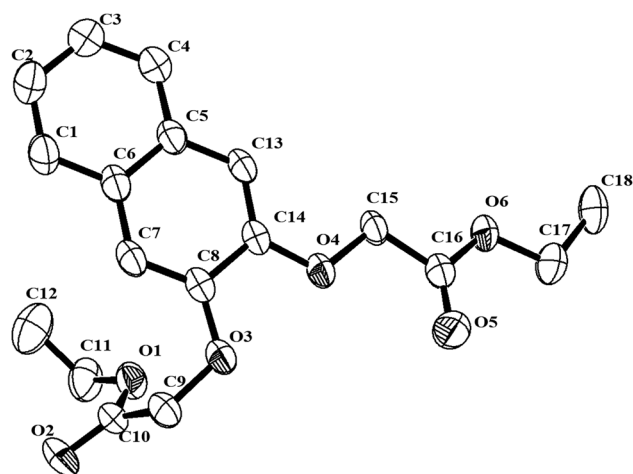


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Crystal structure of diethyl-2,2'-naphthalene-2,3-diylbis(oxy)diacetate, C₁₈H₂₀O₆



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Abstract

C₁₈H₂₀O₆, monoclinic, C2/c (no. 15), $a = 27.191(3)$ Å, $b = 8.7442(3)$ Å, $c = 20.861(2)$ Å, $\beta = 136.337(18)^\circ$, $V = 3424.5(9)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0553$, $wR_{\text{ref}}(F^2) = 0.1625$, $T = 294.7(4)$ K.

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The molecular structure is shown in the Figure (H atoms omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The ethylbromoacetate (8.35 ml, 75 mmol) was added dropwise into the mixture of K₂CO₃ (20.70 g, 150 mmol)

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.80 × 0.60 × 0.40 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ :	0.81 mm ⁻¹
Diffractometer, scan mode:	New Gemini, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9228, 3054, 0.038
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2514
$N(\text{param})_{\text{refined}}$:	220
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

and naphthalene-2,3-diol (4.8 g, 30 mmol) in acetonitrile (150 ml). The reaction solution was refluxed for 24 h, and then it was cooled to room temperature. The insoluble solid was filtered off, and the filtrate was concentrated to obtain the crude product, which was recrystallized from ethyl acetate/petroleum ether the product as a white solid (6.40 g, 79%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.16–8.18 (dd, $J_1 = 3.6$ Hz, $J_2 = 6$ Hz, 2H, Ar-*H*), 7.72–7.74 (dd, $J_1 = 3.6$ Hz, $J_2 = 6$ Hz, 2H, Ar-*H*), 7.23 (s, 2H, Ar-*H*), 4.78 (s, 4H, OCH₂), 4.25–4.31 (q, 4H, COOCH₂), 1.28–1.32 (t, $J = 7.2$ Hz, 6H, COOCH₂CH₃); ¹³C NMR (400 MHz, CDCl₃) δ ppm: 182.91, 168.78, 153.69, 134.13, 133.70, 126.74, 124.83, 124.04, 68.19, 61.67, 14.32; **HRMS** m/z : ($M + \text{Na}^+$) 355.1149, calculated for 355.1158. Crystals of the title compound were obtained from the solvents (ethylacetate: petroleum ether = 1:4).

Experimental details

Comment

To design different crown ether compounds is always a research hotspot. Diethyl-2,2'-(naphthalene-2,3-diylbis(oxy)) diacetate is the synthetic intermediate of some macrocyclic compounds [5–7]. These macrocyclic compounds, especially naphtha-aza-crown ethers (NACEs), exhibited excellent coordination ability with different metal ions. Hence, NACEs have the potential to be used as receptors in molecular recognition, catalysts, separation and so on. Recently, we synthesized some NACEs by cyclocondensating of diethyl-2,2'-(naphthalene-2,3-diylbis(oxy))

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
C1	0.70609 (12)	0.3858 (3)	0.53645 (18)	0.0869 (7)
H1	0.753863	0.358107	0.579384	0.104*
C2	0.66062 (14)	0.3371 (3)	0.4474 (2)	0.0986 (8)
H2	0.677460	0.275898	0.430072	0.118*
C3	0.58920 (14)	0.3777 (3)	0.38181 (19)	0.0961 (7)
H3	0.558420	0.344332	0.320771	0.115*
C4	0.56415 (11)	0.4668 (3)	0.40707 (16)	0.0824 (6)
H4	0.516260	0.493948	0.362657	0.099*
C5	0.60942 (9)	0.5181 (2)	0.49894 (13)	0.0640 (5)
C6	0.68225 (9)	0.4773 (2)	0.56497 (14)	0.0658 (5)
C7	0.72881 (9)	0.5284 (2)	0.65724 (14)	0.0672 (5)
H7	0.776532	0.500098	0.700948	0.081*
C8	0.70512 (8)	0.61839 (19)	0.68332 (12)	0.0597 (4)
C9	0.82028 (9)	0.6529 (3)	0.83588 (14)	0.0796 (6)
H9A	0.828970	0.544436	0.838290	0.096*
H9B	0.841827	0.682709	0.896566	0.096*
C10	0.85683 (9)	0.7379 (3)	0.81734 (14)	0.0808 (6)
C11	0.84294 (16)	0.9090 (3)	0.7163 (2)	0.1076 (9)
H11A	0.892369	0.936423	0.770029	0.129*
H11B	0.816289	1.002198	0.683358	0.129*
C12	0.8376 (2)	0.8085 (4)	0.6553 (3)	0.1340 (12)
H12A	0.788863	0.779146	0.603073	0.201*
H12B	0.866126	0.718776	0.689063	0.201*
H12C	0.854492	0.861616	0.633903	0.201*
C13	0.58555 (8)	0.6098 (2)	0.52822 (13)	0.0646 (5)
H13	0.537681	0.636397	0.485823	0.077*
C14	0.63181 (8)	0.65939 (19)	0.61756 (12)	0.0578 (4)
C15	0.54372 (9)	0.8002 (2)	0.58966 (13)	0.0668 (5)
H15A	0.511636	0.713281	0.558513	0.080*
H15B	0.532952	0.865153	0.543081	0.080*
C16	0.53376 (10)	0.8884 (2)	0.64165 (14)	0.0715 (5)
C17	0.44745 (14)	1.0356 (3)	0.6161 (2)	0.1037 (8)
H17A	0.474591	1.129717	0.644470	0.124*
H17B	0.455963	0.976353	0.662695	0.124*
C18	0.37019 (15)	1.0702 (3)	0.5367 (2)	0.1072 (9)
H18A	0.362154	1.125566	0.490092	0.161*
H18B	0.354879	1.130920	0.558061	0.161*
H18C	0.343677	0.976294	0.510826	0.161*
O1	0.81488 (7)	0.83241 (18)	0.74630 (11)	0.0825 (5)
O2	0.91876 (7)	0.7185 (3)	0.86449 (13)	0.1250 (8)
O3	0.74588 (6)	0.67649 (16)	0.77010 (9)	0.0685 (4)
O4	0.61486 (6)	0.74946 (15)	0.65319 (9)	0.0681 (4)
O5	0.57577 (9)	0.8984 (2)	0.72388 (12)	0.1067 (6)
O6	0.46894 (7)	0.94902 (18)	0.58027 (10)	0.0793 (4)

diacetate with different diamines. The ion selectivities of the NACEs were studied by the square wave voltammetry [8]. Comparing with the optimized structures of NACEs calculated by the density functional theory and the crystal structure of diethyl-2,2-(naphthalene-2,3-diylbis(oxy)) diacetate, the rigid naphthalene ring influenced the structure of the crown ether which played an important role in the ion selectivity.

The crystal structure clearly indicated the chemical structure and configuration of diethyl-2,2-(naphthalene-2,3-diylbis(oxy))diacetate, and all the intramolecular bond lengths and angles are in the expected ranges. The Cambridge Structural Database was searched and five structural related compounds were found [9–11]. By comparison with these compounds, it was observed that the title compound contains a unique naphthalene ring as the center core, which causes one of the two ester side chains to be coplanar with the naphthalene ring, while in the other compounds, both ester side chains are located on the same side of the aryl moiety.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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