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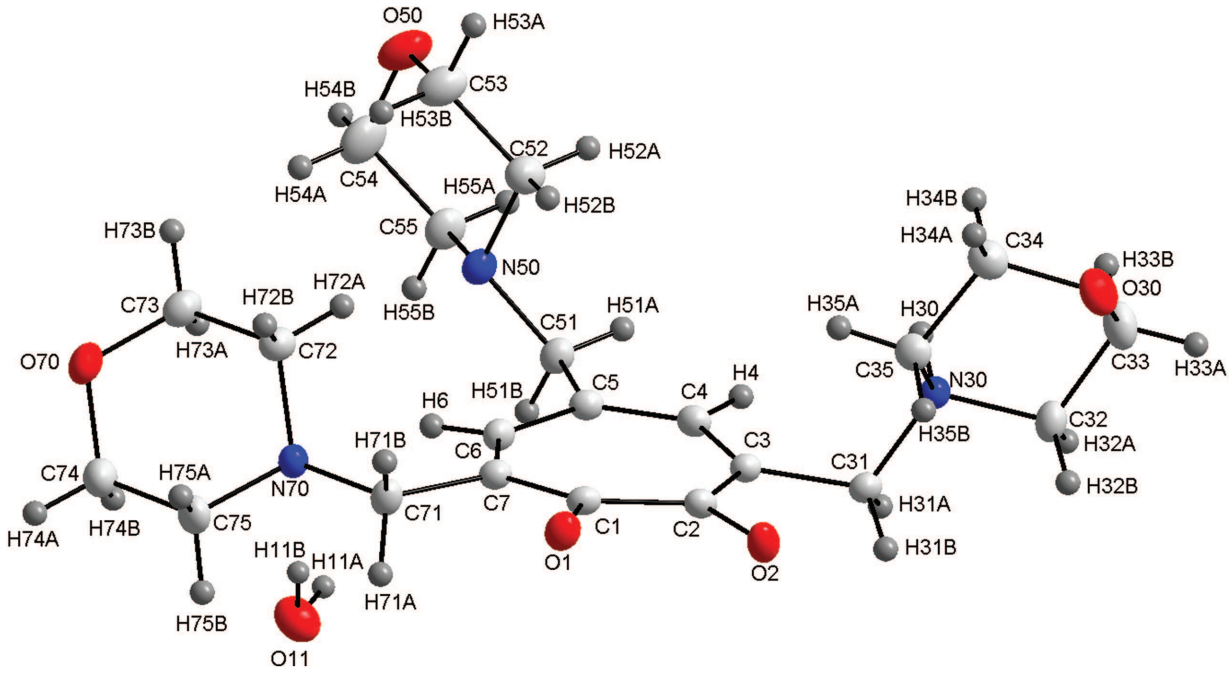
Crystal structure of 3,5,7-tris(morpholinomethyl) tropolone·0.67 hydrate, $C_{22}H_{33}N_3O_5 \cdot 0.67H_2O$



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Abstract

$C_{22}H_{33}N_3O_5 \cdot 0.67H_2O$, monoclinic, $P2_1/c$, $a = 11.9915(6)$ Å, $b = 18.9934(10)$ Å, $c = 10.5332(5)$ Å, $\beta = 112.155(2)°$, $V = 2221.91(19)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0417$, $wR_{ref}(F^2) = 0.1139$, $T = 100(2)$ K.

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The asymmetric unit of the title structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow, plate Size 0.44 × 0.31 × 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.9 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω
$2\theta_{max}$, completeness:	55.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	47649, 5344, 0.045
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4142
$N(param)_{refined}$:	292
Programs:	Bruker programs [35], SHELX [36], WinGX [37], publCIF [38], PLATON [39]

Source of material

A mixture of tropolone (0.46 g, 3.73 mmol) and morpholine (1.18 mL, 13.54 mmol) was treated with 40% aqueous formaldehyde (0.80 mL, 9.61 mmol). After stirring at 60°C for 7 min, a reddish liquid was formed. A yellow precipitate was obtained overnight at ambient temperature. The crude product was crystallized from a ethyl acetate and hexane mixture

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.39736(8)	0.11061(5)	0.21802(9)	0.0216(2)
O2	0.28806(8)	0.22558(5)	0.11278(9)	0.0226(2)
O30	−0.02112(8)	0.31672(6)	−0.35103(10)	0.0286(2)
O70	0.86587(9)	−0.08961(5)	0.22705(10)	0.0280(2)
O50	0.73553(10)	0.06074(6)	−0.36038(11)	0.0348(3)
N50	0.71576(10)	0.14669(6)	−0.14634(11)	0.0192(2)
N30	0.23099(9)	0.31518(6)	−0.18441(11)	0.0164(2)
N70	0.71684(9)	0.02655(6)	0.23533(10)	0.0179(2)
C4	0.50472(11)	0.24913(7)	−0.05380(12)	0.0177(3)
H4	0.5025	0.2825	−0.1194	0.021*
C51	0.69056(11)	0.21264(7)	−0.08938(13)	0.0192(3)
H51A	0.6597	0.2471	−0.1623	0.023*
H51B	0.765	0.2309	−0.0222	0.023*
C3	0.41070(11)	0.25544(7)	−0.00536(12)	0.0165(3)
C1	0.44476(11)	0.14465(7)	0.14896(12)	0.0169(3)
C5	0.59955(11)	0.20249(7)	−0.02175(12)	0.0170(3)
C32	0.15966(12)	0.38163(7)	−0.21589(14)	0.0227(3)
H32A	0.2105	0.4206	−0.2201	0.027*
H32B	0.1299	0.3914	−0.1439	0.027*
C35	0.15039(11)	0.25409(7)	−0.19074(13)	0.0201(3)
H35B	0.1202	0.2579	−0.1176	0.024*
H35A	0.1958	0.2106	−0.1779	0.024*
C75	0.77975(13)	−0.01676(8)	0.35678(14)	0.0247(3)
H75A	0.7275	−0.0545	0.3628	0.03*
H75B	0.8008	0.0118	0.4388	0.03*
C7	0.55900(11)	0.12085(7)	0.14749(12)	0.0171(3)
C2	0.38015(11)	0.21045(7)	0.08333(12)	0.0172(3)
C53	0.63868(14)	0.05226(8)	−0.31342(17)	0.0316(3)
H53B	0.6606	0.017	−0.2416	0.038*
H53A	0.5678	0.0357	−0.3885	0.038*
C6	0.62381(11)	0.14724(7)	0.07443(13)	0.0181(3)
H6	0.6968	0.1245	0.0917	0.022*
C31	0.33490(11)	0.32147(7)	−0.04899(12)	0.0176(3)
H31B	0.3038	0.3334	0.021	0.021*
H31A	0.3861	0.36	−0.0544	0.021*
C34	0.04610(12)	0.25248(8)	−0.32732(14)	0.0239(3)
H34B	0.0762	0.2454	−0.3999	0.029*
H34A	−0.0063	0.2133	−0.3292	0.029*
C52	0.60946(12)	0.12047(8)	−0.25896(14)	0.0250(3)
H52A	0.5829	0.1552	−0.3319	0.03*
H52B	0.5446	0.1128	−0.2267	0.03*
C74	0.89261(13)	−0.04732(8)	0.34678(15)	0.0282(3)
H74B	0.9459	−0.0093	0.3448	0.034*
H74A	0.9341	−0.0757	0.4274	0.034*
C73	0.80074(12)	−0.04976(7)	0.10683(14)	0.0243(3)
H73B	0.78	−0.0799	0.0269	0.029*
H73A	0.8514	−0.0121	0.0969	0.029*
C55	0.81192(12)	0.15699(8)	−0.19832(15)	0.0250(3)
H55B	0.8839	0.174	−0.1252	0.03*
H55A	0.7874	0.1919	−0.2708	0.03*
C33	0.05461(13)	0.37450(8)	−0.35204(15)	0.0285(3)
H33A	0.0078	0.4176	−0.3713	0.034*
H33B	0.085	0.3676	−0.4244	0.034*
C71	0.60834(12)	0.05853(7)	0.24306(13)	0.0197(3)
H71A	0.6263	0.0739	0.3365	0.024*
H71B	0.5462	0.0228	0.2219	0.024*
C72	0.68697(12)	−0.01874(7)	0.11388(14)	0.0218(3)
H72A	0.6452	0.0086	0.0318	0.026*
H72B	0.6339	−0.0564	0.1185	0.026*
C54	0.83852(14)	0.08795(9)	−0.25301(17)	0.0340(4)
H54B	0.9026	0.095	−0.2868	0.041*
H54A	0.8663	0.0539	−0.179	0.041*
O11[a]	0.90093(14)	0.13948(9)	0.36490(16)	0.0327(4)
H11B[a]	0.848(2)	0.1085(13)	0.324(3)	0.056(9)*
H11A[a]	0.914(3)	0.1613(14)	0.301(3)	0.057(9)*
H30	0.2614(15)	0.3083(10)	−0.2560(19)	0.041(5)*

[a]Occupancy: 0.667

(1:1), to form 3,5,7-tri(morpholinomethyl) tropolone as yellow crystals, (1.45 g, 3.47 mmol, 92.85% yield). **MS**: m/z 420.3; **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 7.87,(s, 2H), 3.76–3.72 (m, 8H), 3. 71 (s, 4H), 3.70–3.66 (m, 4H), 3.51 (s, 2H), 2.54 (dd, J = 5.4, 3.9 Hz, 8H), 2.50–2.43 (m, 4H) ppm; **^{13}C NMR** (300 Mhz, CD_2Cl_2) δ 168.35, 138.91, 135.70, 132.86, 67.10, 66.94, 59.46, 53,73, 53.35, 52.76.

Experimental details

Aromatic and methylene hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 1.5U_{eq}(C)$ with C—H distances of 0.93 Å and 0.97 Å respectively. The hydrogen atoms of the water molecule were located from the electron density map.

Discussion

Tropolone, a hydroxide derivative of tropone, is a functional moiety found in a large number of natural products such as colchicine used for the treatment of gout [1, 2]. Tropolone and its derivatives have been reported as antimicrobial agents. It also possess antiviral, antitumor, antioxidant and enzyme inhibiting properties [3–7]. The title compound exhibit antiviral activities [7], while the isopropyl derivatives of tropolone (β-thujaplicin and γ-thujaplicin) were reported to have antifungal and antibacterial properties [6]. Thus these derivatives are used in the preservation of wood [8, 9].

The title compound consists of a tropolone core with three methyl morpholine moieties bound to it at C3, C5 and C7 of the backbone, with additional water (0.67 occupancy) completing the asymmetric unit, as shown in the figure. Earlier in the 1970's, Shimanouchi et al. reported the molecular structure of tropolone [10, 11]. When comparing this structure to that of tropolone, some slight deviations were observed within the tropolone core. The C1—O1 and C2—O2 bond distances of the title compound

of 1.257(2) Å and 1.285(2) Å compare well to that reported for the tropolone structure with C1—O1 and C2—O2 calculated as 1.2603(5) Å and 1.3333(7) Å respectively. The C1—C2 bond distance of the structure reported here and the structure of tropolone are determined as 1.496(2) Å and 1.4542(5) Å respectively and also compare well. All the bond distances and angles are in agreement to similar structures in literature [12, 13]. 3,5,7-tris(morpholinomethyl)tropolone was coordinated to the rhodium(I) showing bond angles and bond distances in the metal complex similar to the uncoordinated molecule [14]. Although, the C—O distances of the coordinated ligand is slightly longer at 1.31 Å (1.257 Å and 1.287 Å for the uncoordinated molecule) and the C1—C2 distance is slightly shorter at 1.44 Å (1.496 Å for the uncoordinated molecule), but still within the normal range. Schutte et al. synthesized the rhenium(I) tricarbonyl complexes with the tropolone and 3,5,7-tribromotropolone ligands coordinated to the metal centre [15–18]. Overall the C1—O1/C2—O2 and the C1—C2 bond distances in these structures vary from 1.276(3) Å to 1.307(8) Å and from 1.462(6) Å to 1.477(8) Å respectively. It is clear that even when these ligand systems are coordinated to a metal centre the bond distances don't vary significantly. In the title compound, the tropolone ring (defined by the atoms C1—C2—C3—C4—C5—C6—C7) is almost planar with the maximum deviation observed for C1 with a distance of −0.0710(9) Å from the plane. The torsion angle O1—C1—C2—O2 of 3.8(2)° indicate the slight twisting of the oxygen atoms with respect to the tropolone plane. The torsion angle in the rhodium(I) structure reported by Hill et al. has a smaller torsion angle of 1.8°, illustrating the effect of the coordination of the metal cenre. Moreover, there exist extensive inter- and intramolecular hydrogen interactions in this molecule. Seven C—H···O (two intramolecular, five intermolecular), two N—H···O (intermolecular), one C—H···N (intramolecular), one O—H···N (intramolecular) and one O—H···O (intermolecular) hydrogen interactions are observed. These hydrogen interactions seems to enhance the solid state ordering of the structure with the molecules packing in alternating layers when viewed along the *ab*-plane. These tropolone type ligand systems and other O,O′, N,O and N,N′ bidentate ligand systems form part of an ongoing study [19–34].

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