

Tris(4-bromophenyl)aminium hexachloridoantimonate ('Magic Blue'): a strong oxidant with low inner-sphere reorganization

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Received 11 May 2010

Accepted 25 May 2010

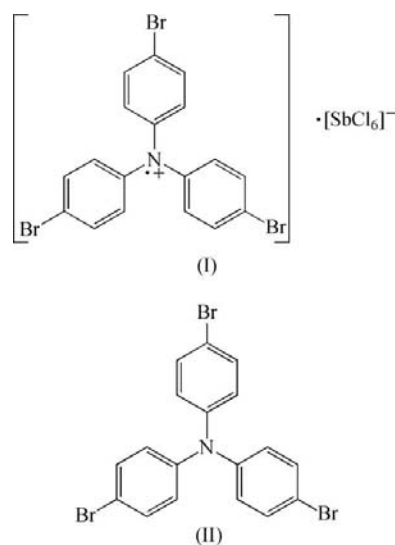
Online 5 June 2010

Both the radical cation tris(4-bromophenyl)aminium hexachloridoantimonate ('Magic Blue'), $(C_{18}H_{12}Br_3N)[SbCl_6]$, (I), and neutral tris(4-bromophenyl)amine, $C_{18}H_{12}Br_3N$, (II), show extremely similar three-bladed propeller structures with planar N atoms. Key geometric features, such as the C–N bond distances and the angles between the planes of the aryl groups and the central NC_3 plane, are identical within experimental uncertainty in the two structures. This contrasts with the significant structural changes observed on oxidation of more electron-rich triaryl amines, where resonance contributes to the stabilization of the radical cation, and suggests that, in general, more strongly oxidizing triarylaminium cations will have lower inner-sphere reorganization energies than their lower-potential analogues.

Comment

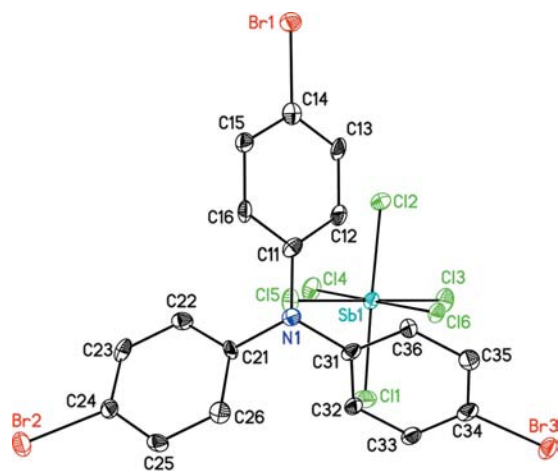
Triarylaminium cations, derived from oxidation of triaryl amines, have found extensive use as chemical oxidants because of their ease of preparation and their strong preference for undergoing simple outer-sphere electron-transfer reactions (Connelly & Geiger, 1996). The commercially available hexachloridoantimonate salt of the tris(4-bromophenyl)aminium cation, 'Magic Blue', has been especially widely used as a stoichiometric and catalytic oxidant (Dapperheld *et al.*, 1991) because of its stability and ease of preparation (Bell *et al.*, 1969) and its high redox potential, $E^{\circ} = 0.70$ V, versus ferrocene/ferrocenium (Connelly & Geiger, 1996). While a number of crystal structures of triarylaminium salts have been determined, no structural data on Magic Blue have been published. Only one structure of a comparably high-potential triarylaminium cation, that of the tris(2,4-dibromophenyl)aminium cation, has been reported, and interpretation of its metrical data is complicated by the fact that the aminium hexafluoroantimonate salt cocrystallizes with $HSbF_6$ (Murata *et al.*, 2004).

Tris(4-bromophenyl)aminium hexachloridoantimonate, (I), crystallizes from dichloromethane as very dark-blue plates. The aminium cation itself has a three-bladed propeller structure (Fig. 1) with a planar central N atom [sum of the angles around N = $360.0(7)^\circ$]. The hexachloridoantimonate anion has a regular octahedral structure, with an average Sb–Cl bond length of $2.371(9)$ Å. While there are no unusually short cation–anion contacts, the anion lies edge-on to the nearest cation, with one Cl atom above the central N atom [$N1 \cdots Cl5 = 3.533(4)$ Å] and one Cl atom above one of the aryl groups [e.g. $C34 \cdots Cl6 = 3.334(5)$ Å].



The reduced form of Magic Blue, *viz.* neutral tris(4-bromophenyl)amine, (II), was previously the subject of a unit-cell determination (Schlemper & Hausmann, 1963). Its molecular structure (Fig. 2) is also that of a three-bladed propeller with a planar central N atom. The propeller shape is typical of triaryl amines unless the benzene rings are constrained to lie roughly in the NC_3 plane by annulation (e.g. 2,2':6',2'':6'',6'-trioxytriphenylamine; Kuratsu *et al.*, 2005). An exception is seen in electronically unsymmetrical 'push–pull' triaryl amines, such as $(4-CH_3OC_6H_4)_2N(C_6H_4-4-COCH_3)$, where the electron-poor aryl ring is roughly coplanar with the NC_3 core in order to maximize electron donation from the central N atom by resonance (Lionetti *et al.*, 2010).

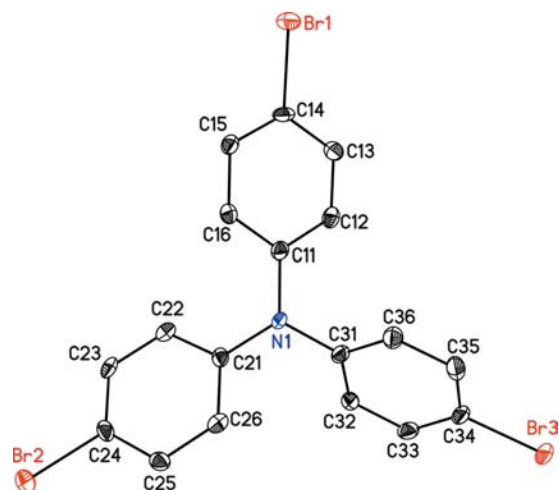
The most striking feature of the structures of the neutral and one-electron oxidized tris(4-bromophenyl)amines is that they are nearly identical (Table 1). While the C–N bond distances in the cation of (I) [mean C–N = $1.411(7)$ Å] are nominally shorter than the corresponding distances in the neutral molecule, (II) [$1.418(5)$ Å], the difference of 0.007 Å is not statistically significant. Even the angles by which the planes of the aryl groups are canted with respect to the central NC_3 plane do not vary significantly between the two structures [the mean dihedral angles are $36.7(17)$ and $35.8(14)^\circ$ in (I) and (II), respectively]. This pattern of extremely close structural correspondence is also observed in the 4-phenyl analogue, $(4-PhC_6H_4)_3N$, the neutral form (Inada *et al.*, 1994).


Figure 1

The structure of $[(4\text{-BrC}_6\text{H}_4)_3\text{N}]\text{SbCl}_6$, (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity, all H atoms have been omitted.

and radical cation (Brown *et al.*, 1977) of which have $\text{N}(\text{C}_6\text{H}_4\text{R})_3$ cores that are essentially identical both to each other and to the cores of (I) and (II).

In contrast, triaryl amines where the radical is stabilized by electron-donating groups do show noticeable structural changes on oxidation. In particular, the C–N bonds shorten by 0.02–0.03 Å on oxidation in triaryl amines with *ortho* or *para* oxygen (Kuratsu *et al.*, 2004, 2005, 2007), nitrogen (Hiraoka *et al.*, 2004), diarylamino phenyl (Low *et al.*, 2004) or diarylamino styryl (Zheng *et al.*, 2006) substituents. Other structural changes, such as increasing alignment of the plane of the electron-donating group with the central NC_3 plane, are also generally observed. These changes are rationalized on the basis of the lone pair on the electron-donating substituent *X* interacting with the triarylamine highest occupied molecular orbital (HOMO) to raise its energy and increase the C–N and C–*X* antibonding character of the HOMO. Oxidation removes an electron from this orbital, decreasing the C–N and C–*X* distances and fostering a planar quinonoid geometry (Lin *et al.*, 2003; Low *et al.*, 2004). The degree of structural rearrangement on oxidation is directly related to the inner-sphere reorganization energy (λ_{IS}), with large changes in bonding on electron transfer corresponding to large values of λ_{IS} . Indeed, diarylamino-substituted triaryl amines are calculated to have more than twice the reorganization energy of simple triaryl amines such as $(\text{C}_6\text{H}_5)_3\text{N}$ in the gas phase (Malagoli & Brédas, 2000; Lin *et al.*, 2003). The reorganization energies in turn have a direct impact on the rates of outer-sphere electron transfer, with lower values of λ corresponding to faster rates, except in reactions sufficiently energetically favourable as to be in the Marcus inverted region of electron transfer. Since low-potential triarylaminium cations are invariably stabilized by electron-donating substituents which induce structural reorganization on electron transfer, this leads to the suggestion that highly oxidizing triarylaminium cations such as Magic Blue are expected to be not only thermodynamically, but also kinetically, better oxidants than


Figure 2

The structure of $(4\text{-BrC}_6\text{H}_4)_3\text{N}$, (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity, all H atoms have been omitted.

their less oxidizing analogues. One factor that complicates this analysis is that it ignores the solvent, or outer-sphere, reorganization energy. Determination of whether that will also correlate with the extent of delocalization (and hence the redox potential) awaits the measurement of the reorganization energies of triaryl amines in solution.

Experimental

Tris(4-bromophenyl)aminium hexachloridoantimonate, (I), was purchased from Acros and was crystallized from anhydrous deuterio-dichloromethane at room temperature under nitrogen. Tris(4-bromophenyl)amine, (II), was purchased from Aldrich and was crystallized by liquid diffusion of methanol into a solution of the compound in chloroform.

Compound (I)

Crystal data

$(\text{C}_{18}\text{H}_{12}\text{Br}_3\text{N})[\text{SbCl}_6]$	$V = 4801.0 (3) \text{ \AA}^3$
$M_r = 816.47$	$Z = 8$
Orthorhombic, <i>Pbcn</i>	Mo $K\alpha$ radiation
$a = 17.4052 (7) \text{ \AA}$	$\mu = 6.82 \text{ mm}^{-1}$
$b = 16.4768 (7) \text{ \AA}$	$T = 100 \text{ K}$
$c = 16.7408 (7) \text{ \AA}$	$0.13 \times 0.13 \times 0.02 \text{ mm}$

Data collection

Bruker d8 APEXII CCD area-detector diffractometer	35891 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)	4956 independent reflections
$T_{\text{min}} = 0.478$, $T_{\text{max}} = 0.905$	3422 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.078$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	262 parameters
$wR(F^2) = 0.075$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.80 \text{ e \AA}^{-3}$
4956 reflections	$\Delta\rho_{\text{min}} = -1.01 \text{ e \AA}^{-3}$

Table 1

Comparison of selected bond lengths (Å) and angles (°) for (I) and (II).

	(I)	(II)
N1—C11	1.414 (6)	1.419 (4)
N1—C21	1.409 (6)	1.416 (4)
N1—C31	1.410 (6)	1.420 (4)
Br1—C14	1.901 (5)	1.891 (3)
Br2—C24	1.899 (5)	1.895 (3)
Br3—C34	1.900 (5)	1.893 (3)
C11—N1—C21	119.3 (4)	122.4 (3)
C11—N1—C31	119.6 (4)	118.2 (3)
C21—N1—C31	121.1 (4)	119.3 (3)

Compound (II)*Crystal data*

$C_{18}H_{12}Br_3N$	$V = 1633.5 (2) \text{ \AA}^3$
$M_r = 482.02$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.3970 (6) \text{ \AA}$	$\mu = 7.40 \text{ mm}^{-1}$
$b = 16.0352 (15) \text{ \AA}$	$T = 100 \text{ K}$
$c = 11.3688 (7) \text{ \AA}$	$0.17 \times 0.12 \times 0.10 \text{ mm}$
$\beta = 107.534 (4)^\circ$	

Data collection

Bruker d8 APEXII CCD area-detector diffractometer	13565 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)	3379 independent reflections
$T_{\min} = 0.366$, $T_{\max} = 0.525$	2692 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	199 parameters
$wR(F^2) = 0.064$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\text{max}} = 1.02 \text{ e \AA}^{-3}$
3379 reflections	$\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$

H atoms were placed in calculated positions and allowed to ride on their parent atoms, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* and *SAINTE* (Bruker, 2007); data reduction: *SAINTE* and *XPRED* (Bruker, 2007; Sheldrick, 2008b); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008b); molecular

graphics: *XP* in *SHELXTL* (Sheldrick, 2008b); software used to prepare material for publication: *XCIF* (Sheldrick, 2008b) and *pubCIF* (Westrip, 2010).

This research was supported by the Donors of the Petroleum Research Fund, administered by the American Chemical Society. The authors thank Dr Allen Oliver for technical assistance and helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3059). Services for accessing these data are described at the back of the journal.

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