

Proton Sponges of 1,2-bis(di-*R*-aminomethyl)benzene Type

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The pK_a values for 1,2-bis(di-*R*-aminomethyl)benzenes (DRAMB) are much higher than for DMAN, 1,8-bis(dimethylamino)naphthalene, the classic proton sponge. On protonation a strong intramolecular N-H \cdots N H bond is formed. The molecule of DRAMB can adopt four idealized conformations with the following symmetries: (i) C_{2v} , (ii) C_2 , (iii) C_s -mirror plane in the benzene ring, (iv) C_s -mirror plane normal to the benzene ring. The C_{2v} symmetry is achieved by symmetric disposition of the alkyl groups above and below the benzene ring with the N atoms exactly in the ring plane, and with the lone pairs oriented away from or towards the aromatic ring. In both conformations, the monoprotonated DRAMBH $^+$ cation cannot form an intramolecular N \cdots H \cdots N bond. Conformation (ii) is characterized by location of the N atoms on the opposite sides of the benzene ring. Formation of a twofold-symmetric intramolecular N \cdots H \cdots N bonds is possible but the proximity of the N atoms in short bridges causes large steric effects even in simple system, such as DMAMB (M=CH $_3$). Form (iii) is compatible with intermolecular N-H \cdots X hydrogen bonds. Form (iv), with the N atoms on one side of the aromatic system, is optimal for minimization of steric hindrance and for the formation of a short intramolecular H bond. A DMAMBH $^+$ cation with exact C_s -symmetry (iv) is observed in the ClO $_4^-$ salt. Pseudo C_s cations are found in the crystals of DMAMBH $^+$ ·NO $_3^-$ and DEAMBH $^+$ ·ClO $_4^-$ (E=ethyl). For bulkier substituents (*R*=propyl, butyl) the symmetry of the bis(aminomethyl)benzene moiety is closer to C_s .

Keywords: proton sponges, N-H \cdots N hydrogen bond, conformation