

Brief Communications

Synthesis and structure of 5-*p*-ethoxyphenyl-3-methoxycarbonyl-1-*p*-tolyl-4-*p*-tolylloxamoylpyrazole

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4-*p*-Ethoxybenzoyl-5-methoxycarbonyl-1-*p*-tolylpyrrole-2,3-dione reacts with *p*-tolylhydrazine to form 5-*p*-ethoxyphenyl-3-methoxycarbonyl-1-*p*-tolyl-4-*p*-tolylloxamoylpyrazole. The molecular and crystal structure of the title compound was studied by X-ray diffraction analysis.

Key words: pyrrole-2,3-dione, arylhydrazine, pyrazole, molecular and crystal structure.

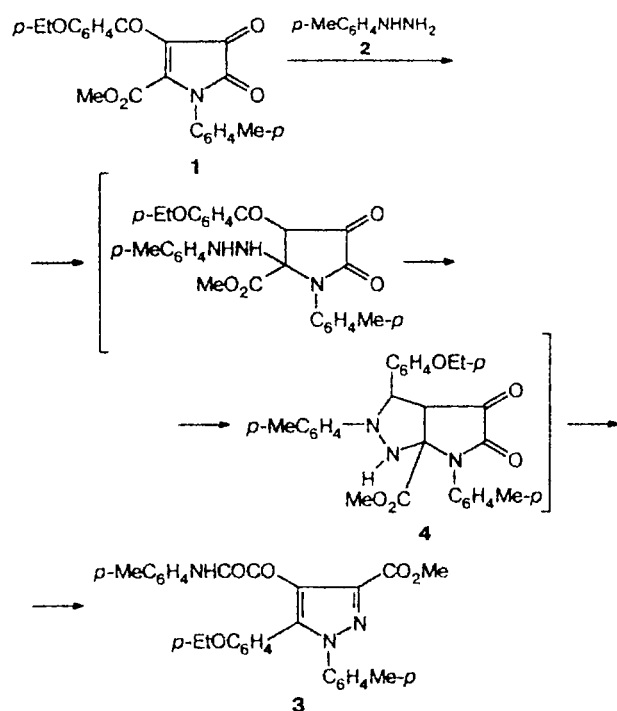
Reactions of 4-unsubstituted, 4-methyl-, and 4-phenyl-1,5-disubstituted pyrrole-2,3-diones with phenyl- and *p*-nitrophenylhydrazines, which involve the attack of the primary amino group of the reagent on the carbonyl group at position 3 of the heterocycle as the initial stage to form 3-arylhya zones, which exist generally as *Z* isomers, were reported in the literature.^{1–4} As part of continuing studies of conversions of 1-aryl-4-aryloxy-5-methoxycarbonylpyrrole-2,3-diones in reactions with various nucleophilic reagents,⁵ we studied the reaction of 4-*p*-ethoxybenzoyl-5-methoxycarbonyl-1-*p*-tolylpyrrole-2,3-dione (1) with *p*-tolylhydrazine (2). Previously, it has been reported^{5–8} that, unlike reactions with 4-unsubstituted, 4-methyl-, and 4-phenyl-1,5-disubstituted pyrrole-2,3-diones,^{1–4} nucleophiles initially add to 4-acylpyrrole-2,3-diones at the carbon atom at position 5 of the heterocycle followed by the attack (by

the second nucleophilic center) on the carbonyl group of the acyl substituent at position 4 of the heterocycle. These data cause one to anticipate that the reaction under study would afford the difficultly accessible fused system of pyrrolo[2,3-*c*]pyrazole.

Pyrroledione 1 reacted with hydrazine 2 taken in a ratio of 1 : 1 upon boiling in anhydrous benzene for 15 min to form a colorless crystalline compound whose structure has not been unambiguously determined by IR and ¹H NMR spectroscopy. X-ray diffraction analysis of the crystalline compound demonstrated that the reaction product is 5-*p*-ethoxyphenyl-3-methoxycarbonyl-1-*p*-tolyl-4-*p*-tolylloxamoylpyrazole (3).

Apparently, compound 3 was formed as a result of successive addition of the primary amino group of hydrazine 2 to the carbon atom at position 5 of pyrroledione 1, as in the case of the reactions of 4-acylpyrrole-2,3-diones with nucleophiles,^{5–8} and addition of the secondary amino group of hydrazine 2 to the carbonyl

[†] Deceased.



group adjacent to the aryl substituent at position 4 of pyrroledione 1 followed by dehydration to pyrrolo-[2,3-*c*]pyrazole (4). The pyrrole ring of the latter underwent cleavage at the N—C bond followed by 1,3-prototropic shift apparently due to strain of the system consisting of two fused five-membered heterocycles and the ease of cleavage of the C—N bond in *gem*-diamines of the NH—C—N type.

The overall view of molecule 3 is shown in Fig. 1. The bond lengths and bond angles are given in Table 1. The pyrazole ring is planar. The bond lengths in this ring are close to the corresponding values in the structurally similar pyrazole compounds.^{9,10} The N(7)=C(10) and C(11)=C(12) double bonds (1.330 and 1.400 Å, respectively) are noticeably elongated and are indicative of delocalization over the pyrazole ring. All four substituents are noncoplanar with the heterocycle and their orientations are characterized by the following torsion angles: N(7)N(6)C(21)C(22), 85.6°; N(6)C(12)C(13)C(14), 115.8°; C(10)C(11)C(28)C(29), 37.4°; and O(4)C(9)C(10)N(7), 35.4°. In the oxamoyl fragment, two carbonyl groups are in *trans* orientations with respect to each other. The C₂H₅O group of the ethoxyphenyl substituent is coplanar with the phenyl ring. There are no intermolecular hydrogen bonds or other shortened contacts in the crystal.

Table 1. Bond lengths (*d*) and bond angles (ω) in molecule 3

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å	Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
O(1)—C(29)	1.214(3)	N(7)—C(10)	1.330(4)	C(14)—C(15)	1.381(4)	C(24)—C(27)	1.495(6)
O(2)—C(28)	1.215(3)	N(8)—C(29)	1.354(4)	C(15)—C(16)	1.387(4)	C(25)—C(26)	1.386(5)
O(3)—C(9)	1.340(3)	N(8)—C(30)	1.408(4)	C(16)—C(17)	1.382(4)	C(28)—C(29)	1.545(4)
O(3)—C(37)	1.455(4)	C(9)—C(10)	1.486(4)	C(17)—C(18)	1.384(4)	C(30)—C(31)	1.379(4)
O(4)—C(9)	1.194(3)	C(10)—C(11)	1.410(4)	C(19)—C(20)	1.495(5)	C(30)—C(35)	1.388(4)
O(5)—C(16)	1.365(3)	C(11)—C(12)	1.400(4)	C(21)—C(22)	1.347(4)	C(31)—C(32)	1.380(5)
O(5)—C(19)	1.436(4)	C(11)—C(28)	1.460(4)	C(21)—C(26)	1.374(4)	C(32)—C(33)	1.386(5)
N(6)—C(12)	1.362(3)	C(12)—C(13)	1.467(4)	C(22)—C(23)	1.394(5)	C(33)—C(34)	1.362(5)
N(6)—N(7)	1.372(3)	C(13)—C(14)	1.384(4)	C(23)—C(24)	1.371(5)	C(33)—C(36)	1.516(6)
N(6)—C(21)	1.439(4)	C(13)—C(18)	1.410(4)	C(24)—C(25)	1.355(5)	C(34)—C(35)	1.386(5)
Angle	ω /deg	Angle	ω /deg	Angle	ω /deg	Angle	ω /deg
C(9)—O(3)—C(37)	116.3(2)	C(14)—C(13)—C(18)	117.7(3)	C(23)—C(24)—C(27)	121.0(4)		
C(16)—O(5)—C(19)	118.1(2)	C(14)—C(13)—C(12)	120.4(2)	C(24)—C(25)—C(26)	122.8(3)		
C(12)—N(6)—N(7)	113.5(2)	C(18)—C(13)—C(12)	121.8(2)	C(21)—C(26)—C(25)	118.1(4)		
C(12)—N(6)—C(21)	126.3(2)	C(15)—C(14)—C(13)	122.4(3)	O(2)—C(28)—C(11)	122.7(3)		
N(7)—N(6)—C(21)	120.1(2)	C(14)—C(15)—C(16)	119.1(3)	O(2)—C(28)—C(29)	118.0(2)		
C(10)—N(7)—N(6)	103.7(2)	O(5)—C(16)—C(15)	124.0(3)	C(11)—C(28)—C(29)	119.3(3)		
C(29)—N(8)—C(30)	130.1(3)	O(5)—C(16)—C(17)	116.1(2)	O(1)—C(29)—N(8)	126.8(3)		
O(4)—C(9)—O(3)	124.7(3)	C(15)—C(16)—C(17)	119.9(3)	O(1)—C(29)—C(28)	122.3(3)		
O(4)—C(9)—C(10)	126.1(2)	C(18)—C(17)—C(16)	120.8(3)	N(8)—C(29)—C(28)	111.0(3)		
O(3)—C(9)—C(10)	109.1(2)	C(17)—C(18)—C(13)	120.1(3)	C(31)—C(30)—C(35)	119.0(3)		
N(7)—C(10)—C(11)	112.5(2)	O(5)—C(19)—C(20)	107.5(3)	C(31)—C(30)—N(8)	124.3(3)		
N(7)—C(10)—C(9)	118.8(2)	C(22)—C(21)—C(26)	120.4(3)	C(35)—C(30)—N(8)	116.6(3)		
C(11)—C(10)—C(9)	128.6(2)	C(22)—C(21)—N(6)	119.8(3)	C(32)—C(31)—C(30)	119.6(3)		
C(12)—C(11)—C(10)	105.1(2)	C(26)—C(21)—N(6)	119.7(3)	C(31)—C(32)—C(33)	122.0(4)		
C(12)—C(11)—C(28)	123.6(2)	C(21)—C(22)—C(23)	120.4(3)	C(34)—C(33)—C(32)	117.8(3)		
C(10)—C(11)—C(28)	131.2(2)	C(24)—C(23)—C(22)	120.3(3)	C(34)—C(33)—C(36)	121.7(4)		
N(6)—C(12)—C(11)	105.3(2)	C(25)—C(24)—C(23)	117.9(3)	C(32)—C(33)—C(36)	120.5(5)		
N(6)—C(12)—C(13)	124.2(2)	C(25)—C(24)—C(27)	121.0(4)	C(33)—C(34)—C(35)	121.5(4)		
C(11)—C(12)—C(13)	130.6(2)			C(34)—C(35)—C(30)	120.1(3)		

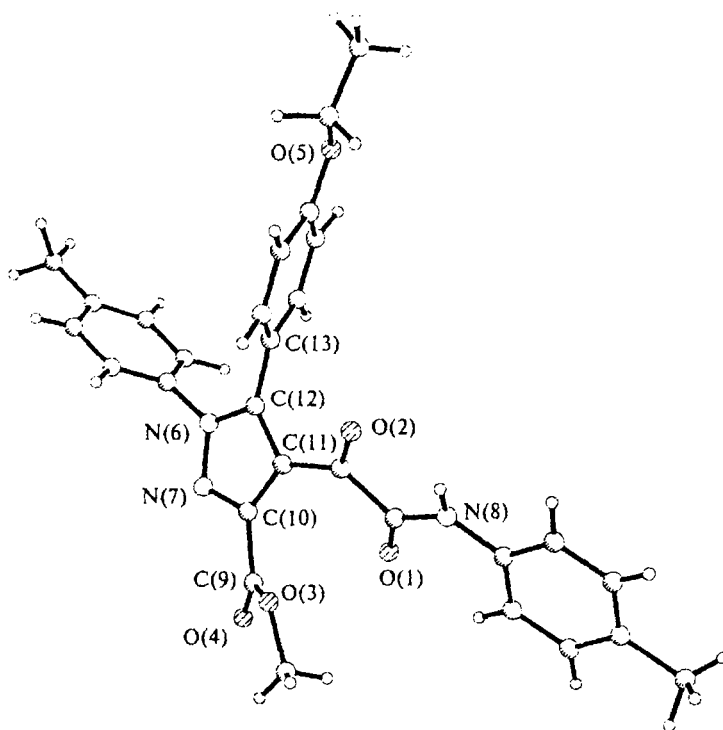


Fig. 1. Overall view of molecule 3.

Experimental

The IR spectrum was obtained on a UR-20 instrument as Nujol mulls. The ^1H NMR spectrum was recorded on an RYa-2310 instrument (60 MHz) with HMDS as the internal standard. The purity of compound 3 was confirmed by TLC on Silufol plates; a 5 : 1 benzene—AcOEt mixture was used as the eluent; spots were visualized with iodine vapor.

5-*p*-Ethoxyphenyl-3-methoxycarbonyl-1-*p*-tolyl-4-*p*-tolyl-oxamoylpyrazole (3). A solution of *p*-tolylhydrazine (0.01 mol)

in anhydrous benzene (10 mL) was added to a solution of 4-*p*-ethoxybenzoyl-5-methoxycarbonyl-1-*p*-tolylpyrrole-2,3-dione (0.01 mol) in anhydrous benzene (20 mL). The reaction mixture was boiled for 15 min and then cooled. The precipitate of compound 3 that formed was filtered off. The yield was 3.04 g (61%), m.p. 196—197 °C (from AcOEt). Found (%): C, 70.12; H, 5.44; N, 8.40. $\text{C}_{29}\text{H}_{27}\text{N}_3\text{O}_5$. Calculated (%): C, 70.01; H, 5.47; N, 8.40. IR, ν/cm^{-1} : 3308 (NH), 1745 (COO), 1695 (C=O), 1535 (amide II). ^1H NMR (CDCl_3), δ : 1.27 (t, 3 H, $\text{CH}_3\text{CH}_2\text{O}$, $J = 8.0$ Hz); 2.25 (s,

Table 2. Coordinates ($\times 10^4$) and isotropic equivalent thermal parameters ($U_{\text{iso}}^{\text{eq}} \times 10^3/\text{\AA}^2$) of nonhydrogen atoms in molecule 3

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^{\text{eq}}$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^{\text{eq}}$
O(1)	7353(2)	467(2)	3401(2)	64(1)	C(20)	-3222(4)	-1063(3)	-1199(5)	72(1)
O(2)	3996(2)	-228(2)	3370(2)	62(1)	C(21)	4201(3)	-3817(2)	-1352(3)	47(1)
O(3)	7451(2)	-1154(2)	4466(2)	53(1)	C(22)	3545(3)	-4663(3)	-1315(3)	62(1)
O(4)	8769(2)	-1799(2)	2912(2)	73(1)	C(23)	2879(4)	-5542(3)	-2624(4)	73(1)
O(5)	-993(2)	-1396(2)	-1275(2)	58(1)	C(24)	2881(4)	-5553(3)	-3965(4)	75(1)
N(6)	4842(2)	-2901(2)	6(2)	47(1)	C(25)	3564(5)	-4696(3)	-3967(4)	102(2)
N(7)	6146(2)	-2834(2)	769(2)	50(1)	C(26)	4238(5)	-3815(3)	-2681(3)	84(1)
N(8)	5926(3)	1427(2)	4664(2)	53(1)	C(27)	2161(7)	-6485(4)	-5379(5)	128(2)
C(9)	7685(3)	-1625(2)	3127(3)	49(1)	C(28)	5071(3)	-391(2)	3056(3)	45(1)
C(10)	6376(3)	-1929(2)	1976(3)	43(1)	C(29)	6272(3)	546(2)	3730(3)	45(1)
C(11)	5244(3)	-1415(2)	2014(3)	41(1)	C(30)	6725(3)	2428(2)	5593(3)	50(1)
C(12)	4247(3)	-2080(2)	719(3)	41(1)	C(31)	8112(4)	2673(3)	5795(4)	69(1)
C(13)	2854(3)	-1971(2)	147(3)	43(1)	C(32)	8810(4)	3668(3)	6786(5)	86(1)
C(14)	1867(3)	-1983(2)	893(3)	48(1)	C(33)	8156(4)	4440(3)	7590(4)	74(1)
C(15)	571(3)	-1807(2)	457(3)	48(1)	C(34)	6786(5)	4186(3)	7383(4)	70(1)
C(16)	244(3)	-1603(2)	-767(3)	45(1)	C(35)	6062(4)	3190(2)	6407(3)	59(1)
C(17)	1196(3)	-1612(3)	-1559(3)	57(1)	C(36)	8953(7)	5529(4)	8653(6)	119(2)
C(18)	2493(3)	-1787(2)	-1116(3)	53(1)	C(37)	8651(4)	-667(4)	5715(4)	70(1)
C(19)	-1995(3)	-1337(3)	-454(4)	61(1)					

Table 3. Coordinates ($\times 10^4$) of hydrogen atoms in molecule 3

Atom	x	y	z	Atom	x	y	z
H(8)	5088(41)	1302(32)	4816(43)	H(27a)	2053(45)	-6406(34)	-6138(47)
H(14)	2092(39)	-2085(29)	1815(42)	H(27b)	1127(42)	-6666(33)	-5420(46)
H(15)	-107(38)	-1802(29)	1029(42)	H(27c)	2378(42)	-7143(35)	-5466(43)
H(17)	939(37)	-1418(29)	-2406(42)	H(31)	8487(40)	2134(32)	5276(43)
H(18)	3202(38)	-1733(29)	-1696(41)	H(32)	9778(42)	3861(31)	6921(44)
H(19a)	-1620(39)	-799(31)	540(46)	H(34)	6348(38)	4705(31)	7986(42)
H(19b)	-2181(38)	-2078(32)	-500(40)	H(35)	5094(40)	3068(30)	6303(42)
H(20a)	-3919(41)	-1051(31)	-711(42)	H(36a)	9961(41)	5441(32)	8920(45)
H(20b)	-3631(39)	-1589(31)	-2308(46)	H(36b)	8919(46)	5703(35)	9504(47)
H(20c)	-2973(40)	-397(33)	-1191(41)	H(36c)	8737(42)	6037(32)	8413(44)
H(22)	3441(38)	-4696(29)	-427(42)	H(37a)	8349(38)	-459(30)	6616(44)
H(23)	2498(42)	-6116(31)	-2641(45)	H(37b)	9066(42)	-56(32)	5740(44)
H(25)	3507(39)	-4632(30)	-4784(45)	H(37c)	9364(42)	-1074(32)	5558(43)
H(26)	4703(40)	-3175(32)	-2640(43)				

6 H, 2 CH₃); 3.70 (s, 3 H, OCH₃); 4.01 (q, 2 H, CH₂O, *J* = 8.0 Hz); 6.71–7.78 (m, 12 H, 3 C₆H₄); 10.61 (s, H, NH).

Crystals of 3 belong to the triclinic system: *a* = 10.174(5), *b* = 14.222(6), *c* = 10.273(8) Å, α = 114.31(6), β = 101.64(2), γ = 94.59(4)°, *V* = 1304.5(1) Å³, *d* = 1.267 g cm⁻³, space group *P* $\bar{1}$, *Z* = 2. The unit cell parameters and X-ray intensity data were obtained on an automated four-circle KUMA diffractometer (KUMA DIFFRACTION) with the use of monochromatic Cu-K α radiation. A total of 3855 independent reflections were measured in the angle range of 4.5° < 66.4°. Absorption was ignored (μ = 0.715 mm⁻¹). The structure was solved by the direct statistical method followed by a series of successive calculated electron density maps. The positions of the nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method to *R* = 0.060. Then all hydrogen atoms were placed in geometrically calculated positions. The final refinement converged to an *R* factor of 0.039 using 1826 reflections with *I* > 2 σ (*I*). The thermal vibrations of the hydrogen atoms were not refined and were set 1.5 times as large as the corresponding values of the nonhydrogen bonds to which the hydrogen atoms are attached. The atomic coordinates are given in Tables 2 and 3. All calculations were carried out on an IBM PC/AT computer using the SHELXS86¹¹ and SHELXL93¹² program packages.

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