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Short Communication

Crystal Structure of 4-[5-(5-Methoxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yloxy)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl]-6-methyl-2-phenylpyridazin-3(2*H*)-one

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In connection with our interest in the reactions of the oxidized dimer of 3-methyl-1-phenyl-2-pyrazolin-5-one ('pyrazolone blue') the crystal structure of one of the products formed in the reaction between 'pyrazolone blue' and diazomethane has been determined.[1,2] The synthesis, reaction mechanism, and spectroscopic data have been published separately.[2]

Experimental

The oxidized dimer of 3-methyl-1-phenyl-2-pyrazolin-5-one ('pyrazolone blue') reacts with diazomethane in diethyl ether forming several products. In the reaction two different intermediates and diazomethane form a structure with two pyrazole and one pyridazinone rings, each having a phenyl and a methyl substituent and an additional methoxy group in the pyrazolyl ring. Spectroscopic methods (^{1}H NMR and MS) showed the compound to have a structure of 4-[5-(methoxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yloxy)-3-methoxy-1-phenyl-1*H*-pyrazol-4-yl]-6-methyl-2-phenylpyridazin-3(2*H*)-one.[2] We report here the crystal structure of the title compound.

Crystal data. $C_{32}H_{28}N_6O_3$, $M_r = 544.59$, triclinic, *P*-1, $a = 13.221(2)$, $b = 13.748(2)$, $c = 9.455(1)$, $\alpha = 87.86(1)$, $\beta = 110.54(1)$, $\gamma = 116.86(1)°$, $V = 1405.4(7)$ Å^3, $Z = 2$, $D_x = 1.28$ Mg m^{-3}, λ(MoKα) = 0.7107 Å, $\mu = 0.8$ cm^{-1}, $F(000) = 572$, $T = 296$ K, final $R = 0.065$ and $R_w = 0.064$ for 2732 unique observed reflections and 370 parameters.

The unit cell was determined by least-squares refinement of 25 carefully centered independent reflections ($6 < 2\theta < 12°$) measured at room temperature on an Enraf-Nonius CAD-4 diffractometer. The data were corrected for Lorenz and polarization effects and for absorption (DIFABS,[3] min. and max. correction coefficients 0.681 and 1.265, respectively).

Data collection and refinement. A total of 4921 reflections were collected ($2\theta_{max} = 25°$) of which 2732 were considered observed according to the criterion $I < 3\sigma(I)$. The two check reflections measured every hour did not show any decay on intensity.

The structure was resolved by direct methods by using the SHELXS86[4] program and subsequent Fourier synthesis. Full-matrix least-squares refinement method using Chebychev weighting (four coefficients) and *F*s, non-H atoms were refined anisotropically and the hydrogen atoms were calculated (1.00 Å) and used as riding atoms with fixed isotropic temperature factors ($U = 0.08$ Å^2). The final difference Fourier map did not show any peaks higher than 0.58 e Å^{-3}.

The scattering factors were taken from Ref. 5. All calculations were performed on a 486-PC (66 MHz) and the refinements and all subsequent calculations were done using the CRYSTALS[6] program (PC version). The figures were drawn using the program SCHAKAL.[7] Final atomic coordinates with e.s.d.s in parentheses with equivalent isotropic temperature factors are listed in Table 1 and bond distances and angles in Table 2. Lists of anisotropic temperature factors, least-squares planes and structure factors are available from the authors on request.

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Table 1. Fractional coordinates with e.s.d.s in parentheses and equivalent isotropic temperature[a] factors for the title compound.

Atom	*x/a*	*y/b*	*z/c*	*U*(iso)	Occ
O(71)	0.8917(2)	0.8965(2)	0.1631(3)	0.0576	1.0000
O(31)	0.6209(2)	0.9873(2)	0.2868(3)	0.0532	1.0000
O(331)	0.8459(2)	0.9478(2)	0.4715(4)	0.0581	1.0000
N(1)	0.7206(3)	1.0973(3)	−0.0082(4)	0.0513	1.0000
N(2)	0.6784(3)	1.0943(2)	0.1072(3)	0.0462	1.0000
N(8)	0.7818(3)	0.7190(2)	0.1940(3)	0.0441	1.0000
N(9)	0.6783(3)	0.6304(2)	0.1976(4)	0.0460	1.0000
N(34)	0.6886(3)	0.8015(3)	0.5222(3)	0.0477	1.0000
N(35)	0.5645(3)	0.7539(3)	0.4836(4)	0.0562	1.0000
C(3)	0.6584(3)	0.9995(3)	0.1673(4)	0.0439	1.0000
C(4)	0.6876(3)	0.9379(3)	0.0922(4)	0.0432	1.0000
C(5)	0.7265(4)	1.0045(3)	−0.0151(4)	0.0490	1.0000
C(6)	0.6813(3)	0.8304(3)	0.1178(4)	0.0424	1.0000
C(7)	0.7934(3)	0.8213(3)	0.1577(4)	0.0460	1.0000
C(10)	0.5798(3)	0.6415(3)	0.1563(4)	0.0468	1.0000
C(11)	0.5778(3)	0.7409(3)	0.1134(4)	0.0449	1.0000
C(21)	0.6761(3)	1.1900(3)	0.1568(4)	0.0450	1.0000
C(22)	0.7554(4)	1.2913(3)	0.1333(5)	0.0556	1.0000
C(23)	0.7554(4)	1.3858(3)	0.1809(5)	0.0631	1.0000
C(24)	0.6777(4)	1.3786(4)	0.2512(5)	0.0622	1.0000
C(25)	0.5971(4)	1.2764(4)	0.2719(5)	0.0603	1.0000
C(26)	0.5951(4)	1.1809(3)	0.2226(4)	0.0520	1.0000
C(32)	0.6282(3)	0.9061(3)	0.3759(4)	0.0460	1.0000
C(33)	0.7287(3)	0.8941(3)	0.4573(4)	0.0455	1.0000
C(36)	0.5285(3)	0.8185(3)	0.3959(5)	0.0519	1.0000
C(51)	0.7639(5)	0.9772(4)	−0.1336(5)	0.0685	1.0000
C(81)	0.8877(3)	0.7004(3)	0.2487(4)	0.0446	1.0000
C(82)	0.9595(4)	0.7208(4)	0.1652(5)	0.0650	1.0000
C(83)	1.0605(5)	0.7022(5)	0.2215(7)	0.0781	1.0000
C(84)	1.0872(4)	0.6629(4)	0.3578(7)	0.0734	1.0000
C(85)	1.0153(4)	0.6431(4)	0.4400(5)	0.0641	1.0000
C(86)	0.9151(4)	0.6628(3)	0.3874(4)	0.0508	1.0000
C(101)	0.4659(4)	0.5431(3)	0.1574(5)	0.0611	1.0000
C(332)	0.9000(4)	1.0658(3)	0.4866(5)	0.0644	1.0000
C(341)	0.7552(4)	0.7460(3)	0.6052(4)	0.0497	1.0000
C(342)	0.8761(4)	0.8051(4)	0.7024(5)	0.0573	1.0000
C(343)	0.9385(5)	0.7471(5)	0.7760(5)	0.0697	1.0000
C(344)	0.8813(6)	0.6350(6)	0.7562(6)	0.0753	1.0000
C(345)	0.7597(5)	0.5770(4)	0.6627(6)	0.0732	1.0000
C(346)	0.6949(4)	0.6320(4)	0.5842(5)	0.0621	1.0000
C(361)	0.3987(4)	0.7957(5)	0.3339(6)	0.0749	1.0000

[a] $U(\text{iso}) = [U(11) \times U822) \times U(33)]^{1/3}$.

Results and discussion

Fig. 1 shows a perspective drawing of the molecule and Fig. 2 a view of the packing. The numbering of the atoms used in Tables 1 and 2 is presented in Scheme 1.

The bond distances and angles are normal (Table 2).[1] The compound can be formulated as an ether derived from three 'pyrazolone blue' and two diazomethane molecules. The pyridazinone and two pyrazole rings are planar. The torsion angles: −164.22° for N(2)–C(3)–O(31)–C(32), 55.49° between the pyridazinone and pyrazolyl rings, 154.22° between the phenyl and pyrazolyl rings, 29.70° between the phenyl and pyrazoloxy rings and 129.91° between the pyridazinone and phenyl rings, respectively, are mainly the result of the packing forces. There are no contacts shorter than the van der Waals radii of the atoms.

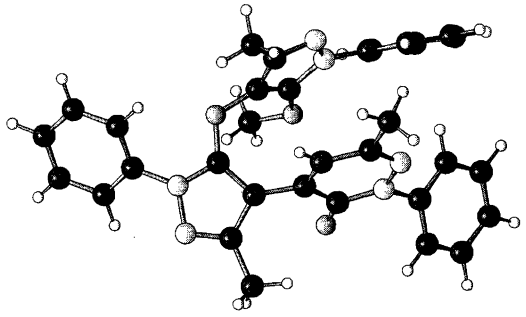


Fig. 1. A perspective drawing of the molecule.

Table 2. Bond distances (Å) and angles (°) for the title compound with e.s.d.s in parentheses.

O(71)–C(7)	1.225(4)	C(3)–O(31)–C(32)	118.5(3)
O(31)–C(3)	1.362(4)	C(33)–O(331)–C(332)	116.3(3)
O(31)–C(32)	1.391(4)	N(2)–N(1)–C(5)	105.2(3)
O(331)–C(33)	1.338(4)	N(1)–N(2)–C(3)	110.2(3)
O(331)–C(332)	1.436(5)	N(1)–N(2)–C(21)	119.2(3)
N(1)–N(2)	1.381(4)	C(3)–N(2)–C(21)	130.1(3)
N(1)–C(5)	1.318(5)	N(9)–N(8)–C(7)	126.5(3)
N(2)–C(3)	1.354(4)	N(9)–N(8)–C(81)	112.6(3)
N(2)–C(21)	1.429(5)	C(7)–N(8)–C(81)	120.6(3)
N(8)–N(9)	1.371(4)	N(8)–N(9)–C(10)	116.8(3)
N(8)–C(7)	1.387(5)	N(35)–N(34)–C(33)	111.0(3)
N(8)–C(81)	1.448(4)	N(35)–N(34)–C(341)	119.9(3)
N(9)–C(10)	1.300(5)	C(33)–N(34)–C(341)	128.7(3)
N(34)–N(35)	1.370(4)	N(34)–N(35)–C(36)	105.7(3)
N(34)–C(33)	1.356(5)	O(31)–C(3)–N(2)	116.6(3)
N(34)–C(341)	1.432(5)	O(31)–C(3)–C(4)	134.7(3)
N(35)–C(36)	1.323(5)	N(2)–C(3)–C(4)	108.7(3)
C(3)–C(4)	1.379(5)	C(3)–C(4)–C(5)	103.4(3)
C(4)–C(5)	1.415(5)	C(3)–C(4)–C(6)	128.5(3)
C(4)–C(6)	1.457(5)	C(5)–C(4)–C(6)	128.1(3)
C(5)–C(51)	1.492(6)	N(1)–C(5)–C(4)	112.5(3)
C(6)–C(7)	1.457(5)	N(1)–C(5)–C(51)	120.0(3)
C(6)–C(11)	1.353(5)	C(4)–C(5)–C(51)	127.4(3)
C(10)–C(11)	1.420(5)	C(4)–C(6)–C(7)	118.1(3)
C(10)–C(101)	1.505(5)	C(4)–C(6)–C(11)	122.8(3)
C(21)–C(22)	1.382(5)	C(7)–C(6)–C(11)	119.0(3)
C(21)–C(26)	1.373(5)	O(7)–C(7)–N(8)	121.2(3)
C(22)–C(23)	1.391(6)	O(71)–C(7)–C(6)	124.5(3)
C(23)–C(24)	1.374(6)	N(8)–C(7)–C(6)	114.3(3)
C(24)–C(25)	1.386(6)	N(9)–C(10)–C(11)	122.7(3)
C(25)–C(26)	1.397(6)	N(9)–C(10)–C(101)	116.5(3)
C(32)–C(33)	1.361(5)	C(11)–C(10)–C(101)	120.8(3)
C(32)–C(36)	1.396(5)	C(6)–C(11)–C(10)	120.5(3)
C(36)–C(361)	1.485(6)	N(2)–C(21)–C(22)	118.1(3)
C(81)–C(82)	1.368(5)	N(2)–C(21)–C(26)	120.8(3)
C(81)–C(86)	1.379(5)	C(22)–C(21)–C(26)	121.1(3)
C(82)–C(83)	1.388(6)	C(21)–C(22)–C(23)	119.3(4)
C(83)–C(84)	1.371(7)	C(22)–C(23)–C(24)	120.4(4)
C(84)–C(85)	1.359(7)	C(23)–C(24)–C(25)	119.8(4)
C(85)–C(86)	1.389(6)	C(24)–C(25)–C(26)	120.3(4)
C(341)–C(342)	1.382(6)	C(21)–C(26)–C(25)	119.1(4)
C(341)–C(346)	1.383(6)	O(31)–C(32)–C(33)	128.6(3)
C(342)–C(343)	1.396(6)	O(31)–C(32)–C(36)	124.6(3)
C(343)–C(344)	1.361(8)	C(33)–C(32)–C(36)	106.7(3)
C(344)–C(345)	1.377(8)	O(331)–C(33)–N(34)	120.0(3)
C(345)–C(346)	1.397(6)	O(331)–C(33)–C(32)	133.3(3)
		N(34)–C(33)–C(32)	106.4(3)
		N(35)–C(36)–C(32)	110.2(3)
		N(35)–C(36)–C(361)	121.9(4)
		C(32)–C(36)–C(361)	127.9(4)
		N(8)–C(81)–C(82)	120.6(3)
		N(8)–C(81)–C(86)	118.5(3)
		C(82)–C(81)–C(86)	120.9(4)
		C(81)–C(82)–C(83)	119.0(4)
		C(82)–C(83)–C(84)	120.6(4)
		C(83)–C(84)–C(85)	119.9(4)
		C(84)–C(85)–C(86)	120.5(4)
		C(81)–C(86)–C(85)	119.0(4)
		N(34)–C(341)–C(342)	120.6(4)
		N(34)–C(341)–C(346)	118.0(4)
		C(342)–C(341)–C(346)	121.4(4)
		C(341)–C(342)–C(343)	118.4(4)
		C(342)–C(343)–C(344)	121.1(5)
		C(343)–C(344)–C(345)	119.9(4)
		C(344)–C(345)–C(346)	120.7(5)
		C(341)–C(346)–C(345)	118.4(4)

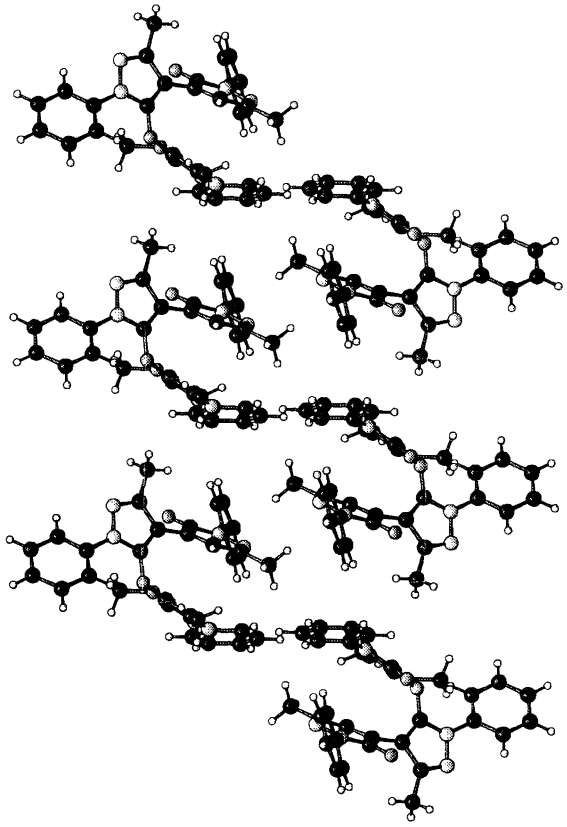
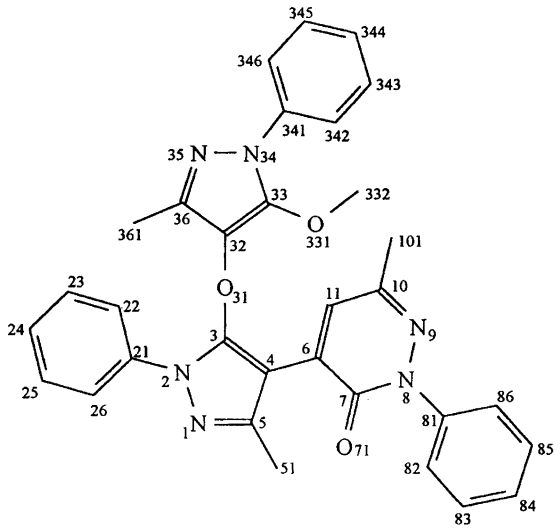


Fig. 2. A packing view of the molecule.



Scheme 1. A schematic drawing of the molecule with the numbering.

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