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Dramatic Steric Distortions and Electronic Demands in 1,3,5-Tris(dialkylamino)-2,4,6-trinitrobenzene: Study of a Severely Warped Benzene

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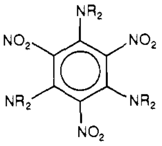
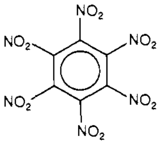
Abstract: The static and dynamic stereochemistry of 1,3,5-tris(dialkylamino)-2,4,6-trinitrobenzene is described by a combination of crystallographic, VT-NMR, and semiempirical calculational methods. Crystal data for the *N,N*-diethyl derivative **1b**: $C_{18}H_{30}N_6O_6$, $M = 426.6$ g·mol^{-1}; monoclinic (space group $P2_1/c$); $a = 10.005$ (2) Å, $b = 21.452$ (5) Å, $c = 10.544$ (2) Å; $\beta = 104.3$ (2)°; and $V = 2193.8$ (8) Å^3; $d_{\text{calc}} = 1.29$ g·cm^{-3}; $Z = 4$. This highly substituted benzene distorts to a boat form in the ground state. The bow and stern angles of the *N,N*-diethyl derivative are 42° and 27°, respectively. This severe out-of-plane distortion is interpreted as a result of a cooperative nonbonded steric repulsion which is reinforced by the demands of a strong push–pull conjugation. Thus, due to a dominant polar resonance form, the molecular skeleton is more quinoid or radialene-like than benzenoid. Evidence for the need of both the electronic and steric factors in order to obtain such a distorted structure is presented. Molecules in this class are found to be fluxional in solution and the boat-C_s and twist-C_2 conformers are seen to interconvert rapidly by means of a pseudorotation pathway. The barrier to interconversion is found by VT-NMR to be 9.1 kcal/mol. Semiempirical calculations (AM1) do a good job of modeling both the ground-state geometry as well as the salient features of the pseudorotation hypersurface for these unusual molecules. On the basis of these calculations, the barrier along the pseudorotation pathway appears to stem from the VDW repulsions that occur as adjacent exocyclic groups pass by one another.

The effective steric bulk of a pendant ligand naturally depends on its conformation. This is the basis underlying the concept of static gearing.[2] Electronic factors can lock in or create a strong preference for a specific conformation and thereby drastically increase the effective bulk of a substituent (gear clashing). This effect is dramatically manifested in 1,3,5-tris(dimethylamino)-2,4,6-trinitrobenzene (**1a**) and 1,3,5-tris(diethylamino)-2,4,6-trinitrobenzene (**1b**). The molecular structure of the parent 1,3,5-triamino-2,4,6-trinitrobenzene (**1c**) is dominated by a quinone-like dipolar resonance form.[3] The structure of **1c** is flat due to the push–pull conjugation between the para-related nitro and amino groups, and the intramolecular H bonding between NH_2 and NO_2 groups. Steric factors are more important in derivatives and analogues of **1c**. Although both hexanitro- (**2**)[4] and hexakis(dimethylamino)benzene (**3**)[5] adopt conformations with their groups turned out of conjugation so as to minimize steric strain, **1a**/**b** retain a conformation which maximizes push-pull conjugation even at the expense of benenoid aromaticity.[6] The skeleton of **1a** thus distorts out of planarity into a boat conformation. We present in this paper our study of the unusual balance between steric and electronic factors in this class of molecules.



1 a R=Me
b R=Et
c R=H



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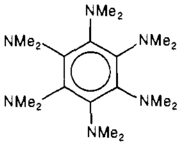

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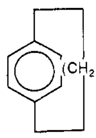
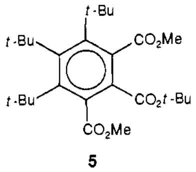


4	n
a	8
b	7
c	6
d	5



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Molecular Structure of Tris(dimethylamino)trinitrobenzene

Crystal Structure of 1b. Crystals suitable for X-ray analysis were obtained for the *N,N*-diethyl compound **1b**. Room temperature data were collected on a crystal grown from ethanol/hexane, and the structure of **1b** was solved and refined in the space group $P2_1/c$ with four molecules per unit cell. All molecules in the cell are in symmetry-related general positions. The molecules have approximate C_s symmetry in the crystal, an unusual consequence for a 1,3,5-trishomo-substituted benzene. A representative structure for **1b** is shown in Figure 1. The most striking

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(1) (a) Princeton University. (b) University of California, San Diego. (c) Presidential Young Investigator, 1988–1993. (d) On leave from Jagiellonian University, Krakow, Poland.

(2) Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* **1980**, *20*, 65.

(3) (a) Cady, H. H.; Larson, A. C. *Acta Crystallogr.* **1965**, *18*, 485. (b) For further discussion of the importance of dipolar resonance forms, see: Hiberty, P. C.; Ohanessian, G. *J. Am. Chem. Soc.* **1984**, *106*, 6963 and ref 1–5 therein. (c) For the structure of *p*-nitro-*N,N*-dimethylaminoaniline, see: Martin, J.; Krygowski, T. M. *J. Mol. Struct.* **1988**, *172*, 413.

(4) Akopyran, Z. A.; Struchov, Y. T.; Dashevskii, V. G. *J. Struct. Chem. (USSR)* **1966**, *7*, 385.

(5) Chance, J. M.; Kahr, B.; Buda, A. B.; Toscano, J. P.; Mislow, K. *J. Org. Chem.* **1988**, *53*, 3226.

(6) Wallis and Dunitz have seen two different conformational preferences in systems with dimethylamino groups proximal to electron-withdrawing groups. In the 2-(*N*-dimethylamino)benzenediazonium cation[7] the dimethylamino group prefers to be coplanar with the benzene ring, suffering severe in-plane bond-angle distortions in order to retain arene planarity. *N,N*-dimethyl-8-nitro-1-naphthylamine,[8] where the nitro and amino groups occupy the peri positions, exhibits a different conformational preference. Here the trigonal groups face-off against one another; the structure shows in-plane distortions and nitro-group pyramidality consistent with an attractive interaction between the amino and nitro groups. The conformational preference in each of the above compounds seems to be linked directly to the possibility for push-pull conjugation.

(7) Wallis, J. D.; Dunitz, J. D. *Helv. Chim. Acta* **1984**, *67*, 1374.

(8) Egli, M.; Wallis, J. D.; Dunitz, J. D. *Helv. Chim. Acta* **1986**, *69*, 255.

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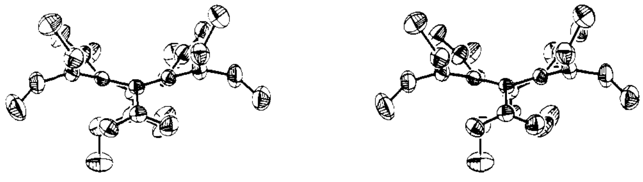

Figure 1. Point-on stereo view that emphasizes the C_s symmetric nature of the structure of **1b**.

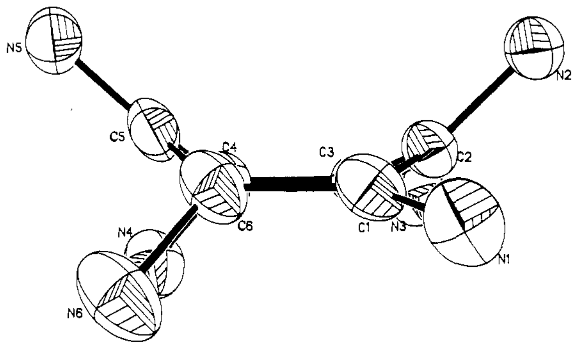

Figure 2. Side view of the principle skeleton of **1b** to show bow and stern distortions. The bow angle is defined as C1-C6-C4-C5; the stern angle is C6-C1-C3-C2.

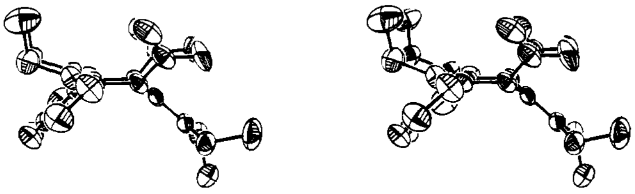

Figure 3. Side-on stereo view of **1b**; hydrogens have been removed for clarity.

feature of this structure is that the benzene ring assumes a boat conformation with extreme out-of-plane deviations (Figure 2).

Distortion of benzenes into chair,[9] twist,[10] and boat[11] forms have been studied; empirically, the chair form is the least[12] and the boat form is the most[11] amenable to out-of-plane conformational distortion. An algorithm for quantifying the degree of boat deformation in paracyclophanes has been introduced by Cram and extended by Maas.[11] Using this analysis of bow and stern angles we find values for the structure of **1b** of 42° and 27°, respectively. These add to give a combined distortion of 69°. This is to be compared with a series of [*n*]-paracyclophanes **4a–d** and the monocyclic compound **5**, where the angle sums are 18°, 34°, 42°, 48° (calc),[13] and 42°,[11] respectively.[14] Clearly, the 20° greater distortion in **1b**, compared to the highly strained **4d**, is remarkable.

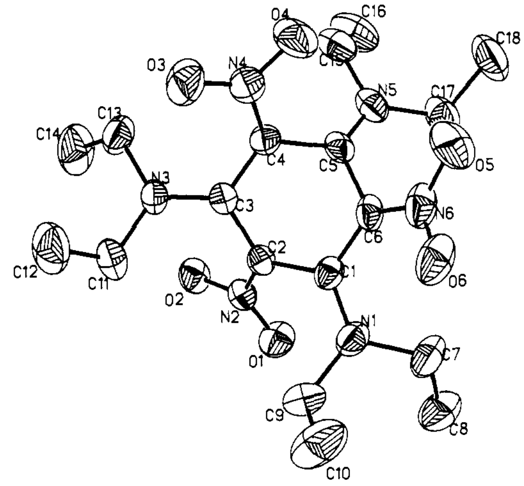

Figure 4. Numbered view of **1b** perpendicular to the basal plane. Numbering corresponds to the data in Table I.

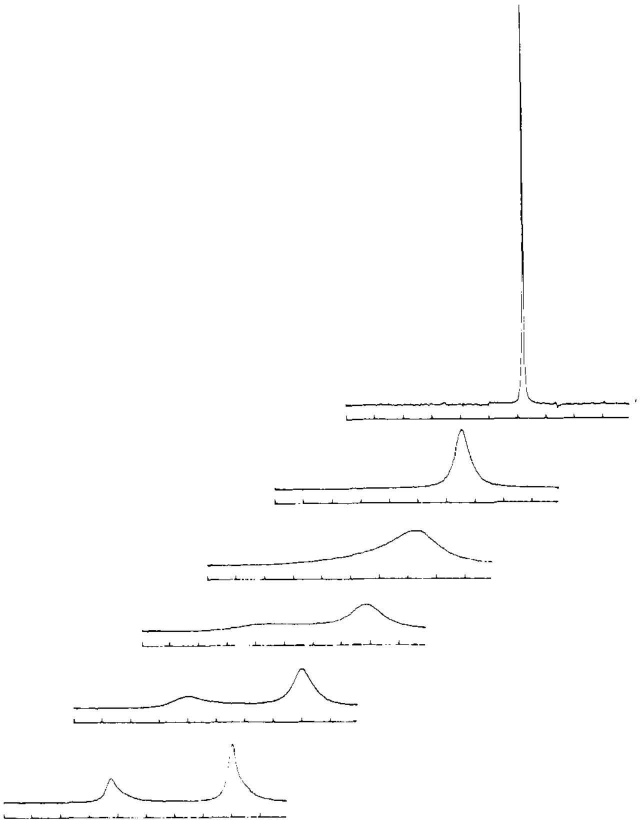

Figure 5. VT-NMR spectra in the region of the methyl groups of **1a** for temperatures of 175, 185, 190, 195, 210, and 294 K (bottom to top). The plot limits are 4 ppm (left) and 3 ppm (right); the tic marks are at 25-Hz separation.

Ortho torsion angles have been used as an alternative gauge of out-of-plane distortion.[11c] This is the torsion angle formed between vicinal exocyclic positions on the benzene ring. For **5** the values are 0.9, −1.5, −30.3, 64.8, −62.3, and 28.8°. For **1b** the values are −48.0, 46.6, 38.4, −72.7, 73.4, and 37.8°. The internal torsion angles compare as follows: [**1b** (**5**)] 29.8, 10.3, −47.0, 45.9, −8.0, −30.9° (−12.3, −12.5, 35.3, −33.9, 8.0, 14.7°).

A rationale for this anomalous torsional distortion can be found by inspection of other geometrical parameters such as the bond lengths in **1b**. Expected values for typical bond lengths are as follows:[15] C(ar)–N(am) = 1.37 Å (planar); C(ar)–C(ar) = 1.40 Å; C(ar)–NO_2 = 1.47 Å; C(sp^2)–C(sp^2) = 1.33 Å; C(sp^2)–N(sp^2) = 1.28 Å; and N-O(nitro)= 1.22 Å. Bond length values for **1b**

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(9) (a) Couldwell, M. H.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1976**, *6*, 59. (b) Weissensteiner, W.; Schuster, I. I.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 6664. (c) Sakurai, H.; Ebata, K.; Kabuto, C.; Sekiguchi, A. Submitted for publication.

(10) (a) Pascal, R. A. P., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660. (b) Mizuno, H.; Nishiguchi, K.; Toyoda, T.; Otsubo, T.; Misumi, S.; Morimoto, N. *Acta Crystallogr. B* **1977**, *33B*, 329.

(11) (a) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204. (b) Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes*; Academic Press: New York, 1983; Chapters 5 and 10. (c) Maas, G.; Fink, J.; Wingert, H.; Blatter, K.; Regitz, M. *Chem. Ber.* **1987**, *120*, 819. (d) Maas, G. *Acta. Crystallogr.* **1985**, *C41*, 1130.

(12) Even in structures with wildly distorted exocyclic geometries, the central ring is considerably less distorted from planarity. In hexakis(trimethylgermy)benzene, the average deviation from a least-squares plane of the exocyclic germanium positions is 0.90 Å as compared to the 0.006 Å for the ring carbon positions. Similarly, the torsion C(1)–C(2)–C(3)–C(4) = 6.8 where as the torsion Ge(1)–C(1)–C(2)–Ge(2) = 57.1.[9c] The crystal structure for hexakis(trifluoromethyl)benzene, as well as the calculated structure of hexa-*tert*-butyl- and hexakis(trimethylsilyl)benzene show similar geometries.[9]

(13) Rice, J. E.; Lee, T. J.; Remington, R. B.; Allen, W. D.; Clabo, D. A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 2902.

(14) As modeled by empirical force-field calculations, the bow and stern angles for boat cyclohexane are roughly 45°.

Table I. Structure Data for **1b**

atoms	exptl (X-ray)	calcd (AM1)
Bond Lengths in Angstroms		
C(1)–C(2)	1.440 (3)	1.452
C(2)–C(3)	1.442 (3)	
C(3)–C(4)	1.416 (3)	1.427
C(4)–C(5)	1.469 (3)	
C(5)–C(6)	1.482 (3)	1.466
C(1)–C(6)	1.412 (3)	
C(1)–N(1)	1.340 (3)	1.359
C(2)–N(2)	1.415 (3)	1.4454
C(3)–N(3)	1.335 (3)	
C(4)–N(4)	1.403 (3)	1.448
C(5)–N(5)	1.296 (3)	1.331
C(6)–N(6)	1.403 (3)	
C(7)–N(1)	1.476 (3)	
C(9)–N(1)	1.474 (3)	
C(11)–N(3)	1.467 (3)	
C(13)–N(3)	1.470 (3)	
C(15)–N(5)	1.478 (3)	
C(17)–N(5)	1.479 (4)	
C(7)–C(8)	1.505 (5)	
C(9)–C(10)	1.496 (4)	
C(11)–C(12)	1.513 (4)	
C(13)–C(14)	1.510 (4)	
C(15)–C(16)	1.510 (4)	
C(17)–C(18)	1.516 (5)	
N(2)–O(1)	1.241 (3)	
N(2)–O(2)	1.246 (3)	
N(4)–O(3)	1.239 (3)	
N(4)–O(4)	1.246 (3)	
N(6)–O(5)	1.243 (3)	
N(6)–O(6)	1.245 (3)	
Bond Angles in Degrees		
C(1)–(2)–(3)	120.1 (2)	118.9
C(2)–(3)–(4)	115.5 (2)	114.5
C(3)–(4)–(5)	115.7 (2)	115.5
C(4)–(5)–(6)	112.4 (2)	112.4
C(2)–(1)–(6)	115.5 (2)	
angle sum at		
N(1)	360.0 (6)	
N(2)	359.9 (6)	
N(3)	359.9 (6)	
N(4)	359.9 (6)	
N(5)	360.0 (6)	
N(6)	360.0 (6)	
C(1)	359.9 (6)	
C(2)	357.3 (6)	359.7
C(3)	359.9 (6)	
C(4)	355.1 (6)	
C(5)	360.0 (6)	359.8
C(6)	354.3 (6)	
Torsion Angles in Degrees		
Internal		
C(1)–C(2)–C(3)–C(4)	29.8 (3)	35.7
C(2)–C(3)–C(4)–C(5)	10.3 (3)	7.0
C(3)–C(4)–C(5)–C(6)	−47.0 (3)	
C(4)–C(5)–C(6)–C(1)	45.9 (3)	47.9
C(2)–C(1)–C(6)–C(5)	−8.0 (3)	
C(6)–C(1)–C(2)–C(3)	−30.9 (3)	
Ortho		
N(1)–C(1)–C(2)–N(2)	−48.0	−43.8
N(2)–C(2)–C(3)–N(3)	46.6	
N(3)–C(3)–C(4)–N(4)	38.4	20.2
N(4)–C(4)–C(5)–N(5)	−72.7	−63.1
N(5)–C(5)–C(6)–N(6)	73.4	
N(6)–C(6)–C(1)–N(1)	−37.8	
Cis Exocyclic		
C(2)–C(1)–N(1)–C(9)	−27.8 (3)	−30.5
C(6)–C(1)–N(1)–C(7)	−26.4 (4)	
C(1)–C(2)–N(2)–O(1)	9.4 (3)	2.7
C(3)–C(2)–N(2)–O(2)	−5.4 (3)	
C(2)–C(3)–N(3)–C(11)	27.5 (3)	
C(4)–C(3)–N(3)–C(13)	29.0 (3)	
C(3)–C(4)–N(4)–O(3)	−8.5 (3)	−20.0
C(5)–C(4)–N(4)–O(4)	13.8 (3)	
C(4)–C(5)–N(5)–C(15)	0.6 (4)	−3.8
C(6)–C(5)–N(5)–C(17)	0.3 (4)	
C(1)–C(6)–N(6)–O(6)	3.6 (4)	
C(5)–C(6)–N(6)–O(5)	−21.3 (4)	

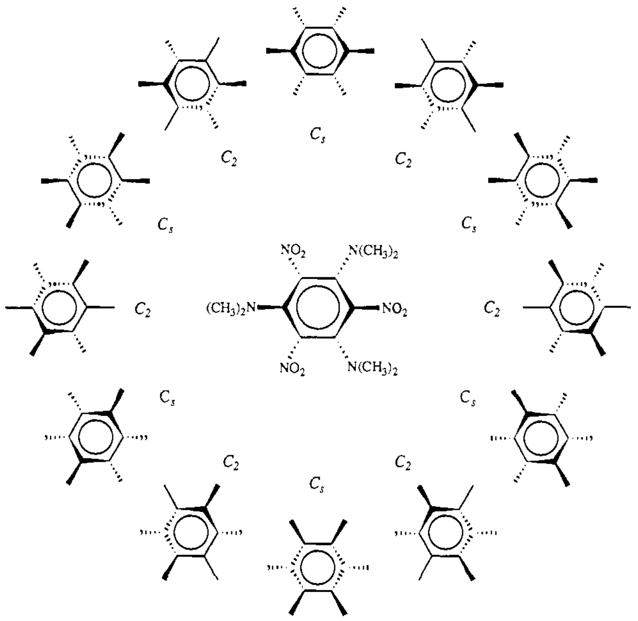

Figure 6. Pseudorotational pathway that interconverts the C_s and C_2 structures of **1a**.

are found to be the following: C(ar)–N(am) = 1.34 Å, 1.30 Å; C(ar)–NO_2 = 1.42 Å, 1.40 Å; C(ar)–C(ar) = 1.48 Å, 1.44 Å, 1.41 Å; and N–O(nitro) = 1.24 Å. By comparison with the above standards, the values for **1b** are more appropriate for a quinoid or even radialene structure rather than a benzenoid structure (Figure 3). Similar bond lengths are seen in **1c** even though it shows no out-of-plane distortion.[3] Interestingly, the structures of duroquinone[16] and 1,4-cyclohexadiene[17] lack benzenoid form and yet retain planarity. Thus, changes in bond lengths alone cannot account for the structure of **1b**. It is reasonable to assume that the out-of-plane modes for a quinoid structure would be softer than for a benzenoid structure, nonetheless, strong nonbonded interactions would still be necessary to destabilize the planar geometry.[18] Therefore, we conclude that it must be the interplay between the effective sterics of the substituents and the nonbenzenoid character of **1b** which leads to the observed boat geometry.

More evidence that the conjugation favors the quinoid geometry and that this resonance form is dominant can be uncovered by looking at the angle sums about C(ar) and N, as well as the exocyclic torsion angles. The long axis of the molecule can be defined by N(2) and N(5), the atoms that sit in "bowsprit" positions.[19] It is interesting to note that the geometry about atoms N(2), N(5), and C(5) is planar. Of the nitro bearing carbons C(2) is the most planar. In addition, the torsions about the C(2)–N(2) and C(5)–N(5) bonds are the smallest of any in **1b**, thus they are the best for vicinal overlap. All this correlates quite nicely with N(5)–C(5) being the shortest bond distance in the molecule.

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(15) For an up to date table of standard bond lengths, see: Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, T. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

(16) Rabinovitch, D.; Schmidt, G. M. J.; Ubell, E. *J. Chem. Soc. B* **1967**, 131.

(17) Burkert, U.; Allinger, N. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

(18) The average internal angle for the 6-membered ring is approximately 116°, and if rigid, it could account for some of the out-of-plane distortion. Considering the structure of TNTAB, we favor an interpretation which assumes the angle contraction to be a consequence, not a cause, of the distortion.

(19) This identification of a long axis in compounds like **1a**/**b** may aid in understanding some of the physical properties of some analogous compounds. Recently, Lehn has looked at some photophysical properties of long-chain *n*-alkyl derivatives of **1**. These compounds do not behave as if they have the optimal D_{3h} symmetry, but appear to have a long axis.[10] This can now be explained by the elucidation of **1a**/**b**.

(20) Lehn, J.-M.; Brienne, J. Personal communication.

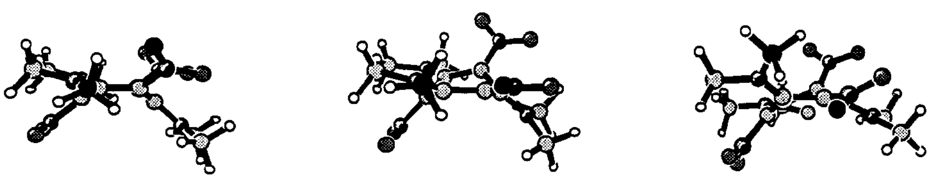

Figure 7. The AM1 geometry of the boat-C_s (left), TS-C_1 (middle), and twist-C_2 (right) conformations of **1a**. The black, filled circles represent the nitrogen from the nitro group and the carbon from the dimethylamino group that pass each other during C_s–C_2 interconversion.

Semiempirical Calculations. Empirical-force-field calculations are not appropriate for modeling molecules with strongly altered electronic structures. Therefore, we decided to use a semiempirical method of the AM1 type.[21] The AMPAC package[22] and GAUSSIAN 86 package of programs were used.[23] Calculations were done on **1a**. The structural parameters thus obtained were then compared to those obtained for **1b** by X-ray crystallography.

The geometry optimization in C_s symmetry, starting from the geometry with all the heavy atoms being coplanar, converged to the boatlike conformation of **1b**. A frequency analysis at this point on the hypersurface revealed it to be a saddle point (one imaginary frequency). The structure was reoptimized without constraints, starting from a conformation obtained by distorting the C_s conformation. The optimized C_1 structure was a minimum within 0.01 kcal/mol of the C_s structure. In addition to the boat conformation, the chair and twist conformation of **1** were calculated. The boat was found to be the lowest energy conformation, the twist following closely (0.9 kcal/mol higher), and the chair being far and away the highest (10.7 kcal/mol higher). A frequency analysis on the symmetry-constrained twist-C_2 and chair-C_s conformations shows the twists to be a minimum and the chair to be a partial maximum.[24] The analysis of the geometrical differences between C_2 and C_s structure leads to the conclusion that during the C_2–C_s interconversion one oxygen from the nitro group and one methyl group from the neighboring dimethylamino group have to pass each other. We assumed, therefore, that the conformation with these two neighbors facing each other should correspond to the transition state between C_2 and C_s structures. The approximate geometry of this transition state was determined by the optimization of the C_1-**1a** geometry with two constraints on the dihedral angles: O–N–C–C = 0° and $C_{(CH_3)}$–N–C–C = 0° as shown in Figure 4 (see also Table I).[25] The energy of this structure is 4.5 kcal/mol higher than the energy of the C_s conformation.

Dynamics and Mechanism of Pseudorotation in 1a/b

VT-NMR Studies. The ^1H NMR spectrum in $CDCl_3$ at ambient temperature shows one quartet and one triplet for **1b** and one singlet for **1a** and is therefore consistent with either a planar D_{3h} structure or a series of rapidly interconverting C_s structures. In order to prove that the structure found in the crystal persists in solution and to quantify the energetics of the pseudorotation process, we undertook a series of variable temperature NMR experiments.

Upon lowering the temperature of a sample of **1a** in CD_2Cl_2 from 290 to 210 K one sees the singlet broaden and at 190 K two broad peaks appear (T_c = 195 K). Final peak separation (110 Hz) is reached at 170 K (super cooled) with the upfield signal twice as intense as the one downfield; two methyl signals are accidentally isochronous (Figure 5). The ^1H NMR spectra for **1b** at various temperatures shows a similar decoalescence behavior for the triplet and quartet with no accidental isochrony.

Taking the low-temperature spectrum as representative of a C_s structure similar to the solid-state structure and assuming that coalescence of the NMR signals is due to conformational interconversion, one can estimate the energetics of the homomerization of **1a**. On the basis of the Gutowsky–Holm approximation,[26] the barrier to homomerization in **1a** is 9.1 kcal/mol.

Prompted by a report that the barrier to rotation about the N(am)–C(ar) bond in 2,4-dinitro-*N*,*N*-dimethylaminoaniline varied with solvent polarity[27] (i.e. high barrier in acetone, low barrier in fluorocarbons), we decided to compare the VT-NMR spectral properties of **1a/b** in acetone with those in dichloromethane. No change in barrier height was seen for **1a/b**, which is suggestive that a mechanism other than rotation about the N(am)–C(ar) bond is responsible for the equivalence of signals in the spectrum of **1a/b** at ambient temperature.

Pseudorotation. From studies in cyclohexane conformational analysis, two distinct conformational domains can be identified. The first is the rigid-chair regime and the second is the fluxional-boat/twist regime. The fluxional interconversion between boat and twist forms has been described as a pseudorotation,[28] where each ground-state twist structure has no greater than D_2 symmetry and the molecule in flux has dynamic symmetry isomorphic to D_{3h}. Such a process has not been elucidated for an all sp^2 carbon 6-membered ring. We, however, believe that this is the most suitable explanation for the observed isomerization of **1**; the mechanism is consistent with experiment and is modeled by calculations which well fit the experimental parameters (e.g. ground-state geometry, barrier height).

In the calculations described above we considered a general point on the hypersurface of **1a** in addition to the symmetry-constrained stationary points (vide supra). The geometry of this constrained structure lies along the pseudorotation path between the twist and boat geometries. By following the changes in the endocyclic and exocyclic dihedral angles, one can describe this pseudorotational path (Figure 6).

The general position calculated above has been constrained to dihedral angles which place it in the middle of the twist and boat extremes (Figure 7). It has an energy roughly 4.5 kcal/mol higher than the ground state. This value for the barrier to interconversion of conformers is in qualitative agreement with the VT-NMR experiments. The particular geometry of the structure indicates that the major reason for the barrier height is due to a steric interaction between neighboring groups and not to an electronic perturbation from loss of push–pull conjugation as in the simple nitroanilines. Indeed, the geometry [N(am)–C(ar) bond lengths and N(am) planarity] shows that the system is still strongly conjugated.

Experimental Section

Chemicals were used as supplied: 40% dimethylamine/ethanol (Fluka); 1,3,5-trichlorobenzene, 1,3,5-tribromobenzene (Aldrich); diethylamine (Eastman Kodak). NMR spectra were recorded at 250.13-MHz

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[24] The imaginary frequency of the chair-C_2 conformation indicates a soft mode for a twisting about the C(ar)–NO_2 bond, similar to those found for the boat-C_s structure. We assume, by analogy to the boat conformation, that the chair-C_1 structure will have very similar geometry and energy to the calculated C_s one.

[25] We were unable, however, to find the fully optimized transition state starting from this approximate geometry.

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[^{1}H] and 62.83-MHz [^{13}C] on a Bruker WM-250 spectrometer. Chemical shifts are based on residual solvent resonances. Melting points are corrected.

1,3,5-Tris(dimethylamino)-2,4,6-trinitrobenzene (1a).[5,29,30] A 500-mL round-bottom flask is charged with 1,3,5-tribromo-2,4,6-trinitrobenzene[31] (1 g) and 250 mL of ethanol. The solution is warmed gently and a 40% solution of dimethylamine in ethanol (5 equiv) is added dropwise. After 1 h the yellow solution is cooled and a precipitate forms (yield 70%). The yellow solid is collected by filtration and can be recrystallized from chloroform and hexane: mp >250 °C dec; ^{1}H NMR ($CDCl_3$) δ 3.40 (s).

1,3,5-Tris(diethylamino)-2,4,6-trinitrobenzene (1b).[29] A mixture of 1,3,5-trichloro-2,4,6-trinitrobenzene[31] (2.2g) and diethylamine (30mL) was heated at reflux under a blanket of argon for 24 h to give a yellow suspension. Addition of water prompted further precipitation. The suspension was filtered to give a yellow solid (2 g) that was washed with water and then dried. Recrystallization from hexane/ethanol yielded yellow needles: mp 99–100 °C (lit.[5] 99–100 °C); ^{1}H NMR (CD_2Cl_2) δ 1.33 (t, 18 H, ^3J = 7.2 Hz), 3.63 (q, 12 H, ^3J = 7.2 Hz).

X-ray Crystallography. Crystals of 1,3,5-tris(diethylamino)-2,4,6-trinitrobenzene were grown by slow evaporation from hexane/ethanol. A bright yellow crystal of approximately 0.06 × 0.18 × 0.51 mm was chosen for the X-ray measurements. Crystal data: $C_{18}H_{30}N_6O_6$, M = 426.6 g·mol^{-1}; monoclinic (space group $P2_1/c$); a = 10.005 (2) Å, b = 21.452 (5) Å, c = 10.544 (2) Å, β = 104.3° (2); and V = 2193.8 (8) Å^3, d_{calc} = 1.29 g·cm^{-3}, Z = 4. X-ray intensities were recorded at room temperature on a Nicolet R3m four-circle diffractometer applying Cu Kα radiation (λ = 1.54178 Å). A total of 2948 independent reflections were recorded with $3° \le 2\theta \le 114°$ of which 2475 with $|F_0| > 3\sigma(F_0)$ were considered unique and observed. The structure was solved by direct methods with the SHELXTL software. All non-hydrogen atoms were refined anisotropically by using a block cascade least-squares procedure. Hydrogen atoms were included at ideal positions (C–H = 0.96 Å and C–C–H = 109.5°). R and R_w factors after refinement of 271 parameters were 0.046 and 0.053, respectively. The largest peak in the final Fourier difference map was 0.17 e·Å^{-3}.

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Registry No. 1a, 121097-10-7; **1b**, 114396-18-8; 1,3,5-tribromo-2,4,6-trinitrobenzene, 83430-12-0; dimethylamine, 124-40-3; 1,3,5-trichloro-2,4,6-trinitrobenzene, 2631-68-7; diethylamine, 109-89-7.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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[29] Tris(dialkylamino)trinitrobenzenes are, in general, explosive! Extreme care should be taken when handling these materials. Do not prepare or store large quantities of these compounds. It is unadvisable to store these compounds in ground glass stoppered vials. Even though we have had no accidental detonations of **1a** or **1b**, we have been able to detonate a few milligrams of **1a** by striking it with a ball peen hammer on a hard surface.

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Communications to the Editor

Structural Characterization of the Pentamolybdate Anion, $[(MoO_4)_2\{Mo_3O_8(OMe)\}]^{3-}$, and Isolation of the $[Mo_3O_8(OMe)]^+$ Trinuclear Core in the Squarate Complex $[\{Mo_3O_8(OMe)\}(C_4O_4)_2]^{3-}$

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Polyoxoanions which are soluble in organic solvents are of continuing interest by virtue of their applications in the elucidation of pathways for interconversions of various polymetalate structural types[2] and in the development of the coordination chemistry of these species with organic substrate molecules.[3,4] The isopolymolybdate anions which can be synthesized or stabilized in organic solvents include the structurally characterized species $[Mo_2O_7]^{2-}$,[5] $[Mo_6O_{19}]^{2-}$,[6] and α-$[Mo_8O_{26}]^{4-}$[7] and the amorphous pentamolybdate $[Mo_5O_{17}H]^{3-}$.[8] In the course of investigations of polymolybdate–carbonyl interactions,[9,10] we have isolated a crystalline derivative of the pentamolybdate species, [(*n*-

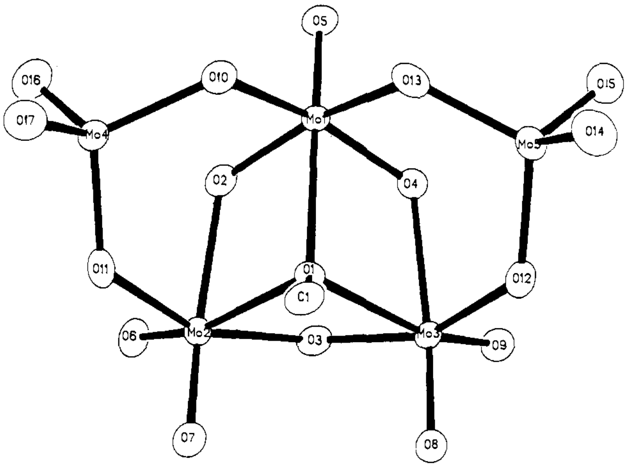

Figure 1. ORTEP view of the structure of $[\{Mo_3O_8(OMe)\}(MoO_4)_2]^{3-}$ (I), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Mo(1)–O(1), 2.446 (9); Mo(2)–O(1), 2.285 (9); Mo(3)–O(1), 2.303 (10); Mo(1)–O_b, 1.801 (14) (av); Mo(1)–O_b', 2.060 (15) (av); Mo(1)–O(3), 1.915 (12); Mo(2)–O(2), 2.237 (10); Mo(2)–O(11), 2.012 (13); Mo(3)–O(3), 1.923 (11); Mo(3)–O(4), 2.240 (9); Mo(3)–O(12), 1.976 (11); Mo(4)–O_b', 1.849 (12) (av); Mo(5)–O_b', 1.837 (11); O(1)–Mo(1)–O(5), 177.9 (6); O(6)–Mo(2)–O(1), 161.8 (6), O(9)–Mo(3)–O(1), 161.8 (5). $O_b \equiv$ bridging oxo groups within $\{Mo_3O_8(OMe)\}^{1+}$ subunit; $O_b' \equiv$ bridging oxo group of $(MoO_4)^{2-}$ subunits.

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