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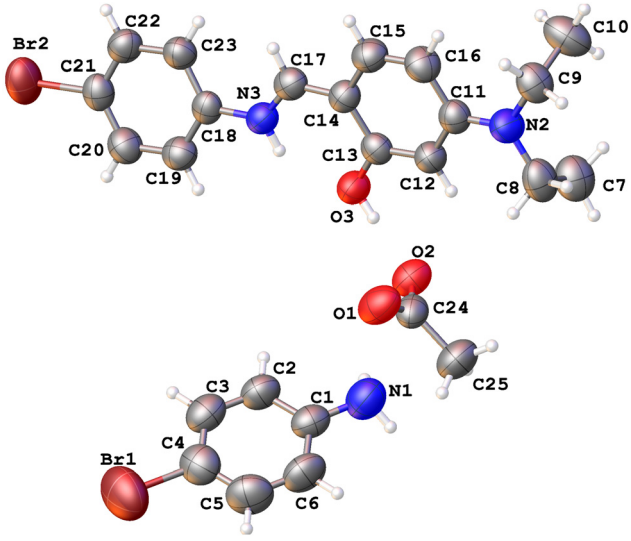
Crystal structure of a (*E*)-4-bromo-*N*-(4-(diethylamino)-2-hydroxybenzylidene) benzenaminium acetate — 4-bromoaniline (1/1)



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Abstract

$C_{25}H_{29}Br_2N_3O_3$, orthorhombic, *Pbca* (61), a = 20.109(5) Å, b = 10.754(5) Å, c = 24.321(5) Å, V = 5,259(3) Å^3, Z = 8, $R_{gt}(F)$ = 0.0464, w$R_{ref}(F^2)$ = 0.1156, T = 295 K.

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A part of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Orange needle
Size:	0.26 × 0.18 × 0.13 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	3.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	62,620, 5,175, 0.068
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,802
$N(param)_{refined}$:	353
Programs:	Olex2,[1,2] SHELX,[3] Mercury[4]

1 Source of material

The titled compound was prepared by adding 6–7 drops of glacial acetic acid to methanolic solution of 4-(diethylamino)salicylaldehyde (0.3 g, 1.5 mmol) and 4-bromoaniline (0.27 g, 1.5 mmol) and the resultant mixture was stirred at room temperature for 12 h. Rotary evaporator was used to remove methanol from the solution to afford an orange crude product. Slow evaporation of dichloromethane solution of the compound yielded mainly yellow block-like crystals of (*E*)-2-((4-bromophenylimino)methyl)-5-(diethylamino)phenol and few orange needle crystals of the title compound.

2 Experimental details

Using Olex2,[1] the structure was solved with the SHELXT[3] structure solution program and refined with the olex2.refine[2] refinement package using Gauss–Newton minimisation. The visual crystal structure information was performed using *Mercury*[4] system software.

3 Comment

A renowned German scientist and a Nobel Prize awardee, Hugo Schiff, firstly discovered Schiff bases in 1864[5] and till date, these compounds are being explored by researchers in various fields.[6] In coordination chemistry, Schiff bases are

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.48429 (8)	0.74278 (14)	0.40079 (6)	0.1522 (8)
N1	0.52520 (18)	0.7484 (3)	0.64863 (13)	0.1010 (12)
H1a	0.4922 (7)	0.784 (2)	0.6646 (2)	0.1211 (14)*
H1b	0.5290 (14)	0.6736 (4)	0.66070 (17)	0.1211 (14)*
C1	0.51439 (19)	0.7463 (4)	0.59187 (18)	0.0731 (10)
C2	0.54121 (19)	0.6535 (4)	0.55945 (18)	0.0798 (11)
H2	0.56544 (19)	0.5899 (4)	0.57586 (18)	0.0958 (13)*
C3	0.5327 (2)	0.6536 (4)	0.5032 (2)	0.0863 (12)
H3b	0.5516 (2)	0.5906 (4)	0.4821 (2)	0.1035 (14)*
C4	0.4966 (2)	0.7462 (5)	0.47801 (19)	0.0904 (13)
C5	0.4696 (2)	0.8396 (4)	0.5098 (2)	0.1039 (15)
H5	0.4453 (2)	0.9029 (4)	0.4933 (2)	0.1246 (18)*
C6	0.4787 (2)	0.8395 (4)	0.5661 (2)	0.0920 (13)
H6	0.4605 (2)	0.9034 (4)	0.5870 (2)	0.1104 (16)*
Br2	0.73770 (6)	−0.30466 (9)	0.50363 (4)	0.0980 (6)
O1	0.57549 (14)	0.5268 (3)	0.70577 (12)	0.0967 (9)
O2	0.55573 (12)	0.3728 (2)	0.76409 (10)	0.0772 (7)
O3	0.65715 (12)	0.2657 (2)	0.73219 (10)	0.0677 (7)
H3	0.62489 (17)	0.306 (2)	0.7424 (14)	0.1016 (10)*
N2	0.76822 (15)	0.5675 (3)	0.84425 (13)	0.0741 (9)
N3	0.73015 (14)	0.1122 (3)	0.67233 (10)	0.0612 (7)
H3a	0.69096 (14)	0.1349 (3)	0.68230 (10)	0.0735 (9)*
C7	0.6750 (2)	0.5462 (4)	0.90902 (17)	0.0999 (14)
H7a	0.6687 (14)	0.4619 (8)	0.8971 (4)	0.150 (2)*
H7b	0.7044 (7)	0.548 (2)	0.9401 (5)	0.150 (2)*
H7c	0.6328 (7)	0.5813 (17)	0.9192 (9)	0.150 (2)*
C8	0.7044 (2)	0.6202 (4)	0.86348 (16)	0.0866 (12)
H8a	0.7116 (2)	0.7049 (4)	0.87595 (16)	0.1039 (15)*
H8b	0.6733 (2)	0.6229 (4)	0.83300 (16)	0.1039 (15)*
C9	0.8286 (2)	0.6246 (3)	0.86756 (15)	0.0792 (11)
H9a	0.8623 (2)	0.6298 (3)	0.83908 (15)	0.0951 (13)*
H9b	0.8183 (2)	0.7087 (3)	0.87926 (15)	0.0951 (13)*
C10	0.8564 (2)	0.5540 (4)	0.91539 (18)	0.1021 (14)
H10a	0.8674 (14)	0.4711 (10)	0.9040 (3)	0.153 (2)*
H10b	0.8957 (9)	0.5950 (17)	0.9286 (8)	0.153 (2)*
H10c	0.8238 (6)	0.551 (2)	0.9443 (5)	0.153 (2)*
C11	0.76977 (18)	0.4710 (3)	0.80829 (14)	0.0632 (9)
C12	0.71136 (18)	0.4148 (3)	0.78867 (13)	0.0620 (9)
H12	0.67052 (18)	0.4436 (3)	0.80127 (13)	0.0744 (11)*
C13	0.71250 (18)	0.3177 (3)	0.75118 (13)	0.0571 (8)
C14	0.77492 (17)	0.2709 (3)	0.73180 (14)	0.0589 (9)
C15	0.83348 (19)	0.3282 (3)	0.75223 (15)	0.0713 (10)
H15	0.87455 (19)	0.2996 (3)	0.74002 (15)	0.0855 (12)*
C16	0.83181 (19)	0.4235 (3)	0.78904 (15)	0.0721 (10)
H16	0.87136 (19)	0.4580 (3)	0.80173 (15)	0.0865 (12)*
C17	0.78055 (18)	0.1729 (3)	0.69465 (14)	0.0628 (9)
H17	0.82321 (18)	0.1482 (3)	0.68473 (14)	0.0754 (11)*
C18	0.73383 (18)	0.0136 (3)	0.63366 (13)	0.0566 (9)
C19	0.67542 (18)	−0.0229 (3)	0.60745 (14)	0.0688 (10)
H19	0.63552 (18)	0.0163 (3)	0.61599 (14)	0.0826 (12)*
C20	0.6765 (2)	−0.1173 (3)	0.56875 (15)	0.0730 (10)
H20	0.6375 (2)	−0.1414 (3)	0.55113 (15)	0.0875 (12)*
C21	0.7356 (2)	−0.1747 (3)	0.55667 (13)	0.0656 (9)
C22	0.7937 (2)	−0.1410 (3)	0.58246 (15)	0.0692 (10)
H22	0.8333 (2)	−0.1808 (3)	0.57360 (15)	0.0831 (12)*
C23	0.79310 (19)	−0.0472 (3)	0.62183 (14)	0.0656 (10)
H23	0.83203 (19)	−0.0253 (3)	0.64007 (14)	0.0787 (11)*
C24	0.54435 (18)	0.4819 (4)	0.74432 (15)	0.0666 (10)
C25	0.4910 (2)	0.5558 (4)	0.77283 (19)	0.0969 (14)
H25a	0.4598 (8)	0.5001 (4)	0.7896 (10)	0.145 (2)*
H25b	0.5109 (3)	0.607 (2)	0.8006 (8)	0.145 (2)*
H25c	0.4684 (10)	0.607 (2)	0.7465 (3)	0.145 (2)*

regarded as one of the major class of ligands due to their ability to coordinate with almost all transition metal ions via imine nitrogen to form complexes.[7] Aside their great coordinating progress, they are also readily available due to their simple method of preparation.[8] Schiff bases are often prepared by the condensation reaction of primary amines with carbonyl compounds (aldehyde or ketones) at appropriate reaction conditions.[9] They have been tested as anticancer, antioxidants, antidiabetics and antimicrobial agents.[10,11]

The crystal structure of the title compound includes three distinct molecular species in the asymmetric unit: a cationic (*E*)-4-bromo–N-(4-(diethylamino)benzylidene)benzenaminium, an acetate counterion, and 4-bromoaniline. The solid-state conformation of this protonated Schiff base is nearly planar, as indicated by the dihedral angle of 11.7(1)° between the two phenyl rings. This angle is significantly narrower than those observed in the neutral Schiff bases (*E*)-2-((4-bromophenylimino)methyl)-5-(diethylamino)phenol (30.31(6)°–32.44(6)°)[12] and (*E*)-4-(((4-bromophenyl)imino) methyl)–N,N-diethylaniline (60.4(2)°–61.1(1)°).[13] The reduced dihedral angle in the title compound may be attributed to intramolecular N–H···O hydrogen bonding between the iminium group's H3a atom and the adjacent hydroxyl group's O36 atom. Nonetheless, other intramolecular bond parameters in both the protonated (this work) and neutral Schiff bases remain similar.[12–14] An analysis of intermolecular interactions in the crystal packing of the title compound reveals that the H1a and H1b atoms of the 4-bromoaniline's amino group interact with the O2 and O1 atoms of the neighbouring acetate molecule via N1–H1a···O2 and N1–H2a···O1 hydrogen bonds, respectively. Additionally, intermolecular O–H···O hydrogen bonds form between the H3 atom of the protonated Schiff base's hydroxyl group and the O2 atom of the acetate molecule. These intermolecular hydrogen bonding patterns result in a one-dimensional, zigzag supramolecular structure extending along the crystallographic *b* axis.

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