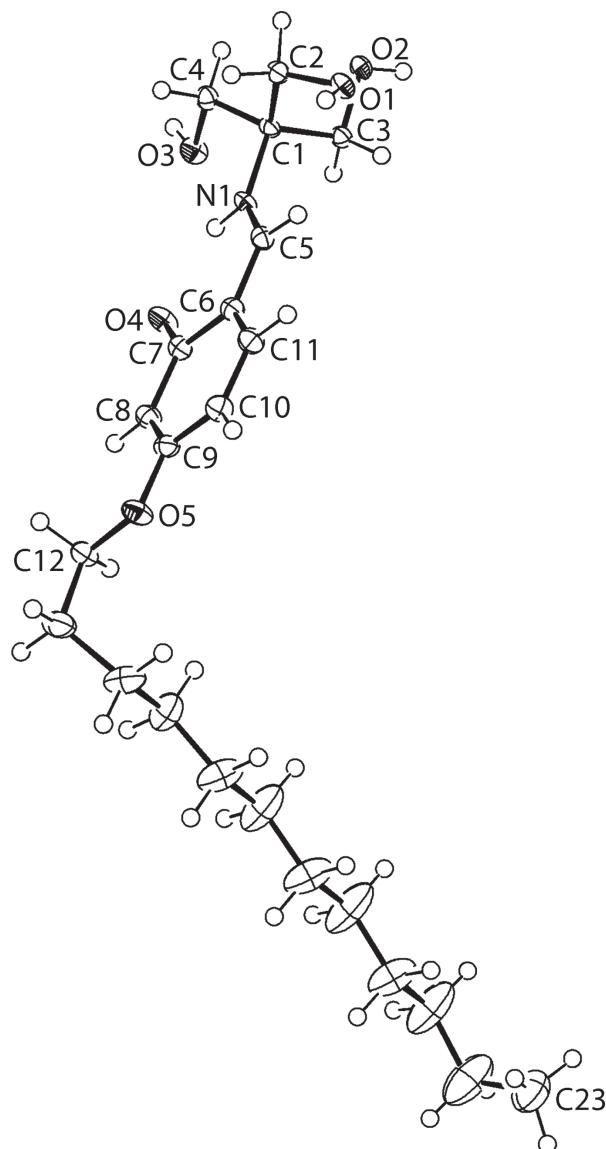


See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Crystal structure of 2-[(1*E*)-{[1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]iminiumyl}methyl]-5-(dodecyloxy)benzen-1-olate, C₂₃H₃₉NO₅



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Abstract

C₂₃H₃₉NO₅, monoclinic, *P*2₁/c (no. 14), *a* = 26.1698(4) Å, *b* = 9.4863(2) Å, *c* = 9.0929(2) Å, β = 97.376(2)°, *V* = 2238.67(8) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0539, *wR*_{ref}(*F*²) = 0.1580, *T* = 100(2) K.

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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.

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.13 × 0.03 × 0.02 mm
Wavelength:	Cu $\text{K}\alpha$ radiation (1.54184 Å)
μ :	0.68 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.0°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	27272, 4004, 0.040
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 3452
<i>N</i> (<i>param</i>) _{refined} :	275
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The melting point of the compound was measured on a Mel-Temp II digital melting point apparatus and was uncorrected. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer as a Nujol mull in a KBr cell from 4000 to 400 cm⁻¹. The ¹H NMR spectrum was recorded in CDCl₃ solution on a Jeol JNM-ECA 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

4-Dodecyloxy-2-hydroxybenzaldehyde was synthesized according to a literature procedure [5]. The prepared aldehyde (0.31 g, 1.0 mmol) was added to an ethanolic solution (10 mL) of tris(hydroxymethyl)aminomethane (Tokyo

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. <https://orcid.org/0000-0003-1401-1520>

See Mun Lee and Kong Mun Lo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */* <i>U</i> _{eq}
O1	0.89812(5)	1.10031(14)	0.50569(14)	0.0184(3)
H1O	0.8900(9)	1.055(2)	0.4268(18)	0.028*
O2	0.93683(5)	1.17452(14)	0.86963(15)	0.0192(3)
H2O	0.9203(9)	1.236(2)	0.911(3)	0.029*
O3	0.97309(5)	0.82780(15)	0.93578(15)	0.0231(3)
H3O	1.0012(6)	0.829(3)	0.991(3)	0.035*
O4	0.87899(6)	0.57144(14)	0.78365(15)	0.0230(3)
O5	0.75800(6)	0.30758(15)	0.45315(16)	0.0247(3)
N1	0.89831(6)	0.83173(16)	0.70445(17)	0.0160(3)
H1N	0.9040(9)	0.7597(17)	0.764(2)	0.019*
C1	0.93071(7)	0.95905(19)	0.7299(2)	0.0146(4)
C2	0.94145(7)	1.0290(2)	0.5849(2)	0.0172(4)
H2A	0.9698	1.0977	0.6078	0.021*
H2B	0.9534	0.9558	0.5195	0.021*
C3	0.90380(7)	1.05744(19)	0.8288(2)	0.0166(4)
H3A	0.8708	1.0908	0.7747	0.020*
H3B	0.8964	1.0065	0.9187	0.020*
C4	0.98251(7)	0.9067(2)	0.8083(2)	0.0182(4)
H4A	0.9997	0.8465	0.7405	0.022*
H4B	1.0053	0.9878	0.8385	0.022*
C5	0.86144(7)	0.8098(2)	0.5962(2)	0.0170(4)
H5	0.8521	0.8854	0.5296	0.020*
C6	0.83438(7)	0.6815(2)	0.5712(2)	0.0172(4)
C7	0.84556(7)	0.5621(2)	0.6670(2)	0.0174(4)
C8	0.81897(8)	0.4341(2)	0.6276(2)	0.0195(4)
H8	0.8253	0.3535	0.6892	0.023*
C9	0.78412(7)	0.4261(2)	0.5006(2)	0.0189(4)
C10	0.77303(8)	0.5445(2)	0.4064(2)	0.0212(4)
H10	0.7487	0.5375	0.3197	0.025*
C11	0.79790(8)	0.6684(2)	0.4427(2)	0.0204(4)
H11	0.7906	0.7480	0.3801	0.024*
C12	0.76677(8)	0.1823(2)	0.5427(2)	0.0238(5)
H12A	0.7570	0.1989	0.6428	0.029*
H12B	0.8036	0.1557	0.5530	0.029*
C13	0.73421(9)	0.0668(2)	0.4658(3)	0.0323(5)
H13A	0.7410	-0.0217	0.5226	0.039*
H13B	0.7448	0.0519	0.3662	0.039*
C14	0.67641(9)	0.0967(3)	0.4485(3)	0.0383(6)
H14A	0.6697	0.1840	0.3894	0.046*
H14B	0.6583	0.0187	0.3911	0.046*
C15	0.65341(9)	0.1135(3)	0.5903(3)	0.0396(6)
H15A	0.6655	0.0345	0.6570	0.048*
H15B	0.6668	0.2018	0.6388	0.048*
C16	0.59630(10)	0.1175(4)	0.5752(3)	0.0480(7)
H16A	0.5848	0.1952	0.5063	0.058*
H16B	0.5835	0.0287	0.5264	0.058*
C17	0.57043(11)	0.1349(4)	0.7065(4)	0.0597(9)
H17A	0.5798	0.2295	0.7474	0.072*
H17B	0.5857	0.0654	0.7806	0.072*
C18	0.51451(11)	0.1220(4)	0.6989(3)	0.0540(8)
H18A	0.4994	0.1906	0.6234	0.065*
H18B	0.5054	0.0271	0.6585	0.065*
C19	0.48748(11)	0.1401(5)	0.8267(4)	0.0707(11)
H19A	0.4950	0.2370	0.8636	0.085*
H19B	0.5040	0.0754	0.9041	0.085*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */* <i>U</i> _{eq}
C20	0.43222(10)	0.1204(4)	0.8214(3)	0.0542(8)
H20A	0.4244	0.0245	0.7820	0.065*
H20B	0.4156	0.1872	0.7464	0.065*
C21	0.40593(12)	0.1355(5)	0.9530(4)	0.0708(11)
H21A	0.4110	0.2342	0.9872	0.085*
H21B	0.4245	0.0751	1.0311	0.085*
C22	0.35122(12)	0.1044(5)	0.9484(4)	0.0739(12)
H22A	0.3420	0.1169	1.0499	0.089*
H22B	0.3461	0.0035	0.9228	0.089*
C23	0.31410(12)	0.1865(4)	0.8462(4)	0.0554(8)
H23A	0.3146	0.2851	0.8784	0.083*
H23B	0.2794	0.1477	0.8466	0.083*
H23C	0.3237	0.1812	0.7456	0.083*

Chemical Industry, 0.12 g, 1.0 mmol) and refluxed for 3 h. The filtrate was evaporated slowly until a yellow precipitate was formed. The precipitate was recrystallized from methanol-hexane by slow evaporation to yield yellow crystals. Yield: 0.16 g (39.1%). **M.pt:** 383–384 K. **IR** (cm⁻¹) 3233 (br) v(O—H), 1634 (s) v(C—N), 1525 (s) v(C—O), 1047 (s) v(C—O), 1016 (m) v(C—O). **¹H NMR** (CDCl₃, ppm): δ 0.86 (s, 3H, CH₃), 1.24–1.79 (m, 20H, CH₂), 3.70–4.00 (m, 8H, OCH₂), 6.40 (d, 1H, Ph—H), 6.51 (d, 1H, Ph—H), 7.37 (1H, Ph—H), 8.41 (s, 1H, N=CH); OH and NH protons were not observed.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C). The O- and N-bound H-atoms were located in a difference Fourier map but were refined with distance restraints of O—H = 0.84±0.01 Å and N—H = 0.88±0.01 Å, respectively, and with *U*_{iso}(H) set to 1.5*U*_{eq}(O) and 1.2*U*_{eq}(N), respectively. As evident from the figure, the long chain suffers from typical disorder. Careful modelling did not reveal any chemically useful information and so, the simpler model was retained.

Comment

In connection with recent studies of diorganotin Schiff bases derived from tris[(hydroxymethyl)aminomethane] [6, 7], largely motivated by the promising cytotoxicities they exhibit [6], the structure of the title tris[(hydroxymethyl)aminomethane] Schiff base derivative, featuring an appended *n*-dodecyl substituent, was prepared and studied crystallographically.

The molecular structure is shown in the figure (50% displacement ellipsoids) and crystallography confirms the molecule existing as a zwitterion in the solid-state.

Proton transfer has occurred from the phenol group to the imine-nitrogen atom (see the figure). An intramolecular, charge-assisted medium-strong imine-N—H···O (phenoxide) hydrogen bond is evident [N1—H1n···O4: H1n···O4 = 1.918(17) Å, N1···O4 = 2.639(2) Å with angle at H1n = 138.9(19)°]. The C5—N1 imine bond length is 1.303(3) Å and the configuration about this bond is *E*. The imine residue is co-planar with the phenyl ring to which it is connected with the N1—C5—C6—C11 and N1—C5—C6—C7 torsion angles being −175.12(18) and 0.5(3)°, respectively. The alpha-methylene atom of the *n*-dodecyl chain is co-planar with the phenyl ring as seen in the values of the C12—O5—C9—C8 and C12—O5—C9—C10 torsion angles of 0.9(3) and −179.71(17)°, respectively. A kink is then evident in the chain with the O5—C12—C13—C14 and C12—C13—C14—C15 torsion angles of −61.5(2) and −61.9(3)°, respectively, being indicative of *–syn*-clinal conformations. The remaining methylene atoms of the chain have an almost all-trans conformation with the maximum deviation in torsion angles being −169.7(2)°, for C13—C14—C15—C16.

There is a single literature precedent for the structure reported herein, that is, with a methyl rather than a *n*-dodecyl substituent [8]. This is also zwitterionic and was characterised as a monohydrate.

In the crystal, the O1-hydroxy group forms a charge-assisted hydrogen bond with the phenoxide-O atom [O1—H1o···O4ⁱ: H1o···O4ⁱ = 1.766(18) Å, O1···O4ⁱ = 2.5927(19) Å with angle at H1o = 167.5(18)° for symmetry operation (i) $x, 3/2 - y, -1/2 + z$] while the other hydroxy groups participate in hydroxy—O—H···O(hydroxy) hydrogen bonds [O2—H2o···O1ⁱⁱ: H2o···O1ⁱⁱ = 1.90(2) Å, O2···O1ⁱⁱ = 2.7279(19) Å with angle at H2o = 166(2)° and O3—H3o···O2ⁱⁱⁱ: H3o···O2ⁱⁱⁱ = 1.93(2) Å, O3···O2ⁱⁱⁱ = 2.7600(19) Å with angle at H3o = 176(3)° for (ii) $x, 5/2 - y, 1/2 + z$ and (iii) $2 - x, 2 - y, 2 - z$]. The molecules assemble head-to-head to form a bi-layer, in the *bc*-plane, sustained by the aforementioned hydrogen bonding interactions. This allows for the inter-digitation of the *n*-dodecyl chains.

Using established procedures [9] and Crystal Explorer 17 [10], the calculated Hirshfeld surfaces were analysed as were the full and delineated two-dimensional fingerprint plots. The presence of multiple conventional hydrogen bonding interactions is reflected in a significant contribution of H···O/O···H contacts, that is, 15.4% to the overall surface.

This notwithstanding, by far the greatest contribution is made by H···H contacts, at 72.9%, reflecting the hydrophobic interactions in the inter-layer region. The only other contribution to the surface contacts of note are from H···C/C···H contacts of 10.9%, which arise largely from methylene-C3—H··· π (phenyl) and methyl-C23—H··· π (phenyl) interactions within the bi-layer constructed from the O—H···O hydrogen bonding.

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