Conformers, Energetics, and Basicity of 2,2′-Bipyridine

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Abstract: The proton affinities of the *cis* and *trans* conformers of 2,2′-bipyridine have been determined at the MP2/6−31G**//HF/6−31G** level of theory. The neutral molecule and its protonated cation are both shown to possess stable *cis* and *trans* conformers: the barriers for cis/trans interconversion, and the roles that electrostatic interactions and π-conjugation play in these barriers, are analyzed. In addition, the barriers to rotation through planar structures are reported. The structures, the effect of electron correlation on the energetics, and the ground state charge distributions are discussed (i) with respect to biphenyl and 2,2′-bipyrimidine and (ii) in the context of dinitrogen proton sponges. With regard to (i) and *cis* → *trans* interconversion, it appears that biphenyl, 2,2′-bipyridine, and 2,2′-bipyrimidine have almost identical conformers and rotational energetics. With regard to (ii), these results indicate that SCF estimates of proton affinities and proton transfer barriers in such compounds are overestimated (by 1−2% and ∼100%, respectively), and that barriers to rotation are underestimated by some 20−30%.

Introduction

With a view to designing novel proton sponges, we recently carried out *ab initio* self-consistent field (SCF) level calculations on a series of such compounds, including 1,8-bis(dimethylamino)naphthalene (DMAN),[1] 1,6-diazabicyclo[4.4.4]tetradecane (DBT),[2] 4,5-bis(dimethylamino)fluorene, and 4,5-bis(dimethylamino)phenanthrene,[3] determining the structures, proton affinities (PAs) and barriers to proton transfer (PT) between nitrogens. All such compounds are currently just beyond the reach of effective electron correlated calculations (density functional methods notwithstanding), although the basicities of much smaller molecules can be very thoroughly studied with high-level methods[4,5]). High-level calculations have been presented[6] for the “model” proton sponge $[N_2H_7]^+$, but results of such studies necessarily have limited relevance to many real proton sponges, because of the absence of aryl groups.

2,2′-Bipyridine (hereafter 22BP) exists in a *trans* conformation in the solid state. In organic solvents and basic solutions, dipole moment measurements indicate a nonplanar *trans* configuration, with an interplanar angle ≈20°.[7] On the basis of UV absorption measurements in solution,[8] the *cis* form (Figure 1b) can be found in acidic solutions. It is evident from Figure 1a that *cis*-22BP potentially has a PA rather larger than monofunctional heterocyclic nitrogen bases, since the protonated species could be stabilized by a cationic hydrogen bond, as in numerous proton sponges.[9,10] However, the measured pK_a of 4.35 and spectroscopic estimates of the PA,[11] clearly indicate that 22BP does not behave as a proton sponge under typical conditions, almost certainly because the *trans* form dominates, and it remains *trans* after protonation. But the reasons for this are not clear—*i.e.*, if there is a large barrier to *trans/cis* rotational interconversion in [22BP]H$^+$, what is its origin? The existence of such a barrier, and the question of whether 22BP also has a stable (presumably non-planar) *cis* conformer, at least in the gas phase, appears to be unresolved either by experiment or calculation.

cis-22BP is the simplest “authentic” model proton sponge, i.e. a dinitrogen compound containing two or more aromatic rings, for which limited electron correlation calculations are feasible. It is therefore one aim of this study to explore the effect of electron correlation at the level of second order Møller−Plesset perturbation theory on the energetics (PA, PT, and rotational barriers), with a view to establishing the accuracy of SCF-level calculations on actual proton sponges. Since the rings can rotate around the linking C−C single bond to relieve repulsive interactions between nitrogen lone pairs (LPs), 22BP would not be considered a proton sponge in the usual sense (and of course it does not show an exceptionally high pK_a). Despite this, it will be shown that *cis*-22BP has a gas phase PA comparable with other proton sponges, in which the protonated form is considerably stabilized by a secondary $[N-H^+\cdots N]$ interaction, as in a typical proton sponge.

The nature of the various conformers of 22BP and [22BP]-H$^+$ is hitherto poorly determined—even the most recent reported calculations have been at the SCF level with small basis sets,[12] or semi-empirical methods.[13] Furthermore, the reliable chararacterization of these conformers and their associated basicity is of interest in the context of coordination chemistry, where 22BP finds extensive application as a versatile ligand (in both *cis* and *trans* forms).

A study of the recent literature indicates intense interest in accurate characterization of the rotational conformers of biphenyl and related bipyridines.[14] This is partly because such

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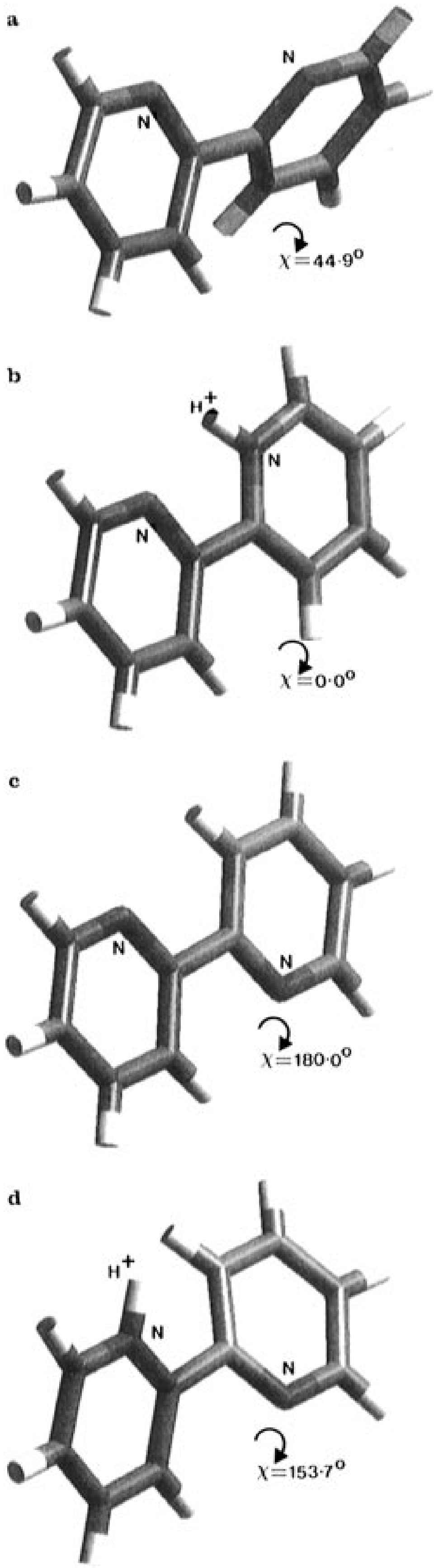

Figure 1. (a) HF/6−31G** optimized structure of *cis*-2,2′-bipyridine. (b) HF/6−31G** optimized structure of *cis*-[2,2′-bipyridine]H$^+$. (c) HF/6−31G** optimized structure of *trans*-2,2′-bipyridine. (d) HF/6−31G** optimized structure of *trans*-[2,2′-bipyridine]H$^+$.

compounds are used as models for parametrizing dynamical simulations with molecules much larger than these simple biaryl or bipyridyl species. A high level (CASSCF/PT) study has recently been published concerning biphenyl,[15] and 2,2′-bipyrimidine has been studied at the Hartree−Fock level with an extended basis set.[16] Extending the "database" of compounds studied to include correlated level calculations on 2,2-bipyridine therefore contributes to these efforts. Indeed, it will be shown that these three species are remarkably similar in terms of their conformers and barriers to rotation.

Computational Details

The restricted Hartree−Fock (RHF) geometry optimizations employed direct SCF techniques with the July 1995 release of GAMESS[17] running on DEC Alpha RISC workstations. Geometries were optimized to a tolerance of 1×10^{-4} au (maximum force on any nucleus) and $<3.3 \times 10^{-5}$ au (rms force for all nuclei). Initial optimizations employed the 6−31G basis set,[18] and harmonic frequency calculations were performed on all structures at this level (including transition states). These calculations verified that four of the nine conformers studied numbers (**1**, **2**, **5**, and **6** in the notation to be introduced shortly) corresponded to true potential energy surface minima at this level. The remaining five conformers showed the expected single imaginary frequency. Subsequent optimizations employed the 6−31G** (6d) basis set.[19] All optimizations initially assumed minimal symmetry (*e.g.* C_2 for 22BP and C_1 for [22BP]H$^+$). Full structural details of the conformers may be obtained from the author on request.

The harmonic frequency calculations and single point MP2(FC)/6−31G** (6d) energies calculated at the HF/6−31G** (6d) geometries were carried out using GAUSSIAN94[20] running on the University of London's Convex 3860 supercomputer. Optimizations to the rotational transition states (TS's) used Schlegel's eigenvalue-following method,[21] and were made feasible at the HF/6−31G** level by using the lower level 6−31G force constants in the initial guess Hessian. Topological analysis of the charge density, ρ, and maps of $-\nabla^2\rho$ utilized the programs SADDLE and GRID, part of the AIMPAC suite of programs.[22]

Results and Discussion

***cis*-2,2′-Bipyridine and *cis*-[2,2′-Bipyridine]H$^+$.** Optimization of 22BP with the 6−31G basis set gives a *cis* conformer with an interplanar angle (we will consistently use the N−C−C−N dihedral angle, χ, since the rings are almost perfectly planar in all conformers) of 57.1°. This falls by 12.2° when the basis set size is increased to 6−31G** (220 basis functions). Some details of this optimum geometry are given in Table 1, conformer **1**. On protonating this C_2 form, χ shrinks to zero, i.e. [22BP]H$^+$ has a stable planar *cis* conformer, Table 1 conformer **2**. The C−C bond linking the rings shortens slightly by around 0.01 Å on protonation; the cationic hydrogen bond distance N···H$^+$ is rather longer than that found in proton

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Table 1. Geometries,[a] Electronic Energies,[b] and Zero-Point Energies for *Cis* Conformers of 22BP and [22BP]H$^+$

	1 (22BP, C_2)	**2** ([22BP]H$^+$, (C_s)	**3** (22BP, C_{2v})	**4** ([22BP]H$^+$, C_{2v})
r(N⋯N)	2.846	2.594	2.709	2.331
r(C−C)	1.496	1.487	1.503	1.493
r(N⋯H$^+$)		2.094		1.288
χ (N−C−C−N)	44.9	0.0	0.0	0.0
N−H$^+$−N		108.5	0.0	129.6
E(HF/6−31G**)	+1062.7	0.0	+1070.4	+71.9
E(MP2[FC]/6−31G**)	+1050.2	0.0	+1060.0	+32.8
zero-point energy[c]	450.1	492.2	450.4	478.7
dipole moment[d]	3.15		3.30	

[a] Optimized at the HF/6−31G** level; values in Å and deg. r(C−C) is the length of the C−C bond joining the pyridine rings. [b] Energies in kJ·mol^{-1} refer to a basis set consisting of 6 Cartesian d-functions on heavier atoms, and are relative to (**2**), the most stable conformer. [c] HF/6−31G//6−31G level, in kJ·mol^{-1}, ignoring the (one) imaginary frequency for the C_{2v} structures. [d] HF/6−31G** level, in D. The (origin-dependent) dipole moment is not reported for the cations.

Table 2. Proton Affinity Calculation for Pyridine[a]

	Py	[Py]$^+$
E(HF/6−31G**)[b]	+995.9	0.0
E(MP2[FC]/6−31G**)[b]	+981.8	0.0
zero-point energy[c]	253.2	294.0
counterpoise correction[d]	1.5 (12.9)	

[a] MP2/6−31G**//HF/6−31G** level. [b] Electronic energies in kJ·mol^{-1}, relative to [Py]$^+$. [c] HF/6−31G//6−31G level, in kJ·mol^{-1}. [d] In kJ·mol^{-1}. HF value is given first, then the MP2 value in parentheses.

sponges.[1−3] The N−H$^+$⋯N angle of 108.5° is perhaps too acute for this to be considered a strong cationic H bond; yet it is evidently strong enough to overcome destabilization of the planar cation by H⋯H interatomic repulsion between *ortho* H atoms.

The gas-phase PA of *cis*-22BP based on the electronic energy and ZPE differences appearing in Table 1 is 1025.0 kJ·mol^{-1} at the HF/6−31G** level, falling to 1012.5 kJ·mol^{-1} at the MP2/6−31G**//HF/6−31G** level. (The ZPE's were scaled by an empirical correction factor of 0.90[23] in deriving these values.) Thus *cis*-22BP has a substantial gas-phase PA, intermediate between the PAs of DMAN[1] and guanidine.[24]

Basis set superposition error (BSSE)[25] is often significant with this basis set.[26] For example, a counterpoise correction in DBT at the HF/6−31G** level lowered the PA by 5 kJ·mol^{-1}.[2] The BSSE correction was estimated from a single-point calculation on conformer **1** with (hydrogen) ghost functions added at the same position relative to one nitrogen as found in the planar optimized cation. The BSSE correction obtained in this way lowers the PA by 1.5 kJ·mol^{-1} (HF/6−31G** level) and 13.9 kJ·mol^{-1} (MP2/6−31G**//HF/6−31G** level). Consequently, the final best estimates of the 0 K gas-phase PA, which include ZPE and counterpoise corrections, are 1023.5 kJ·mol^{-1} (SCF level) and 998.6 kJ·mol^{-1} (MP2 level).

Table 2 summarizes a PA calculation on pyridine at the same level of theory applied to 22BP (i.e. MP2/6−31G**//HF/6−31G**, with a counterpoise correction and an empirically-scaled 6−31G ZPE correction). The PA deduced from these values is 932.2 kJ·mol^{-1}, which is 10 kJ·mol^{-1} higher than the most recent experimental gas-phase value of 922.0 kJ·mol^{-1}.[27] This provides an estimate of the absolute error on the MP2 proton affinities of 22BP presented in this paper. The disagreement between experiment and theory would be much worse without the large MP2 counterpoise correction computed in the way described earlier. The PA of *cis*-22BP is predicted to be ≈67 kJ·mol^{-1} higher than the PA of pyridine at the same level of theory, so this quantifies the effects operating in *cis*-22BP which enhance the PA above the value of its analogous monofunctional base.

The barrier to proton transfer (PT) was obtained by optimizing a C_{2v}-constrained form of the cation, Table 1 conformer **4**, in which the proton is equidistant from both nitrogens. The result, based on the values given in Table 1, is that the barrier is large at 71.9 kJ·mol^{-1} (HF/6−31G** level), falling to 32.8 kJ·mol^{-1} at the MP2 level. (Changes in ZPE, although reported in Table 1, have not been included in this barrier. This is because the time scale of the PT process is likely to be shorter than the time required for the cation to "sense" its change in ZPE, so the latter has little meaning in this context.) This dramatic lowering of the barrier to PT on including electron correlation is consistent with the earlier model study of [N_2H_7]$^+$,[6] although the size of the barrier to PT in that system is much smaller. This seems to be the first calculation of such a PT barrier with an estimate of electron correlation in a much more realistic dinitrogen [N⋯H⋯N]$^+$ cation.

Turning again to (neutral) 22BP, the barrier to rotation through the planar (C_{2v}) structure, Table 1 conformer **3**, including the (very small) change in ZPE, is 7.4 kJ·mol^{-1} at the SCF level and 9.5 kJ·mol^{-1} at the MP2 level. This seems surprisingly low, given that the N⋯N distance shrinks by 0.14 Å on rotation to the C_{2v} structure, and that the planar form of 22BP will also be destabilized by H⋯H interatomic repulsion. The fact that the barrier is reasonably well-represented at the SCF level is consistent with the large body of quantum chemical calculations in the literature on rotational barriers.

***trans*-2,2′-Bipyridine and *trans*-[2,2′-Bipyridine]H$^+$.** With the 6−31G basis set, *trans*-22BP is predicted to be planar (C_{2h}), and a harmonic frequency calculation finds no imaginary frequencies. Increasing the basis size to 6−31G**, the preferred conformation is still planar—Table 3, conformer **5**. This is at odds with the interpretation of solution dipole moment studies, which reported a non-zero molecular dipole moment of ≈0.9 D.[7] It is possible that this discrepancy occurs through not including electron correlation during optimizations—if so, then the barrier to nonplanarity must be rather small (≤5 kJ·mol^{-1}). In fact, it is difficult to see why *trans*-22BP would prefer a nonplanar conformation, at least in the gas phase. A more likely explanation is that solvent−solute interactions can cause non-planarity in solution. The planar *trans* conformer of 22BP is predicted to be around 25 kJ·mol^{-1} lower in energy than the *cis* conformer (this includes ZPE differences).

A frequency calculation on the 6−31G optimized *trans* planar cation gave one imaginary frequency. Relaxing the symmetry to C_1 gives a nonplanar *trans* conformer with an interplanar angle of around 20°, which increases to 26.3° with the 6−31G**

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Table 3. Geometries,[a] Electronic Energies,[b] and Zero-Point Energies for *Trans* Conformers of 22BP and [22BP]H$^+$

	5 (22BP, C_{2h})	**6** ([22BP]H$^+$, C_1)	**7** ([22BP]H$^+$, C_s)
r(H···H)[d]		2.179	1.992
r(C−C)	1.495	1.485	1.488
r(N···H)[e]	2.469	2.533	2.408
χ (N−C−C−N)	180.0	153.7	180.0
E(HF/6−31G**)	+1035.0	+28.5	+30.4
E(MP2[FC]/6−31G**)	+1024.3	+29.4	+32.1
zero point energy[c]	451.4	491.2	491.0

[a−c]See legend of Table 1. [d] Distance from the H added on protonation to the nearest adjacent H on the other pyridine ring. [e] The interring N···H contact opposite to where protonation takes place.

Table 4. *Cis*/*Trans* Transition State Geometries,[a] Electronic Energies,[b] and Zero-Point Energies[c] for 22BP and [22BP]H$^+$

	8 (22BP, C_2)	**9** ([22BP]H$^+$, C_1)
r(N···N)	3.114	3.189
r(C−C)	1.500	1.498
r(N···H$^+$)		3.199
χ (N−C−C−N)	83.3	94.7
E(HF/6−31G**)	+1067.0	+42.1
E(MP2[FC]/6−31G**)	+1055.5	+44.5
zero-point energy	449.7	490.4
dipole moment[d]	2.68	

[a−d]See legend of Table 1.

basis (225 basis functions), Table 3 conformer **6**. The barrier to planarity, deduced from a final 6−31G** optimization with the constraint of C_s symmetry, Table 3 conformer **7**, is very small: only 2.6 kJ·mol^{-1} at the MP2 level, including ZPE changes. So again the planarity or nonplanarity of the *trans* cation in solution will be critically dependent on the solvent−solute interactions. The ZPE-corrected PA at the SCF level is 970.7 kJ·mol^{-1}, lowering to 969.7 kJ·mol^{-1} when a counterpoise correction is carried out in the same way as with *cis*-22BP. Similarly, at the MP2 level the PA is 959.1 kJ·mol^{-1}, with a large counterpoise correction reducing this to 946.5 kJ·mol^{-1}. These PA values assume that the conformation remains *trans* (but nonplanar) after protonation.

***Cis*/*Trans* Transition State Conformers.** At the 6−31G level, the TS of 22BP corresponding to rotation around the linking C−C bond has $\chi = 81.5°$, and a normal mode analysis finds the expected single imaginary frequency. On increasing the basis set size to 6−31G**, Table 4 conformer **8**, χ changes by 1.8° (see Table 3). The rotational energetics of 22BP are summarized in Figure 2a, which shows that the barrier to *cis* → *trans* interconversion is less than 6 kJ·mol^{-1}.

The TS conformer of [22BP]H$^+$ has a similar, near-orthogonal arrangement of the rings, with $\chi = 95.2°$ at the 6−31G level, changing by less than 1° with the larger 6−31G** basis set, Table 4 conformer **9**. The cation rotational energetics are summarized in Figure 2b: unlike the situation in neutral 22BP, it is clear that there is an appreciable barrier to either *cis* → *trans* or *trans* → *cis* interconversion (although the former is significantly larger). The size of this barrier is of central importance in understanding the basicity of 22BP, since without it the *trans* protonated species would instantaneously interconvert to the much more stable *cis* form, giving rise to a much larger observed PA and pK_a.

In the cation, we can identify two types of interaction which should stabilize the *trans* planar conformer of the cation, thus giving rise to the rotational barrier: (i) π -conjugation through the linking C−C bond (optimal when $\chi = 0°$ or 180°) and (ii) a weak electrostatic attraction between the (unprotonated) nitrogen LP and the adjacent hydrogen on the other pyridyl ring. The only destabilizing interaction is the repulsive H$^+$···H electrostatic interaction between the added proton and the corresponding adjacent hydrogen on the other pyridyl ring. The fact that the preferred conformer of [22BP]H$^+$ is nonplanar is evidence that the latter repulsive interaction "wins over" the weaker N···H attractive interaction at small values of the interplanar angle. As χ is decreased from 180°, both interactions are diminished and π -conjugation takes over as the dominant influence determining the rotational energy surface sketched in Figure 2b.

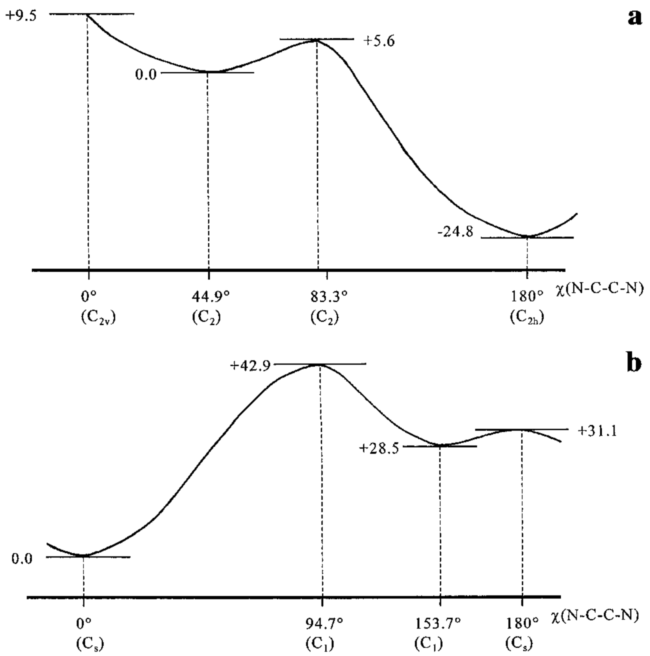

Figure 2. (a) Schematic MP2/6−31G** total energy surface for 2,2′-bipyridine (energies in kJ·mol^{-1}). (b) Schematic MP2/6−31G** total energy surface for [2,2′-bipyridine]H$^+$ (energies in kJ·mol^{-1}).

Unfortunately, there is no rigourous way to separate electrostatic and conjugative effects at the TS conformation. However, we can infer an approximate value for π-conjugative effects from the energy difference between the planar *trans* conformer and the transition state of neutral 22BP, *i.e.* 30.4 kJ·mol^{-1}. This can only be approximate, because the *trans* planar form is destabilized by steric interactions and partially stabilized by a pair of attractive N···H interactions. The extent to which these effects cancel each other is unknown.

Charge Distributions. The preceding arguments concerning π-conjugation can be placed on a more solid basis by quantifying the double bond character of the linking C−C bond in the various conformers. The most appropriate way to do this is via the bond ellipticity: $\epsilon = \lambda_2/\lambda_1 - 1$, where the λ's are the two negative eigenvalues of the Hessian of ρ at the bond critical point (CP) (the point where $\nabla\rho = 0$).[28] A perfect single bond has $\epsilon = 0.0$; the double bond in ethene has $\epsilon \approx 0.4$, and the aromatic C−C bond in benzene has $\epsilon \approx 0.23$.[28] The central C−C bond ellipticities for the nine conformers studied are presented in Table 5. The total charge density at the bond CP, ρ_c, and the Laplacian of the charge density at this point, $\nabla^2\rho_c$, are also reported. These ellipticity values confirm that the conformers which are planar or near planar, *i.e.* **1**, **4**, **5**, **6**, and **9**, show significantly larger double bond character. The small changes in the C−C bond length reported in Tables 1, 3, and 4 also approximately support this picture, but the ellipticity provides a much clearer picture of changes in the double bond

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Table 5. Properties of the Central C−C Bond in 22BP and $[22BP]H^+$

conformer	ϵ	ρ_c (e•Bohr^{-3})	$\nabla^2\rho_c$ (e•Bohr^{-5})
1	0.075	0.282	−0.835
2	0.111	0.281	−0.840
3	0.103	0.276	−0.799
4	0.095	0.280	−0.812
5	0.104	0.281	−0.825
6	0.104	0.282	−0.850
7	0.114	0.279	−0.835
8	0.013	0.281	−0.838
9	0.035	0.277	−0.839

character. Interestingly, the values of ρ_c and $\nabla^2\rho_c$, which have in the past been used to characterize bond strength,[29] show no simple relationship with ϵ or r(C−C). It seems such relationships are not valid when significant changes in conjugative character occur over a small bond length range (only 0.018 Å across all nine conformers).

It is also noteworthy that a "bond" CP is found in the C_2 axis of *cis* 22BP midway between the nitrogen atoms, which has typical properties associated with a closed shell interaction between the nitrogen atoms—a low value of ρ, positive $\nabla^2\rho$, and positive kinetic energy density. This was also found in the four dinitrogen proton sponges we studied previously.[1−3]

Figures 3a and 3b are maps of $-\nabla^2\rho$ for *cis*-22BP and *cis*-$[22BP]H^+$, plotted in the mean plane of one pyridyl ring. Comparing the two figures, the lone pair of the unprotonated nitrogen shows virtually no polarization when the adjacent nitrogen is protonated. This contrasts with the situation in a proton sponge such as DBT, where a similar visual inspection of $-\nabla^2\rho$ reveals a sizable change in the shape of the LP distribution of the unprotonated nitrogen.[2] This indicates that the cationic hydrogen bond in $[22BP]H^+$ is significantly weaker than that found in the most basic proton sponges. This was also suggested by the unfavorable hydrogen-bonding geometry in Table 1.

Conclusions

These calculations indicate the existence of a stable *cis* (albeit nonplanar) conformer of 2,2′-bipyridine, with a substantial proton affinity. However, the *trans* conformer is lower in energy, and the barrier for *cis/trans* interconversion is small (≈6 kJ•mol^{-1}). This explains why only small populations of the *cis* conformer would normally be found either in the gas phase or solution, and together with the somewhat larger barrier for *trans*/*cis* interconversion in the cation, it explains the rather low measured pK_a. In fact, solvent effects on such a small *cis/trans* barrier in 22BP could be large enough to remove it completely. Hence the existence of a stable *cis* conformer in the liquid phase is likely to show dependence on the solvent and/or pH of the solution, as has been verified in a previous experimental study.[8]

The *trans* conformer is predicted to be planar (C_{2h}) in the gas phase, in contrast to the situation in various solvents, where dipole moment measurements suggest a small interplanar angle. The *cis* form of [2,2′-bipyridine]H^+ is predicted to be planar in the gas phase, while the *trans* form has an interplanar angle of ≈26°. The *cis* conformer of the cation is by far the most stable, and the barrier to *trans/cis* interconversion in [2,2′-bipyridine]H^+ of ≈14 kJ•mol^{-1} is probably low enough to observe measurable populations of the *cis* cation at ambient temperatures—and of course, this equilibrium could be further shifted toward the *cis* cation in the presence of an appropriate coordination center.

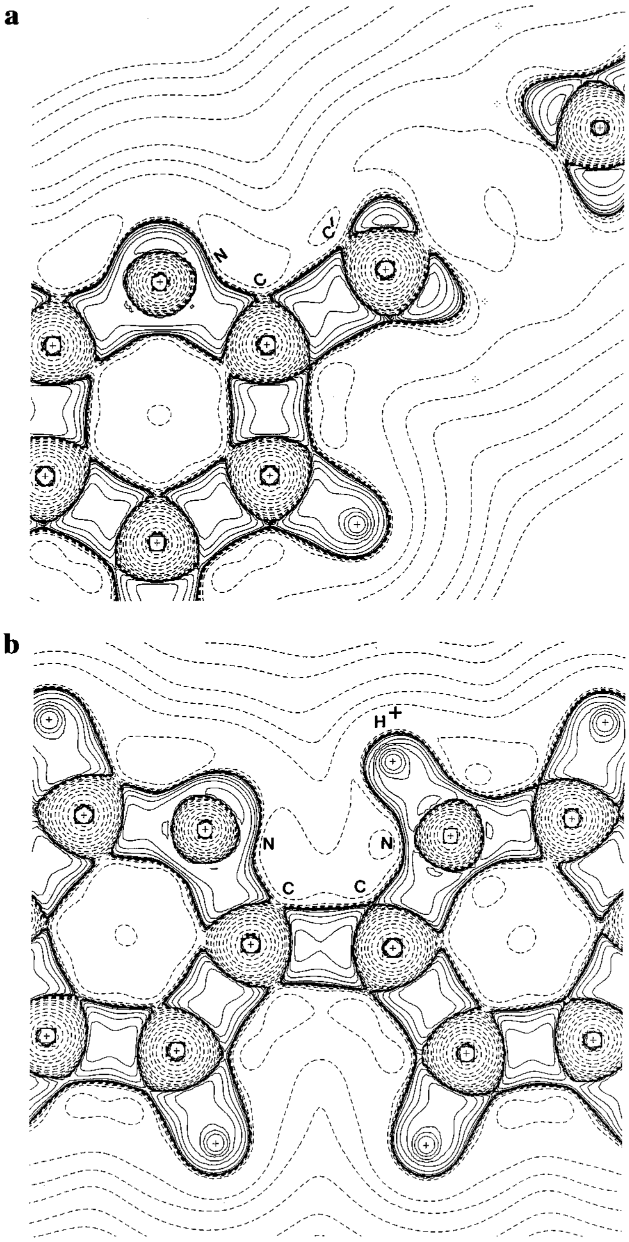

Figure 3. (a) HF/6−31G** $-\nabla^2\rho$ distribution in *cis*-2,2′-bipyridine (in the plane of one ring). (b) HF/6−31G** $-\nabla^2\rho$ distribution in *cis*-[2,2′-bipyridine]H^+ (in-plane).

The *trans/cis* barriers to interconversion in both 2,2′-bipyridine and its protonated cation have their origin in π-conjugative stabilization, which we have roughly estimated as ≈30 kJ•mol^{-1}.

The equilibrium geometry of *cis* 22BP is remarkably similar ($\chi = 44.9°$) to the results of *ab initio* calculations for biphenyl ($\chi = 44.3°$ [15]) and 2,2′-bipyrimidine ($\chi = 49.7°$ [16]). The barrier for *cis*/*trans* interconversion in 22BP (5.6 kJ•mol^{-1}) is also very similar to the results of the biphenyl calculation (6.4 kJ•mol^{-1}) and an experimental gas-phase value for 2,2′-bipyrimidine (4.0 kJ•mol^{-1} [30]). By implication, the size of the π-conjugative effect must be similar in all three compounds.

The PA of *cis*-22BP is 68 kJ•mol^{-1} larger than that obtained for pyridine, at the identical level of theory. This extra stabilization comes almost entirely from the $[N-H^+\cdots N]$ interaction, with a very small contribution from increased π-conjugation, which we can estimate at ≈5 kJ•mol^{-1}, since χ

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[29] Bader R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

[30] Fernholt, L.; Romming, C.; Samdal, S. *Acta Chem. Scand.* **1981**, *A35*, 707.

changes from ≈45° to 0° on protonation of the *cis* conformer. This therefore places a lower limit on the strength of the cationic hydrogen bond in *cis*-[22BP]H^+ at 63 kJ·mol^{-1} (it must be more than this since there is H···H repulsion between *ortho* hydrogens in [22BP]H^+).

As a model dinitrogen proton sponge, *cis* 2,2′-bipyridine can give us guidelines on the accuracy obtainable in Hartree−Fock level calculations on real sponges, where the inclusion of any electron correlation is problematic. The best estimates of its gas-phase proton affinity, barrier to proton transfer and the barrier to rotation through the C_{2v} structure are 998.6, 32.8, and 9.8 kJ·mol^{-1}, respectively. The inclusion of electron correlation at the MP2 level produces a considerable lowering of the proton transfer barrier (reducing it by more than 100%), with a less marked effect on the barriers to rotation (typically these increase by 20−30%). It is reasonable to conclude that SCF level calculations considerably overestimate proton transfer barriers in dinitrogen compounds, whereas reasonable estimates of rotation barriers may be obtained without electron correlated methods.

For both *cis* and *trans* conformers, SCF level calculations give proton affinities ≈2.5% larger then the corresponding MP2 values. This discrepancy is caused by SCF-MP2 differences in total electronic energy and basis set superposition error, in roughly equal measure. The MP2 PAs have their own deficiencies, since the MP2 correction provides only an estimate of electron correlation; the MP2 energies were computed at the SCF/6−31G** geometry; and an empirically-scaled SCF ZPE correction was applied in computing the MP2 proton affinities. Nevertheless, these results suggest that SCF level calculations on dinitrogen proton sponges will systematically overestimate gas phase PAs by at least 10 kJ·mol^{-1}, maybe as much as 20 kJ·mol^{-1}, so the results of such calculations should be downwardly revised.

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