3-21G level. At an appropriately higher level of theory, either the D_{6h} conformer will have the correct single imaginary frequency, or the conformer with C_{2v} symmetry at the HF/3-21G level will lower its symmetry to C_2. Since frequency calculations for SPy with larger basis sets than 3-21G are currently too computationally demanding (already it has 360 basis functions at the 3-21G level, and this rises to 576 functions in a 6-31G* basis), our data cannot distinguish between these two possibilities.

The HF/6-31G* energy difference between D_3 and D_{6h} structures is 101.2 kJ mol^{-1} (including the scaled 3-21G level vibrational energy change) or 101.6 kJ mol^{-1} (exclusive of vibrational energy changes). The traceless quadrupole moment $(2Q_{zz}-Q_{xx}-Q_{yy})$ of free SPy at the B3-LYP/Basis1//HF/6-31G* level is 111.1 Debye.Å.

Complexes with Li^+, Na^+ and K^+

(a) HF/3-21G structures. The results of geometry-optimized complexes of SPy with Li$^+$, Na$^+$ and K$^+$ in D_3, C_{2v} and D_{6h} symmetries are also given in Table 1. The cation is constrained to be at the geometrical centre of the macrocycle in D_3 and D_{6h}. In C_{2v} the cation has the flexibility to move along the C_2 axis, but must remain equidistant from either two or four of the macrocycle nitrogens. The results presented in Table 1 show that only D_3 symmetry complexes of the larger alkali metal cations Na$^+$ and K$^+$ are stable (no imaginary frequencies). That is not to say that Li$^+$ does not complex with SPy, only that it does so in a lower symmetry than C_{2v} (probably coordinating asymmetrically to one or two macrocycle nitrogens). For reasons of computational expediency, such lower-symmetry complexes of Li$^+$ could not be explored.

Complexation with these atomic cations in D_3 symmetry causes the N–C–C–N torsion of adjacent pyridines to reduce below the value in the free macrocycle, from 33.7° for the complex with Li$^+$ (notwithstanding that it is not a stationary point), 34.2° with Na$^+$ and 35.2° with K$^+$. Since the cation binding energies decrease along the series Li$^+ \rightarrow$Na$^+ \rightarrow$K$^+$, this suggests that the macrocycle N–C–C–N angle in such complexes decreases with increasing cation binding energy. The distances $r(\mathrm{N}\cdots\mathrm{M})$ from the macrocycle nitrogen to the cations (in Å) are 2.787, 2.799 and 2.836 in the complexes with Li$^+$, Na$^+$ and K$^+$, respectively.

(b) HF/6-31G* structures (D_3). The same structural trends are evident with the larger basis set, *e.g.* N–C–C–N = 36.7°, 37.2° and 39.1°; $r(\mathrm{N}\cdots\mathrm{M}) = 2.779$ Å, 2.791 Å and 2.831 Å in the complexes with Li$^+$, Na$^+$ and K$^+$, respectively.

(c) Binding energies. Table 2 summarizes the cation binding energies corresponding to: SPy + M$^+ \rightarrow$[SPy·M]$^+$ computed by taking the differences of the appropriate total electronic and vibrational energies (the latter always at the HF/3-21G level, and scaled by the empirical factor 0.893[11]). Energies of complexation with alkali metal cations decrease along the series Li$^+$, Na$^+$, K$^+$. Two previous computational studies of alkali metal cation binding by macrocycles, for 18-crown-6[12] and 1,4,7-trimethyltriazacyclononane (Me$_3$TACN) complexes,[13] have reached the same conclusion. Binding energies for Li$^+$, Na$^+$, K$^+$ in Me$_3$TACN (B-LYP/6-31+G*//HF/6-31+G* level)

Table 2 Larger basis set energies of optimized structures[a]

	HF/6-31G*[b]	HF/Basis1[c,d]//6-31G*	B3-LYP/Basis1[c,e]//HF/6-31G*
SPy	−1473.24564	−1473.25741	−1482.55236
$[SPy{\cdot}Li]^+$	−1480.67460	−1480.68114	−1490.02726
$[SPy{\cdot}Na]^+$	−1635.08734	−1635.09370	−1644.81293
$[SPy{\cdot}K]^+$	−2069.40584[f]	−2069.42928	−2079.46908
$[SPy{\cdot}H_3O]^+$	−1549.72450	−1549.73519	−1559.44393
$[SPy{\cdot}NH_4]^+$	−1529.91624	−1529.92520	−1539.59405
$[SPy{\cdot}C(NH_2)_3]^+$	−1677.83689	−1677.84924	−1688.39399

[a] D_3 symmetry was applied to SPy and its complexes with Li^+, Na^+ and K^+; C_3 symmetry was applied to the $[SPy{\cdot}H_3O]^+$ complex. [b] HF/6-31G* energies for cations (in au): $Li^+ = -7.23554$; $Na^+ = -161.65929$; $K^+ = -596.00659$ (3-21G*); $H_3O^+ = -76.28934$; $NH_4{}^+ = -56.53077$; $C(NH_2)_3{}^+ = -204.52154$. [c] 6-31+G* basis set on Li, N, O, and Na; 3-21+G* on K; and 6-31G* on C,H. [d] HF/Basis1//HF/6-31G* energies for cations (in au): $Li^+ = -7.23554$; $Na^+ = -161.65929$; $K^+ = -596.00683$; $H_3O^+ = -76.29060$; $NH_4{}^+ = -56.53040$; $C(NH_2)_3{}^+ = -204.52479$. [e] B3-LYP/Basis1//HF/6-31G* energies for cations (in au): $Li^+ = -7.28459$; $Na^+ = -162.08124$; $K^+ = -596.74239$; $H_3O^+ = -76.69057$; $NH_4{}^+ = -56.89272$; $C(NH_2)_3{}^+ = -205.76289$. [f] 6-31G* used for all atoms except potassium, for which a 3-21G* basis set was used.

Table 3 Cation binding energies[a] (kJ mol^{-1}) and charge transfers (ΔQ)

Cation	ΔQ[b]	HF/3-21G	HF/6-31G*	HF/Basis1//HF/6-31G*	B3-LYP/Basis1//HF/6-31G*[d,c]
Li^+	0.62	587.2	498.5	484.8	490.4 (485.0)
Na^+	0.37	571.9	466.0	451.8	457.9 (449.6)
K^+	0.27	465.4	392.3	422.3	446.7 (426.2)
H_3O^+	0.18	567.0	481.7	475.5	511.8 (499.5)
$NH_4{}^+$	0.68	434.2	353.8	347.4	377.8 (370.4)
$C(NH_2)_3{}^+$	0.12	204.8[d]	165.8[d]	158.8[d]	189.5[d] (187.3)

[a] Includes the HF/3-21G vibrational energy corrections at 298K (derived from the data in Table 1), scaled by the empirical factor 0.893.[10] [b] In electron units, calculated from a Mulliken population analysis at the B3-LYP/Basis1 level. [c] Values in parentheses are counterpoise-corrected. [d] Includes an estimated vibrational energy correction of 14.6 kJ mol^{-1} (the mean of the scaled HF/3-21G corrections for $[SPy{\cdot}H_3O]^+$ and $[SPy{\cdot}NH_4]^+$).

are 362.6, 248.9, and 157.5 kJ mol^{-1}. The somewhat smaller values are perhaps to be expected in complexes where the cations coordinate to three nitrogens compared to SPy's six. However, the same binding energies for 18-crown-6 (MP2/6-31+G*//HF/6-31+G* level) are also significantly lower: 408, 347 and 299 kJ mol^{-1} (for Li^+, Na^+ and K^+, respectively). The magnitude of the SPy→cation charge transfer ΔQ in the complexes with Li^+, Na^+ and K^+ shows the same trend as the binding energies.

Complex with H_3O^+

Small, planar molecular cations such as hydronium (H_3O^+) and sulfonium (H_3S^+) would seem to be excellent candidate species for forming strongly-bound symmetric complexes. The complex with the first of these, hydronium, has been explored in two symmetries, D_3 and C_3. In the former, the hydrogens of H_3O^+ are constrained to point *at* the macrocycle nitrogens, and in the latter the hydrogens of H_3O^+ are free to point either at or between SPy's nitrogens, the second possibility corresponding to bifurcated hydrogen bonds. The results at the HF/3-21G level (Table 3) show that a C_3 conformer is markedly lower in energy, and in fact frequency calculations show that only this conformer is stable (the D_3 conformer displaying three imaginary frequencies). The hydrogens of H_3O^+ point almost directly at the macrocycle nitrogens: O-H···N(SPy) = 173.3° and H···N(SPy) = 1.883 Å, at the HF/6-31G* level (see Fig. 2). The oxygen atom of H_3O^+ sits 0.77 Å above the mean plane of the macrocycle. At the highest level of theory (B3-LYP), the binding energy of $[SPy{\cdot}H_3O]^+ \approx 512$ kJ mol^{-1}.

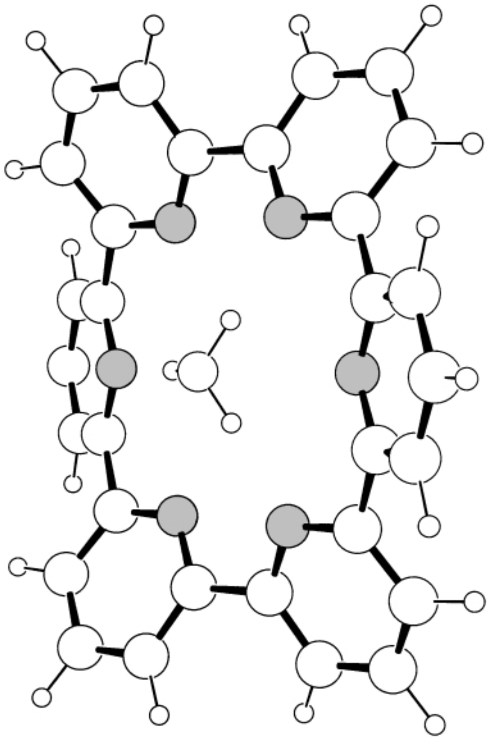

Fig. 2 HF/6-31G* C_3 conformer of $[SPy{\cdot}H_3O]^+$.

Complex with $NH_4{}^+$

Following Toner's suggestion[3] of using the ammonium ion as a template for SPy synthesis, the $[SPy{\cdot}NH_4]^+$ complex has been optimized in C_3 symmetry. The HF/3-21G results find a stable complex (positive binding energy and no imaginary frequencies) with almost linear N–H···N(SPy) hydrogen bonds. The macrocycle retains a D_3-type symmetry, with alternant 'up' and 'down' nitrogens. The HF/6-31G* optimized structure is illustrated in Fig. 3; values of the main hydrogen bond parameters are: N–H···N(SPy) = 176.6° and H···N(SPy) = 1.961 Å. The nitrogen atom of $NH_4{}^+$ sits 1.02 Å above the mean plane of the macrocycle. The binding energy of $[SPy{\cdot}NH_4]^+$ at the B3-LYP level ≈ 378 kJ mol^{-1}.

Complex with guanidinium $[C(NH_2)_3]^+$

Finally, we have considered whether it is possible for SPy to form a highly-symmetric complex with a larger molecular cation such as guanidinium. An intriguing possibility is that the

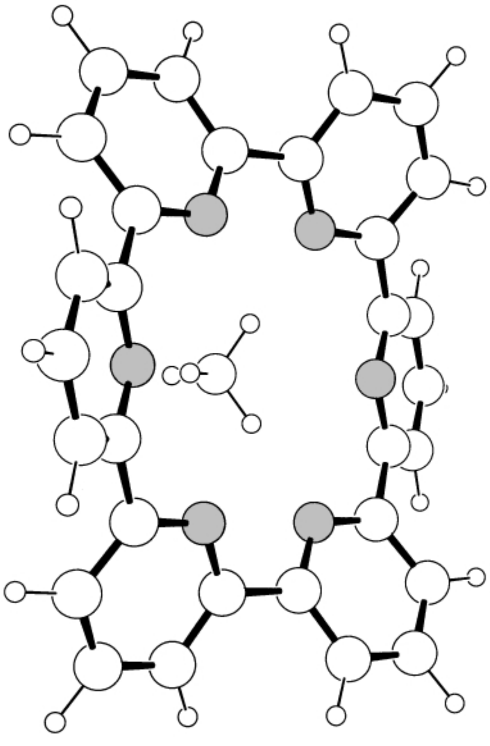

Fig. 3 HF/6-31G* C_3 conformer of $[SPy{\cdot}NH_4]^+$.

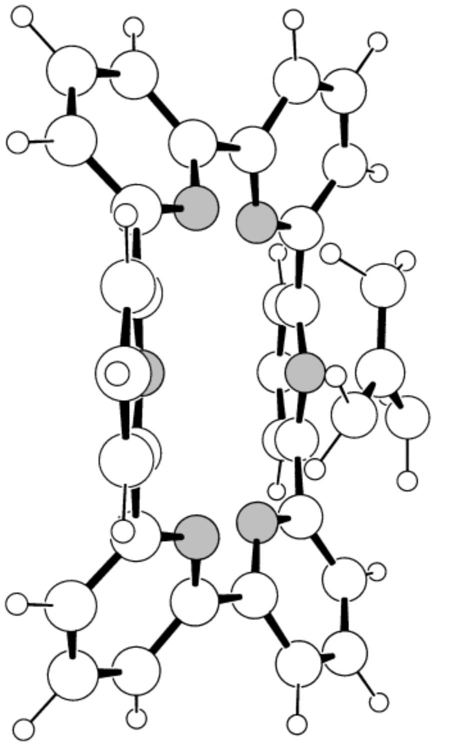

Fig. 4 HF/6-31G* C_3 conformer of $[SPy{\cdot}C(NH_2)_3]^+$.

six hydrogen atoms of guanidinium could each coordinate directly to a nitrogen atom of SPy forming an exceptionally high binding energy complex with six (charged) H-bonds. Given the relative sizes of the guanidinium cation and the SPy cavity, it is clear that SPy would have to adjust its geometry considerably in order to accomodate the ion, incurring an energy 'penalty', but possibly the stabilization due to forming six very strong H-bonds could overcome this.

The complex with guanidinium was first optimized at the 6-31G* level in D_3 symmetry. Each guanidinium hydrogen is indeed coordinated to its own nitrogen atom, and the N···H contact distances of 1.61 Å are realistic for strong, cationic hydrogen bonds. However, the SPy moiety adopts an extremely strained conformation in an attempt to accomodate the ion in this symmetry. The total energy (−1677.45638) demonstrates emphatically that this complex cannot be stable in this symmetry, since it has a negative (*i.e.* unstable) binding energy of −816 kJ mol^{-1}.

Next it was considered whether guanidinium would form a lower-symmetry (C_3) complex with SPy, such that the cation sits above the mean plane of the macrocycle (instead of being constrained to be at its centre) with three of the six guanidinium hydrogens hydrogen bond to (alternate) SPy nitrogens. Optimizations with 3-21G and 6-31G* basis sets lead to a quite credible conformer of this type (shown in Fig. 4 for the larger basis set). The SPy moiety adopts a similar, low-strain conformation found in the other complexes, and N···H = 2.133 Å, N–H–C(guanidinium) = 156.1°. The nitrogens of the cation have become markedly pyramidal in order to form the hydrogen bonds. Isolated guanidinium prefers a totally planar geometry at the HF/6-31G* level (and more sophisticated levels of theory[14]). We may estimate a 'strain' energy for guanidinium in the complex by taking its in-complex geometry, carrying out a HF/6-31G* single point calculation, and comparing this energy to that of the planar (geometry-optimized) cation; this gives a result of 38 kJ mol^{-1}. The binding energy of the complex (Table 2) is positive but not particularly large in comparison to some of the alkali metal cation binding energies). A harmonic frequency calculation at the 3-21G level (408 basis functions) proved just a little too demanding, so there is no direct confirmation of this conformer's stability. The vibrational energy correction to the binding energies for this complex were estimated as the mean of the HF/3-21G values found for $[SPy{\cdot}H_3O]^+$ (15.9 kJ mol^{-1}) and $[SPy{\cdot}NH_4]^+$ 13.3 kJ mol^{-1}).

Conclusions

The calculations presented indicate that 'sexipyridine' $(C_6H_4N)_6$ has a lowest-energy D_3 conformation in the gas phase, with alternate 'up' and 'down' nitrogens, reflecting the 'twisted' gas-phase conformation of 2,2′-bipyridine. There is, however, a saddle-shaped C_{2v} conformer very close in energy, exhibiting one imaginary frequency at the HF/3-21G level. It cannot be ruled out that this lower-symmetry unstable conformer could be (a) stable at a higher level of theory, or (b) that it may lower its symmetry to C_2 at higher level of theory, becoming the likely transtion state for inversion. We also note that the energy-ordering (and stabilities) of D_3 and C_{2v} conformers could be altered in solution, since the current calculations refer only to the gas phase. It should be pointed out, though, that the 3-21G level also predicts instability for *all* of the alkali metal cationic complexes studied in C_{2v} symmetry. Our conclusion that the barrier to inversion of SPy is *either* ≈ 102 kJ mol^{-1} (D_{6h} transition state) *or* ≈ 14kJ mol^{-1} (probable C_2 transition state) will hopefully be resolved either by future experiment or calculation.

High-symmetry (D_3, η^6) complexes with Na^+ and K^+ are predicted to be stable, with the cation at the macrocycle centroid. It may be anticipated that complexes with heavier atomic cations are also stable in this symmetry, whilst Li^+ probably forms a stable η^2 or η^3 complex of lower symmetry. Binding energies for the lighter alkali metal cations are large and show little variation (ranging from 490 to 447 kJ mol^{-1}). Energy differences of ≤100 kJ mol^{-1} between D_3 and D_{6h} conformations for SPy complexes with Li^+, Na^+ and K^+ suggest that the inversion barriers are similar to that of free SPy. The selectivity of the binding for these lighter alkali-metal cations is low, at least in the gas phase.

The hydronium cation appears to be an almost optimal size for forming a very strong complex with SPy. A C_3 conformation with H_3O^+ hydrogens forming near-linear hydrogen bonds to three of the macrocycle nitrogens is predicted. The ammonium cation offers a more experimentally accessible alternative, although the binding energy is significantly lower than for the (planar) H_3O^+.

Our results enable us to predict with some confidence that SPy does not have the cavity size or flexibility to centrally accomodate cations as large as guanidinium in a fully-hydrogen bonded (D_3 symmetry) conformation. Yet there is evidence for the stability of a lower (C_3 symmetry) complex with guanidinium positioned above the mean plane of the macrocycle and coordinated to three of the six macrocycle nitrogens. Despite this, the relatively low binding energy of the complex with guanidinium suggests that it would not be a very effective templating agent for synthesis of sexipyridine and its derivatives.

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