

Formation of a benzenetrienoide resonance structure in a cyclophane containing a trinitrotriaminobenzene unit

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The [6₃](1,5,9)triphenyleno(1,3,5)cyclophane **1** shows a trienoide Kekulé-type structure for the planar donor-acceptor substituted benzene part.

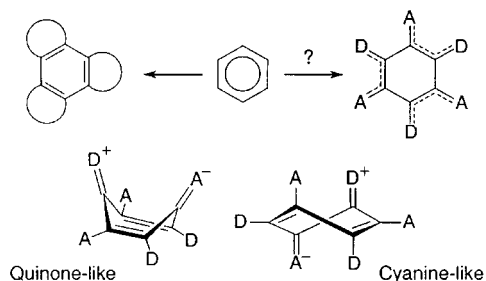
The deviation of small aromatic molecules like benzene and naphthalene from the usual equal bond lengths to bond length alternations has been the object of synthetic and theoretical investigations.^{1,2} The known X-ray structures with considerable bond length alternations reminiscent of the extremum of a Kekulé structure require a threefold incorporation into strained rings which shorten the incorporated bonds. This leads to almost single-bond character for the bonds not incorporated. At first glance, steric strain may not be the only way to ease the formation of such structures with a Kekulé bond length alternation: the complete symmetrical substitution with three electron donating and three accepting groups might also lead to it. In an extreme situation, the interaction between donors and acceptors could equally result in Kekulé-type structures with three groups of separated double bonds that bear one donor and one acceptor, each interacting only with each other. Thus, this type of bond length alternation might also occur within such a ring without great strain.

A closer look, however, shows disappointing results. For example, while all 1,3,5-trinitro-2,4,6-triamino-substituted benzene derivatives known^{3–5} do show bond length alternations, they are far from the threefold symmetry required for a Kekulé structure: the six-membered ring has a clear maximum of C_{2v} or C₂ symmetry. Almost all of the central rings of the molecules analyzed by X-ray adopt either a strongly nonplanar boat or a twist form. The same holds true for substitution with other donors like the hydroxy group or its anion. For these highly nonplanar molecules, the shown quinoid and bis-trimethine cyanoid resonance forms are the only geometric structures observed (Scheme 1). Planar ones correspond to usual benzene derivatives with some substituent-dependent bond length alternation.

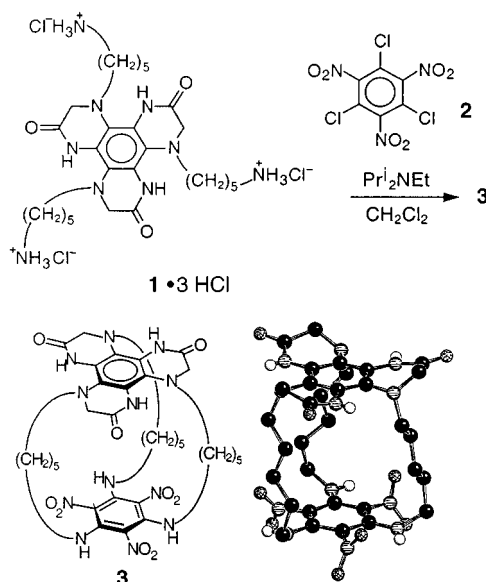
We were therefore surprised when an X-ray structure† (Scheme 2) was obtained of an intermediate **3** in the construction of bis-hexaaminobenzene derivatives⁶ used by us for the study of intramolecular electron transfer.⁷ Both aromatic rings are close to planar.⁸ While this would not be very surprising for most benzene derivatives, it has never been observed before for trinitrotriaminobenzenes, which are only close to planar in the hydrogen-bonded solid state structure of

trinitrotriaminobenzene itself; even with only two amino groups and one alkylamino group, some folding of the ring is observed.⁴ In addition, the donor-acceptor substituted ring shows C₃ symmetry and the bond lengths within the ring are 1.399(4) and 1.416(4) Å. Thus, the clear formation of a benzene ring with a Kekulé structure can be observed which lacks significant steric strain but has symmetrical donor-acceptor substitution. The higher C–C bond length occurs between the nitro and the amino groups that are linked by a weak intramolecular hydrogen bond (2.29 Å). Some interaction is also visible to the other direction, between the other oxygen of the nitro group and a proton of the methylene group next to the nitrogen (2.27 Å).⁹ The oxygen of the nitro group which is engaged in intramolecular hydrogen bonding with the amino group also shows intermolecular contact to the NH of the hexaazatriphenylene (2.34 Å). Both possible enantiomeric forms are present in the crystal, related to each other by inversion symmetry.

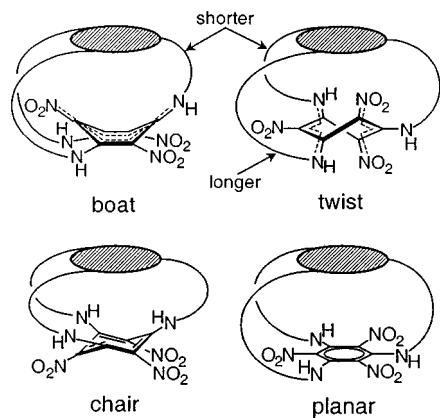
A closer inspection provides a reason for the unexpected planarity. Since the bridges between the two rings need to keep approximately the same distance between them, they have to adopt comparable conformations. The hexaaminobenzene derivative part of **3** is expected to exist with a stable planar conformation for its central benzene ring.^{7,10,11} Then, the second, donor-acceptor substituted ring can adopt neither boat nor twist forms, because the distance of the chains to the first ring would become quite different (Scheme 3). These conformations are thus unlikely to be observed. While equality of the distances would be possible in a chair conformation, it is not truly compatible with the electronic requirements of the push-pull interaction between the substituents and is thus rarely found even for non-polar benzene derivatives with strong steric interactions.¹² The only possible conformation for the usually



Scheme 1



Scheme 2



Scheme 3

highly distorted six-membered ring is therefore a planar one. While in this conformation the donor–acceptor interactions are quite reduced in comparison with known structures, they are nevertheless still present. Therefore a moderate, but definitely existent Kekulé distortion can be detected.

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Notes and references

† *Crystal data for 3*: Orange hexagonal plates, $C_{33}H_{42}N_{12}O_9 \cdot 3H_2O \cdot 0.5 CH_2Cl_2$ (750.3 + 96.5), $T = 298$ K, numerical absorption correction ($\mu = 0.16$ mm⁻¹). Trigonal space group $P\bar{3}$ with $a = b = 15.267(3)$, $c = 10.921(6)$ Å, $Z = 2$; solution by direct methods with SHELXS-97, refinement with SHELXL-97. 3941 reflections, 3549 unique, 1715 observed [$I > 2\sigma(I)$]. N–H refined isotropically, remaining H calculated. $R = 0.067$, $R_w = 0.187$, GOF = 0.98. CCDC 182/1497. See <http://www.rsc.org/suppdata/cc/a9/a908200j/> for crystallographic data in .cif format.

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- 6 *Synthesis of 3*: The synthesis of starting material will be described elsewhere. To a suspension of 1:3 HCl (235 mg, 0.360 mmol) in dry CH_2Cl_2 , a mixture of Hünig's base (282 mg, 2.18 mmol) and 1,3,5-trichloro-2,4,6-trinitrobenzene **2** (ref. 13) (114 mg, 0.360 mmol) in CH_2Cl_2 (100 ml) was added within 3 h. The mixture was stirred overnight and then, after addition of four drops of AcOH, filtered over silica gel (CH_2Cl_2 –MeOH = 25/1). The solvents were removed and the chromatography was repeated. The cyclophane **3** was obtained as a yellow powder (18 mg, 0.024 mmol, 7%), decomp. > 230 °C. Crystals for X-ray analysis were obtained from diffusion of pentane into a solution in CH_2Cl_2 . δ_H (300 MHz, DMSO- d_6) 1.08 (m, 6H), 1.26 (m, 6H), 1.42 (m, 6H), 2.76 (m, 6H), 3.12 (m, 3H), 3.19 (m, 3H), 3.41 (d, J 17.1, 3H), 3.50 (d, J 16.9, 3H), 9.09 and 9.12 (br s, together 6H); δ_C (75.5 MHz, DMSO- d_6) 23.30, 24.82, 27.38, 45.67, 53.53, 56.21, 114.82, 115.07, 126.57, 147.40, 168.97 [FAB-MS: calc. for $C_{33}H_{42}N_{12}O_9$: 750.32, found 750.48 (15, M⁺); $C_{33}H_{42}N_{12}O_9 + Na^+$: 773.31, found: 773.48 (3, M + Na⁺)].
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- 8 The sum of absolute torsional angles within the donor-substituted six-membered ring is 19°, and 15° in the donor–acceptor substituted one.
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