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The Self-Condensation of a Derivative of *o*-Aminobenzaldehyde. Structure of the Polycyclic Bisanhydro Trimer of 2-Amino-5-bromobenzaldehyde

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Abstract

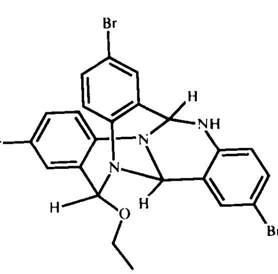
The structure of the title compound 6,14,22-tribromo-19-ethoxy-2,10,18-triazahexacyclo[18.4.0.-$0^{2,11}.0^{3,18}.0^{4,9}.0^{12,17}$]tetracosa-1(24),4(9),5,7,12(17),-13,15,20,22-nonaene monohydrate, $C_{23}H_{18}Br_3N_3O.H_2O$, a bisanhydro trimer hydrate formed from the acid-catalyzed self-condensation of 2-amino-5-bromobenzaldehyde, substantiates the geometry proposed for the similar trimer of *o*-aminobenzaldehyde (OAB). The tricyclic molecule is an ethoxy derivative rather than a hydroxy derivative as previously observed with OAB. Formation of the ethoxy derivative is a direct result of the condensation reaction having been carried out in ethanol. A water molecule of crystallization appears to be strongly hydrogen bonded to one N atom (O—H···N 2.88 Å) and weakly hydrogen bonded to the protonated N atom (N—H···O 3.28 Å).

Comment

The polymeric self-condensation products of *o*-aminobenzaldehyde have been a subject of interest for over 60 years due to the fact that the character of the polymer is strongly dependent upon the experimental reaction conditions. A bisanhydro trimer and a trisanhydro tetramer are formed in the solid state during storage (Seidel & Dick, 1927) though the trimer alone can be obtained through the action of weak or dilute acids (Bamberger, 1927; Seidel, 1926). Strong mineral acids give the bright red tetracondensate as a protonated salt, which is converted slowly to the anhydro tetramer in aqueous media (Seidel & Dick, 1927). In the presence of metal ions, however, an assortment of condensates are observed.

Depending on the coordination preference of the metal ion, the Schiff base ligands tribenzo-[*b,f,j*][1,5,9]triazacyclododecatriene, known as TRI (a trimer), and/or tetrabenzo[*b,f,j,n*][1,5,9,13]tetra-azacyclohexadecatetraene, known as TAAB (a tetramer), are isolated as the metal complex (Skuratowicz, Madden & Busch, 1977). The diacid salt can also function as a precursor to TAAB in reactions with metal acetates (Skuratowicz, Madden & Busch, 1977). Ring substituents have a marked effect on condensation products; for example, condensation of the 5-chloro derivative in the presence of nickel(II) produces Ni(5-Cl TRI) only, with no evidence of the 5-Cl TAAB derivative (Taylor & Busch, 1969). The diacid salt obtained from 2-amino-5-methylbenzaldehyde and HBF_4 gives $Cu(TRI)^{2+}$ as well as $Cu(TAAB)^{2+}$ when reacted with copper acetate (Jircitano, Sheldon & Mertes, 1983). Structures have been proposed for all the condensates based on spectroscopic evidence (McGeachin, 1966; Albert & Yamamoto, 1966; Skuratowicz, Madden & Busch, 1977) and X-ray analyses have corroborated the assigned structures of both the metal complexes and, more recently, several diacid salts (Fleischer & Klem, 1965; Hawkinson & Fleischer, 1969; Owston, Shaw & Tasker, 1982; Owston & Shaw, 1988). Structural characterization of the metal-free condensates, however, can be difficult due to the rapid interconversion.

In order to investigate how condensation is influenced by the steric and electronic nature of ring substituents, we have synthesized a variety of new *o*-aminobenzaldehydes. In an attempt to prepare $Nd(5\text{-}BrTAAB)^{3+}$, the 5-bromo derivative was allowed to react with $Nd(NO_3)_3$ in ethanol. Slow evaporation of the ethanol solvent yielded light yellow crystals which contained no metal ion. Elemental and infrared analysis suggested that the ethanol adduct of the bisanhydro trimer (I) was



(I)

formed under these conditions instead of the Schiff base complex. The crystal structure reported herein supports this assignment. Furthermore, this is the first X-ray structural analysis to substantiate the structure of the bisanhydro trimer of a derivative of aminobenzaldehyde.

The crystals were found to contain a tricyclic trimer with an ethoxy group bonded to C1 rather than a hydroxy group as found in the trimer of *o*-aminobenzaldehyde isolated from weak acid solution. The presence of the ethoxy function could be the result of hemiacetal formation during the reflux of the aminobenzaldehyde in ethanol with the Nd^{3+} acting as a Lewis acid. In the proposed mechanism for the formation of the trimer, a cyclic Schiff base dimer is formed initially and undergoes addition of the amine of a third molecule of OAB at both imine C atoms while one imine N atom attacks the aldehyde. Attack on a hemiacetal with loss of water would indeed give the ethoxy derivative.

Bond distances and angles are quite regular within the molecule with average C—C distances of 1.37 (3) Å in the three benzene rings. The rings are planar with a maximum deviation of ±0.038 Å. The molecule is well ordered, with only atom C5 at the end of the ethoxy group and the water molecule of crystallization showing, not unexpectedly, relatively large thermal motion. The fused C_4N_2 rings have a twisted boat configuration as evidenced by deviations from the mean plane calculated for the six atoms. The water molecule of crystallization appears to be hydrogen bonded to N1 at a distance of 2.88 Å and possibly interacts with the N2 H atom, but only at the limit of interaction, 3.2 Å (Stout & Jensen, 1968).

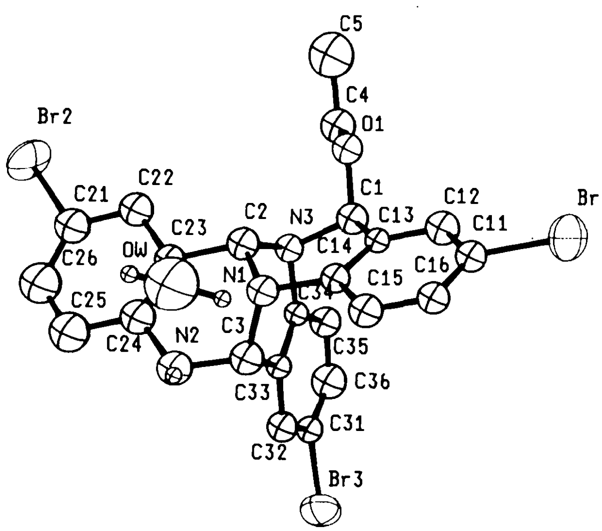


Fig. 1. View of the molecule showing the numbering of the atoms.

Experimental

Crystal data

$C_{23}H_{18}Br_3N_3O.H_2O$
M_r = 610.17
Orthorhombic
Pbca
a = 20.935 (3) Å
b = 22.391 (3) Å
c = 9.756 (3) Å
V = 4573 (1) Å^3
Z = 8
D_x = 1.772 Mg m^{-3}
D_m = 1.72 (1) Mg m^{-3}
D_m measured by flotaion in CH_2BrCH_2Br/C_6H_{14}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 7.32–9.92°
μ = 5.19 mm^{-1}
T = 293 K
Plate
0.60 × 0.30 × 0.08 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: none
2953 measured reflections
2181 independent reflections
1213 observed reflections [$I \geq 2\sigma(I)$]

θ_{max} = 22°
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 10$
3 standard reflections frequency: 100 min intensity variation: 2.99%

Refinement

Refinement on F
R = 0.0830
wR = 0.0895
S = 0.9352
1213 reflections
140 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.012478F^2]$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −0.94 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

B_{iso} for C, N and O; $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$ for Br atoms.

	x	y	z	B_{iso}/B_{eq}
Br1	0.3435 (1)	0.3158 (1)	0.7536 (1)	7.22 (9)
Br2	−0.1884 (1)	0.3916 (1)	0.3611 (1)	6.65 (9)
Br3	0.2072 (1)	0.5055 (1)	−0.0741 (1)	6.80 (10)
C11	0.2705 (9)	0.3152 (9)	0.6342 (9)	2.6 (4)
C12	0.2250 (9)	0.3622 (9)	0.6483 (9)	3.1 (4)
C13	0.1737 (8)	0.3608 (8)	0.5626 (8)	1.9 (3)
C14	0.1660 (9)	0.3143 (9)	0.4696 (9)	2.6 (4)
C15	0.2160 (10)	0.2712 (9)	0.4581 (9)	3.7 (4)
C16	0.2656 (9)	0.2737 (9)	0.5419 (9)	3.6 (5)
C21	−0.1064 (10)	0.3639 (9)	0.2923 (9)	3.9 (5)
C22	−0.0560 (10)	0.3658 (9)	0.3855 (9)	3.8 (5)
C23	0.0029 (9)	0.3451 (9)	0.3354 (9)	3.4 (4)
C24	0.0088 (10)	0.3236 (9)	0.2063 (9)	3.7 (5)
C25	−0.0460 (12)	0.3212 (10)	0.1149 (10)	4.5 (5)
C26	−0.1022 (12)	0.3427 (10)	0.1634 (10)	5.0 (6)
C31	0.1676 (9)	0.4748 (9)	0.0899 (9)	2.7 (4)
C32	0.1563 (9)	0.4157 (9)	0.0977 (9)	3.0 (4)
C33	0.1312 (9)	0.3938 (9)	0.2187 (9)	2.4 (4)
C34	0.1124 (9)	0.4332 (9)	0.3207 (9)	2.3 (4)
C35	0.1268 (9)	0.4936 (9)	0.3081 (9)	3.6 (4)
C36	0.1542 (10)	0.5141 (10)	0.1874 (10)	4.3 (5)
C1	0.1288 (9)	0.4123 (9)	0.5620 (9)	3.1 (4)
C2	0.0606 (9)	0.3499 (9)	0.4316 (9)	3.2 (4)
C3	0.1206 (10)	0.3245 (9)	0.2392 (9)	3.5 (4)
C4	0.0578 (12)	0.4686 (10)	0.7109 (10)	4.8 (6)
C5	0.0232 (13)	0.4622 (13)	0.8411 (13)	7.0 (7)
N1	0.1105 (8)	0.3105 (6)	0.3825 (6)	3.2 (3)
N2	0.0684 (8)	0.3029 (8)	0.1598 (8)	3.8 (4)

N3	0.0837 (8)	0.4111 (6)	0.4459 (6)	3.0 (3)
O1	0.0929 (6)	0.4130 (5)	0.6880 (5)	3.4 (3)
OW	0.0736 (9)	0.1868 (9)	0.3648 (9)	8.2 (5)

Table 2. *Bond distances* (Å) *and angles* (°)

C11—C12	1.43 (3)	C31—C32	1.35 (3)
C12—C13	1.36 (3)	C32—C33	1.38 (3)
C13—C14	1.39 (3)	C33—C34	1.39 (3)
C14—C15	1.43 (3)	C34—C35	1.39 (3)
C15—C16	1.32 (3)	C35—C36	1.39 (3)
C11—C16	1.30 (3)	C31—C36	1.33 (3)
C1—C13	1.49 (3)	C3—C33	1.58 (3)
N1—C14	1.44 (3)	N3—C34	1.45 (3)
C11—Br1	1.92 (2)	C31—Br3	1.93 (3)
C21—C22	1.39 (3)	C1—N3	1.47 (3)
C22—C23	1.41 (3)	C1—O1	1.44 (3)
C23—C24	1.35 (3)	O1—C4	1.46 (3)
C24—C25	1.45 (3)	C4—C5	1.47 (3)
C25—C26	1.36 (3)	C2—N1	1.45 (3)
C21—C26	1.35 (3)	C2—N3	1.46 (3)
C2—C23	1.53 (3)	C3—N1	1.45 (3)
N2—C24	1.41 (3)	C3—N2	1.43 (3)
C21—Br2	1.95 (2)		
Br1—C11—C16	119 (2)	C31—C36—C35	119 (2)
Br1—C11—C12	118 (1)	C32—C31—C36	125 (2)
Br2—C21—C22	116 (2)	C32—C33—C3	121 (2)
Br2—C21—C26	119 (2)	C33—C32—C31	118 (2)
Br3—C31—C32	118 (2)	C33—C34—N3	120 (2)
Br3—C31—C36	117 (2)	C34—C33—C32	120 (2)
C11—C16—C15	121 (2)	C34—N3—C2	112 (2)
C12—C13—C1	119 (2)	C34—N3—C1	112 (2)
C12—C11—C16	123 (2)	C35—C34—C33	119 (2)
C13—C14—N1	121 (2)	C35—C34—N3	120 (2)
C13—C1—O1	110 (2)	C36—C35—C34	119 (2)
C13—C12—C11	117 (2)	C1—C13—C14	120 (2)
C14—N1—C2	111 (2)	C1—O1—C4	114 (2)
C14—C13—C12	121 (2)	C2—C23—C24	121 (2)
C15—C14—C13	118 (2)	C2—C23—C22	117 (2)
C15—C14—N1	120 (2)	C2—N3—C1	108 (1)
C16—C15—C14	120 (2)	C3—C33—C34	119 (2)
C21—C26—C25	120 (3)	C3—N1—C2	107 (2)
C22—C21—C26	125 (2)	C3—N1—C14	116 (2)
C23—C22—C21	115 (2)	N1—C2—C23	109 (2)
C23—C2—N3	113 (2)	N1—C2—N3	111 (2)
C23—C24—N2	120 (2)	N1—C3—C33	111 (2)
C24—C23—C22	121 (2)	N2—C3—N1	110 (2)
C24—N2—C3	113 (2)	N2—C3—C33	112 (2)
C25—C24—C23	121 (2)	N2—C24—C25	119 (2)
C26—C25—C24	117 (2)	N3—C1—C13	113 (2)
O1—C4—C5	107 (2)	N3—C1—O1	109 (2)

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Lists of structure factors, anisotropic displacement parameters for the Br atoms and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71452 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1063]

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Structure of Neostrychnine. An Enamine with a Bridgehead Nitrogen which Undergoes Efficient Chemical Reaction with Singlet Oxygen

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Abstract

Neostrychnine, 20,21-didehydro-21,22-dihydrostrychnidin-10-one, $C_{21}H_{22}N_2O_2$, contains an alicyclic enamine unit in which the N atom is located at a bridgehead, a fact of critical importance to an understanding of the manner in which it reacts with potential electrophiles, including singlet oxygen, $O_2(^1\Delta_g)$. The X-ray structure shows that the steric constraints within the σ framework demand a high degree of pyramidalization of the N atom, which is independent of the fact that this atom is part of an enamine system. These data support the conclusion that the formation of an immonium species with a double bond at the N atom is likely to be highly unfavourable.

Comment

The mechanism of chemical reaction of singlet oxygen, $O_2(^1\Delta_g)$, with electron-rich double bonds,