4480 *J. Org. Chem.* **1996,** *61,* 4480−4482

Ab Initio Studies of Proton Sponges. 3. 4,5-Bis(dimethylamino)fluorene and 4,5-Bis(dimethylamino)phenanthrene

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Received November 29, 1995

The proton sponge properties of the title compounds 4,5-bis(dimethylamino)fluorene (DMAF) and 4,5-bis(dimethylamino)phenanthrene (DMAP) have been much discussed in the literature,[1a,2] with geometric effects of the ring system, linearity of the N−H···N linkage, and overlap of N lone pairs cited as possible sources of enhanced basicity. Certainly, both bases appear to have geometries more likely to result in proton sponge properties than does the archetypal proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN). The ring structure angles the nitrogens toward each other (an N···N separation of 2.31 Å has been suggested for DMAF), forcing close lone pair−lone pair contact and allowing an almost linear H-bond. The primary aim of this paper is to establish the proton affinities (PA) and structures of DMAF and DMAP.

In two previous papers, papers 1 and 2, we have employed *ab initio* MO methods in the investigation of two "proton sponges", 1,8-bis(dimethylamino)naphthalene (DMAN)[3] and 1,6-diazabicyclo[4.4.4]tetradecane ([4.4.4]);[4] here we report a similar study of DMAF and DMAP. A common feature of proton sponges is the proximity of two basic (usually amino) groups, acting in concert to enhance basicity by the formation of a cationic hydrogen bond. Typically a proton sponge has a pK_a of 12 or above, and a PA of well over 1000 kJ mol^{-1}.[1] Our long-term aim is to build a "data-base" of proton sponges at a common, albeit modest, level of theory, with a view to correlating structural and charge density parameters with proton sponge basicity. In this way, we hope to provide useful guidelines for the design of novel proton sponges, by quantifying the separate contributions of H-bond strength, strain relief, N···N repulsion, changes in aromatic character, *etc.* to the intrinsic basicity.

Given the above arguments, the pK_a values of DMAF (12.8) and DMAP (11.5) reported in ref 2a are surprising. While the former is somewhat more basic than DMAN (12.0), the latter's pK_a is *lower* than that of DMAN. The authors ascribed this to the poorer shielding of the H-bond by the methyl groups in DMAPH$^+$ affecting its solvation. Our gas-phase theoretical derived PA's do not include such effects, facilitating a better estimation of the intrinsic basicity of the molecules in question.

Computational Methods

All MO calculations were carried out using GAMESS[5] running on DEC Alpha workstations. Optimization of all geometrical parameters was performed at the HF/6-31G level;[6] 6-31G*[7] single point energy calculations at this geometry were performed to obtain more accurate PA's and charge distributions. As in paper 1,[3] C_2 symmetry was assumed for the free bases and in the initial optimizations of the acids. Further optimization of the acids broke this C_2 symmetry, allowing the proton to move from its central position toward one nitrogen. The asymmetrical proton position was found to be of lower energy in both cases. Zero-point energy (ZPE) corrections to the PA's have been calculated at the STO-3G level, with an estimated correction based on paper 2.[4]

Topological charge density analysis was performed with the AIMPAC suite of programs,[8] using the programs SADDLE and BUFFALO in particular. This analysis relies upon the location and characterization of critical points (CP) in the charge density ρ and its associated scalar field, $-\nabla^2\rho$.[9] A CP in ρ is defined as a point where $\nabla\rho$ vanishes and is characterized by the curvatures of the density at this point. Here we are only interested in (3,−1) CP's, where the density is a minimum in the internuclear direction and a maximum in the two orthogonal directions. Such CP's are characteristic of bonding interactions, even in closed shell interactions such as hydrogen bonding. CP's in $-\nabla^2\rho$ are similarly defined by vanishing first derivatives of $\nabla^2\rho$; our interest is in (3,−3) CP's in $-\nabla^2\rho$ (specifically the nitrogen lone pair features), which reproduce the behavior of Lewis electron pairs.[10]

Results and Discussion

The 6-31G, C_2 optimized bond lengths and angles of DMAF, DMAFH$^+$, DMAP and DMAPH$^+$ are represented in Figure 1. As in Papers 1 and 2, breaking the C_2 symmetry in the acids causes large changes in geometry only in the N−H···N region, the ring system hardly being affected. We therefore report only the C_2 structures in detail. The bond lengths and angles in Figure 1 contain few surprises, with aromatic C−C bonds at around 1.4 Å and C−C−C angles close to 120°. Exceptions to this pattern are found around the central rings, with C−C bonds as long as 1.51 Å and C−C−C angles as large as 134.4°. The two systems differ greatly in the degree of twisting of the ring system, as evidenced by the deviations from the mean plane in Table 1.

DMAF and DMAFH$^+$ behave in a similar fashion to their naphthalene analogues; DMAF is twisted (slightly more than DMAN) with the nitrogens 0.42 Å from the mean plane, which is almost entirely removed on proto-

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S0022-3263(95)02114-1 CCC: $12.00

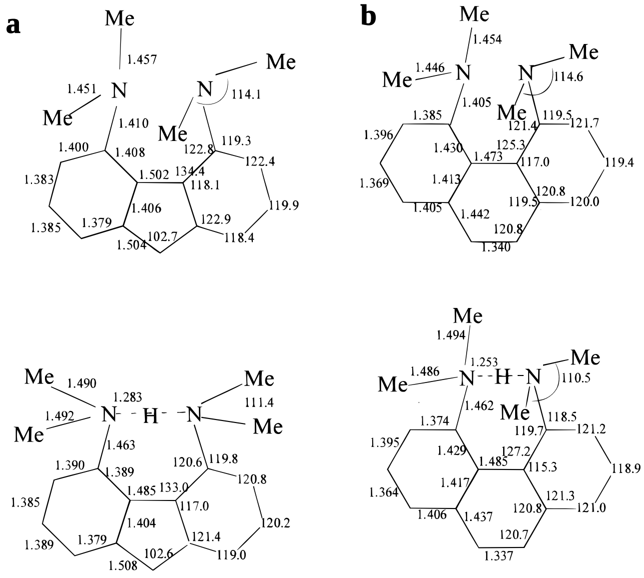

Figure 1. (a) HF/6-31G optimized bond lengths and angles of DMAF and DMAFH$^+$. (b) HF/6-31G optimized bond lengths and angles of DMAP and DMAPH$^+$.

Table 1. Deviations of Heavy Atoms from the Molecular Mean Planes (Å)[a]

	DMAF	DMAFH$^+$	DMAP	DMAPH$^+$
C1	0.218	−0.059	0.601	0.386
C2	0.219	−0.061	0.522	0.303
C3	0.030	−0.022	0.037	−0.025
C4	−0.114	0.007	−0.267	−0.180
C9	0.000	0.000	0.201	0.141
C10	0.093	−0.029	0.310	0.210
C11	0.005	−0.009	0.028	0.020
N1	−0.421	−0.094	−0.944	−0.656
C14	−0.007	1.417	−0.726	−0.331
C15	−1.698	−1.206	−2.245	−2.115

[a] All structures constrained to have C_2 symmetry.

Table 2. Proton Affinities of DMAF and DMAP

	free base energy (hartrees)	cation energy[a] (hartrees)	ΔZPE (kJ mol^{-1})	PA[b] (kJ mol^{-1})
	DMAF			
STO-3G//STO-3G	−755.017222	−755.535737	36.3	1325.1
6-31G//6-31G	−763.972612	−764.397536	–	1074.4
6-31G*//6-31G	−764.270459	−764.687825	–	1054.5
	DMAP			
STO-3G//STO-3G	−792.395038	−792.910806	41.1	1313.0
6-31G//6-31G	−801.820442	−802.243730	–	1065.3
6-31G*//6-31G	−802.127302	−802.543241	–	1046.0

[a] Cation values refer to the asymmetric C_1 form, except in the STO-3G case where the cations have C_2 symmetry. [b] Including an estimated ZPE correction.

Table 3. HF/6-31G* Bond CP and Lone Pair Density Properties (au)[a]

	Bond CP		Lone Pair	
	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
DMAF	0.014	+0.040	0.594	−3.291
DMAFH$^+$ N−H	0.294	−1.454	–	–
N···H	0.065	+0.154	0.592	−3.326
DMAP	0.017	+0.050	0.589	−3.208
DMAPH$^+$ N−H	0.284	−1.341	–	–
N···H	0.085	+0.164	0.589	−3.288

[a] Base bond CP values refer to the N···N "bond"; acid LP values refer to the LP on the unprotonated N.

Table 4. Summary of HF/6-31G*//HF/6-31G Proton Sponge Properties (kJ mol^{-1}, Å, and e bohr^{-5})

	DMAN	[4.4.4]	DMAF	DMAP
PA	1030.1	1082.0	1054.5	1046.0
PT Barrier	22.1	12.5	21.8	13.0
r(N···N)[a]	2.829	2.997	2.981	2.865
N−N shortening on protonation	0.247	0.399	0.273	0.275
$\nabla^2\rho_c$ N···N[a]	+0.0545	+0.0384	+0.0398	+0.0505

[a] In the unprotonated bases.

nation. In contrast, DMAP and DMAPH$^+$ are severely twisted as a result of steric repulsions (the nitrogens are 0.9 Å from the mean plane in DMAP, falling to 0.66 Å in DMAPH$^+$). This deformation of the ring systems, a product of N···N repulsion, leads to much longer N···N separations than anticipated by Staab *et al.*[2a] Another interesting feature of the optimized geometries is the orientation of the methyl groups. In both bases one methyl group lies close to the plane of the ring and one almost perpendicular to this. Protonation causes the nitrogens in DMAFH$^+$ to become almost symmetrically disposed about the mean plane, but in DMAPH$^+$ the "in-out" structure of the methyl groups is maintained.

The optimized geometries agree well with the published X-ray crystal structures for the perchlorate salts of DMAFH$^+$ and DMAPH$^+$;[2] bond lengths generally differ by ≈0.03 Å and angles by 1−2°. The crystal structures also support the findings that DMAFH$^+$ is almost flat but that DMAPH$^+$ is very twisted and that the "in-out" methyl groups are present in DMAPH$^+$. The optimized N···N separations are substantially longer than the crystallographic values, perhaps due to the absence of a counterion. DMAFH$^+$ is found to possess a crystallographic two-fold axis through the center of the molecule, unlike DMAPH$^+$ which is asymmetrically protonated.

As in papers 1 and 2, we find that breaking the C_2 symmetry of the N−H−N linkage results in a lower electronic energy and a more conventional N−H···N hydrogen bond in both systems. In DMAFH$^+$ we find N−H = 1.059 Å, N···H = 1.650 Å and N−H···N = 176.9°; in DMAPH$^+$ N−H = 1.070 Å, N···H = 1.533 Å and N−H···N = 168.3°, with the carbon skeleton hardly changed from the C_2 geometry in Figure 1. At the 6-31G*//6-31G level the barriers to proton transfer are 21.8 and 13.0 kJ mol^{-1} in DMAFH$^+$ and DMAPH$^+$, respectively.

6-31G* single-point energy calculations at the 6-31G equilibrium geometry allow estimation of the PA (papers 1 and 2 indicate that d-type polarization functions on heavy atoms are essential for a reasonable estimation of PA). A crucial factor in determining a theoretical PA is the change in zero-point energy (ZPE) on protonation. The 6-31G harmonic frequency calculation required is very computationally demanding, and it proved possible to do this only at the STO-3G level. Paper 2 showed that STO-3G ZPE corrections to the PA of simple amines are consistently ≈5 kJ mol^{-1} less than the analagous 6-31G results. Thus, we apply the STO-3G ZPE correction plus 5 kJ mol^{-1} to the 6-31G*//6-31G energy differences (Table 2). The PA's so obtained are significantly larger than that found for DMAN (the absolute errors on such values are estimated at around 10 kJ mol^{-1} [4]), but rather less than that of [4.4.4]. The PA's of DMAF and DMAP are similar, differing by around 8 kJ mol^{-1}, remarkable when one considers the highly different geometries and the large observed differences in the pK$_a$'s of the systems. These results apparently support Saupe's[2a] assignment of the anomalously low pK_a of $DMAPH^+$ as being due to solvent effects.

Topological analyses of ρ and $\nabla^2\rho$ around the N···N region of the bases and their acids (Table 3) are broadly similar to those reported in papers 1 and 2. As in those studies we find a (3,−1) CP in ρ between the nitrogens of the free bases, despite the fact they are clearly repelling one another. The asymmetrical H-bonds in the C_1 acids have typical H-bond density properties, with N−H covalent (high ρ and negative $\nabla^2\rho$) and N···H ionic (low ρ and positive $\nabla^2\rho$). Lone pair maxima in $-\nabla^2\rho$ are found on the nitrogens of the bases and on the unprotonated N of each acid. Again the calculated properties at these points are similar to those found in DMAN and [4.4.4], indicating "normal" nitrogen basicity.

The results presented raise an interesting point regarding the relation between basicity and geometry of proton sponges. There seem to be two approaches in the design of new proton sponges: (i) to force the nitrogen atoms closer together and align them so as to maximize their repulsion (as in DMAN, DMAF, and DMAP), (ii) incorporating nitrogens in flexible structures which can minimize the N···N distance on protonation, maximizing the H-bond strength (*e.g.* [4.4.4]). The results for DMAN, DMAF, and DMAP show that decreasing the N···N separation does not lead to enhanced basicity (DMAN has the shortest N···N distance but the lowest PA). DMAF and DMAP show slightly enhanced basicity over DMAN, probably due to an increase in strain. In contrast, a substantial increase in basicity over DMAN is found in the highly flexible [4.4.4].

We emphasize that there is no apparent relation between basicity and the N···N distance in either the unprotonated base or the protonated acid. Such geometrical parameters cannot, on their own, be used to infer basicity, in contrast to the arguments of Saupe *et al.*[2a] An encouraging result, however, is the approximately linear correlation between PA and the *reduction* in N···N distance on protonation. This also suggests that H-bond strength plays a large part in determining proton sponge basicity and may be more important than maximizing N···N repulsion.

JO952114C