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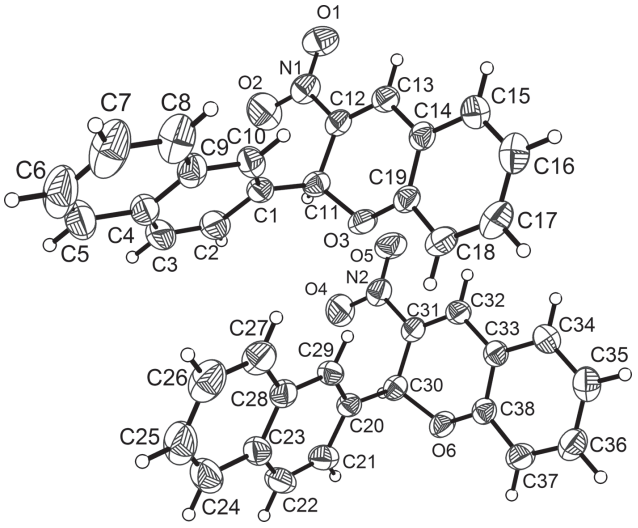
The pseudosymmetric crystal structure of 2-(2-naphthalenyl)-3-nitro-2*H*-1-benzopyran, $C_{38}H_{26}N_2O_6$



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Abstract

$C_{19}H_{13}NO_3$, triclinic, $P\bar{1}$ (no. 2), $a = 9.4457(6)$ Å, $b = 11.0520(7)$ Å, $c = 14.6746(9)$ Å, $\alpha = 100.779(1)°$, $\beta = 102.738(1)°$, $\gamma = 93.065(1)°$, $V = 1460.68(16)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0410$, $wR_{ref}(F^2) = 0.0911$, $T = 291$ K.

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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

The title compound was obtained according to the literature method of preparation of 8,9-dimethoxy-2-nitro-3-(2,4,5-trifluorophenyl)-3*H*-naphtho[2,1-*b*]pyran from 1,2,4-trifluoro-5-[(1*E*)-2-nitroethenyl]-benzene and 2-hydroxy-6,7-dimethoxy-1-naphthalenecarboxaldehyde [1–4]. A mixture of 2-nitroethenylnaphthalene (1.99 g, 10 mmol), *o*-hydroxybenzaldohyde (3.66 g, 30 mmol) and 1,4-diazabicyclo [2.2.2]octane (2.44 g, 2 mmol) dissolved in dry THF (30 mL) was refluxed for 3 hr, and then THF was evaporated, the residues were directly charged on a chromatography column to give the pure product 1.42 g (80.5%). Colourless crystals were obtained by slow evaporation of mixed solution of dichloromethane and ethanol (volume 1:1) at room temperature.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.35 × 0.33 × 0.28 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II area-detector, φ and ω
θ_{max}:	27.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16893, 6612, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4723
$N(param)_{refined}$:	415
Programs:	Bruker programs [10], SHELX [11], DIAMOND [12]

Experimental details

Hydrogen atoms were placed geometrically and refined using a riding model with d(C—H) = 0.93–0.98 Å, U_{iso}(H) = 1.2 U_{eq}(C) for CH groups. The element of pseudo symmetry in the tiltle structure is a translation along the crystallographic *b* direction. Generally reflections hkl with k = odd are weaker than those with k = even. All over the structure the translational pseudosymmetry fit is 86% according to the CheckCif program.

Discussion

The 3-nitrochromenes were reported to have pharmaceutically interesting properties, such as anti-breast cancer agents [5], antifungal activity [6], flavodoxin inhibitors against

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.24900(15)	0.32046(12)	0.38101(10)	0.0473(3)
N2	0.24749(15)	0.81438(12)	0.38340(9)	0.0462(3)
O1	0.28085(14)	0.25661(11)	0.44079(9)	0.0604(3)
O2	0.12406(14)	0.32387(14)	0.33560(11)	0.0796(4)
O3	0.42326(11)	0.57580(9)	0.29709(8)	0.0448(3)
O4	0.12219(14)	0.82197(14)	0.34006(10)	0.0736(4)
O5	0.27881(14)	0.74394(11)	0.43849(9)	0.0597(3)
O6	0.42530(11)	1.08039(9)	0.31461(8)	0.0444(3)
C1	0.26524(15)	0.40583(13)	0.18647(10)	0.0370(3)
C2	0.13272(17)	0.42842(16)	0.12885(13)	0.0517(4)
H2A	0.0742	0.4835	0.1549	0.062*
C3	0.08978(19)	0.37035(17)	0.03552(14)	0.0611(5)
H3A	0.0014	0.3856	−0.0010	0.073*
C4	0.17596(19)	0.28805(16)	−0.00671(11)	0.0519(4)
C5	0.1348(3)	0.2270(2)	−0.10422(14)	0.0775(7)
H5A	0.0470	0.2410	−0.1422	0.093*
C6	0.2215(3)	0.1489(2)	−0.14254(14)	0.0892(8)
H6A	0.1933	0.1105	−0.2067	0.107*
C7	0.3527(3)	0.1257(2)	−0.08672(15)	0.0813(7)
H7A	0.4115	0.0719	−0.1139	0.098*
C8	0.3958(2)	0.18126(18)	0.00761(13)	0.0634(5)
H8A	0.4833	0.1643	0.0443	0.076*
C9	0.30899(17)	0.26403(15)	0.04991(11)	0.0450(4)
C10	0.34958(16)	0.32444(14)	0.14722(10)	0.0411(3)
H10A	0.4361	0.3082	0.1854	0.049*
C11	0.31119(15)	0.47606(13)	0.28858(10)	0.0381(3)
H11A	0.2260	0.5141	0.3045	0.046*
C12	0.36282(16)	0.39791(13)	0.36058(10)	0.0368(3)
C13	0.50148(16)	0.39386(13)	0.40246(10)	0.0385(3)
H13A	0.5269	0.3425	0.4457	0.046*
C14	0.61299(16)	0.47066(13)	0.37989(10)	0.0367(3)
C15	0.76196(17)	0.46305(15)	0.41221(11)	0.0466(4)
H15A	0.7937	0.4059	0.4495	0.056*
C16	0.86248(18)	0.54007(16)	0.38910(12)	0.0547(4)
H16A	0.9618	0.5351	0.4109	0.066*
C17	0.81502(19)	0.62473(16)	0.33333(13)	0.0544(4)
H17A	0.8831	0.6764	0.3179	0.065*
C18	0.66815(18)	0.63365(14)	0.30024(11)	0.0467(4)
H18A	0.6373	0.6902	0.2622	0.056*
C19	0.56747(16)	0.55759(12)	0.32433(10)	0.0367(3)
C20	0.27822(15)	0.91593(13)	0.19336(10)	0.0359(3)
C21	0.20709(17)	0.98466(15)	0.12736(12)	0.0470(4)
H21A	0.1788	1.0619	0.1495	0.056*
C22	0.17998(18)	0.93853(17)	0.03189(12)	0.0520(4)
H22A	0.1339	0.9851	−0.0104	0.062*
C23	0.22040(17)	0.82141(16)	−0.00415(11)	0.0466(4)
C24	0.1960(2)	0.7712(2)	−0.10332(12)	0.0642(5)
H24A	0.1519	0.8167	−0.1471	0.077*
C25	0.2360(2)	0.6580(2)	−0.13518(13)	0.0728(6)
H25A	0.2196	0.6270	−0.2005	0.087*
C26	0.3019(2)	0.58723(19)	−0.07083(14)	0.0674(5)
H26A	0.3281	0.5094	−0.0935	0.081*
C27	0.32780(19)	0.63241(16)	0.02557(12)	0.0537(4)
H27A	0.3716	0.5849	0.0679	0.064*
C28	0.28855(16)	0.75060(14)	0.06116(10)	0.0409(3)
C29	0.31635(15)	0.80138(13)	0.16038(10)	0.0371(3)
H29A	0.3614	0.7557	0.2038	0.044*
C30	0.31370(15)	0.97723(13)	0.29786(10)	0.0377(3)
H30A	0.2254	1.0113	0.3120	0.045*
C31	0.36229(16)	0.89311(13)	0.36583(10)	0.0363(3)
C32	0.50095(16)	0.88535(13)	0.40550(9)	0.0373(3)
H32A	0.5260	0.8301	0.4456	0.045*
C33	0.61304(15)	0.96414(13)	0.38553(9)	0.0356(3)
C34	0.76176(16)	0.95318(15)	0.41492(10)	0.0435(4)
H34A	0.7928	0.8912	0.4475	0.052*
C35	0.86328(17)	1.03392(16)	0.39596(11)	0.0486(4)
H35A	0.9624	1.0265	0.4158	0.058*
C36	0.81691(18)	1.12585(15)	0.34729(11)	0.0490(4)
H36A	0.8855	1.1802	0.3349	0.059*
C37	0.67039(17)	1.13794(14)	0.31694(11)	0.0440(4)
H37A	0.6402	1.1991	0.2834	0.053*
C38	0.56868(15)	1.05810(12)	0.33689(10)	0.0359(3)

helicobacter pylori infection [7], radioprotective activity [8] and so on. There are two crystallographically independent molecules in the asymmetric unit of the title structure (*cf*. the figure). They show pseudo-translational symmetry as discussed before [9]. Bond lengths and angels are all in the expected ranges. The dieder angles of O3-C11-C1-C10 is 75°, while the O6-C30-C20-C29 is 110°. The bond angle of C11–C12–C13 is 124.39(13)°, but the C30-C31-C32 is 123.48(13)°.

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References

1. Li, S.-L.; Xu, H.-L.; Cui, S.-C.; Wu, F.-S.; Zhang, Y.-L.; Su, M.-B.; Gong, Y.-H.; Qiu, S.-B.; Jiao, Q.; Qin, C.; Shan, J.-W.; Zhang, M.; Wang, J.-W.; Yin, Q.; Xu, M.-H.; Liu, X.-F.; Wang, R.; Zhu, L.-L.; Li, J.; Xu, Y.-F.; Jiang, H.-L.; Zhao, Z.-J.; Li, J.-Y.; Li, H.-L.: Discovery and rational design of natural-product-derived 2-phenyl-3,4-dihydro-2*H*-benzo[*f*]chromen-3-amine analogs as novel and potent dipeptidyl peptidase 4 (DPP-4) inhibitors for the treatment of type 2 diabetes. J. Med. Chem. **59** (2016) 6772–6790.
2. Xu, D.-Q.; Wang, Y.-F.; Luo, S.-P.; Zhang, S.; Zhong, A.-G.; Chen, H.; Xu, Z.-Y.: A novel enantioselective catalytic tandem oxa-Michael-Henry reaction: one-pot organocatalytic asymmetric synthesis of 3-nitro-2*H*-chromenes. Adv. Synth. Catal. **350** (2008) 2610–2616.
3. Ballini, R.; Bosica, G.; Fiorini, D.; Palmieri, A.: Neutral alumina catalysed synthesis of 3-nitro-1,2-dihydroquinolines and 3-nitrochromenes, under solvent-free conditions, *via* tandem process. Green Chem. **7** (2005) 825–827.
4. Varma, R. S.; Kadkhodayan, M.; Kabalka, G. W.: The synthesis of 2-naphthyl-3-nitro-2*H*-1-benzopyrans. Synthesis **6** (1986) 486–488.

5. Fouqué, A.; Delalande, O.; Jean, M.; Castellano, R.; Josselin, E.; Malleter, M.; Shoji, K. F.; Hung, M. D.; Rampanarivo, H.; Collette, Y.; van de Weghe, P.; Legembre, P.: A novel covalent mTOR inhibitor, DHM25, shows in *vivo* antitumor activity against triple-negative breast cancer cells. J. Med. Chem. **58** (2015) 6559–6573.
6. Gallo-Ebert, C.; Donigan, M.; Stroke, I. L.; Swanson, R. N.; Manners, M. T.; Francisco, J.; Toner, G.; Gallagher, D.; Huang, C.-Y.; Gygax, S. E.; Webb, M.; Nickels, J. T.: Novel antifungal drug discovery based on targeting pathways regulating the fungus-conserved Upc2 transcription factor. Antimicrob. Agents Ch. **58** (2014) 258–266.
7. Galano, J. J.; Alias, M.; Perez, R.; Velazquez-Campoy, A.; Hoffman, P. S.; Sancho, J.: Improved flavodoxin inhibitors with potential therapeutic effects against helicobacter pylori infection. J. Med. Chem. **56** (2013) 6248–6258.
8. Fatome, M.; Andrieu, L.; Laval, J. D.; Royer, R.; Rene, L.: Radioprotecting effects of *Δ*3-chromenes substituted by an electron-attracting group in the 3-position. Eur. J. Med. Chem. **11** (1976) 81–82.
9. Reiss, G. J.: The pseudosymmetric crystal structure of bis((dimethylphosphoryl)-methanaminium oxonium tribromide. Z. Kristallogr. NCS **228** (2013) 431–433.
10. Bruker: APEX2, SAINT, Bruker AXS Inc. Madison, WI, USA (2009).
11. Sheldrick, G. M.: A short history of *SHELX*. Acta Crystallogr. **A64** (2008) 112–122.
12. Brandenburg, K.: *DIAMOND*. Visual Crystal Structure Information System. Version 3.2i, Crystal Impact, Bonn, Germany (2012).