Crystal structure of 3,3′-[2,2′-(1,2-ethylenedioxy)dibenzyl-methylimino]bis(acetophenone oxime), $C_{32}H_{30}N_4O_4$

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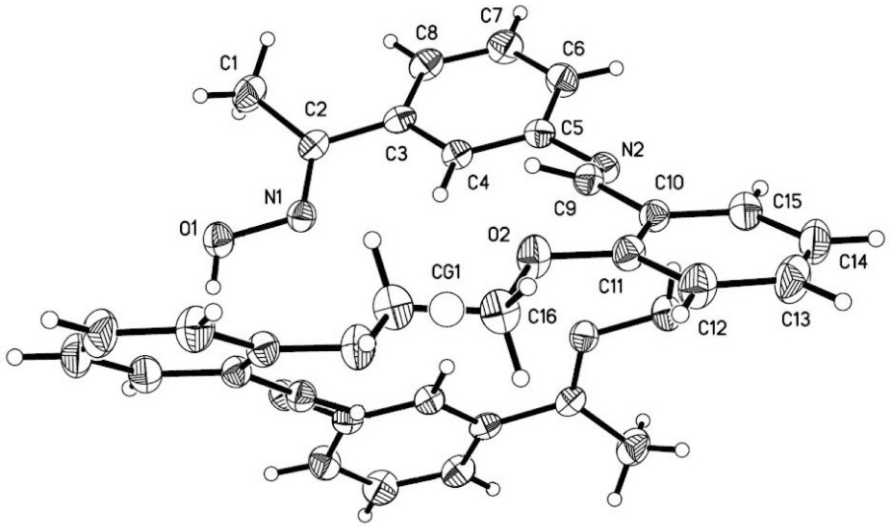

Abstract

$C_{32}H_{30}N_4O_4$, monoclinic, *C*12/*c*1 (no. 15), a = 15.283(2) Å, b = 8.8951(7) Å, c = 19.931(2) Å, β = 93.745(1)°, V = 2703.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.141, T = 298 K.

Source of material

To a hot ethanol solution (7 ml) of 3-amino-acetophenone (818.2 mg, 6.00 mmol) was added a mixture of a hot ethanol solution (10 ml) of hydroxylamine hydrochloride (423.5 mg, 6.00 mmol) and a hot ethanol solution (5 ml) of sodium acetate. After the solution had been stirred at 55 °C for 12 h, the mixture was concentrated. Then 30 ml distilled water was added. After refrigerating at –6 °C for 24 h, the solution gave the yellow solid 3-amino-acetophenone oxime, which was filtered and washed successively with distilled water and ethanol/ hexane (1:4). The isolated compound was dried under vacuum and gave 551.0 mg of yellow crystalline solid (yield 60.9 %; m. p. 135 - 137 °C). The title compound 3,3′-[2,2′-(1,2-ethylenedioxy)dibenzylmethylimino]bis(acetophenone oxime) was prepared in a similar way from 3-amino-acetophenone oxime and 2,2′-(1,2-ethylenedioxy)dibenzaldehyde. The title compound was dried under vacuum and gave 302.2 mg of light pink solid (yield 76.4 %; m. p. 199 - 200 °C). Block-shaped colorless single crystals of the title compound suitable for X-ray diffraction studies could be obtained by slow evaporation of an ethanol solution at room temperature.

Elemental analysis — found: C, 71.89 %; H, 5.66 %; N, 10.48 %; calculated for $C_{32}H_{30}N_4O_4$: C, 71.79 %; H, 5.48 %; N, 10.35 %. IR data are available in the CIF file.

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Discussion

Oxime-type chelating compounds and their derivatives have drawn much attention in the last few decades because these compounds can accommodate one, two or more metal centers and form homo- and heteronuclear metal complexes with interesting properties [1-4], such as excellent catalytic activity for epoxidation and aziridination [5]. In addition, they are also used as models for reaction centers in metalloenzymes [6], non-linear optical materials [7], and molecular recognition and biological activity [8].

The crystal structure of the title compound is built up only by $C_{32}H_{30}N_4O_4$ molecules, in which all bond lengths are in normal ranges. The molecule adopts a symmetrical conformation where the two acetophenone oxime moieties are apart from each other. The oxime groups have *anti*-conformation relative to the center of symmetry in the C16—C16′ bond. There are strong intramolecular O–H···N hydrogen bonds between the hydroxyl (O1–H1) groups and the oxime nitrogen (N2) atoms, with the distances d(N2—O1) = 2.853(2) Å. The results highly indicate that the oxime-OH form is more favorable in the crystalline state in the title compound (d(O1—H1) = 0.82 Å, d(H1···N2) = 2.160 Å, d(O1···N2) = 2.853(3) Å, ∠O1–H1···N2 = 142.36°). In the crystal structure, the molecules are held together by two pairs of intermolecular C12–H12···O1 hydrogen bonds between the oxime-oxygen atom and –C12H12 group of the aromatic ring with the distance d(C12—O1) = 3.518(2) Å. In addition, the adjacent rings (C10-C15) are further linked by a weak intermolecular $\pi\cdots\pi$ stacking interaction (centroid–centroid distance of 4.106 Å). Thus, every molecule is linked with four other molecules into a layer supramolecular structure via intermolecular C–H···O hydrogen bonds and $\pi\cdots\pi$ stacking interactions.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.18 × 0.22 × 0.46 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.88 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6565, 2389
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1462
$N(param)_{refined}$:	182
Programs:	SHELXS-97, SHELXL-97, SHELXTL [9]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.6276	0.1063	0.0970	0.078
H(1A)	8*f*	0.7717	–0.1570	0.1924	0.097
H(1B)	8*f*	0.8189	–0.0672	0.2520	0.097
H(1C)	8*f*	0.8059	0.0064	0.1806	0.097
H(4)	8*f*	0.5773	0.1636	0.2900	0.044
H(6)	8*f*	0.5810	–0.0385	0.4694	0.063
H(7)	8*f*	0.6899	–0.1962	0.4375	0.070
H(8)	8*f*	0.7441	–0.1758	0.3333	0.059
H(9)	8*f*	0.5546	0.3494	0.3610	0.048
H(12)	8*f*	0.3842	0.7768	0.3759	0.068
H(13)	8*f*	0.3092	0.7380	0.4707	0.078
H(14)	8*f*	0.3189	0.5114	0.5273	0.074
H(15)	8*f*	0.4083	0.3257	0.4898	0.060
H(16A)	8*f*	0.4816	0.8063	0.3048	0.059
H(16B)	8*f*	0.4106	0.7140	0.2617	0.059

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	8*f*	0.6380(1)	0.0637(2)	0.1880(1)	0.042(1)	0.041(1)	0.044(1)	0.003(1)	0.007(1)	–0.001(1)
N(2)	8*f*	0.5065(1)	0.1845(2)	0.40679(9)	0.045(1)	0.038(1)	0.038(1)	0.002(1)	0.0026(9)	0.0019(9)
O(1)	8*f*	0.6658(1)	0.0675(2)	0.12220(8)	0.057(1)	0.054(1)	0.047(1)	0.0036(9)	0.0108(9)	–0.0018(9)
O(2)	8*f*	0.4896(1)	0.5870(2)	0.32008(9)	0.062(1)	0.037(1)	0.053(1)	0.0143(9)	0.0174(9)	0.0065(8)
C(1)	8*f*	0.7804(2)	–0.0593(4)	0.2122(2)	0.049(2)	0.074(2)	0.073(2)	0.018(2)	0.015(2)	–0.002(2)
C(2)	8*f*	0.6938(2)	0.0032(3)	0.2301(1)	0.035(1)	0.032(1)	0.053(2)	–0.001(1)	0.006(1)	–0.005(1)
C(3)	8*f*	0.6656(2)	–0.0047(3)	0.2997(1)	0.033(1)	0.029(1)	0.053(2)	–0.002(1)	–0.002(1)	–0.000(1)
C(4)	8*f*	0.6009(2)	0.0921(3)	0.3200(1)	0.038(1)	0.029(1)	0.043(1)	0.001(1)	0.001(1)	0.004(1)
C(5)	8*f*	0.5708(2)	0.0842(3)	0.3838(1)	0.039(1)	0.034(1)	0.043(1)	–0.004(1)	–0.000(1)	0.004(1)
C(6)	8*f*	0.6030(2)	–0.0278(3)	0.4272(1)	0.058(2)	0.051(2)	0.048(2)	0.004(2)	0.005(1)	0.014(1)
C(7)	8*f*	0.6676(2)	–0.1230(3)	0.4078(2)	0.057(2)	0.051(2)	0.065(2)	0.014(2)	0.000(2)	0.019(2)
C(8)	8*f*	0.6996(2)	–0.1118(3)	0.3453(1)	0.044(2)	0.038(2)	0.067(2)	0.010(1)	0.003(1)	0.004(1)
C(9)	8*f*	0.5109(2)	0.3213(3)	0.3888(1)	0.039(1)	0.043(2)	0.039(1)	–0.001(1)	0.005(1)	0.002(1)
C(10)	8*f*	0.4504(2)	0.4361(3)	0.4099(1)	0.038(1)	0.039(2)	0.039(1)	–0.001(1)	0.004(1)	–0.004(1)
C(11)	8*f*	0.4425(2)	0.5730(3)	0.3758(1)	0.043(2)	0.038(2)	0.045(2)	0.004(1)	0.006(1)	–0.008(1)
C(12)	8*f*	0.3894(2)	0.6856(3)	0.3987(1)	0.063(2)	0.046(2)	0.063(2)	0.013(2)	0.013(2)	–0.005(1)
C(13)	8*f*	0.3444(2)	0.6618(4)	0.4552(2)	0.064(2)	0.063(2)	0.071(2)	0.014(2)	0.021(2)	–0.019(2)
C(14)	8*f*	0.3503(2)	0.5270(4)	0.4895(1)	0.060(2)	0.073(2)	0.054(2)	0.001(2)	0.022(1)	–0.011(2)
C(15)	8*f*	0.4035(2)	0.4164(3)	0.4666(1)	0.053(2)	0.050(2)	0.048(2)	–0.003(1)	0.009(1)	–0.003(1)
C(16)	8*f*	0.4716(2)	0.7154(3)	0.2785(1)	0.066(2)	0.029(1)	0.055(2)	0.005(1)	0.009(1)	0.000(1)

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