The solid-state 2:1 molecular complex of 1,5:3,7-dimethano-1,3,5,7-benzo-tetrazonine with hydroquinone

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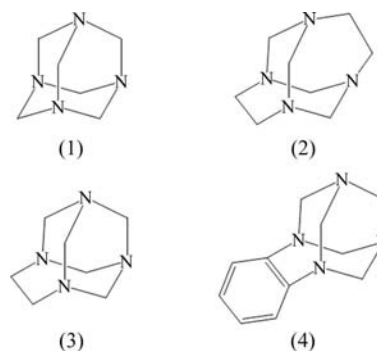
The title compound, 1,5:3,7-dimethano-1,3,5,7-benzotetrazo-nine–hydroquinone (2/1), $2C_{11}H_{14}N_4 \cdot C_6H_6O_2$, crystallizes with the hydroquinone molecule located on a center of inversion. In contrast to other hydroquinone–adamanzane adducts, which form extended hydrogen-bonded networks, in the present case, one hydroquinone molecule is linked to two 1,5:3,7-dimethano-1,3,5,7-benzotetrazonine molecules, forming a 2:1 cluster through O—H···N hydrogen bonds.

Comment

We are interested in investigating the structures and properties, as well as the reactivity, of aminal (aminoacetal) cages by reacting them with electrophiles and nucleophiles. These cyclic polyamines are able to play a role as hydrogen acceptors using the lone pair of an N atom in a hydrogen bond, and have been used as model systems for proton-transfer studies. For instance, there are several reports (MacLean *et al.*, 1999; Mak *et al.*, 1977; Tse *et al.*, 1977; Ghosh *et al.*, 2005, and references 11–13 and 15 therein) on the preparation of adducts between hexamethylenetetramine (urotropine), (1), and phenols. In contrast, the analogue 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]do-decane (TATD), (2), has been shown to be highly reactive with a variety of phenols (Rivera *et al.*, 2006, 2005, 1993). In addition, we were able to crystallize the 1:1 adduct of (2) and hydroquinone (Rivera, Ríos-Motta *et al.*, 2007). Whereas these two aminals maintain similar hydrogen-bonding patterns with the hydroxy groups of hydroquinone, the O—H bond exhibits dramatic changes in length. A comparison of the influence of the lone-pair orbital hybridizations (LPOs) on OH···N distance (Rivera, Ríos-Motta *et al.*, 2007) shows that the major sp^3 character of the N atoms in (1) causes this molecule to possess a slightly shorter hydrogen-bond distance. In connection with our previous work on the synthesis of 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane (TATU), (3) (Riv-

era *et al.*, 2004), where a competition between hydrogen bonding and interactions between π-electron systems may occur and which offers the opportunity to study LPOs owing to the presence of two non-equivalent N atoms, we have recently studied the formation of a 1:1 complex of (3) with hydroquinone. The X-ray data showed that in contrast to the crystal structure of (2) the hydroquinone molecule hydrogen bonds to those N atoms with higher sp^3 character (Rivera, González-Salas *et al.*, 2007).

Recent work from Kuznetsov *et al.* (2007) on a three-component condensation of formaldehyde with a mixture of ammonia and *o*-phenylenediamine, which resulted in the preparation of the new cage amine 1,5:3,7-dimethano-1,3,5,7-benzotetrazonine, (4), caught our attention for two reasons. First, a previous publication from our laboratory reported the synthesis of an analogous compound, (3), but following our methodology (Rivera *et al.*, 2004) all attempts to prepare benzoTATU, (4), were unsuccessful. Second, from the viewpoint of crystal engineering, (4) can provide different hydrogen-bonding interactions since it contains two types of non-equivalent hydrogen-bonding acceptor atoms, and a possible competition between N atoms can occur. Thus, the results from the Kuznetzov group encouraged us to extend our investigation to determine the relationship between nitrogen lone-pair hybridization and hydrogen-bond systems in aminal cages.

The reaction of (4) with hydroquinone yielded a colorless adduct, (I). A view of the molecular structure indicating the atomic numbering is shown in Fig. 1 and a packing diagram is given in Fig. 2.
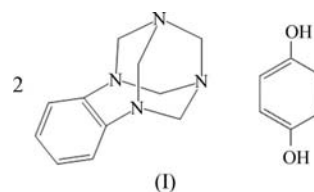
The asymmetric unit of complex (I) contains one molecule of (4) and one-half of a hydroquinone molecule, which is related to the other half by a inversion center, and the monoclinic unit cell contains two adducts. In contrast, the crystal structures of the urotropine (Mak *et al.* 1977), TATD (Rivera, Ríos-Motta *et al.*, 2007) and TATU hydroquinone

adducts (Rivera, González-Salas *et al.*, 2007) show 1:1 molecular complexes. The lattices of these three hydroquinone adducts form extended hydrogen-bonded networks, in which the aminal cages act as a twofold acceptor of hydrogen bonds, leading to the formation of zigzag chains. A previous X-ray structural investigation of (4) showed that the bond angles around the N atoms have close to sp^3 geometry, ranging from 107.1 to 113.6° (the average value was 110.8°; Kuznetsov *et al.*, 2007). On the basis of these X-ray data, the authors suggested that the nonbonding electron pairs on the N atoms directly attached to the benzene ring cannot efficiently delocalize into the aromatic ring. According to these results, the tetrahedral disposition of all nitrogen lone pairs in the aminal cage molecule makes this an attractive candidate as a hydrogen-bond acceptor, and some or all of them may, in principle, form hydrogen-bonded adducts. Thus, we expected that, with the use of hydroquinone, it should be possible to generate an extended hydrogen-bonding network. However, as can be seen in the packing diagram of the title compound (Fig. 2),
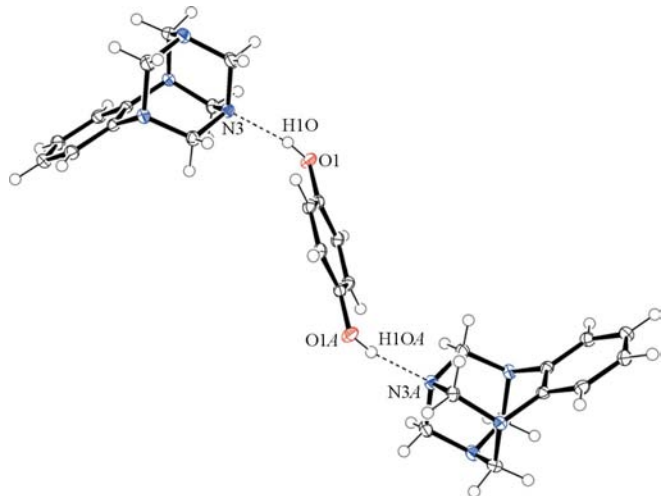

Figure 1
The molecular structure of the benzoTATU–hydroquinone adduct. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres. Atoms labeled with the suffix *A* are at the symmetry position $(-x +1, -y + 2, -z + 1)$.
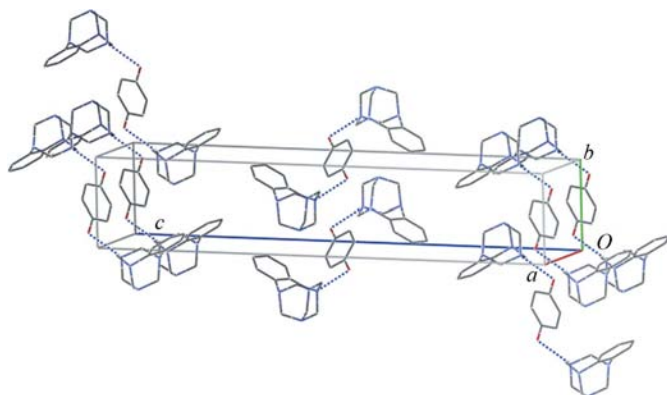

Figure 2
The crystal packing of the benzoTATU–hydroquinone adduct.

although the hydroxy groups of hydroquinone form hydrogen bonds with N atoms of two molecules of (4), the aminal cage is involved in a single intermolecular O—H···N hydrogen bond (Table 1). In contrast to the case of (3) (Rivera, González-Salas *et al.*, 2007), this observation suggests that the common hydrogen-bond network between polyamine and hydroquinone is broken as a consequence of the presence of a benzene ring in the structure of (4). It appears that this group reduces the overall basicity of the aminal cage. Indeed, anilines are weaker bases than aliphatic amines as a result of electron pair delocalization of the nitrogen nonbonding electron pair into the aromatic ring.

Our recent studies on the influence of the nitrogen lone-pair hybridization on O—H and OH···N distances, carried out for structures determined by X-ray crystallography of 1:1 adducts between aminal cages and hydroquinone (Rivera, González-Salas *et al.*, 2007), showed that the hydrogen bond (OH···N distances) is sensitive to the sp^3 character of the N atom. As a continuation of these studies, we found that the current adduct presents slightly longer hydrogen bonds than the TATU–hydroquinone adduct and a different relative orientation of the aromatic rings.

Experimental

Compound (4) was prepared following a procedure described in the literature (Kuznetsov *et al.*, 2007). Hydroquinone was purchased from Merck and used without further purification. To a solution of hydroquinone (11.0 mg, 0.1 mmol) in acetone (10 ml) was added slowly a solution of (4) (20.2 mg, 0.1 mmol) in acetone (10 ml), and the resulting mixture was heated gently for 5 min. Slow evaporation of the solvent at room temperature afforded a hard crystalline mass from which it was possible to break out small air-stable colorless crystals [m.p. 437–440 K (with decomposition)]. The melting point was determined with an electrothermal apparatus and is uncorrected.

Crystal data

$2C_{11}H_{14}N_4 \cdot C_6H_6O_2$	$V = 1245.84$ (12) Å^3
$M_r = 514.64$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.6421$ (4) Å	$\mu = 0.09$ mm^{-1}
$b = 5.9519$ (3) Å	$T = 100$ K
$c = 31.5160$ (18) Å	$0.38 \times 0.21 \times 0.2$ mm
$\beta = 90.687$ (3)°	

Data collection

Bruker APEXII CCD diffractometer	16516 measured reflections
	3840 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	2673 reflections with $I > 2\sigma(I)$
$T_{min} = 0.90$, $T_{max} = 0.98$	$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.121$	
$S = 1.08$	
3840 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
175 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}

The hydroxy H1O atom was located in a difference map and its position refined isotropically [$U_{iso}(H) = 1.2U_{eq}(O)$]. All other H

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1O$\cdots$N3	0.884 (17)	1.924 (18)	2.7711 (15)	159.9 (15)

atoms were placed in geometrically idealized positions, with C—H distances of 0.95 (aromatic) or 0.99 Å (methylene) [U_{iso}(H) = $1.2U_{eq}$(C)].

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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