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Crystal structure of 2-oxo-1-(pyrimidin-5-ylmethyl)-3-(3-(trifluoromethyl)phenyl)-1,2-dihydro-5[4-pyrido[1,2-a]pyrimidin-4-olate, $C_{20}H_{13}F_3N_4O_2$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.16 × 0.14 × 0.12 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.12 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	25.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13789, 6557, 0.018
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4729
$N(\text{param})_{\text{refined}}$:	524
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.64548(15)	0.61208(12)	−0.02771(13)	0.0359(4)
N2	0.60039(16)	0.79195(13)	−0.05909(13)	0.0402(4)
N3	0.4451(2)	0.9377(2)	−0.2909(2)	0.0761(7)
N4	0.5802(2)	1.07862(17)	−0.32960(15)	0.0583(5)
N5	0.28673(17)	0.71963(13)	0.74578(14)	0.0426(4)
N6	0.16724(16)	0.82321(14)	0.65745(13)	0.0419(4)
N7	0.1696(2)	1.15172(17)	0.43342(18)	0.0611(6)
N8	0.2367(2)	1.14491(18)	0.5847(2)	0.0712(6)
O1	0.51386(14)	0.51400(11)	0.11790(12)	0.0476(4)
O2	0.42007(16)	0.87504(12)	0.04180(14)	0.0603(5)
O3	0.21238(17)	0.68711(15)	0.93115(13)	0.0666(5)
O4	−0.02772(15)	0.89287(13)	0.74796(13)	0.0546(4)
F1	0.1578(3)	0.46935(15)	0.47081(18)	0.1224(8)
F2	0.3103(2)	0.53887(18)	0.48375(14)	0.1027(6)
F3	0.1282(2)	0.60544(18)	0.55855(14)	0.1252(9)
F4	−0.1767(4)	0.5352(2)	1.16110(19)	0.1722(14)
F5	−0.1498(3)	0.6141(2)	1.2769(2)	0.1437(11)
F6	−0.3229(2)	0.6230(3)	1.2607(3)	0.1748(14)
C1	0.67559(19)	0.70382(15)	−0.09094(15)	0.0358(4)
C2	0.7812(2)	0.70287(18)	−0.18643(18)	0.0484(5)
H2	0.8005	0.7638	−0.2330	0.058*
C3	0.8556(2)	0.61269(19)	−0.21097(19)	0.0543(6)
H3	0.9264	0.6123	−0.2740	0.065*
C4	0.8263(2)	0.52106(18)	−0.14232(19)	0.0523(6)
H4	0.8785	0.4598	−0.1576	0.063*
C5	0.7214(2)	0.52231(17)	−0.05343(18)	0.0442(5)
H5	0.7001	0.4606	−0.0084	0.053*
C6	0.4833(2)	0.79085(16)	0.02807(17)	0.0421(5)

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Abstract

$C_{20}H_{13}F_3N_4O_2$, triclinic, $P\bar{1}$ (no. 2), $a = 11.3525(10)$ Å, $b = 12.7530(11)$ Å, $c = 13.1926(12)$ Å, $\alpha = 83.894(1)^\circ$, $\beta = 69.314(1)^\circ$, $\gamma = 84.720(1)^\circ$, $V = 1773.7(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0477$, $wR_{\text{ref}}(F^2) = 0.1433$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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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}
C7	0.4508(2)	0.69391(16)	0.09154(16)	0.0400(5)
C8	0.52883(19)	0.60225(16)	0.06985(16)	0.0376(5)
C9	0.3300(2)	0.69155(16)	0.18443(17)	0.0430(5)
C10	0.2207(2)	0.74638(18)	0.1770(2)	0.0540(6)
H10	0.2233	0.7854	0.1127	0.065*
C11	0.1088(3)	0.7433(2)	0.2643(3)	0.0686(8)
H11	0.0372	0.7812	0.2584	0.082*
C12	0.1017(3)	0.6850(2)	0.3597(2)	0.0697(8)
H12	0.0258	0.6826	0.4178	0.084*
C13	0.2088(2)	0.62991(18)	0.36827(19)	0.0557(6)
C14	0.3223(2)	0.63378(17)	0.28196(17)	0.0474(5)
H14	0.3940	0.5974	0.2893	0.057*
C15	0.1999(3)	0.5625(2)	0.4691(2)	0.0702(8)
C16	0.6417(2)	0.89679(15)	−0.11010(17)	0.0419(5)
H16A	0.7329	0.8924	−0.1437	0.050*
H16B	0.6198	0.9456	−0.0538	0.050*
C17	0.5861(2)	0.94077(16)	−0.19411(16)	0.0393(5)
C18	0.4933(3)	0.8965(2)	−0.2154(2)	0.0617(7)
H18	0.4619	0.8344	−0.1753	0.074*
C19	0.4937(3)	1.0261(2)	−0.3447(2)	0.0642(7)
H19	0.4634	1.0545	−0.3993	0.077*
C20	0.6247(2)	1.03481(18)	−0.25337(17)	0.0482(5)
H20	0.6852	1.0695	−0.2393	0.058*
C21	0.2768(2)	0.76818(16)	0.65200(16)	0.0403(5)
C22	0.3796(2)	0.75795(19)	0.55549(19)	0.0516(6)
H22	0.3757	0.7919	0.4907	0.062*
C23	0.4852(2)	0.6985(2)	0.5560(2)	0.0621(7)
H23	0.5532	0.6918	0.4916	0.074*
C24	0.4918(2)	0.6478(2)	0.6526(2)	0.0642(7)
H24	0.5632	0.6061	0.6533	0.077*
C25	0.3932(2)	0.65997(18)	0.7453(2)	0.0534(6)
H25	0.3977	0.6271	0.8103	0.064*
C26	0.0642(2)	0.83797(17)	0.75605(17)	0.0435(5)
C27	0.0771(2)	0.78767(17)	0.85265(17)	0.0438(5)
C28	0.1863(2)	0.72968(17)	0.85416(17)	0.0464(5)
C29	−0.0294(2)	0.79774(19)	0.95717(18)	0.0483(5)
C30	−0.0955(3)	0.8940(2)	0.9842(2)	0.0640(7)
H30	−0.0719	0.9541	0.9370	0.077*
C31	−0.1959(3)	0.9013(3)	1.0808(2)	0.0856(10)
H31	−0.2396	0.9662	1.0976	0.103*
C32	−0.2319(3)	0.8139(3)	1.1524(2)	0.0827(9)
H32	−0.2992	0.8193	1.2174	0.099*
C33	−0.1672(2)	0.7182(2)	1.12660(19)	0.0615(7)
C34	−0.0667(2)	0.7098(2)	1.03022(18)	0.0533(6)
H34	−0.0236	0.6447	1.0140	0.064*
C35	−0.2035(3)	0.6248(3)	1.2050(2)	0.0790(9)
C36	0.1484(2)	0.87329(17)	0.55879(17)	0.0453(5)
H36A	0.0627	0.8640	0.5635	0.054*
H36B	0.2051	0.8380	0.4967	0.054*
C37	0.17099(19)	0.98893(17)	0.54056(16)	0.0414(5)
C38	0.1503(2)	1.04929(19)	0.45452(18)	0.0495(6)
H38	0.1212	1.0165	0.4089	0.059*
C39	0.2129(2)	1.1930(2)	0.5001(2)	0.0639(7)
H39	0.2283	1.2644	0.4855	0.077*
C40	0.2136(3)	1.0427(2)	0.6042(2)	0.0590(6)
H40	0.2271	1.0059	0.6643	0.071*

Source of materials

The synthesis of triflumezopyrim was carried out using 2-[3-(trifluoromethyl)phenyl]malonic acid and *N*-(pyrimidin-5-ylmethyl)pyridin-2-amine as start material, using a modified literature known reaction [3–5]. The educt 2-[3-(trifluoromethyl)phenyl]malonic acid (0.36 g, 1.45 mmol) was dissolved in dichloromethane (20 mL), oxalyl chloride (0.37 mL, 2.9 mmol) and two drops of DMF was added. The reaction was stirred for 1 h at room temperature. The mixture was concentrated under reduced pressure, 10 mL dichloromethane was added for next step use. And then triethylamine (1.1 mL, 7.94 mmol) and *N*-(pyrimidin-5-ylmethyl)pyridin-2-amine (0.27 g, 1.45 mmol) in 10 mL CH₂Cl₂ was slowly added to the above solution at 0 °C and then stirred at room temperature. The reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography to give the title compound (0.15 g), Yield 26%. The product was recrystallized from acetone. m.p. 182–184 °C. Elemental Anal. Calcd. (%) for C₂₀H₁₃F₃N₄O₂ (398.38): C, 60.30; H, 3.29; Found. (%). C, 60.13; H, 3.56.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.93 Å with *U*_{iso}(H) = 1.5 *U*_{eq}(C) for methyl H atoms and 1.2 *U*_{eq}(C) for all other H atoms.

Comment

The title compound Triflumezopyrim is a novel mesoionic insecticide, which has a good internal absorption conduction activity and is the only inhibitory compound in insecticides acting on nicotinic acetylcholine receptors (nAChRs) [6–8]. It mainly controls rice planthoppers and cicadellidae, and has good control effect on various pests such as lepidoptera and homoptera. It can be used in crops like cotton, rice, corn and soybeans [9, 10]. It is used in non-agricultural fields and has a broad market [6]. Herein we report the crystal structure of triflumezopyrim, which makes this kind of compound better understood and paves the way for the development of more novel mesoionic compounds.

There are two crystallographic independent molecules in the asymmetric unit (shown in the figure). There are a pair of external racemate trifluorabrimidine in the figure. In the molecule of the title compound bond lengths and angles are very similar to those given in the literature for 2,4-diphenyl-4,5,6,7-tetrahydro-4,7*a*,12*b*-triazadibenzo(*e,g*)azulene-1,3,8-trione [11]. In the title structure, all the non-hydrogen atoms in pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-dione ring are approximately coplanar. The dihedral angles of pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-dione ring, pyrimidine ring and benzene ring are 80.4, 40.5 and 55.7°, respectively.

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