Crystal structure of (*E*)-ethyl 2-(2-(2-(2,4-dinitrophenyl)hydrazono)-2-phenylethyl)-2,5-dimethyl-7-phenylbenzo[*d*][1,3]dioxole-4-carboxylate, $C_{32}H_{27}N_4O_8$

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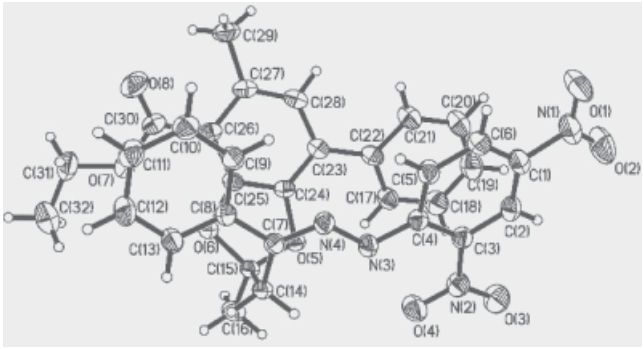

Abstract

$C_{32}H_{27}N_4O_8$, triclinic, $P\bar{1}$ (no. 2), a = 10.085(2) Å, b = 11.302(2) Å, c = 13.269(3) Å, α = 80.76(3)°, β = 78.81(3)°, γ = 82.30(3)°, V = 1456.1 Å^3, Z = 2, $R_{gt(F)}$ = 0.0691, $wR_{ref(F^2)}$ = 0.1756, T = 293 K.

Table 1. Data collection and handling.

Crystal:	red blocks, size 0.2×0.3×0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.99 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14697, 5103
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4057
$N(param)_{refined}$:	400
Programs:	SHELX [4]

Source of material

To a flask containing ethyl 2,5-dimethyl-2-(2-oxo-2-phenylethyl)-7-phenylbenzo[*d*][1,3]dioxole-4-carboxylate (1.0 mmol) and (2,4-dinitrophenyl)hydrazine (1.0 mmol) in ethanol (5 mL) was added anhydrous $CaCl_2$ (2.0 mmol). The solution was stirred at reflux for 48 h, and then concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (*v*:*v* = 1:5) to give the title compound as a mixture of *E*/*Z* isomers with a total yield of 52% (*E*:*Z* = 10:3). Single crystals of title compound were obtained by slow evaporation of its chloroform/petroleum ether solution at room temperature.

Discussion

Benzo[*d*][1,3]dioxole derivatives have driven much attention for their broad spectrum of biological properties [1] and have been used as 5-HT_{2A} receptorantagonist [2] and CB1R inverse agonists. In addition, some benzo[*d*][1,3]dioxole derivatives are indispensable building blocks in functional materials [3]. In spite of their importance, efficient synthetic methods for the preparation of benzo[*d*][1,3]dioxoles derivatives are still limited [3]. In this paper we report the reaction of ethyl 2,5-dimethyl-2-(2-oxo-2-phenylethyl)-7-phenylbenzo[*d*][1,3]dioxole-4-carboxylate with 2,4-dinitrophenylhydrazone to the title compound. All bond lengths and angles of the title structure are in normal ranges. The phenylhydrazone unit is almost coplanar with 14.49(7)° dihedral between ring (C7-C13) and ring (N3/N4/C1-C6). The dihedral angles between the two benzene rings of biphenyl is 27.20(9)°. The crystal packing is stabilized only by van der Waals forces.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(14A)	2*i*	0.0720	0.8418	0.3375	0.053
H(14B)	2*i*	0.0049	0.8021	0.4526	0.053
H(5)	2*i*	0.1973	0.9916	0.6878	0.063
H(28)	2*i*	0.5664	0.6342	0.6344	0.063
H(13)	2*i*	0.1980	0.9521	0.2353	0.063
H(6)	2*i*	0.2098	0.9975	0.8568	0.068
H(2)	2*i*	–0.0474	0.7453	0.9510	0.065
H(9)	2*i*	0.3714	1.0038	0.4696	0.062
H(10)	2*i*	0.5307	1.1067	0.3539	0.072
H(17)	2*i*	0.1719	0.4979	0.6679	0.066
H(12)	2*i*	0.3579	1.0560	0.1202	0.075
H(11)	2*i*	0.5247	1.1332	0.1794	0.076
H(19)	2*i*	0.1387	0.4872	0.9740	0.086
H(21)	2*i*	0.4236	0.6649	0.7822	0.076
H(18)	2*i*	0.0671	0.4348	0.8344	0.083
H(29A)	2*i*	0.7420	0.7997	0.4669	0.107
H(29B)	2*i*	0.7913	0.6829	0.4145	0.107
H(29C)	2*i*	0.7709	0.6757	0.5354	0.107
H(31A)	2*i*	0.6867	0.7388	0.0918	0.087
H(31B)	2*i*	0.5839	0.8564	0.0992	0.087
H(20)	2*i*	0.3158	0.6020	0.9473	0.088
H(32A)	2*i*	0.5024	0.6393	0.0681	0.156
H(32B)	2*i*	0.5496	0.7372	–0.0253	0.156
H(32C)	2*i*	0.4186	0.7664	0.0558	0.156
H(16A)	2*i*	0.1615	0.5265	0.3511	0.089
H(16B)	2*i*	0.0881	0.6372	0.2886	0.089
H(16C)	2*i*	0.0184	0.5848	0.4000	0.089

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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}
O(6)	2*i*	0.3056(2)	0.6962(2)	0.3438(1)	0.039(1)	0.059(1)	0.043(1)	–0.0103(8)	–0.0097(8)	–0.0037(8)
O(5)	2*i*	0.1893(2)	0.6330(2)	0.5065(1)	0.042(1)	0.056(1)	0.045(1)	–0.0158(8)	–0.0121(8)	0.0034(8)
N(4)	2*i*	0.1535(2)	0.9190(2)	0.5368(2)	0.049(1)	0.049(1)	0.040(1)	–0.012(1)	–0.003(1)	–0.003(1)
O(7)	2*i*	0.5392(2)	0.7248(2)	0.2169(2)	0.055(1)	0.077(1)	0.053(1)	–0.017(1)	–0.002(1)	–0.003(1)
N(3)	2*i*	0.0682(2)	0.8525(2)	0.6118(2)	0.054(1)	0.058(1)	0.036(1)	–0.014(1)	–0.004(1)	–0.001(1)
C(7)	2*i*	0.1658(2)	0.8990(2)	0.4418(2)	0.042(1)	0.042(1)	0.042(2)	–0.004(1)	–0.009(1)	–0.002(1)
C(26)	2*i*	0.5252(3)	0.7096(2)	0.3954(2)	0.038(1)	0.040(1)	0.057(2)	–0.003(1)	–0.010(1)	–0.012(1)
C(4)	2*i*	0.0695(3)	0.8613(2)	0.7123(2)	0.044(2)	0.047(2)	0.042(2)	–0.005(1)	–0.007(1)	–0.005(1)
C(24)	2*i*	0.3230(2)	0.6453(2)	0.5119(2)	0.039(1)	0.039(1)	0.052(2)	–0.007(1)	–0.014(1)	–0.004(1)
C(25)	2*i*	0.3911(3)	0.6836(2)	0.4146(2)	0.044(1)	0.038(1)	0.046(2)	–0.005(1)	–0.014(1)	–0.007(1)
C(8)	2*i*	0.2656(3)	0.9675(2)	0.3656(2)	0.047(2)	0.039(1)	0.041(1)	–0.004(1)	–0.007(1)	–0.004(1)
C(14)	2*i*	0.0912(2)	0.8100(2)	0.4061(2)	0.038(1)	0.056(2)	0.042(1)	–0.012(1)	–0.011(1)	–0.002(1)
N(2)	2*i*	–0.1017(2)	0.7120(2)	0.7789(2)	0.063(2)	0.057(2)	0.054(2)	–0.016(1)	–0.005(1)	0.001(1)
O(4)	2*i*	–0.1057(2)	0.6979(2)	0.6888(2)	0.091(2)	0.087(2)	0.059(1)	–0.044(1)	–0.014(1)	–0.007(1)
C(23)	2*i*	0.3827(3)	0.6257(2)	0.5991(2)	0.053(2)	0.037(1)	0.047(2)	–0.004(1)	–0.016(1)	–0.004(1)
C(27)	2*i*	0.5906(3)	0.6905(2)	0.4829(2)	0.039(2)	0.047(2)	0.071(2)	–0.003(1)	–0.016(1)	–0.016(1)
C(3)	2*i*	–0.0088(3)	0.7909(2)	0.7956(2)	0.049(2)	0.049(2)	0.044(2)	–0.008(1)	–0.005(1)	–0.006(1)
O(8)	2*i*	0.6857(2)	0.8201(2)	0.2715(2)	0.069(2)	0.085(2)	0.090(2)	–0.039(1)	0.001(1)	–0.008(1)
C(5)	2*i*	0.1491(3)	0.9404(2)	0.7398(2)	0.056(2)	0.054(2)	0.049(2)	–0.013(1)	–0.004(1)	–0.009(1)
C(28)	2*i*	0.5200(3)	0.6485(2)	0.5788(2)	0.053(2)	0.051(2)	0.061(2)	–0.003(1)	–0.027(1)	–0.010(1)
O(3)	2*i*	–0.1737(3)	0.6620(2)	0.8531(2)	0.091(2)	0.100(2)	0.067(2)	–0.051(2)	–0.000(1)	0.014(1)
C(13)	2*i*	0.2644(3)	0.9835(2)	0.2598(2)	0.063(2)	0.054(2)	0.042(2)	–0.013(1)	–0.012(1)	–0.003(1)
C(6)	2*i*	0.1571(3)	0.9440(3)	0.8407(2)	0.057(2)	0.061(2)	0.056(2)	–0.010(1)	–0.011(1)	–0.017(1)
C(1)	2*i*	0.0868(3)	0.8678(3)	0.9190(2)	0.065(2)	0.058(2)	0.042(2)	0.001(1)	–0.013(1)	–0.012(1)
C(2)	2*i*	0.0023(3)	0.7936(2)	0.8974(2)	0.059(2)	0.053(2)	0.044(2)	–0.003(1)	–0.002(1)	–0.001(1)
C(30)	2*i*	0.5935(3)	0.7578(2)	0.2904(2)	0.040(2)	0.047(2)	0.066(2)	–0.004(1)	–0.005(1)	–0.009(1)
C(9)	2*i*	0.3679(3)	1.0143(2)	0.3992(2)	0.057(2)	0.055(2)	0.046(2)	–0.015(1)	–0.011(1)	–0.004(1)
C(10)	2*i*	0.4634(3)	1.0757(3)	0.3300(2)	0.061(2)	0.058(2)	0.064(2)	–0.021(2)	–0.015(2)	–0.003(2)
C(17)	2*i*	0.2026(3)	0.5189(2)	0.7237(2)	0.067(2)	0.052(2)	0.048(2)	–0.013(1)	–0.015(1)	–0.000(1)
C(22)	2*i*	0.3112(3)	0.5873(2)	0.7055(2)	0.057(2)	0.040(1)	0.052(2)	–0.003(1)	–0.022(1)	–0.002(1)
C(12)	2*i*	0.3603(3)	1.0453(3)	0.1908(2)	0.082(2)	0.059(2)	0.044(2)	–0.016(2)	–0.006(2)	0.004(1)
C(11)	2*i*	0.4600(3)	1.0915(3)	0.2262(2)	0.070(2)	0.056(2)	0.062(2)	–0.022(2)	–0.003(2)	0.004(2)
C(19)	2*i*	0.1817(4)	0.5125(3)	0.9069(2)	0.089(3)	0.069(2)	0.051(2)	–0.007(2)	–0.012(2)	0.010(2)
C(21)	2*i*	0.3518(3)	0.6182(3)	0.7917(2)	0.080(2)	0.061(2)	0.055(2)	–0.012(2)	–0.023(2)	–0.005(2)
N(1)	2*i*	0.1028(3)	0.8650(3)	1.0263(2)	0.095(2)	0.084(2)	0.050(2)	0.006(2)	–0.017(2)	–0.020(2)
O(2)	2*i*	0.0425(3)	0.7963(3)	1.0937(2)	0.160(3)	0.124(2)	0.047(2)	–0.030(2)	–0.018(2)	0.004(2)
C(18)	2*i*	0.1392(3)	0.4814(3)	0.8236(2)	0.078(2)	0.064(2)	0.063(2)	–0.018(2)	–0.014(2)	0.004(2)
C(29)	2*i*	0.7372(3)	0.7144(3)	0.4741(3)	0.043(2)	0.088(2)	0.090(2)	–0.010(2)	–0.017(2)	–0.024(2)
C(31)	2*i*	0.5917(3)	0.7690(3)	0.1101(2)	0.071(2)	0.080(2)	0.055(2)	–0.008(2)	0.008(2)	0.007(2)
C(20)	2*i*	0.2871(4)	0.5806(3)	0.8908(2)	0.099(3)	0.075(2)	0.051(2)	–0.010(2)	–0.026(2)	–0.006(2)
O(1)	2*i*	0.1771(3)	0.9337(3)	1.0435(2)	0.129(2)	0.125(2)	0.069(2)	–0.019(2)	–0.036(2)	–0.034(2)
C(32)	2*i*	0.5082(5)	0.7240(4)	0.0466(3)	0.121(4)	0.128(4)	0.061(2)	–0.018(3)	–0.021(2)	0.004(2)
C(15)	2*i*	0.1708(2)	0.6848(2)	0.4025(2)	0.040(1)	0.055(2)	0.040(1)	–0.014(1)	–0.011(1)	–0.001(1)
C(16)	2*i*	0.1036(3)	0.6007(3)	0.3564(2)	0.061(2)	0.066(2)	0.061(2)	–0.022(2)	–0.019(2)	–0.012(2)

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