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Crystal structure of (2*E*,4*Z*)-dimethyl 4-((phenylamino)methylene)pent-2-enedioate, $C_{14}H_{15}N_1O_4$

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Abstract

$C_{14}H_{15}N_1O_4$, triclinic, $P\bar{1}$, $a = 8.2018(4)$ Å, $b = 11.5512(5)$ Å, $c = 14.4121(7)$ Å, $\alpha = 79.242(2)^\circ$, $\beta = 78.647(3)^\circ$, $\gamma = 85.496(3)^\circ$, $V = 1313.93(11)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0548$, $wR_{\text{ref}}(F^2) = 0.1805$, $T = 296(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.26 \times 0.24 \times 0.18$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	27.6° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	20977, 5899, 0.017
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3894
$N(\text{param})_{\text{refined}}$:	347
Programs:	Bruker APEX system [1], SHELX [2, 3]

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

Source of material

Methyl propiolate (0.4203 g, 5.0 mmol), aniline (0.1863 g, 2.0 mmol), water (4 mL) and potassium sulfate (15.0 mg) were heated and stirred at 353 K for ten hours, then dichloromethane (15 mL) was added and the reaction mixture was poured into a separator funnel. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (333–363 K) : ethyl acetate (6:1, v/v) to give colourless block asymmetric unit of the title.

Experimental details

The non-methyl hydrogen atoms were identified in difference Fourier syntheses, but included using a riding model $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The methyl groups were idealized and refined using rigid groups allowed to rotate about the C–C bond (AFIX 137 option of the SHELXL-2015 program). There are two crystallographically independent molecules in the asymmetric unit. They show non-crystallographic (pseudo) translational symmetry. This phenomenon is known for small molecule structures as well as for biological systems [4] and may be checked by automated procedures [5].

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O7	0.82537(15)	0.62219(10)	0.75870(8)	0.0605(3)
O3	0.83969(15)	0.43118(10)	0.46707(9)	0.0607(3)
O4	0.71137(16)	0.42066(10)	0.61983(9)	0.0638(3)
O5	0.80262(16)	0.91956(10)	0.50978(8)	0.0632(4)
O6	0.64784(17)	1.08640(10)	0.51680(8)	0.0691(4)
O1	0.77740(18)	0.70625(10)	0.20914(8)	0.0703(4)
O8	0.71188(16)	0.61463(11)	0.91433(9)	0.0684(4)
O2	0.68179(19)	0.89080(10)	0.21902(9)	0.0745(4)
N1	0.49067(16)	0.59313(10)	0.66189(9)	0.0503(3)
H1	0.539924	0.527202	0.681547	0.060*
N2	0.49905(17)	0.79047(11)	0.95934(9)	0.0540(4)
H2	0.546581	0.723685	0.978604	0.065*
C18	0.69641(19)	0.84022(12)	0.70105(10)	0.0451(3)
H18	0.775211	0.799546	0.661877	0.054*
C8	0.53875(19)	0.63916(12)	0.56918(11)	0.0457(4)
H8	0.490213	0.711800	0.546611	0.055*
C6	0.73413(19)	0.47397(13)	0.53767(11)	0.0481(4)
C5	0.65401(19)	0.58790(12)	0.50454(11)	0.0452(4)
C22	0.54497(19)	0.83624(13)	0.86660(10)	0.0476(4)
H22	0.498156	0.909819	0.844825	0.057*
C19	0.65539(19)	0.78393(13)	0.80070(11)	0.0463(4)
C20	0.7313(2)	0.66769(13)	0.83123(11)	0.0495(4)
C9	0.3710(2)	0.63771(13)	0.73128(11)	0.0469(4)
C4	0.69484(19)	0.64128(12)	0.40386(11)	0.0475(4)
H4	0.763220	0.595024	0.364360	0.057*
C16	0.6924(2)	0.99066(13)	0.55655(11)	0.0484(4)
C23	0.3829(2)	0.83753(13)	1.02953(11)	0.0486(4)
C2	0.7012(2)	0.79044(14)	0.25783(11)	0.0525(4)
C17	0.6367(2)	0.94246(13)	0.65769(11)	0.0524(4)
H17	0.555412	0.985021	0.693859	0.063*
C28	0.2854(2)	0.93922(15)	1.00824(12)	0.0610(5)
H28	0.294166	0.979222	0.945284	0.073*
C10	0.3468(2)	0.57444(15)	0.82455(12)	0.0585(4)
H10	0.407962	0.504172	0.838282	0.070*
C14	0.2781(2)	0.74213(15)	0.71127(12)	0.0589(4)
H14	0.291918	0.785525	0.649245	0.071*
C24	0.3650(3)	0.77924(16)	1.12374(13)	0.0654(5)
H24	0.428938	0.710530	1.138385	0.078*
C3	0.6484(2)	0.74683(14)	0.36010(11)	0.0556(4)
H3	0.578455	0.795488	0.396742	0.067*
C11	0.2339(3)	0.61424(16)	0.89659(12)	0.0671(5)
H11	0.219312	0.571263	0.958773	0.080*
C13	0.1650(3)	0.78041(17)	0.78491(13)	0.0709(5)
H13	0.102876	0.850376	0.771701	0.085*
C27	0.1756(3)	0.98000(16)	1.08157(13)	0.0704(5)
H27	0.110535	1.048271	1.067512	0.085*
C15	0.8677(3)	0.96535(17)	0.41106(12)	0.0709(5)
H15A	0.777904	0.983005	0.376127	0.106*
H15B	0.943798	0.907734	0.383888	0.106*
H15C	0.925005	1.035972	0.407032	0.106*
C12	0.1417(3)	0.71829(18)	0.87677(13)	0.0714(5)
H12	0.064800	0.745704	0.925300	0.086*
C21	0.9084(3)	0.50944(16)	0.78300(15)	0.0726(5)
H21A	0.970825	0.485415	0.725528	0.109*
H21B	0.827358	0.452171	0.814081	0.109*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H21C	0.982579	0.515446	0.825626	0.109*
C7	0.9226(2)	0.31916(15)	0.49457(15)	0.0702(5)
H7A	0.995494	0.297071	0.439310	0.105*
H7B	0.841264	0.260447	0.520203	0.105*
H7C	0.986218	0.325230	0.542548	0.105*
C1	0.8426(3)	0.74309(18)	0.10951(12)	0.0754(6)
H1A	0.875329	0.675029	0.079748	0.113*
H1B	0.937647	0.789687	0.102514	0.113*
H1C	0.758878	0.789366	0.079223	0.113*
C26	0.1600(3)	0.92208(17)	1.17525(13)	0.0720(5)
H26	0.085824	0.951311	1.223952	0.086*
C25	0.2547(3)	0.82105(18)	1.19600(12)	0.0725(5)
H25	0.244244	0.780778	1.258943	0.087*

Comment

Enyne compounds are not only important raw materials and intermediates in the organic synthesis, but also they are important building blocks for some anticancer drugs and antibiotics [6, 7]. The compounds having a conjugated alkenyl structure is known to have the strongest anticancer antibacterial activity at present [8, 9]. The synthesis and screening of reagents with high anticancer activity and stable low toxicity have become a research hotspot in chemistry, pharmacology, and molecular biology, especially the construction method of the conjugated alkyne structure of its core skeleton [10, 11]. Hence, there is considerable interest in the development of effective methods for the synthesis of it and its analogues [12, 13].

However, the crystal structure of (2*E*,4*Z*)-dimethyl 4-((phenylamino)methylene)pent-2-enedioate has not been reported before. The title compound, built up by the C₁₄H₁₅N₁O₄ molecules, has been synthesized. The single-crystal structure verifies that all bond lengths and angles are in normal ranges.

The *E*, *Z* constitution was verified (*cf.* the figure).

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