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Crystal structure of 3-[(triisopropylsilyl)-ethynyl]-6*a*,12*a*-dihydro-1*H*-1,4-diaza-benzo[α]anthracene-2,7,12-trione, C₂₇H₂₈N₂O₃Si

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Abstract

C₂₇H₂₈N₂O₃Si, triclinic, $P\bar{1}$ (no. 2), $a = 7.5098(4)$ Å, $b = 7.8881(4)$ Å, $c = 20.8904(14)$ Å, $\alpha = 97.002(5)^\circ$, $\beta = 98.703(5)^\circ$, $\gamma = 95.739(5)^\circ$, $V = 1205.25(12)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0586$, $wR_{\text{ref}}(F^2) = 0.1610$, $T = 100(2)$ 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, atomic coordinates and displacement parameters.

Source of material

In an argon atmosphere, a one pot reaction of 1-(triisopropylsilyl)-1-propyne (4.0 g, 0.020 mol), *n*-butyl lithium (14 mL, 0.022 mol, 1.6 M in hexane), cuprous bromide (3.6 g, 0.025 mol), lithium bromide (4.3 g, 0.050 mol), and oxalyl chloride (1.9 g, 0.015 mol) in 200 mL distilled

Table 1: Data collection and handling.

Crystal:	Block
Size:	0.18 × 0.17 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.13 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
θ_{max} , completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7540, 4243, 0.033
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2823
$N(\text{param})_{\text{refined}}$:	304
Programs:	Bruker [1], SHELX [2], Olex2 [3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Si1	0.12039(12)	0.76505(11)	0.36455(4)	0.0417(3)
O1	0.1918(3)	0.0973(2)	−0.01227(10)	0.0390(5)
O2	0.8446(3)	0.3137(2)	−0.06824(10)	0.0424(5)
O3	0.0634(3)	0.3276(3)	0.17191(10)	0.0411(5)
N1	0.2580(3)	0.3079(3)	0.09893(11)	0.0293(5)
H1	0.1781	0.2343	0.0713	0.035*
N2	0.5073(3)	0.5492(3)	0.18363(11)	0.0312(5)
C1	0.5715(4)	0.1275(3)	−0.09989(13)	0.0291(6)
C2	0.6220(4)	0.0559(3)	−0.15751(14)	0.0356(7)
H2	0.7390	0.0894	−0.1671	0.043*
C3	0.5010(4)	−0.0647(4)	−0.20094(15)	0.0403(8)
H3	0.5360	−0.1148	−0.2401	0.048*
C4	0.3302(4)	−0.1125(4)	−0.18757(14)	0.0393(7)
H4	0.2480	−0.1948	−0.2177	0.047*
C5	0.2776(4)	−0.0414(3)	−0.13058(14)	0.0334(7)
H5	0.1595	−0.0740	−0.1218	0.040*
C6	0.3988(4)	0.0784(3)	−0.08612(13)	0.0277(6)
C7	0.3424(4)	0.1484(3)	−0.02435(13)	0.0287(6)
C8	0.4720(3)	0.2760(3)	0.02242(13)	0.0252(6)
C9	0.6458(3)	0.3252(3)	0.00906(13)	0.0262(6)
C10	0.7001(4)	0.2579(3)	−0.05408(14)	0.0297(6)
C11	0.7703(4)	0.4419(3)	0.05378(14)	0.0304(6)
H11	0.8880	0.4729	0.0442	0.036*
C12	0.7237(4)	0.5123(3)	0.11150(14)	0.0296(6)
H12	0.8097	0.5910	0.1417	0.036*
C13	0.5509(3)	0.4691(3)	0.12608(13)	0.0279(6)
C14	0.4255(3)	0.3489(3)	0.08187(13)	0.0256(6)
C15	0.2084(4)	0.3746(3)	0.15628(13)	0.0308(6)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C16	0.3462(4)	0.5079(3)	0.19685(13)	0.0295(6)
C17	0.2911(4)	0.5937(4)	0.25420(14)	0.0363(7)
C18	0.2316(4)	0.6646(4)	0.29931(15)	0.0417(8)
C19	−0.1281(4)	0.6901(4)	0.33738(18)	0.0553(9)
H19	−0.1605	0.7295	0.2939	0.066*
C20	−0.1749(5)	0.4952(5)	0.3255(2)	0.0681(11)
H20A	−0.0988	0.4450	0.2958	0.102*
H20B	−0.3030	0.4660	0.3057	0.102*
H20C	−0.1532	0.4495	0.3671	0.102*
C21	−0.2495(5)	0.7736(7)	0.3810(3)	0.111(2)
H21A	−0.2306	0.7326	0.4237	0.166*
H21B	−0.3768	0.7432	0.3605	0.166*
H21C	−0.2192	0.8989	0.3869	0.166*
C22	0.0862(6)	1.0637(5)	0.3039(2)	0.0718(12)
H22A	0.1325	1.0026	0.2673	0.108*
H22B	0.1197	1.1878	0.3060	0.108*
H22C	−0.0463	1.0384	0.2973	0.108*
C23	0.1688(5)	1.0044(4)	0.36818(17)	0.0538(9)
H23	0.1094	1.0592	0.4038	0.065*
C24	0.3715(5)	1.0664(5)	0.3849(2)	0.0704(11)
H24A	0.4189	1.0399	0.4285	0.106*
H24B	0.3912	1.1910	0.3846	0.106*
H24C	0.4347	1.0081	0.3525	0.106*
C25	0.1623(6)	0.7852(6)	0.50264(18)	0.0737(12)
H25A	0.1836	0.9102	0.5039	0.111*
H25B	0.2292	0.7522	0.5423	0.111*
H25C	0.0323	0.7498	0.5001	0.111*
C26	0.2270(5)	0.6972(5)	0.44297(17)	0.0604(10)
H26	0.3542	0.7548	0.4482	0.072*
C27	0.2556(9)	0.5208(7)	0.4426(3)	0.137(2)
H27A	0.1382	0.4487	0.4342	0.205*
H27B	0.3223	0.5052	0.4852	0.205*
H27C	0.3260	0.4874	0.4082	0.205*

THF at 0 °C for 3 h furnished triisopropylsilyl-alkynyl- α -oxo-acetic acid (0.53 g, 0.002 mol) in 6% yield [4]. The product was purified by chromatography and was then treated with 1, 2-diamino-9,10-anthracenedione (0.47 g, 0.002 mol) in 20 mL glacial acetic acid at 60 °C for 30 min to afford the title product (0.77 g, 0.0017 mol) in 85% yield. Crystals of the title compound were obtained by slow evaporation from dichloromethane/hexanes stored in a freezer overnight.

Experimental details

The raw data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs [1]. The structure was solved by direct methods with SHELXL [2]. Final unit cell parameters were determined by least-squares refinement of 4243 reflections taken from the data set. Subsequent difference Fourier calculations and least-squares refinement

against F² were performed with SHELXL-2014 [2] using OLEX2 [3]. Hydrogen atoms on the aromatic rings and iso-propyl groups were placed in geometrically idealized positions and refined as riding atoms.

Comment

Tetracyanoquinodimethane (TCNQ) based molecules have attracted much attention due to their applications as organic semiconductor materials and fluorescent probes [5–8]. The introduction of nitrogen atoms to TCNQ molecules can bring extra chemical stability and higher electronegativity, reducing highest molecular filling orbital and the lowest unfilled orbital levels. The title compound was synthesized by a cyclocondensation reaction of 1,2-diaminoanthracenedione with triisopropylsilyl-alkynyl- α -oxo-acetic acid and was expected to serve as a useful building block for the construction of new TCNQ molecules.

In the asymmetric unit cell the molecule is discrete and contains only one independent molecule. All ring atoms and alkynyl C17, C18 atoms are coplanar while Si1 is slightly displaced out of the plane. This is probably due to steric effects from the bulky triisopropylsilyl group. Angles and bond lengths fall in their normal ranges compared with previously studies [9, 10].

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