A Planar Hydrazine: Bi(1,2,3-azadiboriridin-1-yl)

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Both 1-amino-1,2,3-azadiboriridine and bi(1,2,3-azadiboriridin-1-yl) are found by *ab initio* molecular orbital calculations to prefer conformations with coplanar lone-pair orbital axes on the adjacent nitrogen atoms; the latter molecule is predicted to prefer a fully coplanar (D_{2h}) conformation.

Since an initial study[1] by electron diffraction in 1960, the structure of hydrazine (1) has been the subject of several experimental[2] and many theoretical[3] studies. The consensus of all these studies is that the equilibrium structure is the so-called *gauche* conformation (1a) of C_2 symmetry with a dihedral angle between *vicinal cis* NH bonds close to 90°. This angle may alternatively be thought of as that between the axes of the lone-pair orbitals on the adjacent nitrogen atoms, and a value close to 90° may be explained[4] as facilitating delocalization of the adjacent lone pairs of electrons and at the same time minimizing the repulsive interaction that would occur if the axes were coplanar. Similar values are obtained for the corresponding angles in 1,1-dimethyl-[5] and 1,2-dimethyl-[6] hydrazine.

In each of these molecules, there are four lone-pair electrons. The hydrazine radical cation, however, which has only three electrons in the lone-pair orbitals, prefers a parallel, near-planar structure,[7] and the hydrazine dication (isoelectronic with ethylene) is fully planar.[8] We therefore reasoned that substitution at either or both nitrogen atoms in hydrazine by strongly electron-withdrawing (π-acceptor) groups might lead to preference for a structure in which the axes of the (depleted) lone-pair orbitals are coplanar. We have now investigated this matter by means of *ab initio* molecular orbital calculations with the Gaussian 80 system of programs[9] and use of various basis sets.

Preliminary calculations[10] on 1,1-dicyano-, 1,1-diformyl-, 1,1-diboryl-, and tetracyano-hydrazine with STO-3G[11] and 3-21G[12] basis sets showed that the preferred conformation for each of these molecules is one having perpendicular lone-pair orbital axes, the three bonds at the substituted nitrogen atoms

being coplanar and those at the amino-nitrogen atoms pyramidal.

For 1-amino-1,2,3-azadiboriridine (2),‡ however, calculations with these basis sets suggested that the 'parallel' C_s conformation (2a) was of lower energy than the 'perpendicular' C_s conformation (2b) by 13.4 (STO-3G) or 14.4 kJ mol⁻¹ (3-21G). As these values (and the corresponding optimized geometries) might not be quantitatively reliable, we also carried out calculations on this molecule (2) with basis sets including polarization functions on all first-row atoms (6-31G*)[14] or on the nitrogen atoms only [3-21G(N*)];[15] again, conformation (2a) was of lower energy than conformation (2b), but now by 18.1 (6-31G*) or 16.9 kJ mol⁻¹ [3-21G(N*)]. In these calculations, the N–N bond in (2a) was found to be tilted out of the B–N–B plane slightly (*ca.* 4°), and the NH₂ group remained pyramidal (with its hydrogen atoms on the other side of the B–N–B plane from the nitrogen atom); the B–H bonds also lay marginally (0.2°) out of the B–N–B plane. Compound (2) appears to be the first 1,1-disubstituted hydrazine derivative in which coplanar lone-pair orbital axes are preferred.§

Calculations on bi(1,2,3-azadiboriridin-1-yl) (3) then showed that the fully coplanar (D_{2h}) conformation (3a) was of lower energy than the perpendicular (D_{2d}) conformation (3b) by 8.8 kJ mol⁻¹ [3-21G(N*)]; it was confirmed that the planar conformation (3a) was a local minimum on the energy surface by its recovery upon reoptimization [3-21G(N*)] of a C_{2h} conformation in which the N–N bond lay initially 5° out of each B–N–B plane. By contrast, the energy of the D_{2h} conformation (1b) of hydrazine itself is *higher* than that of the D_{2d} conformation (1c) by 92.7 (6-31G*)[5] or 95.8 kJ mol⁻¹ [3-21G(N*)].[5]

(1) (1a) (2a) (2b) (2c) (2d) (3a) (3b) (1b) (1c)
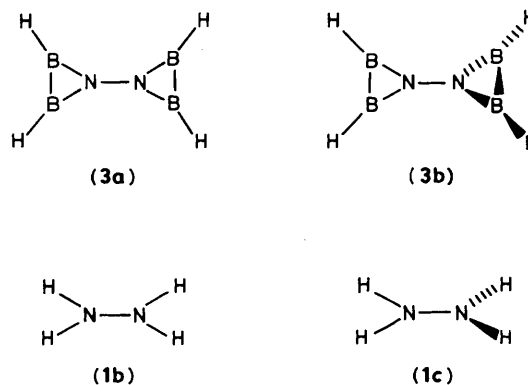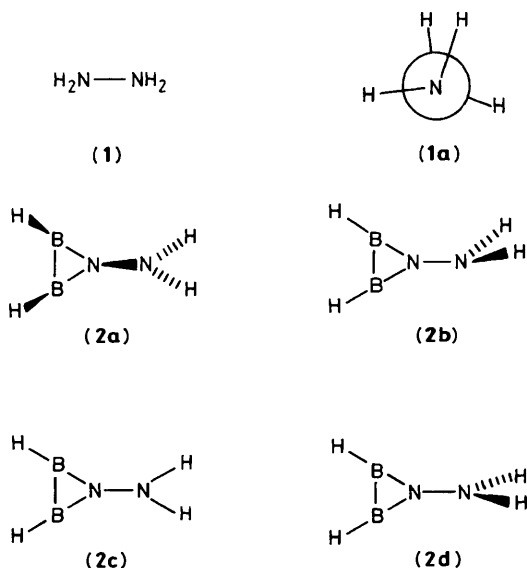
‡ Since our calculations on this model system were carried out, synthesis of a highly substituted 1,2,3-azadiboriridine derivative has been reported (ref. 13).

§ 1,2-Diformylhydrazine has been found (ref. 16) to be fully planar in the crystal, but the isolated molecule was found with the 3–21G basis set to prefer a C_2 structure having a CNN'C' dihedral angle of 84.5° and pyramidal N atoms, and lying 5.4 kJ mol⁻¹ below the planar (constrained) structure.

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We believe that the above results support the thesis upon which this work was based and, to that extent, the contention that hydrazine and many of its derivatives adopt a near-perpendicular conformation in order to avoid the net anti-bonding (repulsive) interaction that would arise from four π-type electrons on the adjacent nitrogen atoms in the parallel conformation. In the molecules (2) and (3), as a result of delocalization over the three-membered, two-π-electron, 'aromatic' NBB rings, the 'lone-pair' electron densities on the ring-nitrogen atoms are lowered substantially (into the range 1.41—1.47, according to Mulliken population analyses of the 3–21G results); in consequence, as in the hydrazine radical cation (nominal 'lone-pair' electron density 1.5 on each nitrogen atom), the conformations (2a) and (3a), which have coplanar lone-pair orbital axes, become preferred.

The energy difference between (3a) and (3b) is much smaller than that between (2a) and (2b) but, for a more appropriate comparison, we have calculated also the energies of the optimized (but non-equilibrium) planar C_{2v} (2c) and perpendicular C_{2v} (2d) conformations of 1-amino-1,2,3-azadiboriridine: the former is of lower energy than the latter by 36.3 kJ mol^{-1} [3–21G(N*)]. Restricting our comments to conformations of hydrazine and its derivatives containing only planar nitrogen centres, we see that incorporation of one nitrogen atom only into 1,2,3-azadiboriridine results in a very large change [132.1 kJ mol^{-1} by 3–21G(N*)] in favour of the fully coplanar system; incorporation of the second nitrogen atom into such a ring, however, benefits the perpendicular system with its more localized lone pair on the amino-N atom more than it does the planar system, and the preference for the planar system is reduced by 27.5 kJ mol^{-1} [3–21G(N*)].

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