## Structures of Tris(donor)-Tris(acceptor)-Substituted Benzenes, 1[1]

# Steric, Polar and Hydrogen-Bonding Effects in Triaminotrinitrobenzenes☆

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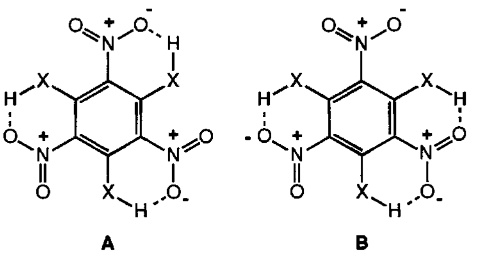
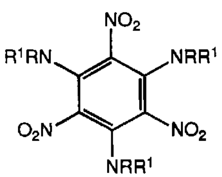
The X-ray analyses of three 1,3,5-tris(alkylamino)-2,4,6-trinitrobenzenes (alkyl = *i*Pr, neopentyl, *t*Bu; **1d**−**f**) show their benzene rings to be highly distorted towards boat (**1d** · *i*PrNH$_2$) and twist-boat (**1e,f**) forms. The patterns found for intramolecular donor-acceptor interaction and hydrogen bonding depend on the conformation of the benzene core: boat structures have the "stern" amino group strongly donating to the "bow" nitro group in the *para* position and two stronger hydrogen bonds between the substituents on the "side" of the boat, whereas twist-boat structures have two amino groups strongly interacting with the nitro group in their common *ortho* position to which there are also two strong hydrogen bonds. **1d**−**f** undergo conformational exchange on the $^{13}$C-NMR time scale at room temperature. Cooling to 220 K allows detection of all carbon signals and shows $C_1$ symmetry to be present. AM1 calculations reproduce the distortions of **1d**−**f**. Computations on several 2,4,6-tridonor-substituted 1,3,5-trinitrobenzenes indicate that the pronounced deviations from planarity in **1a**−**f** originate largely from electronic effects.

There has been much interest in hexanitrogen-substituted benzenes[2]. These compounds display unusual static and dynamic features, and they afford stable highly oxidized species which may find application as conducting or ferromagnetic materials. One of us was first concerned with triple-proton transfer reactions in benzotris(imidazole)[3], but the focus in this work is upon conformations of triamino-trinitro intermediates in the synthesis of this type of compound.

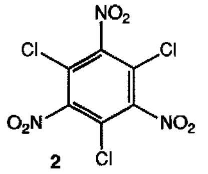
Scheme 1



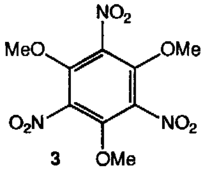


**1**

| 1 | a | b | c | d | e | f | g | h |
|---|---|---|---|---|---|---|---|---|
| R | H | Me | Et | *i*-Pr | *neo*-Pentyl | *t*-Bu | Me | Et |
| R$^1$ | H | Me | Et | H | H | H | H | H |



**2**



**3**

There are two classes of structures which would at first glance seem likely for 1,3,5-trinitro-2,4,6-tris(XH)-substituted benzenes (Scheme 1) in which intermolecular hydrogen bonding is important: type **A**, which has each nitro group hydrogen-bonded, and could have $C_3$ symmetry, and type **B**, of $C_1$ symmetry, which has one doubly bonded and one free nitro group. The implicit assumption of a planar benzene ring in either **A** or **B** need not be true. Studies on tris(dialkylamino)trinitrobenzenes **1b,c** by Siegel et al.[2d] have shown that they exist in boat conformations best described as adopting quinonoid structures. Other results in this work were that the barrier for conformational interchange is 9.1 kcal/mol in **1c**, and that AM1 semiempirical calculations[4] reproduce the structure of **1b,c** well. It was argued from the AM1 structure of the transition state for conformational interconversion that both electronic and steric factors are required to obtain such a distorted structure.

We were interested to see whether in this class of compounds, a decrease in steric bulk of the amino substituents by changing NR$_2$ to NHR and concomitant introduction of hydrogen bonding would greatly alter the static or dynamic features of the benzene ring. In addition, we sought to find a relationship between hydrogen bonding and the donor-acceptor pattern of the substituents on the benzene ring.

## Results and Discussion

**1d**−**f** were prepared from either **2**[3] or **3**[5] by heating with the appropriate amine in toluene. **1d** crystallized from the reaction mixture as 1:1 complex with isopropylamine, which could not be removed by crystallization, but by sublimation.

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The amine-free product crystallized as a 1:1 complex with toluene from that solvent. The melting points were identical in all cases; apparently, the amine and toluene are lost on heating. Neither **1e** nor **1f** crystallized with incorporation of the corresponding amine or solvent.

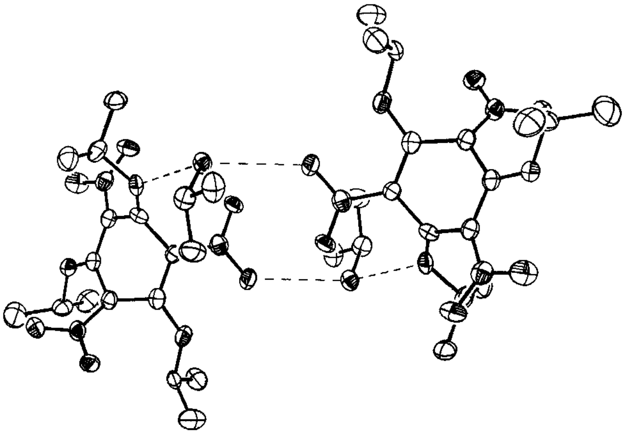


Figure 1. ORTEP plot of **1d** · *i*PrNH$_2$

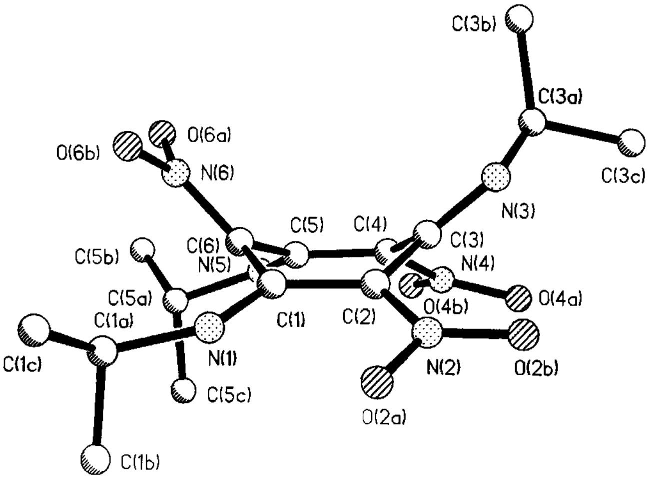


Figure 2. Edge-on view of **1d**

The $^{13}$C-NMR spectra of **1d,e** – including **1d** · *i*PrNH$_2$, but not **1f** – show no aromatic ring carbon atoms at 300 K because of excessive broadening, indicating that the rates of conformational changes correspond to the region of signal coalescence. Only **1f** gave a spectrum consistent with $C_3$ symmetry, the peak for the amino-vinyl carbon atoms being considerably broadened. Cooling to 200 K allowed observation of all carbon resonance lines, although for **1d** · *i*PrNH$_2$, solubility problems allowed measurements only down to 220 K, so that the exchange could not be completely frozen out. $C_1$ symmetry is present in all compounds, with substantial chemical-shift differences within the sets of signals expected to be identical if $C_3$ symmetry prevailed. However, a clear pattern for these sets of signals is found for **1e**: Two carbon atoms of each set of three display resonance lines close together and at lower field from the third one, a pattern that is preserved for the corresponding proton signals at 210 K. For **1d** · *i*PrNH$_2$, this pattern is also observed. In this compound, the signal for one nitro-bearing carbon atom is about 2.5 times broader than the signals for the other two. Apparently, the excess amine has a preferential interaction with one nitro group. With uncomplexed **1d**, this broadening vanishes, and the grouping of signals as in **1d** · *i*PrNH$_2$ and **1e** is no longer observed.

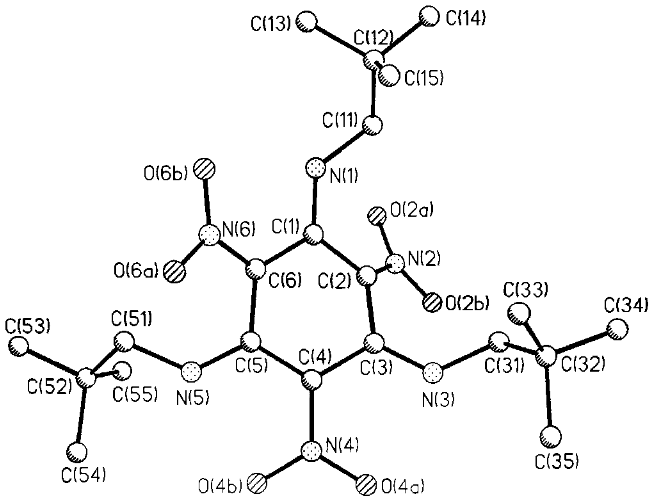


Figure 3. Ball-stick diagram of **1e**

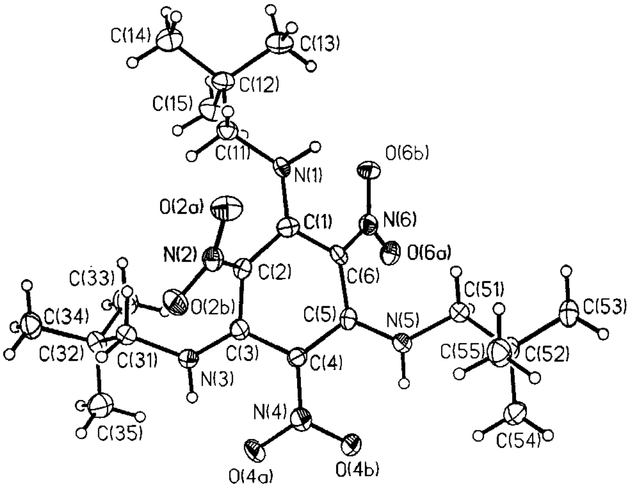


Figure 4. ORTEP plot of **1e**

The solid-state structures for **1d** · *i*PrNH$_2$, **1e**, and **1f** were determined by X-ray crystallography (Table 1 and Figures 1 – 5). All compounds have benzene rings that are much more distorted than expected on the basis of steric interactions alone (even a highly strained compound like 8,11-dichloro[5]metacyclophane shows only about one half of the sum of absolute torsional angles in the benzene ring[6]). **1d** · *i*PrNH$_2$ is found to adopt a boat-like structure rather similar to **1c**[2d] (Table 2 allows a comparison). The boat ring of **1d** · *i*PrNH$_2$ is a little less distorted but also less twisted than that of **1b**, and there are some minor differences in the twist of substituents. An "ideal" non-twisted boat geometry

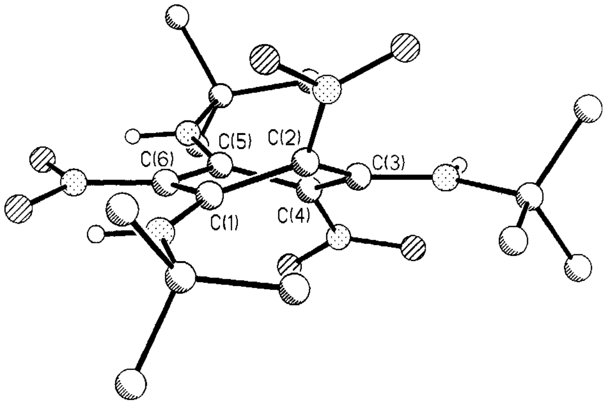


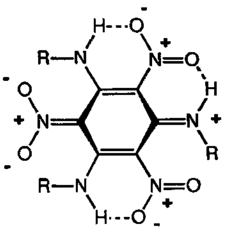
Figure 5. Edge-on view of **1f**

Table 1. Selected structural data for **1d–f**

| | **1d**·$i$PrNH$_2$ | | **1e** | | **1f** |
|---|---|---|---|---|---|
| Bond lengths [Å] | | | | | |
| C1-C2 | 1.412(7) | | 1.428(6) | | 1.461(6) |
| C2-C3 | 1.482(7) | | 1.449(6) | | 1.426(7) |
| C3-C4 | 1.474(7) | | 1.451(6) | | 1.434(7) |
| C4-C5 | 1.411(8) | | 1.431(5) | | 1.451(7) |
| C5-C6 | 1.452(7) | | 1.437(6) | | 1.439(7) |
| C6-C1 | 1.471(7) | | 1.433(6) | | 1.457(7) |
| C1-N1 | 1.322(7) | | 1.328(6) | | 1.303(6) |
| C3-N3 | 1.281(7) | | 1.314(5) | | 1.336(6) |
| C5-N5 | 1.327(6) | | 1.319(5) | | 1.315(6) |
| C2-N2 | 1.377(6) | | 1.404(5) | | 1.386(6) |
| C4-N4 | 1.393(7) | | 1.396(6) | | 1.406(6) |
| C6-N6 | 1.366(7) | | 1.410(5) | | 1.390(6) |
| C-C(ave) | 1.450 | | 1.438 | | 1.445 |
| C-NHR(ave) | 1.310 | | 1.320 | | 1.318 |
| C-NO$_2$ (ave) | 1.379 | | 1.403 | | 1.394 |
| Nonbonded Distances [Å] | | | | | |
| H1a-O2a | 1.911 | O6b | 1.988 | O6b | 1.769 |
| H3a-O2b | 2.402 | O4a | 1.842 | O4a | 2.093 |
| H5a-O4b | 1.960 | O4b | 1.819 | O6a | 1.784 |
| N1-O2a | 2.571 | O6b | 2.608 | O6b | 2.550 |
| N3-O2b | 2.842 | O4a | 2.565 | O4a | 2.611 |
| N5-O4b | 2.586 | O6b | 2.544 | O6a | 2.544 |
| Torsional Angles [deg] | | | | | |
| C1C2C3C4 | -41.3(7) | | 39.5(4) | | 21.7(6) |
| C2C3C4C5 | 39.5(7) | | -19.2(5) | | 17.8(6) |
| C3C4C5C6 | -1.0(8) | | -14.1(5) | | -39.5(6) |
| C4C5C6C1 | -38.0(7) | | 29.8(5) | | 20.8(6) |
| C5C6C1C2 | 36.0(7) | | -10.1(5) | | 15.9(6) |
| C6C1C2C3 | 4.8(7) | | -24.7(4) | | -38.9(6) |
| Σ\|dih.∠\| | 161 | | 137 | | 155 |
| H1aN1C11H11a | | | -78.9 | | |
| H1aN3C11H11b | | | 162.6 | | |
| H3aN3C31H31a | | | -176.8 | | |
| H3aN1C31H31b | | | 65.1 | | |
| H5aN5C51H51a | | | -157.9 | | |
| H5aN5C51H51b | | | 84.2 | | |

would have $C_{2v}$ symmetry (disregarding substituents) and internal dihedral angles of 4 × ($\pm a$) and 2 angles with a value of 0°; the sum of absolute values of internal torsional angles therefore equals $4a$. The bond lengths within the ring show even more difference than in **1c**; these differences correspond to a quinonoid structure with short "side"-C–C, "bow"- and "stern"-C–N bond lengths and long C–C bonds leading to "stern" and "bow" (Scheme 2). The principal differences between corresponding bond lengths in the two compounds are the 0.046 Å shorter "bow"-C–NO$_2$ bond length and the 0.048 Å shorter C–C bonds to the bow carbon atom. **1d** · $i$PrNH$_2$ shows intramolecular hydrogen bonding corresponding to type **B** (Scheme 1): Two stronger interactions occur between the side-NH and -O$_2$N and a very weak one between the stern-NH and side-O$_2$N groups. The distances found for the stronger interactions are within the range of those reported for nitroanilines[7]. The third nitro group does not engage in intramolecular hydrogen bonding. The isopropylamine is disordered, but appears to have interactions with N(3)–H(3A) of one molecule and with the oxygen atoms of side- and bow-nitro groups in other molecules in the unit cell.

Scheme 2



In contrast to **1c,d**, twist-boat structures are adopted by **1e,f** in the solid state. An "ideal" twist boat in $C_2$ symmetry has dihedral angles of 4 × ($\pm a/2$) and 2 × ($-a$). To our knowledge, these are the first examples of uncharged "benzene" rings strongly deformed to twist boats. There is less bond alternation than in the boat forms of **1c,d**, and the variations cannot be rationalized in terms of a clear-cut equivalent resonance structure. An admixture of "radialene character" may be claimed ([6]radialenes[8], oxidized benzene derivatives[2c] as well as cyclohexanes[9] that are stablest in twist-boat forms are known). However, the amounts of distortions in **1e,f**, as measured by the sum of absolute values of torsional angles, are of comparable magnitude to those in **1c,d**. The averaged C–C bond lengths are shorter, and the C–N bonds are longer (Table 1 shows a comparison of all structures). In addition, the intramolecular hydrogen bonding is more pronounced, and its pattern is different although also conforming to type **B**: Two strong interactions occur to only one nitro group, and a weaker one to the second; the third nitro group does not engage in intramolecular hydrogen bonding. The C–NHR bonds are shorter for the two substituents showing hydrogen bonding. Taken together, these structural features are reflected in the splitting pattern prominent in the $^{13}$C-NMR spectrum: Two signal lines of each set lie close together and are shifted downfield in comparison to the third signal. A $^{1}$H-NMR spectrum for **1e** has been obtained at 210 K to further the evidence beyond that gathered from the $^{13}$C-NMR data. As expected, at least three signals for each set of protons are found. In addition, the methylene protons are diastereotopic. One set of these couples very strongly with the protons of the amino group ($^3J$ = 9.7–10.6 Hz), whereas the coupling of the other set is not resolved ($^3J$ < 1 Hz). According to the Karplus relationship, one set of HNCH torsional angles should therefore be close to 180° and the other close to 90°. The torsional angles derived from the X-ray data bear close resemblance to these predictions, the most pronounced deviation is found for the torsion around N(3)-C(31). Since this is also the group with the weak intramolecular hydrogen bond, we do not find this discrepancy surprising. We believe the NMR results to clearly indicate that structures similar to those adopted in the solid state are also present in solution.

Therefore, it is reasonable to assume that the conformations of the benzene rings adopted in **1b–f** are governed by principally intramolecular rather than the intermolecular forces present in the crystal. Computations on molecules of this class hold great promise to further gain information about the causes of the distortions observed. They are too large, however, to allow performing meaningful ab initio calculations with computational facilities presently available. The most recent semiempirical method AM1[4] may therefore be called a "state-of-the-art" tool, especially since it proved so fruitful in modeling the X-ray analysis of **1c**[2d]. Furthermore, AM1 has proved to be superior to previous semiempirical methods for modeling hydrogen bonding[10], which is present in **1c–f**. In addition, AM1 has even been useful in modeling intermolecular hydrogen bonding in nitroanilines[11].

Table 2. Comparison of selected structural features for **1c** and **1d**

| | **1c**[a] | **1d**·$i$PrNH$_2$[b] | **1d** (AM1) |
|---|---|---|---|
| **Torsional angles [deg]** | | | |
| side bonds[c] | 10.3, -8.0 | 4.8, -1.0 | 9.7, 11.1 |
| bonds[d] to "stern" $NO_2$ | -29.8, 30.9 | -38.0, 36.0 | -46.8 35.6 |
| bonds[d] to "bow" $CNNR^1$ | -47.0, 45.9 | -41.3, 39.5 | -44.0, 32.2 |
| **Average difference in CC bond lengths [Å]** | | | |
| bonds to "stern"-side bonds[c] | 0.027 | 0.050 | 0.013 |
| bonds to "bow"-side bonds[c] | 0.061 | 0.068 | 0.021 |
| Intramolecular hydrogen-oxygen distances [Å] | | | |
| H1a-O2a (side interaction) | - | 1.911 | 2.029 |
| H3a-O2b ("bow" interaction) | - | 2.402 | 2.079 |
| H5a-O4b (side interaction) | - | 1.960 | 2.073 |

[a] Ref.[2d]. — [b] This work. — [c] Shown as double bonds in Scheme 2. — [d] Shown as single bonds in Scheme 2.

Table 3. Ring Distortions in 1,3,5-Triamino-2,4,6-trinitrobenzenes (AM1)

| | dihedral angles (dih. ∠) [deg] at side bonds[a] | to stern $NO_2$ | to bow CHNR | Σ\|dih.∠\| |
|---|---|---|---|---|
| **1a** ($C_s$ boat) | 1.5, -1.5 | 32.6, -32.6 | 30.6, -30.6 | 129 |
| ($C_2$ twist)[b] | -34.8, -34.8 | 16.9, 16.9 | 17.4, 17.4 | 138 |
| **1f** ($C_2$ twist) | 15.5, 18.3 | 29.5, -48.8 | 29.8, -47.9 | 190 |
| **1g** ($C_s$ boat) | 6.7, 9.3 | 30.9, -39.9 | 35.2, -43.8 | 166 |
| **1h** ($C_s$ boat) | 7.1, 9.8 | 31.2, -40.6 | 35.5, -44.6 | 169 |

[a] Shown as double bonds in Scheme 2 for boat structures; bonds with smaller twist for twist-boat structures. — [b] 0.06 kcal/mol lower in $\Delta H_f$ than the $C_s$ boat; the other geometries respresent the structures of lowest energy found.

AM1 calculations on **1d** (without additional amine) yield an optimized structure strongly resembling that of the isopropylamine complex. We know of no way to assure finding the global AM1 energy minimum for a structure as complicated as that of **1d**, but believe that the structure discussed is the minimum closest in geometry to the X-ray structure. It is also the structure with the lowest energy found. Optimizations of dihedral angles which involve concerted motions of several atoms are difficult, and the dihedral angles are not optimized better than about 0.5°. In comparison to the X-ray structure, that computed by AM1 (Table 2) may be described as having larger side-bond twists, a 4° larger average out-of-plane angle for the $CNO_2$ moieties, and a 5° smaller angle for the CNH*i*Pr moieties; there are also some differences in $NO_2$ and *i*Pr twist angles. Greater deviations are found for the internal hydrogen bond distances which vary only by 0.05 Å, about an order of magnitude less than those of the crystal. The rather minor structural differences between the AM1 and the crystal structure might well be caused by optimizing intramolecular hydrogen bonding in the isolated molecule; the crystal structure is for an intermolecular complex. We rather believe that the substantial similarities between calculated and experimental structure are quite notable[12].

Structures for other examples of **1** have also been computed, internal torsional angles are shown in Table 3. Those for **1g** and **1h** are slightly twisted boats closely resembling the structure for **1d** (Table 2). The twists at the side bonds and the sums of absolute internal dihedral angles increase rather slightly with the size of the alkyl group. Changing R to *t*Bu (**1f**) does not only increase the sum of dihedral angles but also leads to a pattern of a $C_2$ twist boat, in basic agreement with the crystal structure for **1f**.

For the "parent" compound **1a**, $C_s$ boat and $C_2$ twist-boat conformations have almost the same energy and angle sums of 129° and 138°. The significant distortion calculated for **1a** by AM1 is in contradiction to its reported crystal structure[13], for which all heavy atoms are essentially coplanar. A factor in the great discrepancy between the geometry for **1a** found in the crystal and that predicted by AM1 for the isolated molecule may be the very strong intermolecular hydrogen bonding which clearly occurs in the solid state[13]. Further evidence for this assumption is provided in the accompanying publication[1]. A measure of the strength of these interactions[7] is provided by a mp > 360°C with decomposition[2f] for **1a**, its IR spectrum[3], and the lack of solubility in almost any solvent which precludes to obtain meaningful solution-state NMR spectra[14]. In this context, we note that 3,5-diamino-2,4,6-trinitrophenol[15], 3,5-diamino-2,4,6-trinitrobenzoic acid[16], and 3,5-diamino-2,4,6-trinitrobenzamide[17], which have one amino group replaced by a more poorly donating group, but less favorable intermolecular hydrogen bonding, exhibit sums of absolute torsional angles of 41°, 38°, and 51° in the solid state. AM1 calculations on 3,5-diamino-2,4,6-trinitrophenol located two twist-boat structures and one boat structure within a range of 0.3 kcal/mol and angle sums ranging from 90–101°.

Clearly, AM1 calculations do consistently overestimate the values for the sums of absolute dihedral angles, for the boat structures of **1c**[2c] and **1d** by 9° and 18°, and by 35° for the twist-boat structure of **1f**. Nevertheless, it is obvious that for compounds of type **1**, the resistance of the benzene ring towards distortion is greatly weakened by the electronic push-pull interactions present, and even the relatively small steric interaction between the $NH_2$ and $NO_2$ groups in **1a** is sufficient to cause considerable deviation of the aromatic ring from planarity.

## Conclusion

In this work we have shown by X-ray crystallography on **1c−f** that only one alkyl group on each nitrogen atom is needed to cause severe distortion of the aromatic ring to boat or twist-boat forms. We have identified the patterns of intramolecular hydrogen bonding and donor-acceptor interaction associated with each conformer. AM1 calculations have proved valuable in modeling these structures. No steric interactions larger than those of NH hydrogen atoms are calculated to be necessary for an out-of-plane deviation of over 30° for compounds of type **1**, leading to very similar structures and resulting in high calculated dipole moments (2.5 D for **1d**) for these symmetrically looking compounds. It remains to be seen how accurate these predictions are.

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## Experimental

*General Comments:* Melting points are uncorrected. – Routine $^1$H NMR: Bruker WP-200 (200.133 MHz for $^1$H); variable-temperature (VT) NMR: Bruker AC-500 (500.133 MHz for $^1$H). Samples for VT experiments were prepared from solvents dried with active basic alumina which were condensed into the NMR tubes under vacuum; the tubes were then sealed. – HR MS: Kratos MS-80RFA with DS55/DS 90. **1d−f** have weak molecular ions, but strong peaks corresponding to [M$^+$ − OH] and [M$^+$ − NO$_2$], analyzing for the exact masses, are always found, too. – Microanalyses: Spang Microanalytical Laboratories.

*1,3,5-Tris(isopropylamino)-2,4,6-trinitrobenzene* (**1d** · *i*PrNH$_2$): Dry isopropylamine [0.18 ml (2.1 mmol)] was added to a solution of 1,3,5-trimethoxy-2,4,6-trinitrobenzene[3] [0.20 g (0.66 mmol)] in toluene (4 ml) with stirring. The solution immediately turned yellow, and an oil separated which crystallized after ca. 5 min. The mixture was stirred for 24 h, and additional amine [0.05 ml (0.06 mmol)] was added. Subsequent boiling to reflux for 30 min and cooling to room temp. gave yellow prisms which were filtered and washed with toluene, and then with pentane. Drying at 0.05 Torr yielded **1d** · *i*PrNH$_2$ [0.25 g (85%)], mp 185°C (dec.). The crystals were suitable for X-ray analysis. – $^1$H NMR (CDCl$_3$, 200 MHz, room temp.): δ = 1.08 (d, *J* = 6.2 Hz, 6H), 1.38 (d, *J* = 6.3 Hz, 18H), 3.12 (sept, *J* = 6.4 Hz, 1H), 3.91 (sept, *J* = 6.4 Hz, 3H); the signals at δ = 1.08 and 3.12 increased when isopropylamine was added to the solution. – $^{13}$C NMR (CDCl$_3$, 125 MHz, 300 K): δ = 27.25, 32.01, 61.68 (br.); (CD$_2$Cl$_2$, 220 K): δ = 19.84, 20.38, 20.72, 23.70, 23.95, 24.34 (one CH$_2$ group hidden by the isopropylamine CH$_3$ at δ = 23.95), 42.48, 51.18, 52.08, 52.38, 102.22, 111.52, 117.07, 148.86, 151.04 (br.), 152.13.

$C_{15}H_{24}N_6O_6 \cdot C_3H_9N$ (443.5) Calcd. C 48.75 H 7.50 N 22.11
Found C 49.00 H 7.64 N 22.03

Sublimation at 140°C/0.05 Torr resulted in loss of isopropylamine, and a yellow powder, mp 185°C (dec.), was obtained. – $^1$H NMR (CDCl$_3$, 200 MHz, room temp.): δ = 1.38 (d, *J* = 6.3 Hz, 18H), 3.91 (br. sept, *J* = 6.4 Hz, 3H), ca. 10.7 (very br. s, ca. 3H). – $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz, 300 K): δ = 22.59, 52.27 [although long relaxation delays (15 s) and a pulse angle of 60° were used to ensure maximum intensity of quaternary carbon atoms, they could not be observed]; (220 K): δ = 19.22, 19.91, 20.38, 23.34, 23.49, 24.15, 51.39, 51.82, 52.49, 101.98, 110.61, 116.56, 148.12, 152.14, 152.27.

$C_{15}H_{24}N_6O_6$ (384.4) Calcd. C 46.87 H 6.29 N 21.86
Found C 47.07 H 6.04 N 21.81

Table 4. Structure determination summary of **1d−f**

| | **1d·*i*PrNH$_2$** | **1e** | **1f** |
|---|---|---|---|
| Empirical Formula | $C_{18}H_{33}N_7O_6$ | $C_{21}H_{36}N_6O_6$ | $C_{18}H_{30}N_6O_6$ |
| Color; Habit | yellow prisms | yellow prisms | yellow prisms |
| Crystal Size [mm] | 0.20 x 0.30 x 0.35 | 0.15 x 0.25 x 0.45 | 0.20 x 0.35 x 0.40 |
| Crystal System | monoclinic | monoclinic | monoclinic |
| Space Group | $P2_1/c$ | C2/c | $P2_1/n$ |
| Unit Cell [Å] *a* | 8.504(2) | 19.679(8) | 10.375(6) |
| *b* | 17.368(3) | 15.214(6) | 11.286(8) |
| *c* | 16.040(3) | 17.245(6) | 18.330(13) |
| β | 101.24(3)° | 108.89(3)° | 97.61(6)° |
| Volume [Å$^3$] | 2323.6(8) | 4879(5) | 2122(2) |
| Z | 4 | 8 | 4 |
| Formula Weight | 443.5 | 468.6 | 426.5 |
| Density (calcd.) [g·cm$^{-3}$] | 1.268 | 1.276 | 1.335 |
| Absorption Coeff. [mm$^{-1}$] | 0.767 | 0.088 | 0.808 |
| F(000) | 952 | 2016 | 912 |
| Radiation | CuK$_\alpha$ | MoK$_\alpha$ | CuK$_\alpha$ |
| Temperature [°C] | -165(2) | -165(2) | -165(2) |
| 2θ Range | 3.5-110.0° | 3.5-45.0° | 3.5-110.0° |
| Reflections collected | 3371 | 6371 | 3472 |
| Indep. Reflections | 2922 ($R_{int}$ = 4.56%) | 3209 ($R_{int}$ = 3.76%) | 2662 ($R_{int}$ = 2.49%) |
| Obsvd. Reflections[a)] | 2319 | 2012 | 2144 |
| Absorption Corr. | Semi-empirical | N/A | N/A |
| Min/max Transmiss. | 0.5002/0.6722 | | |
| Hydrogen Atoms | Riding Model<br>Isotropic U | Riding Model<br>Isotropic U | Riding Model<br>Isotropic U |
| Weighting Scheme[b)] | y = 0.0019 | 0.0004 | 0.0001 |
| Parameters refined | 282 | 326 | 272 |
| Final *R* indices [%] (obsd. data) | $R = 7.42$ $R_w = 11.50$ | $R = 4.80$ $R_w = 4.62$ | $R = 7.33$ $R_w = 7.01$ |
| *R* indices [%] (all data) | $R = 9.48$ $R_w = 12.16$ | $R = 9.16$ $R_w = 5.70$ | $R = 9.59$ $R_w = 7.36$ |
| Goodness-of-fit | 2.11 | 1.13 | 2.88 |

a) $[F > 4.0\sigma(F)]$. – b) $w^{-1} = \sigma^2(F) + y \cdot F^2$.

Crystallization of sublimed **1d** from toluene and drying at 0.05 Torr led to well-developed yellow prisms of a 1:1 complex with that solvent, mp 185°C. – $^1$H NMR (CDCl$_3$, 200 MHz, room temp.): δ = 1.38 (d, *J* = 6.5 Hz, 18H), 2.36 (s, 3H), 3.91 (dsept, *J* = 9.7 and 6.4 Hz, 3H), 7.15−7.28 (m, 5H), ca. 10.5 (br. d).

$C_{15}H_{24}N_6O_6$ Calcd. 384.1757 Found 384.1746 (MS)

*1,3,5-Tris[(2,2-dimethyl)propylamino]-2,4,6-trinitrobenzene* (**1e**): Dry neopentylamine [0.35 ml (3.0 mmol)] was added to a solution of 1,3,5-trimethoxy-2,4,6-trinitrobenzene[3] (303 mg [1.00 mmol)] in toluene (4 ml). The solution, which turned yellow immediately, was stirred for 14 h at room temp. and was then heated to reflux for 1 h. After cooling, pentane (ca. 30 ml) was added, and the precipitate was filtered. **1e** was obtained as fine yellow needles [0.43 g (92%)], mp 206−208°C (dec.). Crystals for X-ray analysis were grown from hot toluene; the fine needles which separated from the solution on cooling were transformed into prims on standing for 2 d. – $^1$H NMR (CDCl$_3$, 200 MHz, room temp.): δ = 1.06 (br. s, 9H), 3.17 (br. s, 2H); amino proton peaks not visible; (CD$_2$Cl$_2$/CFCl$_3$, 500 MHz, 210 K): δ = 0.99 (s, 9H), 1.05 (s, 9H), 1.06 (s, 9H), 2.55 (dd, *J* = 14.1 and 9.3 Hz, 1H), 2.84 (dd, *J* = 13.6 and 10.1 Hz, 1H), 2.88 (dd, *J* = 14.4 and 10.3 Hz, 1H), 3.45 (d, *J* = 14.2 Hz, 1H), 3.66 (d, *J* = 13.7 Hz, 1H), 3.73 (d, *J* = 13.9 Hz, 1H), 10.31 (d, *J* = 10.6 Hz, 1H), 11.76 (d, *J* = 10.5 Hz, 1H), 11.84 (d, *J* = 9.7 Hz, 1H). – $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz, 300 K): δ = 27.22, 31.12, 61.78 (br.); (200 K): δ = 26.47, 26.67, 26.84, 31.47, 31.84

Table 5. Atomic coordinates (× 10⁴) and equivalent isotropic displacement coefficients (× 10⁴) [Å²] for **1d** · *i*PrNH₂; *U*(eq) defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2807(6) | 1832(3) | 1666(3) | 275(18) |
| C(2) | 2449(6) | 1038(3) | 1639(3) | 254(18) |
| C(3) | 2713(6) | 619(3) | 2460(3) | 266(18) |
| C(4) | 4208(6) | 847(3) | 3037(3) | 270(18) |
| C(5) | 4636(6) | 1633(3) | 3074(3) | 278(19) |
| C(6) | 3532(6) | 2129(3) | 2512(3) | 271(18) |
| N(1) | 2579(5) | 2276(3) | 983(3) | 324(16) |
| C(1A) | 3200(6) | 3053(3) | 900(3) | 275(18) |
| C(1B) | 4679(8) | 3003(4) | 521(4) | 452(23) |
| C(1C) | 1890(8) | 3516(4) | 342(4) | 514(25) |
| N(2) | 1889(5) | 647(3) | 893(3) | 314(17) |
| O(2A) | 1630(5) | 1022(2) | 192(2) | 380(14) |
| O(2B) | 1638(4) | -58(2) | 875(2) | 317(14) |
| N(3) | 1647(5) | 156(3) | 2632(3) | 283(15) |
| C(3A) | 1765(7) | -165(3) | 3479(3) | 337(20) |
| C(3B) | 309(7) | 106(4) | 3815(4) | 421(22) |
| C(3C) | 1832(7) | -1040(3) | 3457(4) | 383(21) |
| N(4) | 5282(5) | 276(3) | 3392(3) | 326(17) |
| O(4A) | 5049(5) | -401(2) | 3162(3) | 393(15) |
| O(4B) | 6504(5) | 466(2) | 3944(3) | 427(15) |
| N(5) | 5976(5) | 1900(3) | 3553(3) | 297(16) |
| C(5A) | 6800(7) | 2630(3) | 3463(4) | 343(20) |
| C(5B) | 7214(9) | 3038(4) | 4303(4) | 594(28) |
| C(5C) | 8277(8) | 2447(4) | 3114(4) | 517(25) |
| N(6) | 2867(5) | 2745(3) | 2844(3) | 296(16) |
| O(6A) | 3365(5) | 2934(2) | 3606(2) | 385(15) |
| O(6B) | 1753(4) | 3133(2) | 2397(2) | 330(13) |
| N(7) | -1236(5) | -507(3) | 1561(3) | 293(16) |
| C(7A) | -2511(6) | 96(3) | 1607(4) | 344(20) |
| C(7B) | -4115(7) | -195(4) | 1184(4) | 481(24) |
| C(7C) | -2039(8) | 823(3) | 1214(4) | 505(25) |

Table 6. Atomic coordinates (× 10⁴) and equivalent isotropic displacement coefficients (× 10³) [Å²] for **1e**; *U*(eq) defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 1499(2) | -979(3) | 9778(2) | 20(1) |
| N(1) | 1131(2) | -1151(2) | 10285(2) | 21(1) |
| C(11) | 1071(2) | -624(3) | 10969(2) | 21(1) |
| C(12) | 1121(2) | -1207(3) | 11712(2) | 23(2) |
| C(13) | 550(2) | -1932(3) | 11475(3) | 28(2) |
| C(14) | 968(2) | -620(3) | 12352(3) | 34(2) |
| C(15) | 1870(2) | -1599(3) | 12057(3) | 34(2) |
| C(2) | 1806(2) | -139(3) | 9729(2) | 18(1) |
| N(2) | 1411(2) | 638(2) | 9688(2) | 22(1) |
| O(2A) | 791(1) | 587(2) | 9734(2) | 29(1) |
| O(2B) | 1664(1) | 1353(2) | 9554(2) | 28(1) |
| C(3) | 2431(2) | -106(3) | 9461(2) | 19(1) |
| N(3) | 2955(2) | 463(2) | 9752(2) | 23(1) |
| C(31) | 3091(2) | 1031(3) | 10468(2) | 25(2) |
| C(32) | 3844(2) | 879(3) | 11080(2) | 23(2) |
| C(33) | 3881(2) | -19(3) | 11484(3) | 37(2) |
| C(34) | 3951(2) | 1605(3) | 11723(3) | 32(2) |
| C(35) | 4428(2) | 954(3) | 10672(3) | 34(2) |
| C(4) | 2423(2) | -702(3) | 8801(2) | 21(1) |
| N(4) | 2856(2) | -536(2) | 8317(2) | 30(1) |
| O(4A) | 3351(2) | 21(2) | 8528(2) | 42(1) |
| O(4B) | 2740(2) | -935(2) | 7644(2) | 42(1) |
| C(5) | 1945(2) | -1438(3) | 8646(2) | 19(2) |
| N(5) | 1807(2) | -1897(2) | 7963(2) | 21(1) |
| C(51) | 1289(2) | -2606(3) | 7657(2) | 22(2) |
| C(52) | 918(2) | -2539(3) | 6723(2) | 21(1) |
| C(53) | 429(2) | -3337(3) | 6473(3) | 26(2) |
| C(54) | 1481(2) | -2557(3) | 6279(3) | 32(2) |
| C(55) | 482(2) | -1697(3) | 6510(3) | 31(2) |
| C(6) | 1629(2) | -1655(3) | 9265(2) | 19(1) |
| N(6) | 1620(2) | -2547(2) | 9481(2) | 22(1) |
| O(6A) | 2008(1) | -3081(2) | 9269(2) | 26(1) |
| O(6B) | 1249(1) | -2793(2) | 9914(2) | 29(1) |

(double intensity), 59.46, 61.70, 61.91, 104.34, 112.53, 116.95, 150.22, 152.85, 153.26.

$C_{21}H_{36}N_6O_6$ (468.6) Calcd. C 53.83 H 7.74 N 17.94
Found C 53.75 H 7.61 N 17.84

Calcd. 468.2696 Found 468.2689
([M⁺ + 1] confirmed by peak-matching; MS)

*1,3,5-Tris(tert-butylamino)-2,4,6-trinitrobenzene* (**1f**): To a solution of 1,3,5-trichloro-2,4,6-trinitrobenzene[5] [1.000 g (3.160 mmol)] in toluene (10 ml), dry *tert*-butylamine [4.0 ml (38 mmol)] was added. The resulting yellow solution was stirred at room temp. for 2 h and was then heated to reflux for 5 h. The solvent was removed in vacuo, and the residue was treated with pentane (20 ml), filtered, and washed with pentane. It was then thoroughly washed with water (4 × ca. 10 ml) and dried at 0.05 Torr. **1f** was obtained as a bright yellow powder [1.296 g (96%)], mp 171–173°C (dec.). Crystals for X-ray analysis were grown from hot toluene to give dark yellow prisms. – $^1$H NMR ($CDCl_3$, 200 MHz, room temp.): δ = 1.41 (s, 9H), 9.19 (br. s, 3H). – $^{13}$C NMR ($CDCl_3$, 125 MHz, 300 K): δ = 29.71, 60.24, 122.88 (br.), 145.33.

$C_{18}H_{30}N_6O_6$ (426.5) Calcd. C 50.69 H 7.09 N 19.71
Found C 50.57 H 7.00 N 19.67

Calcd. 426.2227 Found 426.2230 (MS)

Table 7. Atomic coordinates (× 10⁴) and equivalent isotropic displacement coefficients (× 10³) [Å²] for **1f**; *U*(eq) defined as one third of the trace of the orthogonalizcd $U_{ij}$ tensor

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2642(4) | 4558(4) | -791(2) | 15(2) |
| C(2) | 3060(4) | 5643(4) | -394(2) | 17(2) |
| C(3) | 2455(4) | 5975(4) | 230(3) | 17(2) |
| C(4) | 1841(4) | 5018(4) | 566(2) | 16(2) |
| C(5) | 2171(4) | 3800(4) | 416(3) | 20(2) |
| C(6) | 2355(5) | 3562(4) | -334(3) | 18(2) |
| N(1) | 2566(4) | 4403(3) | -1500(2) | 20(1) |
| C(1A) | 2571(5) | 5181(4) | -2163(3) | 19(2) |
| C(1B) | 2501(5) | 6485(4) | -1990(3) | 27(2) |
| C(1C) | 1344(5) | 4825(4) | -2664(3) | 27(2) |
| C(1D) | 3758(5) | 4871(4) | -2536(3) | 27(2) |
| N(2) | 4291(4) | 6053(3) | -479(2) | 21(1) |
| O(2A) | 4928(3) | 5580(3) | -940(2) | 26(1) |
| O(2B) | 4787(3) | 6876(3) | -77(2) | 29(1) |
| N(3) | 2397(4) | 7048(3) | 532(2) | 21(1) |
| C(3A) | 2470(5) | 8309(4) | 284(3) | 23(2) |
| C(3B) | 2426(5) | 8453(4) | -542(3) | 29(2) |
| C(3C) | 1238(5) | 8881(4) | 512(3) | 30(2) |
| C(3D) | 3670(5) | 8903(4) | 708(3) | 33(2) |
| N(4) | 760(4) | 5184(3) | 943(2) | 21(1) |
| O(4A) | 538(3) | 6187(3) | 1206(2) | 29(1) |
| O(4B) | 17(3) | 4329(3) | 1005(2) | 24(1) |
| N(5) | 2270(4) | 2951(3) | 912(2) | 22(1) |
| C(5A) | 2422(5) | 2890(4) | 1733(3) | 22(2) |
| C(5B) | 3652(5) | 2148(5) | 1916(3) | 32(2) |
| C(5C) | 2624(5) | 4090(4) | 2119(3) | 28(2) |
| C(5D) | 1252(5) | 2229(5) | 1965(3) | 33(2) |
| N(6) | 2356(4) | 2405(4) | -595(2) | 26(2) |
| O(6A) | 2304(3) | 1531(3) | -163(2) | 30(1) |
| O(6B) | 2379(4) | 2186(3) | -1266(2) | 35(1) |

*X-ray Analyses on* **1d–f**: Data collection: Syntex P-1 and Siemens P3f diffractometer, highly oriented graphite-crystal monochromator; scan type: Wyckoff; scan speed: variable, 2.00–12.00° min⁻¹ in ω; scan range (ω): 0.40°; background measurement: stationary crystal and stationary counter at beginning and end of scan, each for 16.7% of total scan time. Solution and refinement: Siemens SHELXTL PLUS (VMS)[18], direct methods, refinement by full-matrix least squares. Further parameters are listed in Table 4[19], atomic coordinates and equivalent isotropic displacement coefficients in Tables 5–7.

CAS Registry Numbers

**1a**: 3058-38-6 / **1d**: 132699-66-2 / **1d** · *i*PrNH$_2$: 132699-69-5 / **1e**: 132699-67-3 / **1f**: 132699-68-4 / **1g**: 132699-65-1 / **1h**: 91881-07-1 / *i*PrNH$_2$: 75-31-0 / *t*BuNH$_2$: 75-64-9 / neopentylamine: 5813-64-9 / 1,3,5-trichloro-2,4,6-trinitrobenzene: 2631-68-7 / 1,3,5-trimethoxy-2,4,6-trinitrobenzene: 18523-16-5

[*] Dedicated to Professor *Horst Prinzbach* on the occasion of his 60th birthday.

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[32/91]