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Ab Initio Studies of Proton Sponges: 1,8-Bis(dimethylamino)naphthalene

J. A. Platts and S. T. Howard*

Department of Chemistry, University of Wales, College of Cardiff, Cardiff CF1 3TB, U.K.

K. Woźniak

Chemistry Department, Warsaw University, Ul. Pasteura 1, 02-093 Warszawa, Poland

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The structures of 1,8-bis(dimethylamino)naphthalene and its protonated forms have been determined by *ab initio* geometry optimization. The title compound is found to possess C_2 symmetry in the gas phase, and the $N(C_{10}H_6)N$ fragment is markedly nonplanar. Protonation causes the molecule to become more planar, as it approaches (without quite attaining) C_{2v} symmetry. Asymmetric protonation at one nitrogen is energetically preferred to the symmetric N⋯H⋯N bridged form. The predicted proton affinity is within a few kilojoules per mole of an experimental value. The changes in structure and the electron distribution are discussed in terms of the topology of the charge density ϱ and of $\nabla^2\varrho$, for this and related amines.

Introduction

The title compound 1,8-bis(dimethylamino)naphthalene (DMAN) illustrated (Figure 1) is an exceptionally strong base, in comparison with other aromatic amines with a pK_a value of around 12. It invariably forms ionic complexes, with a cationic hydrogen bond $[NHN]^+$, and is a model example of so-called "proton sponges". Their basic strength derives from the proximity of amino groups (the "proximity effect"), and it has been described in two excellent reviews.[1,2] The gas-phase proton affinity (PA) of DMAN has been experimentally determined as 1030.1 kJ mol^{-1} by measurement of proton-transfer equilibria.[3] This is one of the highest known values for an organic base, hence the interest in DMAN and its related compounds. The crystal and molecular structure of DMAN has been determined by X-ray diffraction.[4] It was found that the naphthalene ring moiety is twisted considerably away from planarity. This was interpreted in terms of minimizing the strain between the dimethylamino groups and the associated lone pair (LP) repulsions.

The calculations presented here indicate that the isolated molecule has C_2 symmetry, although the crystal structure determination gave a molecule without symmetry. This is presumably due to packing forces in the crystal. The lack of symmetry in the solid state has been confirmed from ^{13}C solid-state NMR measurements.[5] A number of DMAN complexes have been successfully crystallized, in which DMAN always acts as the proton acceptor.[6] In many of these complexes, the cation is symmetric with a bridging proton on a 2-fold crystallographic axis. In others, one nitrogen has been protonated.

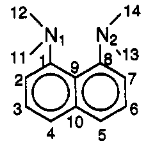

Figure 1. DMAN, with labeling scheme.

The X-ray diffraction results reveal substantial changes in geometry between the protonated and unprotonated forms. These changes must be accompanied by significant changes in the distribution of electronic charge, although this can only be inferred from the X-ray measurements, and its interpretation is complicated by the presence of interactions with surrounding molecules in the crystal. Given the considerable interest in proton sponges, and the apparent lack of high-level calculations which could shed light on their basic properties, it was decided to perform Hartree−Fock calculations on DMAN and its protonated cation DMANH$^+$. The main objectives were to optimize the structures in the absence of any crystal packing forces; to compute a theoretical gas-phase PA for DMAN, and to relate changes in structure on protonation to those in the electron distribution. This work is part of a study of hydrogen bonding and protonation, particularly with regard to its influence on electronic structure.

Computational

The GAUSSIAN92[7] suite of programs was used on the University of London's Convex C3800 supercomputing facility. *Ab initio* calculations were additionally performed at Cardiff on a DEC Alpha RISC workstation running GAMESS.[8] Direct SCF methods were used in both cases. The optimizations employed the algorithm due to Schlegel[9] with analytical first and second deriva-

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Table 1. Selected Geometrical Parameters (in Angstroms and Degrees)

parameter	DMAN (HF/6-31G)	DMAN expt (ref 4)	DMANH$^+$ (HF/6-31G)	DMANH$^+$ expt (ref 6)	$C_{10}H_8$ (HF/6-31G)
r(C1–C2)	1.372	1.383, 1.373	1.361	1.363	1.363
r(C2–C3)	1.407	1.387, 1.410	1.412	1.410	1.415
r(C3–C4)	1.356	1.337, 1.333	1.360	1.353	1.363
r(C4–C10)	1.419	1.419, 1.408	1.419	1.412	1.420
r(C9–C10)	1.424	1.425	1.416	1.434	1.413
r(C1–C9)	1.447	1.429, 1.449	1.428	1.422	1.420
r(C1–N1)	1.416	1.395, 1.399	1.466	1.466	
r(N1–C11)	1.451	1.458, 1.458	1.488	1.469	
r(N1–C12)	1.456	1.467, 1.465	1.489	1.464	
C9–C1–C2	119.4	119.4, 118.6	121.2	121.58	120.8
C1–C2–C3	122.3	121.4, 121.4	120.5	120.28	120.2
C2–C3–C4	119.7	120.7, 121.0	119.9	120.12	120.2
C3–C4–C10	120.5	120.5, 120.3	121.0	121.42	120.8
C4–C10–C9	120.7	120.0, 120.5	119.5	121.6	119.0
C10–C9–C1	117.1	117.0, 117.2	117.9	117.26	119.0
C1–C9–C8	125.9	125.8	124.3	125.48	122.0
C4–C10–C5	118.6	119.5	120.9	119.24	122.0
C9–C1–N1	121.6	120.8, 120.1	117.6	117.73	
C9–C1–N1	121.6	120.8, 120.1	117.6	117.73	
C1–N1–C11	119.1	118.5, 118.0	113.6		
C1–N1–C12	117.5	117.1, 117.2	113.4		
C1–C2–C3–C4	2.7	3.0, 3.0	0.07	−1.8	0.0
C2–C3–C4–C10	−3.0	−5.1, −4.6	−0.08	1.3	0.0
C3–C4–C10–C9	−1.5	−1.1, −2.4	−0.02	0.8	0.0
C4–C10–C9–C1	6.2	8.9, 10.5	0.14	−2.5	0.0
C10–C9–C1–C2	−6.5	−10.9, −11.8	−0.15	2.3	0.0
C10–C9–C1–N1	172.2	168.5, 167.9	179.7	176.1	
C9–C1–N1–C11	148.8	162.7, 160.9	116.1	108.2	
C9–C1–N1–N12	−67.1	−59.4, −60.6	−115.0	55.2	
N1–H–N2			161.9	154.8	

tives of the Restricted Hartree–Fock (RHF) wave function, at the 3-21G[10] and 6-31G[11,12] levels of theory. The geometry optimization of DMAN began with the 3-21G basis set and nuclear coordinates from the crystal structure analysis. Despite the lack of any symmetry constraints, this resulted in a structure with C_2 symmetry, so many of the subsequent calculations with the 6-31G and 6-31G* basis sets applied this symmetry as a constraint. Initially, the 6-31G geometry optimization of DMANH$^+$ was also constrained to have this symmetry, with the proton symmetrically positioned on the C_2 axis, bridging the two nitrogens. The 6-31G-optimized DMAN structure was used as the starting point. Following this, the C_2 symmetry constraint was lifted and a geometry optimization was attempted, in order to investigate the possibility of an unsymmetrical N···H···N hydrogen bond being formed. The C_2 constrained form of DMANH$^+$ will be referred to as DMANH$^+$ (i) and the unconstrained form as DMANH$^+$ (ii). A 6-31G optimization on naphthalene is also reported for comparison.

In order to better estimate the PA of DMAN, single-point energy calculations using the 6-31G* basis set[13] were carried out on both DMAN and DMANH$^+$ at their respective 6-31G-optimized geometries (6-31G*//6-31G). Calculations at the same level were also carried out for methylamine, dimethylamine, trimethylamine, and *N*,*N*-dimethylaniline. Computation of harmonic vibrational frequencies for DMAN in order to estimate the zero-point energy (ZPE) correction to the PA proved to be beyond the available computing resources. To circumvent this problem, 6-31G frequency calculations were undertaken for the related amines listed above, which were used as models to estimate the DMAN ZPE correction.

The critical-point (CP) analysis of the scalar fields ϱ and $\nabla^2\varrho$ developed by Bader and co-workers[14] has been utilized to explore how the electron distribution is affected by protonation. The set of CPs in $\varrho(\mathbf{r})$, $\{\mathbf{r}_c\}$, are defined such that $\nabla\varrho(\mathbf{r}_c) = 0$. The value of ϱ_c in a bond may be used to measure its strength;[15] the trace of the Hessian of ϱ at $\mathbf{r}_c$ measures the extent of depletion or concentration of charge;[16] and the ratio of eigenvalues of this matrix (the bond "ellipticity" ϵ) measures the extent of conjugation or double-bond character.[17] More precisely, $\epsilon = \lambda_2/\lambda_1 - 1$, where the λ's are the two (negative) eigenvalues of the Hessian corresponding to directions perpendicular to the bond. The set of stationary points where $\nabla(\nabla^2\varrho) = 0$, the points of maximum charge concentration or depletion, may be utilized in studies of reactivity,[18-20] much in the same way as the electrostatic potential (EP).[21] A local maximum, or (3,−3) critical point in $-\nabla^2\varrho$, occurs in the region of the density associated with a LP of electrons.

The CP analyses of ϱ were carried out using the SADDLE program.[22] The search of $\nabla^2\varrho$ to determine the nitrogen LP properties employed a modified version of Laidig's FORTRAN program SADD2R.[22]

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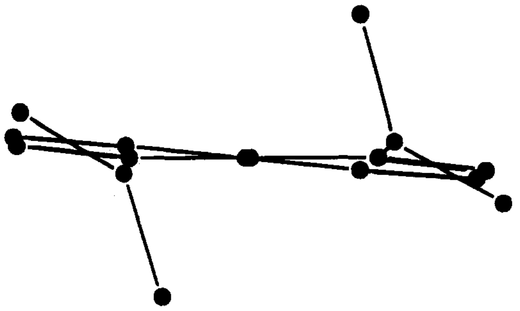

Figure 2. DMAN, *ab initio* optimized structure, view along the C_2 axis.

Results and Discussion

Table 1 shows selected bond lengths, bond angles, and torsion angles for the optimized structures of DMAN, DMANH$^+$ (i), and naphthalene with the 6-31G basis set. Our optimized parameters for naphthalene are almost identical to those published recently by Hinchliffe and Machado using the 6-31G** basis set.[23] The bond lengths in DMAN differ systematically from the analogous values in naphthalene. The largest deviation is 0.027 Å for r(C1—C9), and the average difference is 0.010 Å. This may be ascribed to the delocalization of the nitrogen LP electrons through the π system of naphthalene, which results in changes in the π character of the C—C bonds. This can also be seen in r(C1—N1), which is shorter than typical N(sp^3)—C(ar) bond lengths, and in r(N1—C11) and r(N1—C12), which are again shorter than normal N(sp^3)—C(sp^3) bonds.[24] Table 1 also reports the geometry from the X-ray diffraction study of Einspahr *et al.*[4] Two values are reported for each experimental geometrical parameter, since the left and right halves of DMAN were not identical (no C_2 symmetry). The largest differences between the average bond lengths found in the crystal and the optimized lengths are 0.021 Å for r(C3—C4), 0.019 Å for r(C1—N1), and 0.020 Å for r(N1—C12). These are approximately twice as large as the average left-right discrepancy reported in the experimental structure.

The most remarkable feature in the bond angle data is the value of 125.9° for C1—C9—C8 (122° in naphthalene), which is indicative of the repulsion between the NMe$_2$ groups. The remaining ring angles are much nearer to the analogous values in naphthalene, and these derivations are due to the electronic effect of the amino groups and the relaxation of the ring geometry caused by the very large C1—C9—C8 angle. The angles C1—N1—C11 and C1—N1—C12 are both close to 120°, which further supports the idea that the nitrogen is sp^2 hybridized with the LP density partially delocalized. Most predicted bond angles are within 1° of the corresponding experimental values: the largest differences from the averaged crystallographic bond angles are found in C1—C2—C3 (0.9°), C2—C3—C4 (1.1°), C4—C10—C5 (0.9°), and C1—N1—C11 (0.9°).

The torsion angle data reveals possibly the most interesting feature of this molecule, i.e. that the naphthalene ring system is not planar but twisted (see Figure 2). Dihedral angles for the ring carbon atoms vary from 1.5° to 6.5° in their absolute values, while that defining the N atom has an even larger deviation from 180.0° (7.8°). In general, the degree of planarity is slightly higher for the *ab initio* optimized structure. The dihedral angles describing the positions of the methyl carbons relative to the mean plane, C9—C1—N1—C11 and C9—C1—N1—C12, are 148.8° and −67.1°, respectively. They are qualitatively similar to those found in the crystal structure, with one methyl group close to the mean plane of the ring and the other one almost perpendicular to it. However, there are significant quantitative differences of 14° and 7°. This can be attributed to intermolecular interactions of the dimethylamino groups in the crystal. Distances of atoms from the mean plane of the ring are shown in Figure 3. The largest deviations occur for N1 (0.27 Å) and C1 (0.09 Å); in the crystal structure these atoms are even further from the mean plane (0.40 and 0.15 Å, respectively). The "in-plane" methyl groups are more shifted from the mean plane in the isolated molecule (0.30 Å) than in the molecule in the crystal lattice (0.13 and 0.17 Å). The reverse is true for the "axial" methyl groups (1.53 for the isolated molecule and 1.63 for the crystal structure).

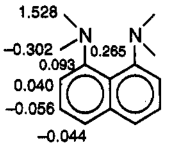

Figure 3. DMAN, with distances of atoms from the mean plane.

The results of a CP analysis of ϱ for DMAN are given in Table 2. The total charge density ϱ_c, the Laplacian of the charge density $\nabla^2\varrho_c$, and the ellipticity at bond CPs are reported. The large values of ϱ_c and $\nabla^2\varrho_c$ in the C1—N1 bond support the idea that the nitrogen LP density has become partially delocalized over the π system of the molecule. The results also show that the C1—C2 and C3—C4 bonds have the most double-bond character, which would be anticipated from a consideration of resonance structures.

A search of the valence shell of one of the nitrogens was also performed, for the purpose of locating the LP and evaluating the properties of the charge density at that point. Concentric spherical shells were explored for small values of $\nabla(\nabla^2\varrho)$, followed by application of the Newton—Raphson minimizer in SADD2R to precisely locate the stationary points. Analogous 6-31G*//6-31G calculations and CP analyses are reported in Table 3 for the LP of ammonia, methylamine, dimethylamine, trimethylamine, and *N,N*-dimethylaniline. The values of ϱ and $\nabla^2\varrho$ indicate that the nitrogen LP in DMAN has properties intermediate between those of methylamine and dimethylamine. It is therefore clear that the very high basicity observed for DMAN cannot be assigned to the LP properties on one nitrogen and that it must have its origin in some other effect, such as the cooperative action of both LPs.

Geometrical parameters from the 6-31G optimization of DMANH$^+$ (i) are also reported in Table 1. In general, the C—C bond lengths are much closer to the values found in naphthalene than the analogous values for DMAN, and r(C1—N1) is much longer than in DMAN. These results suggest that there is little delocalization of the nitrogen LP density in DMANH$^+$ (i). The bond lengths r(N1—C11) and r(N1—C12) are also significantly longer than in DMAN, which is consistent with the nitrogens having very little sp^2 character.

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Table 2. Critical Point Analyses of ϱ[a]

	ϱ_c (e Bohr^{-3})			$\nabla^2\varrho_c$ (e Bohr^{-5})			ϵ		
bond	DMAN	DMANH$^+$	$C_{10}H_8$	DMAN	DMANH$^+$	$C_{10}H_8$	DMAN	DMANH$^+$	$C_{10}H_8$
C9—C1	0.295	0.306	0.3092	−0.85	−0.90	−0.93	0.20	0.22	0.16
C1—C2	0.338	0.342	0.3397	−1.06	−1.09	−1.07	0.33	0.35	0.30
C2—C3	0.315	0.312	0.3110	−0.96	−0.95	−0.94	0.18	0.16	0.17
C3—C4	0.344	0.342		−1.10	−1.09		0.31	0.29	
C4—C10	0.310	0.311		−0.94	−0.94		0.16	0.15	
C9—C10	0.307	0.321	0.3144	−0.90	−0.93	−0.95	0.20	0.19	0.19
C1—N1	0.300	0.268		−1.06	−0.84		0.07	0.01	
N1—C11	0.275	0.250		−0.89	−0.68		0.05	0.03	
N1—C12	0.269	0.250		−0.84	−0.68		0.04	0.03	
N1—H		0.163			−0.33			0.00	

[a] At the 6-31G*//6-31G level.

Table 3. Lone Pair Properties[a]

	ϱ (e Bohr^{-3})	$\nabla^2\varrho$ (e Bohr^{-5})	r_c (Bohr)
ammonia	0.5803	−3.1408	0.7347
methylamine	0.5931	−3.3051	0.7322
dimethylamine	0.6021	−3.4208	0.7303
trimethylamine	0.6083	−3.5054	0.7289
N,N-dimethylaniline	0.6103	−3.5153	0.7282
DMAN	0.5996	−3.3593	0.7302

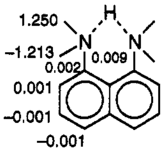

Figure 4. DMANH$^+$, with distances of atoms from the mean plane.

The internal ring angles found for DMANH$^+$ (i) mostly differ little from those in DMAN. Two significant changes are in the angles C1—C9—C8 and C4—C10—C5, which both move away from their highly strained values in DMAN. This may be indicative of some relief of strain occurring on protonation. Other major changes are found for C9—C1—N1, which falls by about 4° to accomodate the proton, and for the angles C1—N1—C11 and C1—N1—C12, which fall by an average of 5° due to the large loss of sp^2 character in the nitrogens. The angle N1—H—N2 formed by the hydrogen bond is 161.9°, which is at the high end of the values found from crystallographic studies of complexes of DMAN.

The torsion angles shown in Table 1 are dramatically different from those found for unprotonated DMAN. They show that DMANH$^+$ (i) is far less twisted than DMAN, and is near to possessing C_{2v} symmetry. The largest deviation from C_{2v} symmetry is observed for C10—C9—C1—N1, which is only 0.3°, compared with 7.8° for the same torsion angle in DMAN. Other torsion angles are even closer to planarity of the ring system. This is also shown by the deviation of the atoms from the mean plane of the ring, which are shown in Figure 4.

Table 1 also contains averaged geometrical data from five symmetrically protonated DMAN complexes, in each case with a different counter ion.[6] The agreement between the theoretical protonated structure and these mean parameters is also very good. Only r(N1—C11) and r(N1—C14) deviate more than 0.020 Å between theory and experiment, and r(C9—C10) also differs by 0.018 Å. The angles C1—C9—C8 and C4—C10—C5 differ by 1.2° and 0.6°. The large discrepancy of 7.1° in N1—H—N2 angle can be readily explained by the lack of a counterion in the theoretical case, which would tend to attract the proton from the NHN$^+$ group. It should also be noted that the proton can only be located with low accuracy from X-ray diffraction. The average experimental hydrogen-bond distance r(N1—H$^+$) = 1.32 Å for symmetrically protonated species, which is comparable to the 6-31G theoretical result of 1.27 Å.

The CP analysis for the charge density of DMANH$^+$ (i) is also reported in Table 2. Unsurprisingly, the biggest changes are found in the C—N bonds, all of which have large depletion of charge at the bond CP. In the ring system, the bonds closer to the amino groups have an increase in charge, while those farther away are depleted slightly. This is probably due to polarization of the electron density toward the positively charged N⋯H⋯N moiety. The large value of ϱ_c and the negative value of $\nabla^2\varrho_c$ for the N⋯H bond are uncommon for hydrogen bonds, but have been found in calculations on other strong, symmetrical hydrogen bonds such as in the [F—H—F]$^-$ anion.[26] Compared with DMAN, the ellipticity of the charge density in bonds C1—C2 and C3—C4 is more *dissimilar* in DMANH$^+$ (i), which is at odds with the idea that aromaticity has increased (they would be identical in naphthalene).

Optimization calculations on the asymmetrically protonated form DMANH$^+$ (ii) were extremely slow to converge, and it did not prove possible to optimize the geometry to the same accuracy as in DMAN or DMANH$^+$ (i). (The largest residual force on a nucleus was 1 order of magnitude greater than the 1 × 10^{-4} au criterion achieved in the latter two cases.) Consequently we do not report the structure here in the same detail. In fact, the structure obtained was virtually identical to DMANH$^+$ (i), except for the asymmetric proton position. Both (i) and (ii) protonated forms are characterized by a naphthalene ring which is extremely close to planarity (see the distances in Figure 4), and methyl groups which are nearly symmetrical about the plane of the ring. The hydrogen-bond distances in form ii are r(N1—H$^+$) = 1.05 Å and r(N2—H$^+$) = 1.64 Å. The angle N1—H—N2 is 156.8°. The energy of DMANH$^+$ (ii) with the 6-31G* basis set at the near-optimized 6-31G geometry is some 0.008 Hartrees (22 kJ mol^{-1}) below that for DMANH$^+$ (i). Hence there can be little doubt that this asymmetric form is preferred for the free protonated species.

Table 4 reports the predictions of gas-phase PAs for DMAN and some smaller amines. The PAs show the same linear trend with the nitrogen LP $-\nabla^2\varrho_c$ values in Table 3, which was first reported by Tang *et al.*[27] (and these optimizations are at a higher level of theory). The

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[26] Platts, J. A. Unpublished results; calculations on [F-H-F]$^-$ at the MP2/6-311++G(3d,3p) level give $\nabla^2\varrho_c$ = −0.491 e Bohr^{-5}. The optimized value for r(F—H) = 1.143 Å, at the same level of theory.

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Table 4. Proton Affinities[a]

	PA,[b] without ZPE	ZPE correction[c]	PA with ZPE	exp PA at 600 K (ref 3)
ammonia	923.0	45.9	877.1	866.1
methylamine	962.2	44.8	917.4	907.9
dimethylamine	988.0	44.6	943.4	939.3
trimethylamine	1004.0	44.1	959.9	960.2
N,N-dimethylaniline	1007.9	44.3	963.6	953.5
DMAN[d]	1060.5	(51)	1009.5	
DMAN[e]	1082.2	(51)	1031.2	1030.1

[a] Values in kilojoules per mole. [b] At the 6-31G*//6-31G level. [c] At the 6-31G level. [d] (i) Protonated symmetrically. [e] (ii) Protonated at one nitrogen.

calculation on *N,N*-dimethylaniline[28] refers to protonated and unprotonated forms in which the molecule has C_s symmetry, with the methyl groups on opposite sides of the mirror plane. This does not correspond to the lowest energy conformation—nearly coplanar methyl groups and an sp^2 nitrogen are preferred.[28] This geometry was selected as a closer model for DMAN, which has sp^3-like nitrogens.

It is clear that the 6-31G*//6-31G calculations, in the absence of a correction for the change in stored thermal energy on protonation, consistently overestimate the PA. The application of a ZPE correction using harmonic frequencies computed at the 6-31G level dramatically improves the agreement with experiment, to within an average accuracy of 0.7%. The ZPE corrections are remarkably constant, lying between 45.9 and 44.1 kJ mol^{-1}, despite the wide range in size of molecules considered. Evidently it is an excellent approximation to assume that three new degrees of freedom (each with 15 kJ mol^{-1}) corresponding to local modes of vibration are present in each protonated species, barely perturbing the parent molecule normal mode frequencies. Therefore we might apply this correction to DMAN, at least for the asymmetrically protonated form where only one nitrogen is protonated. However, calculations on the proton-bound dimers of ammonia, methylamine, and dimethylamine[29] give ZPE corrections of around 51 kJ mol^{-1}. We consider that this provides a closer estimate of the DMAN ZPE correction. (In Table 4 we assume that the experimental value for the DMAN PA applies to the asymmetric form, since our calculations indicate this has the lowest energy—consequently the PA for symmetric protonation of DMAN is not known experimentally.) Thus we have a 6-31G*//6-31G PA for DMAN of 1031.2 kJ mol^{-1}, barely 1 kJ mol^{-1} from the experimental value, which is much better than the mean error in predicted PAs for the five smaller amines. This is an encouraging result, given that only moderately sized basis sets can currently be used for such molecules.

Conclusions

On comparing the free molecule *ab initio* optimized structure of DMAN to that in the crystal, it was found that the nonplanarity is enhanced by the influence of packing forces. The nonplanarity was greatly diminished on protonation, suggesting that relief of strain may well be an important factor in the basicity of DMAN. Asymmetric protonation is energetically preferred for the free base, although in the solid state, the minimization of the packing energy can evidently favor the symmetric structure.[5] Protonation also results in a ring structure closer to that of naphthalene, presumably due to increased localization of charge in the LPs. The critical point ϱ_c and $\nabla^2\varrho_c$ values for ring bonds are also brought closer to the corresponding values in naphthalene upon protonation, although the ellipticities do not follow this trend. Whether this corresponds to increased "aromaticity" is arguable, given that there is no agreed definition of this concept.

These calculations alone only partly investigate the extent to which the proximity effect influences the basic nature of DMAN. Further calculations on related systems, such as the $N_2H_7^+$ cation, are underway.[29] We have established that HF calculations at the 6-31G*//6-31G level predict amine gas-phase PAs with an average absolute accuracy of around 0.7%, or typically 6−7 kJ mol^{-1}. The predicted PA for DMAN is in far better agreement with experiment (0.11% error), but this is purely fortuitous since there remains uncertainty about the ZPE correction. While this average error of 0.7% remains 1 order of magnitude poorer than the best experimental accuracy, it should be quite sufficient for predicting basicities of new proton sponges.

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(28) Howard, S. T. Unpublished results.

(29) Platts, J. A. Manuscript in preparation.