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Balancing Steric and Electronic Factors in Push–Pull Benzenes: An ab Initio Study on the Molecular Structure of 1,3,5-Triamino-2,4,6-trinitrobenzene and Related Compounds

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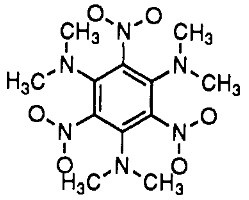
Abstract: The structures of 1,3,5-triamino-2,4,6-trinitrobenzene (**2**) and related compounds (**3–5**) are studied using ab initio Hartree–Fock (6-31G(D)) and local density functional (LDF) computational methods. In contradiction to published structures for **2** predicted from semiempirical data, both ab initio methods predict a planar structure in accord with the experimental X-ray crystallographic study. It is concluded that appreciable "push–pull" conjugation is present in **2** and that the interaction between flanking groups is mainly attractive through cyclic hydrogen bonding. Computations on **3–5** were used to gauge the affinity for some rings to distort into boat instead of chair forms. The relative electron density distributions for **2** and **5** are discussed. The planar forms of **2** and **5** are shown to support the concept that static "gear clashing" in combination with push–pull effects are responsible for the warped structure of alkyl substituted cognates of **2**.

Benzene rings, bearing push–pull substituents, contain polar resonance forms with quinone and radialene-like bonding patterns in their overall valence bond structure (Figure 1).[2] Such resonance forms can be important enough to enforce strong conformational preferences on the pendant substituents and thereby increase the effective in-plane steric bulk of the substituents.[3,4] For example, the molecular structure of 1,3,5-tris(dimethylamino)-2,4,6-trinitrobenzene (**1**) displays a dramatic warping of the benzene ring into a deep boat conformation, while at the same time retaining planarity around each of the push–pull conjugated nitrogens. This extraordinary out-of-plane distortion has been attributed to the combination of steric and electronic effects in **1** and has been well-modeled by semiempirical computations with the AM1 Hamiltonian.[4]



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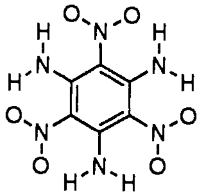

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In contrast, the X-ray crystallographic structure of 1,3,5-triamino-2,4,6-trinitrobenzene (**2**) presents a planar structure consistent with the replacement of steric repulsion by an attractive hydrogen bonding interaction.[5] As logical as this analysis seems, the question of whether this planarity *is* inherent in **2** or a result of the crystal environment has been raised on the basis of semiempirical calculations that predict **2** to have a nonplanar gas-phase structure similar to that of **1**.[6] The fact that the semiempirical level of theory is inappropriate for the prediction of molecular structures where significant hydrogen bonding is important[7] motivates one to investigate the claim[6] that "a contradiction between theory and experiment" remains for the structure of **2**. The importance of understanding the push–pull phenomenon and the balance between steric and electronic effects in organic compounds makes it imperative that such questions be laid to rest. We now reconcile the above "contradiction" through the implementation of appropriate level ab initio Hartree–Fock (6-31G(D)) and local density function theory (LDF) computations to the structure of **2** and related compounds.

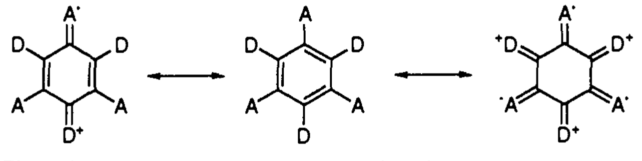

Figure 1. Possible resonance contributors for a fully-substituted "push–pull" benzene.

Methods

The molecular structures of all stationary points have been determined with both the semiempirical and ab initio methods at the restricted Hartree–Fock (RHF) self-consistent-field (SCF) level of theory. The semiempirical calculations were performed with the AM1[8] parametrization of the MNDO Hamiltonian. The ab initio calculations were performed using the 6-31G(D)[9a,b] basis set. This basis set includes a set of six d polarization functions on all heavy atoms. For illustration of effects of basis sets, several calculations were also performed using the STO-3G[9c,d] and 6-31G[9e] basis sets, as well as the local density functional

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[1] (a) San Diego Supercomputer Center. (b) University of California, San Diego.

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(LDF) approach at the ab initio level. The LDF calculations were performed with a double numerical basis set augmented by polarization functions. This basis set is comparable in size to a polarized double-ζ basis set in traditional Hartree–Fock molecular orbital theory.

Geometry optimizations were performed with the aid of analytically determined gradients and the search algorithms contained in MOPAC,[10] GAMESS,[11] and DMOL.[12] The semiempirical calculations were done using the PRECISE and GNORM criteria to ensure tight geometries. The nature of each SCF-stationary point was established by calculating (analytically for ab initio Hartree–Fock wave functions, numerically for semiempirical and ab initio LDF methods) and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies. All minima are determined to have zero imaginary frequencies as well as transition states with one imaginary frequency. Full structural information on all molecules is available as supplementary material.

The molecular electrostatic potential maps were generated using the program MEPMAP.[13] This program draws a contour map of a molecular electrostatic potential grid. The grid is produced by the GAMESS program before MEPMAP is run. The MEP plot shows the energy of attraction or repulsion for a test positive charge, +q. The units of the contour lines are kcal/(mol·e), where e is the electron charge.

Molecular Structure of 2

Several structural features highlight the X-ray crystallographic investigation of **2**. The molecules pack in a centrosymmetric array with extensive inter- and intramolecular hydrogen bonding, adopt a planar geometry with both nitro and amino groups positioned for maximum conjugation, and evince short carbon–nitrogen (single) and long carbon–carbon (aromatic) bond lengths with planar-trigonal geometries at each atom. All of these features indicate that strong push–pull conjugation exists among the amino (donor) and nitro (acceptor) groups around the ring. Studies on the electron density distribution in **2** also support the increased radialene-like bonding.[14]

Relief from steric congestion caused by clashing substituents can occur via two modes in **2**: exocyclic torsions and out-of-plane buckling. Exocyclic torsion is the dominant mode for sterically congested hexaalkylbenzenes, where the aromatic nature of the ring resists out-of-plane distortions and the exocyclic torsions are free rotors.[15] The force constant for out-of-plane buckling should weaken and that for exocyclic torsion should stiffen in push–pull aromatic molecules as compared to hexaalkylbenzenes, where such conjugation is impossible. Thus, out-of-plane distortions should be feasible for cases where steric repulsion is large and push–pull conjugation is strong, as in **1**.

Thermal motion analysis of the X-ray structure of **2** predicts that the nitro groups librate with an average torsional amplitude of 12° with respect to the ring and the benzene ring remains flat.[5] This fits well with the picture that the oxygens of the nitro and the hydrogens of the amino groups attract one another through hydrogen bonds, and that a slight torsion is necessary to optimize this hydrogen bonding interaction. Various crystallographic studies support this view of the nitro/amino interaction.[16] Indeed, the cost of exocyclic torsions up to ca. 30° is quite modest when weighed against the benefit of forming a cyclic network of hydrogen bonds.

Table I. Calculated and Experimental Geometries of **2** and **5**

parameter	LDF	**2** 6-31G(D)	X-ray[a]	**5** 6-31G(D)
bond lengths				
C–C	1.433	1.427	1.444	1.433
C–N	1.318	1.323	1.319	1.335
C–N	1.403	1.435	1.426	1.510 (C–B)
N–H	1.042	0.992		0.990
N–O	1.258	1.202	1.266	1.194 (B–H)
bond angles				
C–C_{amino}–C	119.1	117.8	117.9	123.6
C–C_{nitro}–C	120.8	122.1	122.0	116.3 (C–C_B–C)
C–C–N_{amino}	120.4	121.0	121.1	118.1
C–C–N_{nitro}	119.6	118.9	119.0	121.8 (C–C–B)
C–N–H	115.0	119.8		120.8
H–N–H	129.8	120.2		118.4
C–N–O	120.8	119.4	121.0	123.3 (C–B–H)
O–N–O	118.3	121.2	117.9	113.2 (H–B–H)
torsion angles				
C–C–N–H	2.9	9.3		0.0
C–C–N–H	−177.0	−170.6		0.0
C–C–N–O	−6.1	−27.9	12[b]	0.0
C–C–N–O	173.6	152.0		0.0

[a] Reference 4. [b] Estimated from residual thermal motion analysis of X-ray anisotropic refinement parameters.

On the other hand, semiempirical calculations on **2** predict that the benzene ring distorts strongly out-of-plane, and the conformation of each exocyclic bond retains a ca. 0° torsion angle of nitro and amino groups. This implies that the oxygen-to-hydrogen interaction is primarily sterically repulsive and the ring warps in order to move these groups outside of van der Waal's contact. This analysis is only tenable through serious neglect of the hydrogen bonding attraction between nitro and amino groups in **2**. Such erroneous neglect is one facet of the notoriety of semiempirical methods.[7]

Computations of the planar (D_{3h}) conformation of **2** at the HF/6-31G(D) level reveal a structure very close in geometry to that found in the crystal (Table I). Normal mode analysis shows this structure to be a partial maximum (multiple negative eigenvalues). Optimization of the structure along one of these negative eigenvectors resulted in a minimum energy D_3 structure (2.5 kcal/mol below D_{3h}), with a planar benzene ring and nitro (25°) and amino (8°) groups slightly turned out of plane. The structural parameters for this slightly perturbed structure corroborate even better with experiment. Using the semiempirical boat structure as the initial geometry of **2** and optimizing at HF/6-31G(D) results in a C_s structure (1.8 kcal/mol below D_{3h}; 0.8 kcal/mol above D_3) with an almost planar ring (bow and stern dihedrals of less than 3°) and two of the three nitro groups twisted slightly out of plane. Full turning of the nitro groups alone or both the nitro and amino groups perpendicular to the plane raises the energy to 29.2 or 48.0 kcal/mol, respectively.

Local density functional theory (LDF) predicts a D_3 minimum energy structure for **2** similar to that found by HF, with torsion angles for the nitro and amino groups of 6° and 3°, respectively. The corresponding C_s minimum energy structure, with a planar ring, lies ca. 0.5 kcal/mol above the D_3 structure. Thus, the most consistent picture of the structure of **2** interprets the interaction between oxygen and hydrogen as primarily attractive, with no motivation for the benzene ring to warp out of plane. Indeed, no stationary points have been found by either HF or LDF methods where the structure of the benzene ring is in a boat or chair conformation (Table II). Clearly, there is excellent agreement between the appropriate level of theory and the X-ray experiment; any previous discrepancy came from an imprudent application of the semiempirical method.[6]

Molecular Structure of Related Structures 3, 4, and 5

A Dreiding model of the planar structures of [6]radialene (**3**), 2,3,5,6-tetramethylquinodimethide (**4**), and 1,3,5,-triamino-2,4,6-

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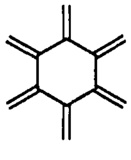
Table II. HF 6-31G(D) Energies for Various Conformations of **2–5**

	flat		chair		boat	
compd	sym	E^a	sym	E^a	sym	E^a
2	$D_{3h}{}^c$	−1006.195257 (2.5)	C_{3v}	*b*	C_s	−1006.198084^f (0.8)^f
	D_3	−1006.199319^f (0.0)^f				
	$D_{3h}{}^d$	−1006.122771 (48.0)				
	$D_{3h}{}^e$	−1006.152759 (29.2)				
3	D_{6h}	−461.247791 (24.3)	$D_3{}^d$	−461.286468 (0.0)	C_{2v}	−461.282383 (1.7)
4	D_{2h}	−463.669276 (12.7)	C_{2h}	−463.680666 (0.2)	C_{2v}	−463.680951 (0.0)
5	D_{3h}	−471.593776	C_{3v}	*b*	C_s	*b*

[a] Energy in hartrees (relative energy for conformation in kcal/mol). [b] No stationary point found. [c] Partial maximum. [d] Nitro and amino groups rotated perpendicular to the aromatic ring. [e] Nitro groups rotated perpendicular to the aromatic ring. [f] LDF-DMOL energies: D_3, −1004.694515 (0.0); C_s, −1004.6903701 (0.5).

triboranobenzene (**5**) indicate close hydrogen to hydrogen contacts (i.e. within the sum of van der Waal's radii: 2.0 Å). In **3**, the ring bonds are formally single bonds with some double bond character, in **4** there are four single and two double ring bonds, and in **5** the ring bonds are formally all aromatic bonds. How these structures accommodate the in-plane steric strain of their hydrogens serves as a good model for assessing the balance between steric and electronic factors in these systems.



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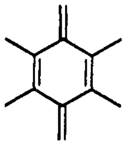

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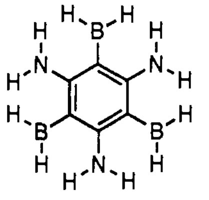

5

Six-membered rings take on three basic conformations: planar (D_{nh}), chair (D_{nd}), and twist/boat (C_n/C_s). Structural optimizations, initiated from each of these conformations, were carried out at the HF/6-31G(D) level for **3**, **4**, and **5** (cf. Table II). In the case of **3**, the planar structure was energetically unfavorable compared to the chair and boat forms, with the boat form being slightly higher in energy than the chair. Similarly, the planar structure of **4** is not favored compared to the chair and the boat forms; however, the boat form is slightly more stable than the chair. The chair distortion in **4** requires a transoid distortion of the double bonds in the ring and strains the π-bond. In contrast to both **3** and **4**, all optimizations of **5** result in the same planar structure. The normal-mode analysis of the planar optimized structure of **5** reveals it to be a true minimum (zero negative eigenvalues).

Both the chair and the boat forms of **3** display relatively normal bond lengths and angles, no close hydrogen–hydrogen contacts, and torsion angles about each double bond of essentially 0°. Thus, the ring bonding in **3** presents no electronic imperative to create an effective retaining force against out-of-plane distortion and simple steric interactions cause the ring to warp severely to reduce strain. Distortion of **4** into the chair form introduces torsional strain in the double bonds and therefore only small out-of-plane distortions occur; however, the force needed to create an out-of-plane boat distortion is small and this form relieves the in-plane steric congestion without jeopardizing the integrity of the double bonds. Dominance of the quinoidal form is likely the basis for the boat rather than chair distortion in **1** and related monoalkylamino compounds.

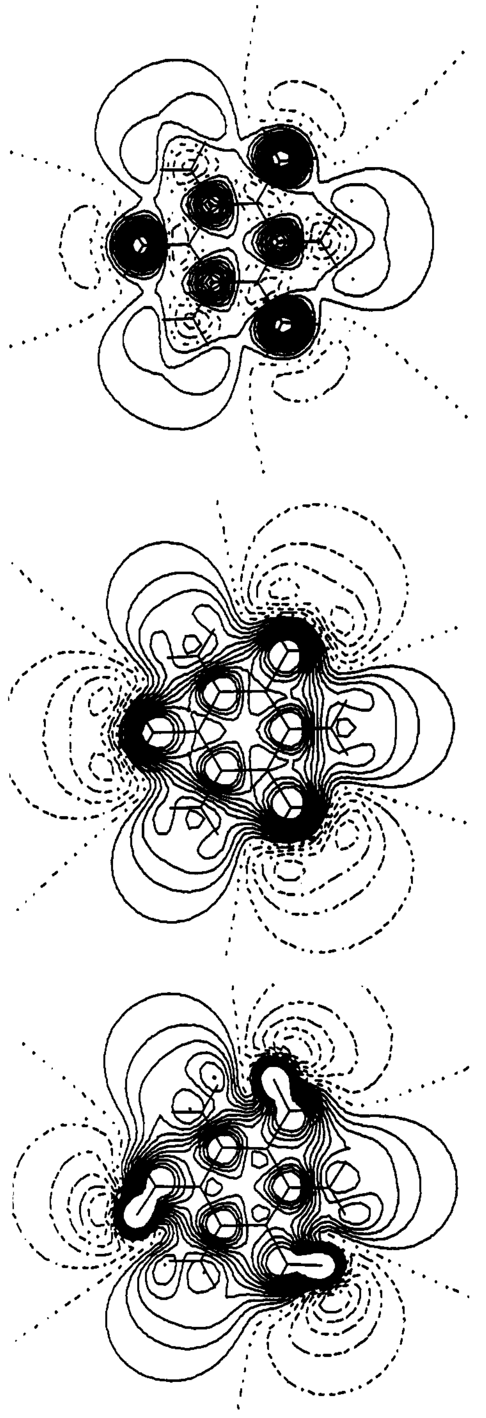

Figure 2. MEPMAPs of (a, top) **5** (D_{3h}), (b, middle) **2** (D_{3h}), and (c, bottom) **2** (D_3). Substitution starts with the acceptor group (BH2-, **5**; NO_2, − **2**) at 1 o'clock and alternates with amino groups around the ring. Solid and dotted contours indicate a repulsive and attractive interaction with the positive point charge, respectively.

In **5**, the importance of the benzene resonance, although weakened, still presents a significant restraint to out-of-plane distortion, and simple steric repulsions cannot overcome the electronic benefit of planarity. The planar structure of **5** shows several structural features consistent with push–pull conjugation from amino (donor) to borano (acceptor) groups: short carbon–nitrogen and carbon–boron bond lengths, long carbon–carbon bond lengths, and torsions of 0° with respect to the benzene ring for both amino and borano groups. Focusing on these features, the structure of **5** closely resembles that of **2**. Bond angles in the benzene ring, however, distort according to Bent's rule (electronegativities) in preference to π effects.[17]

The distortion of the internal angles in **2** can be rationalized in two ways: (1) The nitrogen of the nitro group in **2** is more electronegative than the nitrogen of the amino group, and the $C–C_{nitro}–C$ angle increases forcing the $C–C_{amino}–C$ angle to decrease; (2) The π-donation from the amino group causes the $C–C_{amino}–C$ angle to decrease and, in response, the $C–C_{nitro}–C$ angle must increase. The π and electronegativity effects oppose one another in **5** with electronegativity dominating; the nitrogen is more electronegative than the boron and the $C–C_{amino}–C$ is larger than the $C–C_{boron}–C$ angle.[18]

The fact that **5** adheres to a planar structure, adapting to the hydrogen interactions through in-plane distortions, further supports the concept that out-of-plane distortions in push–pull benzenes result only in response to strong steric interactions within the plane. Thus, we reaffirm our previous claim that steric and electronic effects both play an important role in dictating the severely warped structure of **1** and related compounds.[4]

Electron Density Distribution in 2 and 5

Several experimental papers have revisited the original X-ray data on **2** in order to deduce something about the electron density in this strange compound.[5,14,19] The resonance forms given in the first structural paper predict a relative ranking of electron densities that was later subject to further interpretation. The 6-31G(D) data allow the construction of a potential energy map that represents the interaction of a positive point charge with **2** or **5** in a fixed plane (MEPMAP). MEPMAPs of the plane 1.2 Å from the molecular best plane of **2** (planar) and **5** show qualitatively similar results in the relative electron richness at various atom sites (Figure 2, a and b). The nitrogen of the amino group and the carbon α to the acceptor (nitro or borano) group are richer in electrons than the central atom (boron or nitrogen) of the acceptor group or the carbon α to the amino group. In **5** the richer atoms manifest an overall attractive interaction with the point charge, whereas in **2** the oxygens of the nitro group remove so much electron density that all atoms appear on the repulsive side. These trends are consistent with the standard valance bond picture for push–pull conjugated systems. The MEPMAP for **2** (D_3), with the nitro and amino groups twisted, shows a strong distortion, in harmony with the molecular symmetry. This could be a harbinger of the ease with which **2** can distort to a non-centrosymmetric mode and thereby serve as a starting point for a discussion of the anomalous second harmonic generation activity of "centrosymmetric" **2**.[20]

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Supplementary Material Available: Tables of Cartesian coordinates for the optimized geometries of all molecules calculated (13 pages). Ordering information is given on any current masthead page.

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