This material was recrystallized (ethyl acetate–hexane) to give 125 mg (26%) of pure **9**: mp 123–125 °C; IR (CH_2Cl_2) 1780, 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–1.95 (m, with s at 1.78, 9 H, $CH_2CH_2CH_2$, CH_3), 2.59, 2.81 (AB q, J_{AB} = 20, 2 H, $=CCH_2$), 3.12, 3.31 (AB q, J_{AB} = 18, 2 H, $CH_2C=O$), 3.50–3.60 (m, 1 H, OCH), 3.82–3.92 (m, 1 H, OCH), 4.25, 4.51 (d of AB q, J_{AB} = 13, J = 5, 2 H, OCH_2), 4.67 (m, 1 H, OCHO), 4.81 (m, 1 H, CHOC=O), 5.31 (d, J = 6, 1 H, CHI), 5.41 (br d, J = 9, 1 H, =CH), 5.90 (br d, J = 9, 1 H, =CH), 6.80 (br t, J = 10, 1 H, CH=CC=O); ^{13}C NMR ($CDCl_3$) δ 11.46 (q), **19.45** (t), 24.40 (t), 25.32 (d), 30.54 (t), 36.52 (t), 47.22 (s), 62.30 (s), **62.49** (t), 64.47 (t), 76.39 (d), **98.88** (d), 127.61 (d), 129.28 (d), 137.10 (s), 139.70 (d), 171.26 (s), 196.55 (s) (the boldfaced signals were slightly doubled, indicating the presence of compounds diastereomeric at the THP methine); exact mass calcd for $C_{18}H_{24}IO_5$ (M + 1) m/e 447.0670, found m/e 447.0669 (FAB). Anal. Calcd for $C_{18}H_{23}IO_5$: C, 48.44; H, 5.19. Found: C, 48.21; H, 4.61.

***rel*-(1*S*,4a*S*,7*S*,8*S*,8a*R*)-1,7,8,8a-Tetrahydro-7-methyl-8-[[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl]-2*H*-1,4a-(epoxymethano)naphthalene-6,9(5*H*)-dione (43).** To a solution of 115 mg (0.258 mmol) of **9** and 3 mg of 1,2-bis(diphenylphosphino)ethane in 49 mL of benzene was added 134 mg (0.460 mmol) of tri-*n*-butyltin hydride and 6 mg of azobis(isobutyronitrile) in 4 mL of benzene. The mixture was degassed with argon and warmed under reflux for 1 h. The benzene was evaporated and the residue was dissolved in 20 mL of dichloromethane. The resulting solution was washed with two 5-mL portions of 10% aqueous potassium fluoride solution (the white precipitate was filtered off), dried ($MgSO_4$), and concentrated in vacuo. The residual oil was chromatographed over 6 g of silica gel (eluted with ethyl acetate–hexane, 1:3 to 1:1) to give 44 mg (53%) of pure **43** and 12 mg of a less pure sample, which was recrystallized to afford 6 mg (7%) of additional **43**: mp 135–137 °C. This material was a 1:1 mixture of tetrahydropyranyl diastereomers that could be separated by MPLC (Lobar size A column, eluted with ethyl acetate–hexane, 1:10): IR (CH_2Cl_2, mixture) 1775, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$, less polar diastereomer) δ 1.21 (d, J = 6, 3 H, CH_3), 1.30–1.70 (m, 6 H, $CH_2CH_2CH_2$), 2.28 (m, 1 H, CH), 2.35 (d, J = 18, 1 H, $CH_2C=O$), 2.42 (quintet, J = 5, 1 H, C*H*Me), 2.58 (br s, 2 H, $=CCH_2$), 2.62 (d, J = 6, 1 H, CH), 3.25 (d, J = 18, 1 H, $CH_2C=O$), 3.32 (d, J = 10, 1 H, OCH), 3.50 (br d, J = 11, 1 H, OCH), 3.65 (td, J = 10, 3, 1 H, OCH), 3.89 (dd, J = 10, 4, 1 H, OCH), 4.55 (br s, 1 H, CHOC=O), 4.75 (br s, 1 H, OCHO), 5.75 (br d, J = 9, 1 H, =CH), 5.82 (br d, J = 9, 1 H, =CH); ^{1}H NMR ($CDCl_3$, more polar diastereomer) δ 1.10 (d, J = 6, 3 H, CH_3), 1.15–1.90 (m, 6 H, $CH_2CH_2CH_2$), 2.25 (q, J = 4, 1 H, CH), 2.35 (d, J = 18, 1 H, CHC=O), 2.42 (quintet, J = 5, 1 H, C*H*Me), 2.57 (m, 2 H, $=CCH_2$), 2.63 (d, J = 6, 1 H, CH), 3.25 (d, J = 18, 1 H, CHC=O), 3.33 (dd, J = 10, 4, 1 H, OCH), 3.48 (dt, J = 10, 3, 1 H, OCH), 3.79 (m, 1 H, OCH), 3.88 (d, J = 10, 1 H, OCH), 4.45 (br s, 1 H, CHOC=O), 4.80 (br s, 1 H, OCHO), 5.70–5.85 (m, 2 H, =CH); ^{13}C NMR ($CDCl_3$, mixture) δ 11.81 (q), 11.95 (q), 17.91 (t), 18.09 (t), 25.17 (t), 25.48 (t) 28.60 (t), 29.12 (t), 33.54 (t), 41.21 (t), 41.34 (t), 42.68 (d), 42.92 (d), 45.04 (d), 45.35 (d), 45.98 (s), 48.20 (d), 48.28 (d), 61.53 (t), 61.75 (t), 61.86 (t), 63.66 (t), 75.79 (d), 75.92 (d), 98.27 (d), 101.16 (d), 126.02 (d), 135.46, 135.57 (d), 175.77 (s), 176.04 (s), 205.94 (s), 206.42 (s); exact mass calcd for $C_{18}H_{24}O_5$ m/e 320.1623, found m/e 320.1676. Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 66.91; H, 7.22.

***rel*-(1*S*,4*R*,5a*S*,9*S*,9a*R*,12*S*)-1,4,5,8,9,9a-Hexahydro-4-methoxy-2-methyl-2*H*-9,5a-(epoxymethano)-1,4-methano-3-benzoxepin-11-one (44).** To a solution of 4.9 mg (0.0153 mmol) of **43** in 3 mL of methanol was added 3.7 mg of Dowex-50 (H^+), and the mixture was heated at reflux for 3.5 h. The resin was removed by filtration and the solvent was removed in vacuo. The residue (4 mg) was chromatographed over 0.5 g of silica gel (eluted with ethyl acetate–hexane, 1:5) to give 3.3 mg (86%) of **44** as a colorless oil: IR (CH_2Cl_2) 1775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (d, J = 6, 3 H, CH_3), 1.62 (d, J = 14, 1 H, CHC(OMe)O), 1.85 (q, J = 7, 1H, $CHCH_3$), 2.12 (t, J = 4, 1 H, CH), 2.31 (d, J = 4, 1 H, CH), 2.50 (m, 2 H, $=CCH_2$), 3.05 (d, J = 14, 1 H, CHC(OMe)O), 3.45 (s, 3 H, OCH_3), 3.95 (d, J = 10, 1 H, OCH), 4.02 (dd, J = 10, 3, 1 H, OCH), 4.58 (br s, 1 H, CHOC=O), 5.67 (br d, J = 10, 1 H, =CH), 5.81 (dt, J = 10, 3, 1 H, =CH); exact mass calcd for $C_{14}H_{18}O_4$ m/e 250.1179, found m/e 250.1192.

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Supplementary Material Available: Crystallographic details and ORTEP drawing for compound **36** (6 pages). Ordering information is given on any current masthead page.

Stereochemistry of Hexakis(dimethylamino)benzene and Its Dication

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The crystal structures of hexakis(dimethylamino)benzene (**4**) and its dication bis(triiodide) (**8**) have been determined. Crystals of **4** are monoclinic, space group $C2/c$, a = 18.440 (6) Å, b = 9.461 (3) Å, c = 12.017 (4) Å, β = 104.74 (3)°, Z = 4. Like hexaisopropylbenzene, hexakis(dimethylsilyl)benzene, and hexakis(dichloromethyl)benzene, molecules of **4** adopt approximate C_{6h} symmetry in the crystal, but, unlike these otherwise closely related compounds, **4** does not manifest an orientational disorder. Reaction of **4** with iodine yields **8**, crystals of which belong to the monoclinic system, space group $P2/c$, a = 16.243 (5) Å, b = 11.051 (4) Å, c = 20.358 (7) Å, β = 112.02 (3)°, Z = 4. Molecules of **8** have crystallographic C_2 symmetry and approximate D_2 symmetry, with the benzene ring in a twist conformation. Variable-temperature NMR studies on 1,3,5-tris(diethylamino)-2,4,6-tris(dimethylamino)benzene (**9**) and hexakis(diethylamino)benzene, two molecules that are structurally related to **4**, show that pyramidal inversion of the nitrogen atoms requires 8.2 and 10.0 kcal mol^{-1}, respectively. As shown by the interconversion of the diastereomers of 1,3,5-tris(ethylmethylamino)-2,4,6-tris(dimethylamino)benzene, which requires 16.0 kcal mol^{-1}, barriers to rotation about the C_{ar}–N bonds in this class of compounds are substantially higher than barriers to pyramidal inversion. According to AM1 calculations, the homomerization (topomerization) of **4** is not concerted but involves stepwise inversion of the dimethylamino groups. The calculated activation energy, 10.5 kcal mol^{-1}, is in reasonable agreement with the experimentally observed barrier of 8.2 kcal mol^{-1} for **9**. Variable-temperature NMR studies on **8** reveal a site exchange of the methyl groups which is rationalized by a pseudorotational motion of the twisted benzene ring.

Hexaisopropylbenzene (**1**),[2] hexakis(dimethylsilyl)benzene (**2**),[3] and hexakis(dichloromethyl)benzene (**3**)[4] assume ground-state conformations of approximate C_{6h} symmetry in which the α-hydrogen in each side chain is

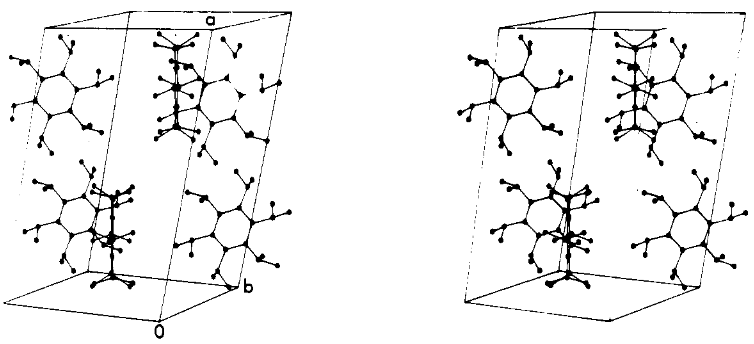


Figure 1. Stereoview of the unit cell of hexakis(dimethylamino)benzene (4). The orientation is parallel to the mean plane of the aromatic carbons in the molecule seen edge on. Hyrogen atoms have been deleted for clarity.

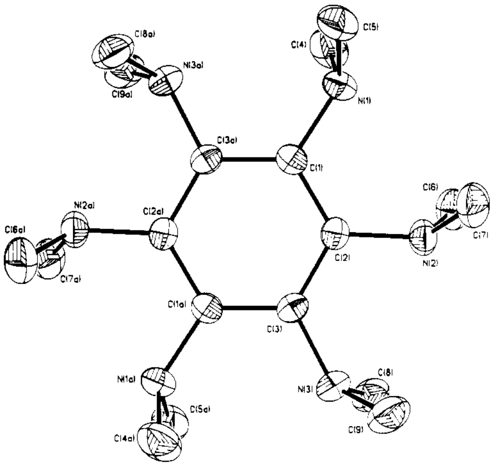
tucked into the cleft formed by the two methyls or chlorines of a neighboring group.[5] Unlocking of these tongue-and-groove arrangements requires internal rotation about the bonds to the benzene ring. In the otherwise closely related hexakis(dimethylamino)benzene (4), the α-hydrogen is replaced by an unshared electron pair, and atomic inversion at nitrogen thus provides an additional degree of freedom that does not exist in the previously studied systems. Electron-rich 4 also affords the opportunity for redox chemistry not available for 1, 2, and 3, and the dication of 4 provides an alternative mechanism for unlocking the static-gear arrangement of the side chains by eliminating the restriction of planarity imposed by the benzene ring. The present work was undertaken in order to determine the structure of 4, to explore the mechanisms of internal motion available to this molecule, and to study the stereochemistry of the derived dication.

Structural Studies

Hexakis(dimethylamino)benzene. The procedure described by Backer and van der Baan[6] for the synthesis of 4 (ammonolysis of 1,3,5-trichloro-2,4,6-trinitrobenzene to 1,3,5-trinitro-2,4,6-triaminobenzene, reduction to hexaaminobenzene, and exhaustive methylation) was followed in all essential details,[7] except that the reduction was carried out with sodium in ammonia and methanol[8] rather than by heating with phenylhydrazine[9] or by catalytic hydrogenation.[10] Pentakis(dimethylamino)aniline (5) was obtained as a byproduct in the methylation step.

X-ray data for a crystal of 4 grown from acetone were collected at 175 ± 3 K. The crystals belong to the monoclinic system, space group $C2/c$, with a = 18.440 (6) Å, b = 9.461 (3) Å, c = 12.017 (4) Å, β = 104.74 (3)°, and Z = 4. The cell parameters are in agreement with those previously reported by Backer and van der Baan.[6] An ORTEP view of 4 is shown in Table I along with a listing of final atomic parameters. The molecule is located on a crystallographic center of symmetry and, like 1, 2, and 3, possesses approximate C_{6h} symmetry. All bond distances and angles have normal values, and the structural parameters are for the most part in excellent agreement with those calculated by the AM1 method[11] (Table II).[13] Be-

Table I. Final Fractional Crystal Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å$^2 \times 10^3$) for Hexakis(dimethylamino)benzene (4)^a



atom	x	y	z	U^b
C(1)	3234 (1)	2127 (2)	4991 (1)	25 (1)
C(2)	2626 (1)	1325 (2)	4365 (1)	25 (1)
C(3)	1891 (1)	1700 (2)	4372 (1)	26 (1)
N(1)	3969 (1)	1678 (2)	4933 (1)	30 (1)
N(2)	2719 (1)	95 (2)	3710 (1)	32 (1)
N(3)	1243 (1)	930 (2)	3739 (1)	32 (1)
C(4)	4352 (1)	2648 (2)	4344 (2)	48 (1)
C(5)	4457 (1)	1183 (2)	6009 (2)	44 (1)
C(6)	3006 (1)	345 (2)	2715 (2)	46 (1)
C(7)	3089 (1)	−1086 (2)	4390 (2)	44 (1)
C(8)	1105 (1)	1030 (2)	2495 (2)	41 (1)
C(9)	1184 (1)	−512 (2)	4121 (2)	45 (1)

^{a} Standard deviations are in parentheses. For numbering of atoms see structure above (ORTEP plot of 4 with thermal ellipsoids at 50% probability). Hydrogen parameters are given in the supplementary material. ^{b} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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(1) On leave from the Jagiellonian University, Krakow, Poland.

(2) Siegel, J.; Gutiērrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569.

(3) (a) Schuster, I. I.; Weissensteiner, W.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 6661. (b) Unpublished results.

(4) Kahr, B.; Biali, S. E.; Schaefer, W.; Buda, A. B.; Mislow, K. *J. Org. Chem.* **1987**, *52*, 3713.

(5) For related work from our laboratory, see: (a) Weissensteiner, W.; Gutiērrez, A.; Radcliffe, M. D.; Siegel, J.; Singh, M. D.; Tuohey, P. J.; Mislow, K. *J. Org. Chem.* **1985**, *50*, 5822. (b) Mislow, K. *Chimia* 1986, *40*, 395. (c) Singh, M. D.; Siegel, J.; Biali, S. E.; Mislow, K. *J. Am. Chem. Soc.* **1987**, *109*, 3397. (d) Biali, S. E.; Buda, A. B. *J. Org. Chem.* **1988**, *53*, 135. (e) Biali, S. E.; Buda, A. B.; Mislow, K. *Ibid.* **1988**, *53*, 1289. (f) Biali, S. E.; Kahr, B.; Okamoto, Y.; Aburatani, R.; Mislow, K. *J. Am. Chem. Soc.* **1988**, *110*, 1917. (g) Biali, S. E.; Gutiērrez, A.; Mislow, K. *J. Org. Chem.* **1988**, *53*, 1316. (h) Biali, S. E., Mislow, K. *Ibid.* **1988**, *53*, 1318.

(6) Backer, H. J.; van der Baan, Sj. *Recl. Trav. Chim. Pays-Bas* **1937**, *56*, 1175.

(7) Alternatively, 4 may be synthesized by reduction of tris(dimethylamino)cyclopropenium at a mercury cathode. See: Johnson, R. W. *Tetrahedron Lett.* **1976**, 589.

(8) Rogers, D. Z. *J. Org. Chem.* **1986**, *51*, 3904.

(9) Flürscheim, B.; Holmes, E. L. *J. Chem. Soc.* **1929**, 330. Kohne, B.; Praefcke, K. *Liebigs Ann. Chem.* **1985**, 522.

(10) Breslow, R.; Maslak, P.; Thomaides, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 6453. Kohne, B.; Praefcke, K.; Derz, T.; Gondro, T.; Frolow, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 650. Kohne, B.; Praefcke, K. *Liebigs Ann. Chem.* **1987**, 265.

(11) This method[12a] is a semiempirical version of the Roothan-Hall/RF/SCF LCAO MO method in the NDDO approximation and is implemented in the AMPAC program package.[12b]

Table II. Comparison of Experimental and Calculated Structural Parameters of 4

atoms[a]	exptl (X-ray)[d]	calcd (AM1)[e]
	Bond Lengths	
C_{ar}–C_{ar}	1.402 (2)	1.422
C_{ar}–N	1.440 (2)	1.436
N–C_m	1.450 (3)	1.445
	Bond Angles	
C_{ar}–C_{ar}–C_{ar}	120.0 (2)	120.0
C_{ar}–C_{ar}–N[b]	122.9 (2)	123.1
C_{ar}–C_{ar}–N[c]	117.0 (1)	116.9
C_{ar}–N–C_m	115.1 (1)	114.9
C_m–N–C_m	112.0 (2)	114.1
	Torsion Angle	
C_{ar}–C_{ar}–N–C_m	66.3 (2)	67.6

[a] C_{ar} = benzene (aryl) carbon; C_m = methyl carbon. [b] Angle anti with respect to the nitrogen lone pair. [c] Angle syn with respect to the nitrogen lone pair. [d] Structure averaged over C_{6h} symmetry. Average deviations in parentheses. Bond lengths in angstroms; angles in degrees. [e] C_{6h} symmetry assumed.

cause the dimethylamino groups are forced to adopt a conformation in which the nitrogen lone pairs cannot participate in the benzene π system, the length of the C_{ar}–N bond reflects its single-bond character.[14]

Despite its similarity to the molecular structures of **1**, **2**, and **3**, **4** is crystallographically unique in being the only member of the set that does not manifest an orientational disorder in which the molecules are flipped and enantiotopic faces are exchanged at the lattice sites.[16] This distinction appears to result from differences in the packing arrangements. The centrosymmetric molecules of **4** are oriented in face-to-edge fashion, with a 71.8° angle between the mean planes of the benzene rings (Figure 1), whereas **1** and **3**, though also centrosymmetric (space group $P\bar{1}$), crystallize with one molecule per unit cell[2,4] and are therefore stacked in parallel planes. The mean C_{ar} planes of the two independent molecules in **2** are at 4.7° and no other relationship between these planes in the crystal exceeds 9°;[3b] the molecules of **2** thus also pack in nearly parallel planes. Judging from these observations, the face-to-face interactions that dominate the packing arrangements in **1**, **2**, and **3**, and that are absent in **4**, are implicated in the origin of the observed disorder.[17]

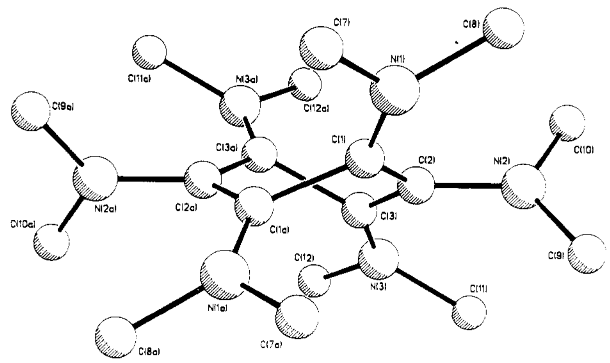

Figure 2. View of hexakis(dimethylamino)benzene dication **8A** along the crystallographic twofold axis.

Table III. Selected Bond Lengths[a] in Dications 7 and 8

	7		8	
bond[b]	exptl (X-ray)[c]	calcd (AM1)[d]	exptl (X-ray)[e]	calcd (AM1)[f]
N(1)–C(1)	1.306 (6)	1.340	1.34 (3)	1.337 (0)
C(1)–C(2)	1.382 (5)	1.415	1.38 (3)	1.439 (1)
C(1)–C(1a)	1.529 (8)	1.517	1.57 (5)	1.526 (2)
C(2)–N(2)			1.43 (3)	1.398(0)

[a] In angstroms. [b] See Figure 2. [c] Crystallographic D_2 symmetry. Standard deviations in parentheses.[19] [d] D_2 symmetry constraint. [e] Average values for **8A** and **8B**, each averaged over D_2 symmetry. Averaged standard deviations in parentheses. [f] C_2 symmetry constraint, values averaged over D_2 symmetry. Average deviations in parentheses.

Hexakis(dimethylamino)benzene Dication. In contrast to 1,2,4,5-tetrakis(dimethylamino)benzene (**6**), a strong electron donor that is easily and reversibly oxidized to the dication at −0.266 V vs Ag/Ag^+ in acetonitrile,[19] **4** undergoes irreversible oxidation at +0.32 V vs Ag/AgCl in CH_2Cl_2,[7] evidently because of steric restrictions imposed by the six dimethylamino groups.[20] However, in close analogy to the reaction of **6** with iodine, which yields the iodide–triiodide salt of **6** dication (**7**),[19] reaction of **4** with iodine in acetonitrile/ether affords the bis(triiodide) salt of **4** dication (**8**). Crystals of the salt are black and belong to the monoclinic system, space group $P2/c$, with a = 16.243 (5) Å, b = 11.051 (4) Å, c = 20.358 (7) Å, β = 112.02 (3)°, and Z = 4.[18] The unit cell contains two independent molecules of the dication, **8A** and **8B**, each with crystallographic C_2 symmetry and approximate molecular D_2 symmetry.[21] The two I_3^- ions are nearly linear.

The molecular structures of **8A** and **8B** are closely similar. A projection of structure **8A** along its crystallographic C_2 axis is shown in Figure 2. The most striking structural feature is the twist conformation of the benzene ring, which closely resembles the conformation of the benzene ring in **7**.[19] Also in analogy to **7**, **8A** and **8B** each contain two nearly planar five-center six-electron π systems, N(1)–C(1)–C(2)–C(3)–N(3) and its symmetry-related counterpart. Electron delocalization in these systems results in partial double-bond character and bond shortening, particularly of the C_{ar}–N bonds, relative to **4** (Tables II and III).[22] By the same token, the C(1)–C(1a) and C(3)–C(3a) bonds

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[12] (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Available as QCPE No. 506 and described in: *QCPE Bull.* **1986**, *6*(4), 24.

[13] As previously noted for bonding parameters calculated for **3** by MNDO,[4] the only significant discrepancy from the experimental geometric parameters is found for the C_{ar}–C_{ar} bond lengths: as calculated by AM1, these are 0.02 Å longer than observed. This is, however, consistent with a general tendency of the MNDO-type methods to overestimate C_{ar}–C_{ar} bond lengths. See: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

[14] In this connection it is instructive to compare the C_{ar}–N bond length and C_{ar}–C_{ar}–N–C_m torsion angle in **4** (1.44 Å, 66.3°) with the corresponding parameters in 2,6-dichloro-4-nitrodimethylaniline (1.41 Å, 60.5°)[15a] and *p*-nitroaniline (1.37 Å, 0.0°).[15b]

[15] (a) Stuchkov, Y. T.; Khotsyanova, T. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, *8*, 1369. (b) Donohue, J.; Trueblood, K. N. *Acta Crystallogr.* **1956**, *9*, 960.

[16] The disorder is expressed by the fraction of the major orientational isomer, 0.67 (2) and 0.646 (4) for **1** and **3**, respectively.[2,4] Crystals of **2** are monoclinic with two independent molecules in general positions in the space group $P2_1/c$, and the fractions of the major orientational isomers are 0.857 (1) and 0.943 (1) for the two independent molecules.[3b] In all these cases the disorder results in characteristic elongations of the anisotropic thermal motion ellipsoids of C_{ar} tangential to the ring. Such elongations are absent in **4** (see ORTEP in Table I), and no minor nitrogen positions were found in the final Fourier maps.

[17] Crystals of **5** also exhibit a twofold orientational disorder similar to that in **1**, **2**, and **3**, and the molecules pack in a face-to-face manner with an angle of 14.5° between adjacent faces.[18]

[18] Toscano, J. P. A.B. Thesis, Princeton University, 1987.

[19] Elbl, K.; Krieger, C.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1023.

[20] Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927.

[21] The site symmetry of **7** is D_2.[19]

[22] The lone electron pairs of the two additional dimethylamino groups in **8A** (N(2) and N(2a)) are nearly orthogonal to these π ribbons and are therefore effectively out of conjugation. This is manifest in the C(2)–N(2) bond lengths, which are not substantially changed from the C_{ar}–N bond lengths in **4**.

acquire single-bond character and are significantly lengthened relative to the C_{ar}–C_{ar} bonds in **4** (Tables II and III). This trend parallels similar observation in **7**[19] and is at least *qualitatively* borne out by AM1 calculations (Table III). A more detailed analysis of the structure is unwarranted in light of the mediocre quality of the crystals ($R = 0.132$, $R_w = 0.102$). Most interestingly, distortion of the benzene ring in **8** unlocks the tongue-and-groove arrangement of dimethylamino groups in **4**, with consequences on the internal dynamics that are discussed below.

In further analogy to **6**,[19] **4** forms a deeply colored 1:2 complex with tetracyanoquinodimethane (TCNQ); evidently **4**, like **6**, is a strong two-electron donor. Finally, in light of the report[6] that **4** forms a trihydrochloride, it is conceivable that **4** acts as a kind of proton sponge and forms triprotonated salts that are structurally analogous to the diprotonated salts of **6** recently reported by Staab et al.,[23] with hydrogens shared by pairs of adjacent dimethylamine groups through N–H···N hydrogen bonds.

Stereodynamics

Hexakis(dimethylamino)benzene. The observation by NMR of a homomerization (topomerization) process whose *net* effect, by whatever mechanism, is the reversal of the sense of cyclic directionality[24] requires the exchange of nuclei in nonequivalent sites. Since the methyl groups in **1**, **2**, and **3** are symmetry equivalent, it is necessary to lower the symmetry in order to make rotation NMR-visible. Such desymmetrization was achieved for **1** and **2** by selective replacement of CH_3 by CD_3 groups[2,25] and by π-complexation of the benzene ring with $Cr(CO)_3$.[3a] These strategies are in principle also applicable to **4**, even though a complication is introduced by the possibility that homo- or isomerization in compounds derived from **4** can take place either by rotation or by inversion, or by a combination of the two. Thus the two mechanisms may have different stereochemical consequences. For example, consider a hypothetical pair of conformational cycloenantiomers[5c] derived from **4** by selective replacement of CH_3's by CD_3's: as previously noted,[5c] inversion at nitrogen results in homomerization, whereas rotation about the C_{ar}–N bonds without inversion results in enantiomerization. But even if the stereochemical consequences are the same, the mechanisms may still be differentiable. For example, consider a hypothetical π complex of the type **4**·$Cr(CO)_3$:[26] although inversion and rotation both result in enantiomerization, proximal and distal methyl groups are exchanged only under rotation, as in **2**·$Cr(CO)_3$.[3a]

For reasons of convenience we chose a somewhat different approach, which involved the selective replacement of methyl groups in **4** by ethyl groups. 1,3,5-Tris(diethylamino)-2,4,6-tris(dimethylamino)benzene (**9**) and hexakis(diethylamino)benzene (**10**), prepared from 1,3,5-trichloro-2,4,6-trinitrobenzene by treatment with diethylamine followed by reduction and exhaustive methylation and ethylation, respectively, are similar in structure to **4**. In the ground states of **9** and **10** the nitrogen atoms are pyramidal and the geminal methylene hydrogens within each ethyl group are diastereotopic. They remain so even under conditions of rapid rotation about the C_{ar}–N bonds, provided that the nitrogen atoms do not become planar. On the time scale of rapid inversion or inversion–rotation, however, the geminal hydrogens become enantiotopic. The operation of an inversion mechanism is therefore revealed by the observation of a process that equivalences the methylene hydrogens.

When a solution of **9** in methylcyclohexane-d_{14} was cooled to 173 K, the signal due to the methylene protons at δ 3.11 decoalesced into two signals of equal intensity, and an ultimate shift separation of 0.30 ppm was realized at 150 K. In **10** the methylene signal at δ 3.12 similarly decoalesced at 215 K, with a shift separation of 0.50 ppm at 190 K that did not change upon further cooling. A value of 8.2 and 10.0 kcal mol^{-1} was calculated for the homomerization barriers ($\Delta G^{\ddagger}_{173}$ and $\Delta G^{\ddagger}_{215}$) of **9** and **10**, respectively, by use of the Gutowsky–Holm expression.[27] These observations show that an inversion mechanism is operative. Note that it is not necessary to lower the symmetry of the parent system (**4**) to evince this mechanism: the idealized ground-state symmetry of **10** is also C_{6h}.

That the barrier to rotation in this class of compounds is higher than that to inversion was shown in a VT-NMR study of 1,3,5-tris(ethylmethylamino)-2,4,6-tris(dimethylamino)benzene (**11**), a compound prepared by reduction of 1,3,5-tris(ethylamino)-2,4,6-trinitrobenzene[28] followed by exhaustive methylation. On the assumption that the ground-state conformation of **11** resembles that of **4**, two diastereomers are distinguishable: the "cis" isomer, in which all three ethyls are on the same side of the benzene plane, and the "trans" isomer, in which only two ethyl groups are on the same side. On the time scale of slow inversion and rotation, the two diastereomers exist as *dl* pairs, with C_3 (cis) and C_1 (trans) symmetry; on the time scale of rapid inversion and slow rotation, the diastereomers are achiral, with C_{3v} (cis) and C_s (trans) symmetry. However, only rotation about the C_{ar}–N bonds is capable of interconverting the two diastereomers, and the observation of such an interconversion is therefore evidence for internal rotation.

When a solution of **11** in a 3:1 mixture of toluene-d_8 and methylcyclohexane-d_{14} was cooled below 290 K, the methylene carbon resonance at δ 51.14 separated into three peaks of relative intensity 1:2:1 at δ 50.92, 50.99, and 51.05. The resonance at δ 41.52 due to the *N*-methyl carbons of the ethylmethylamino groups also separated into three peaks, also in the ratio of 1:2:1, at δ 41.21, 41.30, and 41.37. The methyl carbon resonances of the dimethylamino groups however remained accidentally isochronous. These observations are consistent with two diastereomers that are undergoing rapid inversion but slow rotation on the NMR time scale. The ratio of intensities is consistent with a 3:1 mixture of trans to cis isomers as would be expected from statistical arguments.[29] Further cooling caused no change in the spectrum until 170 K, at which point the spectrum increased in complexity, consistent with a slow-

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[23] Staab, H. A.; Elbl, K.; Krieger, C. *Tetrahedron Lett.* **1986**, *27*, 5719.

[24] A cycle is defined by three or more noncollinear points in the molecular model. A cycle is undirected if it is bisected by a molecular C_{2n} axis in, or by a molecular σ plane perpendicular to, the mean plane of the cycle. Otherwise it is directed. Specification of the sense of cyclic directionality requires a reference point above the cycle that defines the side from which the cycle is viewed.[5b]

[25] In related work,[5c,h] selective replacement of methyl groups in **1** by halogen atoms opened the way for the observation of site-exchange processes in the derived stereoisomers.

[26] Attempts to prepare transition metal complexes of **4** have thus far been unsuccessful.[18]

[27] Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; p 96.

[28] Mustafa, A.; Zahran, A. A. *J. Chem. Eng. Data* **1963**, *8*, 135.

[29] A 3:1 ratio of trans to cis is expected if the diastereomers are essentially equal in energy, since there are three degenerate ways to construct the trans diastereomer while there is only one way to construct the cis isomer. Another way to explain this ratio is to consider the number of ways that each diastereomer can convert to the other. For the cis-to-trans conversion, rotation of any one of the three equivalent ethylmethylamino groups is successful. For the trans-to-cis conversion only one of three rotations is successful. Thus cis converts to trans three times as often as trans to cis.

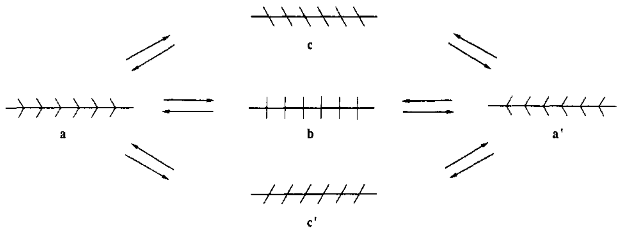

Figure 3. Homomerization of hexakis(dimethylamino)benzene (**4**) by concerted inversion mechanisms. The homomers a and a′ and the midpoints of the achiral (b) and chiral (c, c′) reaction paths are schematically represented by projections that indicate the conformational disposition of the six pyramidal (a, a′) or planar (b, c, c′) dimethylamino groups viewed along the N–C_{ar} bond axes.

ing of inversion on the NMR time scale. A value of 16.0 kcal mol^{-1} was calculated for the barrier to interconversion ($\Delta G^{\ddagger}_{290}$) of the diastereomers by use of the program DNMR3.[30] Accidental isochrony of signals precluded determination of the rotation barrier by ^1H NMR spectroscopy. At 180 K the methylene proton resonance of the diastereomeric mixture at δ 3.05 decoalesced into two signals, and although the more upfield resonance became isochronous with and obscured by the *N*-methyl resonances, it was possible to estimate an ultimate shift difference of 0.70 ppm at temperatures of 165 K and below, to give a value for enantiomerization by inversion ($\Delta G^{\ddagger}_{180}$) of 8.2 kcal mol^{-1}. This barrier is the same, within experimental limits, as that for **9** and strongly suggests that the barrier in **4** is quite close to this value.

The barrier to rotation in **11**, and presumably in **4**, is thus substantially higher than to inversion, but still far lower than the rotation barriers observed in **1** and related molecules.[31] Although the shorter C_{ar}–N bond length (as compared to C_{ar}–C) should lead to an increase in the height of the rotation barrier, the extra degree of freedom offered by inversion evidently facilitates rotation.

It remains to discuss the details of the structural changes that accompany homomerization of **4**. The simplest conceivable mechanism is correlated (concerted or synchronous) inversion of all six dimethylamino groups through a transition state or intermediate in which the $(C_m)_2NC_{ar}$ planes are perpendicular to the plane of the benzene ring. That is, the homomers (topomers) a and a′ undergo a reversal in sense of directionality by way of a D_{6h} midpoint (b) in which the ring is undirected (Figure 3). According to AM1 calculations, however, b[32] lies 25.1 kcal mol^{-1} above the ground state a. The a $\rightleftharpoons$ b $\rightleftharpoons$ a′ mechanism is therefore not in accord with observations.

Alternatively, correlated inversion may proceed through a transition state or intermediate in which the $(C_m)_2NC_{ar}$ planes are tilted relative to the plane of the ring. This D_6 midpoint corresponds to two enantiomeric structures, c and c′ (Figure 3), in which the ring is also undirected. This pathway is particularly appealing because the tilt allows partial overlap of the nitrogen lone pair electrons with the benzene π system and thus lowers the energy of c relative to b.[33] Indeed, structures formally analogous to c have been reported for hexanitrobenzene[34] and hexaphenylbenzene,[35] both of which adopt conformations of approximate D_6 symmetry. However, the optimized (AM1) structure with D_6 symmetry (C_{ar}–C_{ar}–N–C_m = 63.2°) still lies 18.7 kcal mol^{-1} above the ground state, and the a $\rightleftharpoons$ c $\rightleftharpoons$ a′ mechanism thus also fails to account for the experimental findings.

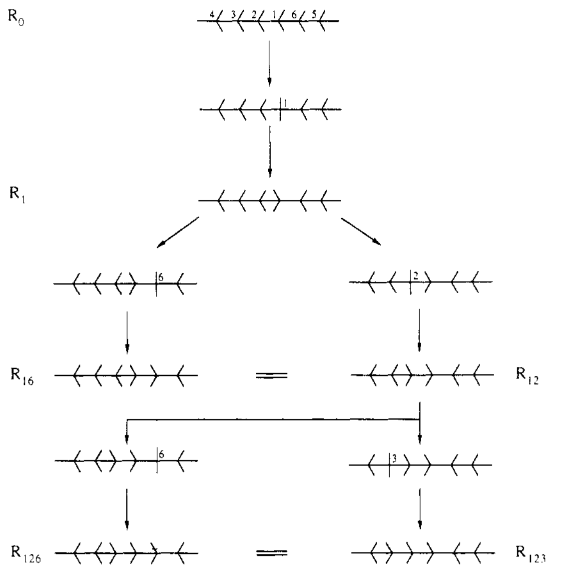

Figure 4. Schematic representation of stepwise inversions that lead from the ground state of **4** (R_0) to a symmetrical structure (R_{123} = R_{126}) midway along the homomerization itinerary. Conformational descriptors follow the convention adopted for **1**[2] and related molecules.[3,4]

With correlated inversion ruled out of consideration, the way is opened to a choice among mechanisms in which inversion proceeds in a stepwise manner, one dimethylamino group at a time. In the absence of labeling, inversion has precisely the same stereochemical consequences as rotation by π, and stepwise inversions in **4** are therefore represented by the same reaction graph as stepwise rotations in **1**.[2] A segment of this graph (Figure 4) depicts stepwise inversion sequences that lead from the ground state of **4** (R_0) to a symmetrical structure midway along the pathway connecting R_0 with its homomer R_{123456}. Other inversion pathways may be safely excluded since, as was shown in previous, closely related studies,[2-4] all other intermediates (R_{13}, R_{14}, etc.) are substantially higher in energy because of the increase in the number of repulsive gear-clashing interactions. Furthermore, the energy profile for $R_0 \rightarrow R_{123}$ is the mirror image of the one for $R_{123} \rightarrow R_{123456}$, and the analysis may therefore be restricted to the half of the itinerary shown in Figure 4.

Structures and energies of the intermediary states were calculated by the AM1 method.[36] Inversion of one dimethylamino group leads to R_1 which does not, however, correspond to a minimum on the potential energy hypersurface. Inversion of two vicinal (ortho) groups yields R_{12}, which is a stable intermediate and whose steric energy

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(30) Kleier, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165.

(31) Rotation barriers (ΔG) in **1**,[2] 1,2-bis(1-bromoethyl)-3,4,5,6-tetraisopropylbenzene,[5c] and 1,2-bis(bromochloromethyl)-3,4,5,6-tetraisopropylbenzene[5h] are 22 (lower limit), 24 (lower limit), and 26.8 kcal mol^{-1}, respectively.

(32) The molecular structure was optimized with the heavy atoms constrained to D_{6h} symmetry.

(33) Complete overlap is achieved only at the cost of intolerable steric strain: the D_{3d} conformation of **4**, in which the six lone pairs point alternately up and down around the benzene ring periphery, lies 82.1 kcal mol^{-1} above the ground state (AM1). The corresponding conformation of **1** has a steric energy of 90.0 kcal mol^{-1} (MM2).[2]

(34) Akopyan, Z. A.; Struchkov, Yu. T.; Dashevskii, V. G. *J. Struct. Chem. (Engl. Transl.)* **1966**, *7*, 385.

(35) Bart, J. C. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 1277.

(36) With some exceptions, all structures were optimized with no symmetry constraints on the heavy atoms. A C_2 symmetry constraint was imposed on R_{123} because that is the symmetry adopted by the corresponding minimum-energy conformations of **1**[2] and **2**.[3] The four $(C_m)_2NC_{ar}$ atoms of the inverting dimethylamino groups were kept coplanar in the optimization of all transition structures. In addition, the hydrogen atoms of all calculated structures were kept fixed in the conformation adopted in R_0.

relative to R_0 (RSE) is 9.1 kcal mol^{-1}. Two symmetry-nonequivalent paths lead to R_{12} and its homomer R_{16}. The path that leads to R_{16} involves planarization of the dimethylamino group in position 6 and takes place in the relatively unencumbered environment of the lone pairs on the nitrogen atoms in positions 1 and 5 (Figure 4). The path that leads to R_{12} involves planarization of the dimethylamino group in position 2 and takes place in the congested environment of the methyl groups in positions 1 and 3 (Figure 4). In both cases the planarization is associated with an increase in energy which, for the latter path, is partially compensated by the diminished steric interactions between the gear-clashing dimethylamino groups in positions 1 and 2 of R_1 (Figure 4). The RSE of the transition state leading to R_{12}, 10.2 kcal mol^{-1}, is therefore slightly lower than the RSE of the transition state leading to R_{16} (10.9 kcal mol^{-1}). Starting from R_{12} there are again two symmetry-nonequivalent paths, one leading to R_{123} and the other to its homomer R_{126}. Planarization of the dimethylamino group in position 3 requires 10.5 kcal mol^{-1} and is preferred over planarization of the group in position 6 (11.9 kcal mol^{-1}) for the reasons given above. Accordingly, R_{123} is formed in preference over R_{126}.

Within the error limits of the method,[12a] and given the many assumptions and approximations involved, the activation energy of 10.5 kcal mol^{-1} calculated for the homomerization of **4** is in reasonable accord with the experimentally observed barrier of 8.2 kcal mol^{-1} for the homomerization of **9**. The homomerization mechanism is therefore established as a stepwise inversion process whose sequence, $R_0 \rightarrow [R_1] \rightarrow R_{12} \rightarrow R_{123} \rightarrow R_{1234} \rightarrow [R_{12345}] \rightarrow R_{123456}$, closely parallels corresponding sequences of stepwise rotations in **1**,[2] **2**,[3a] and **3**.[4]

Hexakis(dimethylamino)benzene Dication. Variable-temperature ^{1}H NMR spectra of **8** were obtained in dilute CD_2Cl_2 solution. The sharp singlet at δ 3.30 broadened below 240 K, decoalesced below 200 K, and at 175 K had separated into two peaks, δ 3.44 and 2.64, with relative intensities 2:1. Below 175 K the more intense downfield resonance decoalesced into two peaks of equal intensity. From 165 to 150 K (supercooled solution) the spectrum remained unchanged, with three equally intense signals at δ 3.45, 3.41, and 2.61. The three resonances are assigned to the three nonequivalent methyl groups in the D_2 conformation of **8** (C(7) or C(12), C(8) or C(11), and C(9) or C(10) in **8A**, Figure 2), which is frozen out at low temperatures.

Rates of exchange were obtained by line-shape analysis, by use of the program DNMR3,[30] under the assumption that all methyl positions are interchanged by a single process. Fitting of the rate data to the Eyring equation gave a value for $\Delta G^{\ddagger}_{200}$ of 9.1 kcal mol^{-1}. The site-exchange process responsible for the coalescence evidently entails a pseudorotational motion of the twisted benzene ring that equivalences the dimethylamino group on C(2) with the groups on C(1) and C(3) (Figure 2).

Experimental Section

Solution 250.13-MHz ^{1}H and 62.83-MHz ^{13}C NMR spectra were recorded at ambient temperature on a Bruker WM-250 spectrometer. Residual solvent resonances were used as an internal reference. UV–visible spectra were recorded on a Hewlett-Packard 8450A Diode Array Spectrometer. Mass spectra were measured on a KRATOS MS50 RFA high-resolution mass spectrometer, with an ionizing voltage of 70 eV. Melting points were recorded on a Thomas-Hoover melting point apparatus and are corrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Chemicals used were reagent grade.

Hexakis(dimethylamino)benzene (4). Hexaaminobenzene was obtained in 97% yield by reduction of 1,3,5-trinitro-2,4,6-triaminobenzene[6] according to the procedure of Rogers.[8] Dimethyl sulfate (77 mL) and 81 mL of a 10 M KOH solution were slowly added in alternating portions to a stirred suspension of hexaaminobenzene (4.5 g) in 228 mL of water (argon atmosphere), without cooling. The hot reaction mixture was stirred for an additional 1.5 h. The brownish solid was collected by filtration and dissolved in dilute HCl. The solution was warmed with charcoal and filtered through Celite, and 10 M KOH was added to the filtrate. The cream-colored precipitate was collected by filtration, washed with methanol, and recrystallized from acetone to give 0.50 g (5.6%) of **4** as a white, crystalline solid: mp 235–237 °C (lit.[6] mp 236 °C); ^{1}H NMR (benzene-d_6) δ 2.84 (s); ^{13}C NMR (benzene-d_6) δ 45.23 (CH_3), 152.81 (C_{ar}); mass spectrum (high resolution), m/z 336.3011 (336.3001 calculated for $C_{18}H_{36}N_6$). The mother liquors yielded a small quantity of **5**, a compound more directly accessible by the procedure described below.

Iodine (0.31 g) in 10 mL of acetonitrile was stirred into a solution of **4** (0.054 g) in 10 mL of ether. There was an immediate precipitate of shiny black crystals. After 15 min the mixture was filtered to give 0.15 g (83%) of **hexakis(dimethylamino)benzene dication bis(triiodide) (8).** Well-formed needles of **8** were grown by allowing ether vapor to diffuse into an acetonitrile solution. These crystals, which proved to be unsuitable for X-ray analysis, melted above 123 °C with evolution of iodine: UV λ_{max} (CH_3CN) nm (log ϵ) 292 (4.88), 361 (4.61), 460 (3.91), 654 (3.13); ^{1}H NMR (CD_2Cl_2) δ 3.30 (s); ^{13}C NMR (DMSO-d_6) δ 44.08 (CH_3), 143.92 (C_{ar}). Anal. Calcd for $C_{18}H_{36}N_6I_6$: C, 19.69; H, 3.31; N, 7.65; I, 69.35. Found: C, 19.93; H, 3.10; N, 7.96; I, 69.46.

Tetracyanoquinodimethane (0.20 g) was added to a suspension of **4** (0.10 g) in acetonitrile. After an interval of 12 h the blackish-green solution was cooled and the precipated **hexakis(dimethylamino)benzene TCNQ complex** was collected by filtration to yield black needles (0.20 g): UV λ_{max} (CH_3CN) nm (log ϵ) 249 (4.76), 394 (5.18), 744 (4.65). Anal. Calcd for $C_{42}H_{44}N_{14}$: C, 67.72; H, 5.95; N, 26.32. Found: C, 68.00; H, 4.89; N, 26.70.

Pentakis(dimethylamino)aniline (5). A 10 M KOH solution (41 mL) was slowly added to a stirred mixture of hexaaminobenzene (2.3 g), water (117 mL), and dimethyl sulfate (39 mL) maintained at ice-bath temperature. After an additional 6 h, the light brown solid was collected by filtration and dissolved in dilute HCl. The solution was warmed with charcoal and filtered through Celite. Addition of 10 M KOH to the filtrate produced a white precipitate, which was collected by filtration, washed with ethanol, and recrystallized from acetone to yield **5** as a white, crystalline solid (0.10 g, 2.5%): mp 171–172 °C; ^{1}H NMR (benzene-d_6) δ 2.72 (s, 6 H), 2.83 (s, 12 H), 2.92 (s, 12 H), 4.20 (br s, 2 H); ^{13}C NMR (acetone-d_6/benzene-d_6) δ 43.14, 45.18, 45.63 (CH_3), 136.61, 142.34, 145.06, 151.10 (C_{ar}); mass spectrum (high resolution), m/z 308.2678 (308.2688 calculated for $C_{16}H_{32}N_6$). Anal. Calcd for $C_{16}H_{32}N_6$: C, 62.30; H, 10.46; N, 27.24. Found: C, 62.04; H, 10.35; N, 27.07.

1,3,5-Tris(diethylamino)-2,4,6-trinitrobenzene. A mixture of 1,3,5-trichloro-2,4,6-trinitrobenzene[6] (2.2 g) and diethylamine (30 mL) was heated under reflux (argon atmosphere) for 24 h to give a suspension of a yellow solid in a red liquid. The mixture was filtered and the filtrate was diluted with water (150 mL). The yellow powder (2.4 g) that precipated was collected by filtration and washed with water. Recrystallization from ethanol/hexane gave the desired product, yellow needles: mp 99.5–100.5 °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). Anal. Calcd for $C_{18}H_{30}N_6O_6$: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.72; H, 7.21; N, 19.75.

1,3,5-Tris(diethylamino)-2,4,6-tris(dimethylamino)benzene (9). 1,3,5-Tris(diethylamino)-2,4,6-trinitrobenzene (2.2 g) and methanol (30 mL) were placed into a flask fitted with a dry ice condenser and stir bar. The solution was cooled in a dry ice/acetone bath and ammonia (ca. 100 mL) was condensed into the flask. Sodium (3.5 g) was added in small chunks over a period of 5 min. After addition was complete, the mixture was allowed to warm to room temperature and the ammonia was evaporated. The methanol slurry was poured into 100 mL of water and extracted twice with 30-mL portions of ether and once with benzene (30 mL). The extracts were combined and dried over $MgSO_4$. The light brown solution was concentrated to 5 mL and water (80 mL) was added. Dimethyl sulfate (60 mL) and 10 M KOH

(80 mL) were added in alternate portions of 5–10 mL. The product was worked up as described above for 4 and 5 to yield 0.62 g (29%) of 8 after crystallization from acetone: mp 92–93 °C; ^1H NMR (8:1 methylcyclohexane-d_{14}/toluene-d_8) δ 1.06 (t, 18 H, ^3J = 7.3 Hz), 2.74 (s, 18 H), 3.11 (q, 12 H, ^3J = 7.3 Hz); ^{13}C NMR (CD_2Cl_2) δ 10.11 (CH_2CH_3), 44.96 (NCH_3), 48.40 (CH_2CH_3), 150.55, 151.37 (C_{ar}). Anal. Calcd for $C_{24}H_{48}N_6$: C, 68.52; H, 11.50; N, 19.98. Found: C, 68.03; H, 11.82; N, 19.94.

Hexakis(diethylamino)benzene (10). 1,3,5-Tris(diethylamino)-2,4,6-trinitrobenzene was reduced as described above and then ethylated in water with a 10-fold excess of ethyl trifluoromethanesulfonate added in alternate portions, with enough 10 M sodium hydroxide solution to keep the mixture strongly basic. The mixture was stirred for 30 min and extracted with ether. The ether extracts were combined and dried over magnesium sulfate, and the ether was evaporated to give a brown residue. Crystallization from acetone gave the desired product: mp 211–213 °C; ^1H NMR (methylcyclohexane-d_{14}) δ 0.97 (t, 18 H, ^3J = 7.3 Hz), 3.12 (q, 12 H, ^3J = 7.3 Hz); ^{13}C NMR (methylcyclohexane-d_{14}) δ 15.58 (CH_2CH_3), 50.72 (CH_2CH_3), 152.70 (C_{ar}); mass spectrum (high resolution), m/z 504.4889 (504.4879 calcd for $C_{30}H_{60}N_6$).

1,3,5-Tris(ethylmethylamino)-2,4,6-tris(dimethylamino)benzene (11). 1,3,5-Tris(ethylamino)-2,4,6-trinitrobenzene was prepared by the method of Mustafa and Zahran,[28] mp 206–207 °C (lit.[28] mp 206 °C). The compound was reduced by the method of Rogers[8] and methylated as described for hexakis(dimethylamino)benzene. An identical workup, followed by crystallization from acetone, gave white, chunky crystals: mp 121.5–122.5 °C; ^1H NMR (methylcyclohexane-d_{14}) δ 1.14 (t, 9 H, ^3J = 7.2 Hz), 2.66 (s, 9 H), 2.99 (s, 18 H), 3.05 (q, 6 H, ^3J = 7.2 Hz); ^{13}C NMR (toluene-d_8/methylcyclohexane-d_{14}, 3:1) δ 14.30 (CH_2CH_3), 41.52 ($EtNCH_3$), 45.16 ($N(CH_3)_2$), 51.14 (CH_2CH_3), 151.93, 154.06 (C_{ar}); mass spectrum (high resolution), m/z 378.3464 (378.3471 calcd for $C_{21}H_{42}N_6$).

X-ray Crystallography. Crystals of 4 were obtained by slow evaporation from acetone. A crystal of approximately 0.26 × 0.26 × 0.52 mm^3 was chosen for the X-ray measurements. Crystal data: $C_{18}H_{36}N_6$, M = 336.6 g·mol^{-1}; monoclinic (space group $C2/c$); a = 18.440 (6) Å, b = 9.461 (3) Å, c = 12.017 (4) Å, and β = 104.74 (3)°, V = 2027 (1) Å^3, d_{calcd} = 1.10 g·cm^{-3}, Z = 4. X-ray intensities were collected at 175 ± 3 K on a Nicolet R3m four-circle diffractometer equipped with a nitrogen-flow cooling device by applying Mo Kα radiation (λ = 0.71069 Å). A total of 1794 independent reflections were recorded with $3° \leq 2\theta \leq 50°$ of which 1500 with $[|F_o| > 3\sigma(F_o)]$ were considered unique and observed. The structure was solved by direct methods with the SHELXTL software. Carbon and nitrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in the refinement at idealized positions (C–H = 0.96 Å, N–C–H = 109.5°) and were refined isotropically by using a riding model. R and R_w factors after refinement were 0.048 and 0.055, respectively.

Crystals of 5 and 8 suitable for X-ray analysis were grown from acetone and 1:1 methanol/dichloromethane, respectively. The thin needles of 8 were extremely brittle and diffracted very poorly at $2\theta > 40°$. Crystal data and structural parameters for 5 and 8 are given in ref 18 and in the supplementary material, respectively.

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Registry No. 4, 114396-17-7; 4·TCNQ, 114422-55-8; 5, 114422-56-9; 7, 114396-19-9; 8, 114396-21-3; 9, 114396-22-4; 10, 114396-23-5; 11, 114396-24-6; hexaaminobenzene, 4444-26-2; 1,3,5-trinitro-2,4,6-triaminobenzene, 3058-38-6; 1,3,5-trichloro-2,4,6-trinitrobenzene, 2631-68-7; 1,3,5-tris(diethylamino)-2,4,6-trinitrobenzene, 114396-18-8; 1,3,5-tris(ethylamino)-2,4,6-trinitrobenzene, 91881-07-1.

Supplementary Material Available: Bond lengths and bond angles with standard deviations, anisotropic thermal parameters, hydrogen atom coordinates for 4 (Tables IV–VII); crystal parameters, data measurements, atomic coordinates, bond lengths and bond angles with standard deviations, anisotropic thermal parameters for 8 (Tables VIII–XIV) (8 pages). Structure factor tables are available from the author. Ordering information is given on any current masthead page.

Ab Initio Calculations of Hydrogen Transfers. A Computational Test of Variations in the Transition-State Structure and the Coefficient of Rate-Equilibrium Correlation

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Hydrogen atom transfers from R–H (R = Me, Et, i-Pr, or t-Bu) to X$^\bullet$ (X = H or Cl) were investigated by using the ab initio molecular orbital method with the object of gaining insight into the relation between transition-state (TS) structures and reactivities and into the significance of the coefficient, α, of rate–equilibrium correlation. Structures of the reactants, TSs, products, and σ complexes were fully optimized with the 3-21G basis set. Single-point energy calculations were carried out for all the structures at the MP2/6-31G* level. It was found that the TS structure becomes more reactant-like for a more reactive R–H when X = H while it is unchanged when X = Cl. The $\Delta E^\ddagger$–ΔE correlation gave straight lines with slopes of 1.0 and 1.4 respectively for X = H and Cl. These results were discussed in terms of Marcus' equation. It was concluded that (1) the coefficient α is an experimentally (or computationally) derived index of selectivity but not always a reliable measure of the TS structure, (2) the variation in the intrinsic barrier is an important factor in determining the magnitude of α, and (3) the α value becomes anomalously sizable when a new interaction occurs between the two reacting fragments in the TS and therefore the arithmetic mean assumption breaks down.

Correlation between rates and equilibria (eq 1) is one of the most commonly used free energy relationships in organic chemistry, and the coefficient α has usually been taken as a measure of the position of the transition state (TS) along the reaction coordinate. When the TS has an

$$\log k = \alpha \log K + C \qquad (1)$$

intermediate character between the reactant and the product, the value of α should be between 0.0 and 1.0. The Hammond postulate[2] and its Leffler[3] generalization pro-

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