Structures of Tris(donor)-Tris(acceptor)-Substituted Benzenes, 5[1]

Organization and Reorganization of the π System in a Symmetric Tris(alkylamino)trinitrobenzene: Balance Between Cyanine and Quinoid Structures[☆]

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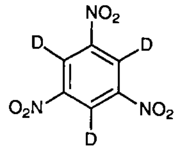
The π system of **1a** may adopt markedly different electronic structures with concomitant strong conformational preferences for the six-membered ring. Neutral **1a** can exist either in a quinoid boat form or as a twist boat, formally resulting from the coupling of an anionic with a cationic trimethinecyanine. Deprotonation gives a rigid quinoid boat structure; protonation occurs at a ring atom to form an equally rigid cyanine.

Knowledge of the electronic and geometric features of donor-acceptor-substituted π systems is of decisive importance to the rational design of molecules with nonlinear-optical properties[2]. In this respect, non-aromatic π systems seem to be the most promising[2b,c]. They may result, for example, from the attachment of several strong donors and acceptors to the benzene nucleus (Jahn-Teller distortion). Qualitatively, these distortions are rationalized by the „cyanine concept“[3]; exceptions, however, are known[3b]. With aid of this concept, no predictions are possible about the conformation of the distorted molecule.

The non-aromatic[4c], [6]radialene-like trifold donor-substituted 1,3,5-trinitrobenzenes **1**–**3**[1,4] are ideal objects for experimental studies of the interplay between electronic and geometric organization of the π system since they are conformationally flexible: mainly for electronic reasons[5] they adopt strongly non-planar boat[1,4a,b,d] or twist boat conformations[4a–c] which hardly differ energetically. The differences in geometries, however, are reflected by changes in the electronic structures of their π systems. So far, the direct comparison of both forms has been possible only for **1a**, which crystallizes in a boat form in the cosolvate with isopropylamine, but in a twist-boat form in the cosolvate with toluene. The strong alternation of the C–C bonds within the ring, and of the exocyclic C–N bonds found in the boat form[4a,b,d] could be satisfactorily explained by invoking a quinoid resonance form (**NQ** in Schemes 1 and 2). The electronic structure of the π system in the twist-boat form could not be discussed in detail, because the numerical uncertainties of the geometric parameters were increased by the disorder of the cosolvated toluene[4a]. We therefore report on a more precise X-ray analysis of solvate-free **1a**. On the other hand, we were interested in the behavior of **1a** on protonation and deprotonation. Its π system, again, may prefer an aromatic, a quinoid or a (cationic or anionic pentamethine-)cyanine-like structure (Scheme 1; **PQ**, **PC** and **DQ**, **DC**, respectively; the aromatic form is not shown), and all forms appear reasonable at first glance. Fortunately, **1a** behaves as an amphoteric molecule, and stable salts are formed in both cases. Thus, the rare possibility is given to study the different geometric and electronic forms of the π system with slight changes in steric effects[5]. Therefore, we have not only determined the structure of solvate-free **1a**, but also those of its potassium and tetrafluoroborate salts **1a-D** and **1a-P** in the solid state and in solution. We have discovered a remarkable relationship between electronic structures of the π systems and the respective molecular conformations.



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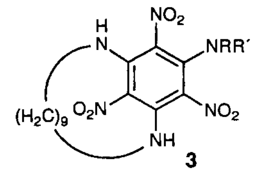

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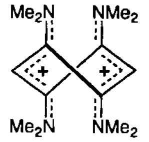
1: D = NHR: R = *i*Pr (**1a**), Et (**1b**), *t*Bu (**1c**), *neo*-Pent (**1d**); D = NEt_2
2: D = OX; X = H, K

3a: R = H, R′ = *neo*-Pent



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For solvate-free **1a**, an X-ray analysis indicates a highly distorted six-membered ring in a twist conformation (Figure 1; Schemes 1 and 2). The geometric parameters, like bond lengths or the sum of absolute torsional angles within the ring (representing a measure of its absolute deforma-

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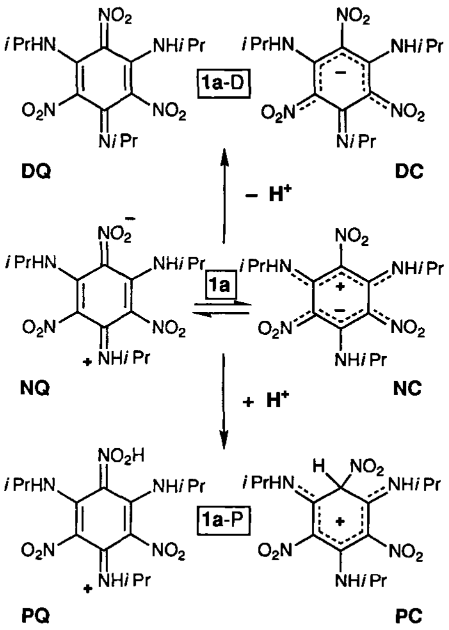
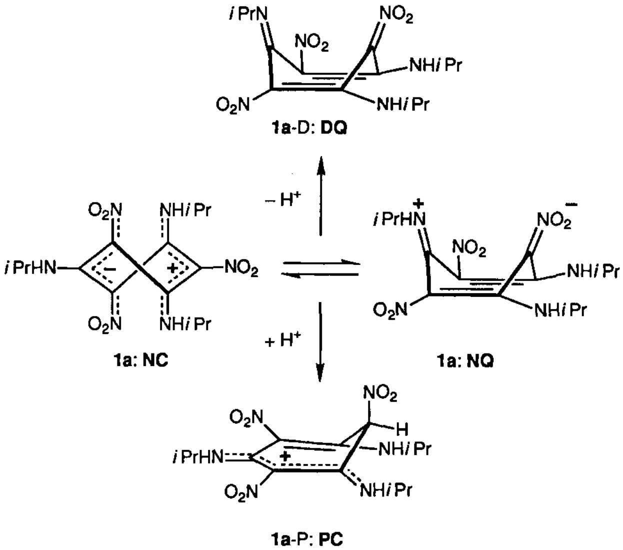
Scheme 1. Structural alternatives for the π systems in **1a**, **1a**-D, and **1a**-P



Scheme 2. Electronic structures and geometries of the six-membered rings in **1a**, **1a**-D, and **1a**-P in the solid state



tion[1,4a–c]), fall within the range expected for twist-boat forms of **1**[4a–c]. The π system adopts a structure analogous to the dications of alkylated tetra- and hexaaminobenzenes. If sterically possible, their six-membered rings form twist-boats[6] in which two cationic trimethinecyanine units with short C–C bonds are coupled by two long bonds (as in **4**[6a]). By analogy, in the neutral molecule **1a** (**NC** in Schemes 1 and 2) one cyanine moiety should be formally anionic (along N5–C5–C6–C1–N1), and the other cationic (along N2–C2–C3–C4–N4). Charge separation in a neutral molecule is unfavorable, and a strong coupling between both moieties is expected with concomitant (formal) back transfer of charge; the differences in the geometric parameters are, therefore, small. In accordance with this description, however, all bonds within the cyanine units (1.421 – 1.447 Å) are significantly shorter than the remaining bonds (1.454 and 1.461 Å), on an average by 0.023 Å. While the differences are not large, the inspection of all known twist-boat structures of **1a**–**d**[4a–c,7] and **2** yields a uniform averaged shortage of 0.007–0.024 Å for the C–C bonds in the cyanine moieties, with the exception of **1a** · toluene (where the *R* value is high): −0.002 Å. The two C–N(amino) bonds in the "cationic" unit should also be shorter than the remaining one. While in all structures their average is shorter by 0.005–0.027 Å (with **1d** as the sole exception: −0.005 Å) the differences are mostly below 3σ and are not discussed further. The C–NO_2 bonds do not follow this pattern which is most likely due to the moderate π-acceptor strength of the nitro group[8]. This is particularly evident in the anion of **1a**.

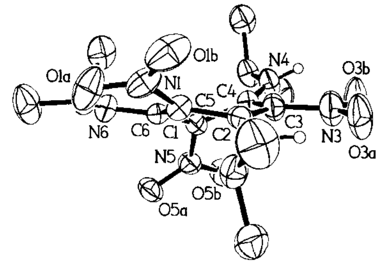


Figure 1. ORTEP of **1a**; selected bond lengths [Å], bond angles, and torsional angles [°]: C1–C2 1.454(4), C2–C3 1.432(4), C3–C4 1.440(5), C4–C5 1.461(4), C5–C6 1.447(4), C6–C1 1.421(4), C1–N1 1.420(4), C3–N3 1.413(4), C5–N5 1.373(4), C2–N2 1.322(4), C4–N4 1.306(4), C6–N6 1.319(4); C1→C3 117.0(3), C2→C4 119.3(3), C3→C5 114.5(3), C4→C6 117.4(3), C5→C1 115.6(2), C6→C2 120.1(2); C1→C4 −15.3(4), C2→C5 −18.8(4), C3→C6 42.7(4), C4→C1 −30.3(4), C5→C2 −5.4(4), C6→C3 28.5(4)

1a-D · MeOH crystallizes in a boat form (Figure 2; **DQ** in Schemes 1 and 2). The sum of absolute torsional angles within the ring is larger than in all known structures of **1**–**3**; it amounts to 180°[9]. As documented by the strong C–C bond length alternation, **1a**-D adopts a cross-conjugated quinoid form (**DQ**)[10]. The C–N bond length of the deprotonated amino group is markedly shortened (as expected), but not the C–N bond length of the nitro group in its *para* position whose double-bond character is, therefore, not increased. The deprotonated amino group adopts a position at the "stern" position[11]. A planar, anionic pentamethinecyanine (**DC**) in a ring of sp^2 centers seems to be generally unfavorable[11].

Likewise, only one conformer of **1a**-D can be detected by NMR spectroscopy in solution. This must be the boat form, as inferred from a comparison of the ^{13}C-NMR signals of the ring atoms with those of the cyclophane **3a** which is frozen in a boat form for steric reasons[1]. In **1a**-D, the barrier to conformational inversion boat ⇌ boat (> 16 kcal/mol[12]) is drastically increased in comparison with **1a** (ca. 9 kcal/mol[4a,d]): **1a**-D is a rigid, C_1-symmetric molecule on the NMR time scale at room temperature[13]. The boat form

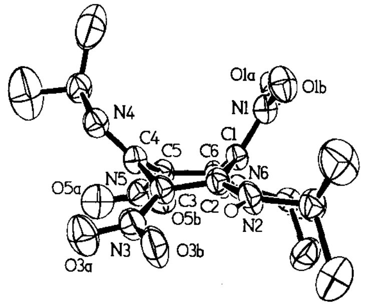


Figure 2. ORTEP of **1a**-D · MeOH; the countcrion K^+ has been omitted for clarity; selected bond lengths [Å], bond angles, and torsional angles [°]: C1–C2 1.464(3), C2–C3 1.417(3), C3–C4 1.488(3), C4–C5 1.488(3), C5–C6 1.415(3), C6–C1 1.467(3), C1–N1 1.372(3), C3–N3 1.373(3), C5–N5 1.388(3), C2–N2 1.322(3), C4–N4 1.270(3), C6–N6 1.319(3); C1→C3 114.1(2), C2→C4 116.5(2), C3→C5 111.9(2), C4→C6 116.9(2), C5→C1 114.3(2), C6→C2 118.1(2); C1→C4 13.3(3), C2→C5 −48.9(3), C3→C6 39.4(3), C4→C1 3.7(3), C5→C2 −41.9(3), C6→C3 32.7(3)

in **DQ** must, therefore, be strongly preferred to other conformers. This finding is corroborated by deprotonation of the sterically constrained **3a**: according to the NMR spectra, **3a** is exclusively deprotonated at the neopentylamino group at the "stern" of the boat which must, therefore, be much more acidic than the "side" positions.

1a may be protonated at the ring, at the amino nitrogen atoms, or at the oxygen atom of a nitro group, which results in a cationic pentamethinecyanine, a quinoid, and an aromatic (or quinoid) structure, respectively. In 1,3,5-triaminobenzenes, the strong, sterically not encumbered donor pyrrolidino[14] is needed to effect complete ring protonation. **1a**-P is sterically encumbered and bears donors whose strength is drastically diminished by the presence of three nitro groups in the molecule. These features decrease the stabilities of both the ring- and nitrogen-protonated forms. However, **1a** still reacts as a base, and the ring-protonated form is found in the solid (Figure 3; **PC** in Schemes 1 and 2). The π system does not form a pentamethinecyanine, but a trimethinecyanine (N2–C2–C3–C4–N4), which is coupled *via* a long bond (1.470 Å) with a nitro-enamine moiety (C1–C6) (Scheme 2). Crystal-packing forces or the counterion exert a marginal influence on the molecular parameters of **1a**-P since it follows from the NMR spectra that **1a** is protonated on a nitro-group-bearing carbon atom also in solution[15]. **1a**-P does not show either chemical (proton) exchange or conformational inversion (barrier to both processes > 16 kcal/mol[12]). Like the quinoid form in **1a**-D, the ring-protonated form of **1a**-P must correspond to a deep energy minimum. Whether its π system is dissymmetric also in solution, cannot be decided, because the C_1 symmetry[13] present in **1a**-P is caused in any case by the hindered rotation about the C–N(amino) groups.

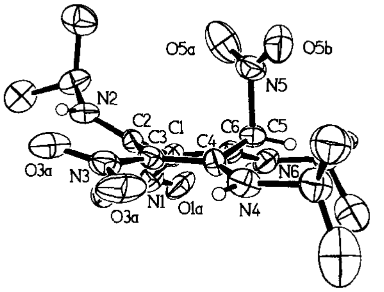


Figure 3. ORTEP of **1a**-P; the counterion BF_4^- has been omitted for clarity; selected bond lengths [Å], bond angles, and torsional angles [°]: C1–C2 1.470(5), C2–C3 1.449(5), C3–C4 1.404(5), C4–C5 1.517(5), C5–C6 1.497(5), C6–C1 1.389(6), C1–N1 1.409(5), C3–N3 1.412(5), C5–N5 1.535(5), C2–N2 1.299(4), C4–N4 1.305(5), C6–N6 1.327(5); C1→C3 115.6(3), C2→C4 118.5(3), C3→C5 115.6(3), C4→C6 112.9(3), C5→C1 115.9(3), C6→C2 119.5(3); C1→C4 −26.7(5), C2→C5 −12.6(5), C3→C6 44.3(4), C4→C1 −36.1(4), C5→C2 −2.9(5), C6→C3 35.6(5)

In conclusion, the symmetrically substituted tris(donor)-tris(acceptor)benzene **1a** may adopt two markedly different structures of its π system, its salts only one. Each of these forms leads to a strong preference for one conformation of the six-membered ring (Scheme 2). **1a** is a paradigm for the different forms of organization of a benzene derivative which avoids an aromatic structure due to strong conjugative interactions between its substituents[16].

This work was supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* (Liebig and equipment grant to J.J.W.), and Prof. Dr. *R. Gleiter*. Mrs. *C. Steinle*'s skillful collaboration is gratefully acknowledged.

Experimental

Diffractometer: CAD4 (Enraf-Nonius) with Mo-K_α radiation, highly oriented graphite-crystal monochromator, ω-2Θ scans.

X-ray Analysis of **1a**[4a]: Yellow prisms (0.35 × 0.40 × 0.40 mm) from acetone; $C_{15}H_{24}N_6O_6$ (384.4); monoclinic; *C*2/*c*; $a = 18.759(5)$, $b = 11.767(5)$, $c = 36.604(9)$ Å; $\beta = 104.259(3)°$; $Z = 16$; $\varrho_{calcd.} = 1.304$ gcm^{-3}; $\mu = 95.6$ mm^{-1}; $F(000) = 3264$; $\Theta = 2.0-28.0°$; 9673 reflections, 9395 independent and 4450 observed [$I > 2.5\sigma(I)$]; no absorption correction; solution by direct methods (SHELXS-86[17]); refinement by full-matrix procedure to F^2: heavy atoms refined anisotropically, H atoms on N isotropically, all other H atoms fixed; 511 parameters refined; $R = 0.053$ ($R_w = 0.071$); $S = 2.76$; largest and smallest difference peak: 0.35 and −0.09 eÅ^{-3}[18].

1a-D: By treatment of **1a**[4a] with KH in dry THF and filtration of the precipitate. Yellow platelets of a 1:1 complex with methanol separated from a concentrated methanolic solution, m.p. > 200°C (dec.). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 0.83 (d, J = 5.9 Hz, 3H), 1.16 (d, J = 6.1 Hz, 9H), 1.32 (d, J = 6.4 Hz, 3H), 1.34 (d, J = 6.7 Hz, 3H), 3.16 (d, J = 5.2 Hz, 3H), 3.29 (sept, J = 6.0 Hz, 1H), 3.80 (dsept, $J \approx 10$ and 6.3 Hz, 1H), 3.85 (dsept, $J \approx 10$ and 6.4 Hz, 1H), 4.09 (d, J = 5.2 Hz, 1H), 10.36 (pseudo-t, J = 8.9 Hz, 2H). – ^{13}C NMR ([D$_6$]DMSO, 75.5 MHz): δ = 21.15, 21.45, 21.84, 24.26, 24.35, 24.48, 48.54, 49.08, 49.26, 53.42, 101.68, 113.99, 118.32, 145.18, 150.30, 151.54. – The sodium salt of **1a** gave practically identical spectra. – $C_{15}H_{23}KN_6O_6 \cdot CH_3OH$ (454.5): calcd. C 42.28, H 5.99; found C 42.13, H 5.80.

X-ray Analysis of **1a**-D: Yellow prisms (0.50 × 0.35 × 0.20 mm); $C_{15}H_{23}KN_6O_6 \cdot CH_3OH$ (454.5); monoclinic; *P*2$_1$/*n*; $a = 10.098(5)$, $b = 14.819(8)$, $c = 15.332(4)$ Å; $\beta = 98.60(21)°$; $Z = 4$; $\varrho_{calcd.} = 1.25$ gcm^{-3}; $\mu = 27.6$ mm^{-1}; $F(000) = 960$; $\Theta = 2.0-28.0°$; 5710 reflections, 5417 independent and 3333 observed [$I > 2.5\sigma(I)$]; no absorption correction; solution by direct methods (SIR 88[19]), refinement by full-matrix procedure to F^2: heavy atoms refined anisotropically, H2, H6, H7, H of OH isotropically, remaining H atoms fixed; 15% disorder of the isopropyl group at N6, coordinates of C13″, C14″ refined, thermal parameters fixed; 293 parameters refined; $R = 0.044$ ($R_w = 0.056$); $S = 2.10$; largest and smallest difference peak: 0.34 and −0.05 eÅ^{-3}[18].

1a-P: By treatment of **1a** · toluene[4c] with $HBF_4 \cdot Et_2O$ in THF. The pale yellow precipitate was washed with diethyl ether and dried, m.p. >150 °C (dec.). – ^1H NMR (CD_3CN, 300 MHz): $\delta = 1.25$ (d, $J = 6.3$ Hz, 3H), 1.40 (d, $J = 6.2$ Hz, 6H), 1.46 (d, $J = 6.2$ Hz, 3H), 1.47 (d, $J = 6.3$ Hz, 6H), 3.78 (dsept, $J = 9.6$ and 6.3 Hz, 1H), 4.44 (dsept, $J = 9.6$ and 6.2 Hz, 1H), 4.67 (dsept, $J = 9.7$ and 6.1 Hz, 1H), 6.77 (s, 1H), 10.58 (br. d, $J \approx 7$ Hz, 1H), 11.03 (br. s, 1H), 11.36 (br. s, 1H). – ^{13}C NMR (CD_3CN, 75.5 MHz): $\delta = 20.11$ (CH_3), 22.54 (CH_3), 22.75 (CH_3), 22.78 (CH_3), 23.27 (CH_3), 24.13 (CH_3), 50.92 (CH), 52.48 (CH), 55.74 (CH), 77.88 (CH), 114.95 (C), 116.70 (C), 147.80 (C), 150.74 (C), 155.01 (C). – $C_{15}H_{24}N_6O_6 \cdot HBF_4$ (472.2): calcd. C 38.15, H 5.34; found C 38.20, H 5.51.

$[(^{15}NO_2)_3]$-**1a**-P: $[(^{15}NO_2)_3]$-**1a** was obtained by reaction of $[^{15}N_3]$-1,3,5-trimethoxy-2,4,6-trinitrobenzene[20] with isopropylamine in chloroform and subsequent filtration through neutral aluminum oxide (yield, 93%); it was protonated as described above. – The following signals were split into doublets: ^1H NMR: $\delta = 6.79$ ($J = 2.5$ Hz); ^{13}C NMR: $\delta = 77.88$ ($J = 8.4$ Hz), 114.94 ($J = 20.2$ Hz), 116.68 ($J = 18.9$ Hz).

X-ray Analysis of **1a**-P: Yellow prisms (0.50 × 0.35 × 0.20 mm) from acetonitrile/diethyl ether by the vapor diffusion technique; $C_{15}H_{24}N_6O_6 \cdot HBF_4$ (472.2); orthorhombic; $Pna2_1$; $a = 16.424(4)$, $b = 18.514(3)$, $c = 7.173(1)$ Å; $Z = 4$; $\varrho_{calcd.} = 1.45$ gcm^{-3}; $\mu = 12.5$ mm^{-1}; $F(000) = 984$; $\Theta = 2.0-26.0°$; 2308 reflections, 2308 independent and 1546 observed $[I > 2.5\sigma(I)]$; no absorption correction; solution by direct methods (Sir88[19]), refinement by full-matrix procedure to F^2: heavy atoms refined anisotropically, H2, H4, H6, H7, H10, H13 isotropically, remaining H atoms fixed; 316 parameters refined; $R = 0.041$ ($R_w = 0.045$); $S = 1.83$; largest and smallest difference peak: 0.24 and -0.12 eÅ^{-3}[18].

3a: In analogy to the procedure described in ref.[1] and recrystallized from dichloromethane; a 1:1 cosolvate with this solvent was thus formed. – ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.01$ (s, 9H), 1.35–1.55 (m, 10H), 1.63 (m, 2H), 1.74 (m, 2H), 2.52 (dd, $J = 9.1$ and 14.0 Hz, 1H, CH_AH_B of the neopentyl group), 3.34–3.49 (m, 3H), 3.67–3.88 (m, 2H), 10.01 (br. d, $J = 7.6$ Hz, 1H), 11.25 (br. d, $J = 8.4$ Hz, 1H), 11.65 (br. d, $J = 8.4$ Hz, 1H). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 23.13$, 23.27, 25.52, 25.64, 26.01, 27.27 (triple intensity), 27.47, 28.20, 31.76, 48.57, 49.24, 60.18, 104.92, 113.03, 117.42, 150.47, 153.71, 153.92. – $C_{20}H_{32}N_6O_6 \cdot CH_2Cl_2$ (537.4): calcd. C 46.93, H 6.38, N 15.64; found C 47.22, H 6.39, N 15.57.

Na Salt: In analogy to **1a**, **3a** was deprotonated with NaH in THF. The coupling between NH and the diastereotopic methylene protons of the neopentyl group, detected in neutral **3a**, disappeared. – ^1H NMR ($[D_6]$DMSO, 300 MHz): $\delta = 0.78$ (s, 9H), 1.08–1.41 (m, 10H), 1.58 (m, 4H), 2.52 (d, $J = 14.3$ Hz, 1H, CH_AH_B of the neopentyl group), 3.27 (d, $J = 14.1$ Hz, 1H, CH_AH_B of the neopentyl group), 3.22–3.50 (m, 4H), 10.53 (pseudo-d, $J = 8.7$ Hz, 2H). – ^{13}C NMR ($[D_6]$DMSO, 75.5 MHz): $\delta = 22.86$, 23.21, 24.74, 27.22, 27.42, 27.68 (triple intensity), 31.83, 46.20, ca. 46.21 (shoulder), 65.25, 102.78, 114.57, 118.32, 147.97, 151.30, 152.70.

☆ Dedicated to Prof. Dr. *Reinhard W. Hoffmann* on the occasion of his 60th birthday.

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[5] The "push-pull" effect causes elongation of the C–C bonds within the ring and decreases the resistance of the benzene ring against bending. Steric interactions between the substituents only determine the actual amount of ring distortion[4c].

[6] [6a] K. Elbl, C. Krieger, H. A. Staab, *Angew. Chem.* **1986**, *98*, 1024; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1023. – [6b] J. M. Chance, B. Kahr, A. B. Buda, J. P. Toscano, K. Mislow, *J. Org. Chem.* **1988**, *53*, 3226. – [6c] J. S. Miller, D. A. Dixon, J. C. Calabrese, C. Vazquez, P. J. Krusic, M. D. Ward, E. Wasserman, R. L. Harlow, *J. Am. Chem. Soc.* **1990**, *112*, 381.

[7] In addition, we have included an X-ray analysis of the *N*-ethyl derivative **1b** (J. J. Wolff, S. F. Nelsen, D. R. Powell, unpublished results), which also crystallizes in a twist-boat form.

[8] [8a] J. R. Holden, C. Dickinson, *J. Phys. Chem.* **1977**, *81*, 1505. – [8b] S. Sorriso in *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives, Part I* (Ed.: S. Patai), Wiley, Chichester, **1982**, p. 1. – [8c] A. Domenicano in *Accurate Molecular Structures*, (Eds.: A. Domenicano, I. Hargittai), Oxford University Press, New York, **1992**, p. 437.

[9] For the boat form of cyclohexane (consisting of sp^3 centers!), AM1 finds 210°, and MM2 gives 212°.

[10] The comparable Meisenheimer complexes of 1,3,5-trinitrobenzene derivatives show similar bond alternations; the ring is much less distorted, however: R. Destro, C. M. Gramaccioli, M. Simonetta, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, **1968**, *B24*, 1369; R. Destro, T. Pilati, M. Simonetta, *ibid.* **1979**, *35*, 733; H. Ueda, N. Sakabe, J. Tanaka, A. Furusaki, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2866.

[11] In two structures of anions of nitrogen-substituted 1,3,5-trinitrobenzenes listed in the Cambridge Structural Data File (F. H. Allen in Lit. [8c], p. 355; F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rogers, D. G. Watson, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2331) the (much less distorted) six-membered ring also adopts a quinoid boat form with the deprotonated group at a "stern" position: These are the K salts of 1,1-diphenyl-2-(2,4,6-trinitrophenyl)hydrazine [Σ | dihedral angles | = 84°] and of hexanitrodiphenylamine [Σ | dihedral angles | = 22°], respectively: R. Gopal, B. E. Robertson, J. A. Weil, *Can J. Chem.* **1983**, *61*, 2735; M. L. Kundu, S. K. Gosh, *Acta Crystallogr., Sect. B.: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 941.

[12] The lower value for the barrier was determined from the smallest distance of those signals which would coalesce on conformational interconversion.

[13] In the ^{13}C-NMR spectra of **1a**-D and **3a**, all possible resonance signals are observable; the rotations around the C–N(amino) bonds and the ring inversion are strongly hindered in solution.

[14] [14a] F. Effenberger, F. Reisinger, K. H. Schönwälder, P. Bäuerle, J. J. Stezowski, K. H. Jogun, K. Schöllkopf, W.-D. Stohrer, *J. Am. Chem. Soc.* **1987**, *109*, 882. – [14b] F. Effenberger, *Acc. Chem. Res.* **1989**, *22*, 27. – [14c] W. Knoche, W. W. Schoeller, R. Schomäcker, S. Vogel, *J. Am. Chem. Soc.* **1988**, *110*, 7484, and literature cited.

[15] Characteristic signals for the ring-bound proton at $\delta = 6.9$ (cf. ref. [14]) and for the respective carbon atom at $\delta = 77.9$ are found which are split into doublets on labeling the nitro groups with ^{15}N.

[16] Theoretical investigations of the electronic situation in **1**—**3** will be published elsewhere: G. Frenking, P. Bischof, J. J. Wolff, manuscript in preparation.

[17] G. M. Sheldrick, *SHELXS-86: Program for Crystal Structure Solution*, Göttingen **1986**.

[18] Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-400188 (**1a**), -400189 (**1a**-D), -400190 (**1a**-P), the names of the authors, and the journal citation.

[19] M. C. Burla, M. Camalli, G. Cascarano, G. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, *J. Appl. Crystallogr.* **1989**, *22*, 389.

[20] J. J. Wolff, H.-H. Limbach, *Liebigs Ann. Chem.* **1991**, 691.

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