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REACTIONS OF 4-CHLORO-3-FORMYL-COUMARIN WITH ARYLHYDRAZINES

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The interaction of 3-formyl-4-coumarin with arylhydrazine hydrochlorides in the presence of sodium acetate gave the corresponding 3-arylhydrazonomethyl-4-chlorocoumarin, and with phenylhydrazine, 4-bromo- and 4-chlorophenylhydrazine hydrochlorides in the presence of two equivalents of triethylamine gave either 1-aryl- or 2-aryl[1]benzopyrano[4,3-c]pyrazol-4-ones depending on the reaction conditions. In reactions of 4-chloro-3-formylcoumarin with 2,4-dichloro-, 2,4-difluoro-, 2-hydroycarbonyl-, 4-nitro- and 3,5-di(trifluoromethyl)phenylhydrazine,2-pyridyl- and 2-quinoxalyl-hydrazine in the presence of excess of triethylamine the 2-aryl[1]benzopyrano[4,3-c]-pyrazol-4(2H)-ones were obtained exclusively. The structures of 1-phenyl- and 2-(2-pyridyl)[1]benzopyrano[4,3-c]-pyrazolo-4(1H)ones were confirmed by X-ray crystallography. A simple method is proposed to distinguish between 1- and 2-substituted [1]benzopyrano[4,3-c]pyrazolo-4-ones on the basis of the ^1H NMR chemical shifts of the C(3)-H proton in two solvents – DMSO-d_6 and $CDCl_3$.

Keywords: 3-arylhydrazonomethyl-4-chlorocoumarins, 1-aryl- and 2-aryl[1]benzopyrano[4,3-*c*]pyrazol-4-ones, 4-chloro-3-formylcoumarins.

Formylation of 4-hydroxycoumarin (**1**) and the reactions of the product, 4-chloro-3-formylcoumarin (**2**) [1-5], and also of 4-azido-3-formylcoumarin with nitrogen nucleophiles – amines and hydrazines – are described in a series of papers [13].

We used a method [14] which we had used previously for the formylation of 4-oxo-1-(2-pyridyl)-4,5,6,7-tetrahydroindazole, the key characteristic is the preliminary preparation of the formylating reagent, and obtained 4-chloro-3-formylcoumarin, identical to the product described elsewhere [5], in 67% yield.

The reaction of the formyl derivative **2** with arylhydrazine hydrochlorides in the presence of an equimolar amount of anhydrous sodium acetate gave 3-arylhydrazonomethyl-4-chlorocoumarins (**3**) which precipitated on mixing hot ethanolic solutions of the aldehyde **2** and the arylhydrazine. The structure of the arylhydrazones **3** were confirmed by ^1H NMR (δ_{NH} 10.82-11.62 ppm) and IR spectroscopy (ν_{CO} 1745-1735, ν_{NH} 3300-3280 cm^{-1}), and elemental analysis (Tables 1 and 2).

The synthesis of 1-phenyl- and 2-phenyl[1]benzopyrano[4,3-*c*]pyrazol-4-ones is the subject of a number of papers [1, 4, 6] in which presence of 1- or 2-substitution was determined by the method of synthesis and confirmed by ^1H and ^{13}C NMR spectroscopy. When equimolar amounts of the chlorocoumarin **2** and a hydrazine hydrochloride with an excess of triethylamine (Scheme 1) were refluxed for 5 h in ethanol we obtained mixtures of 1-aryl- (**4**) and 2-aryl[1]benzopyrano[4,3-*c*]pyrazol-4-ones (**5**) in the case of phenylhydrazine, 4-bromo-,

* To J. Stradins in appreciation of your speech in defence of science and order given in 1957.

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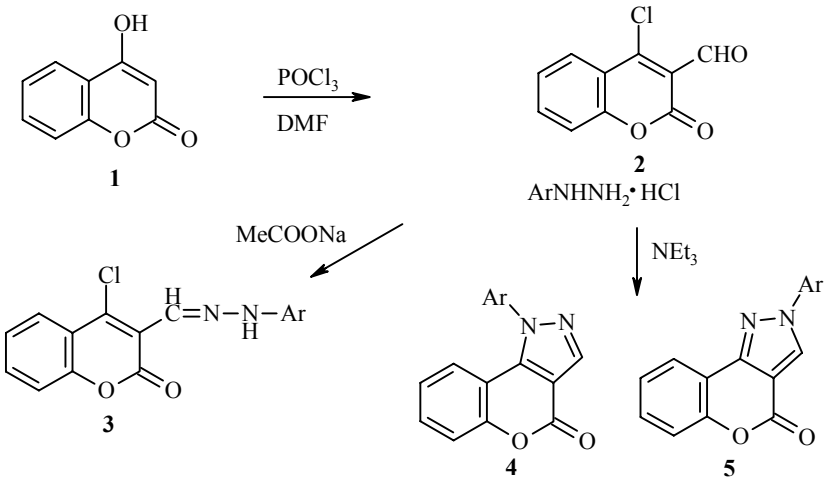
3- and 4-chlorophenylhydrazines, and 4-methoxyphenylhydrazine. For the mixtures of compounds **4a,b,e, 5a,b,e** by the choice of reaction conditions followed by many recrystallizations we were able to isolate the 1- and 2-arylisomers **4a**, **5a**, **4b**, **5b**, **4e**, and **5e** in pure form. From the mixtures formed from 2-, 3-chlorophenyl- and 4-fluorophenylhydrazines we isolated only the 2-aryl-substituted benzopyranopyrazolones **5c**, **d**, and **f**. We were unable to separate the mixture of compounds **4g** and **5g** prepared from methoxyphenylhydrazine.

Scheme 1



3–5 a Ar = C_6H_5, **b** Ar = C_6H_4Br-4, **c** Ar = C_6H_4Cl-2, **d** Ar = C_6H_4Cl-3, **e** Ar = C_6H_4Cl-4, **f** Ar = C_6H_4F-4, **g** Ar = C_6H_4OMe-4, **h** Ar = $C_6H_3Cl_2$-2,4, **i** Ar = $C_6H_3F_2$-2,4, **j** Ar = C_6H_4COOH-2, **k** Ar = $C_6H_4NO_2$-4, **l** Ar = $C_6H_3(CF_3)_2$-3,5, **m** Ar = C_5H_4N-2, **n** Ar = 2-quinoxalyl

As the result of the reactions of 2,4-dichloro-, 2,4-difluoro-, 2-hydroxycarbonyl-, 4-nitro- and 3,5-di(trifluoromethyl)phenylhydrazines, 2-pyridyl- and 2-quinoxalylhydrazine with aldehyde **2** (refluxing for 5 h followed standing in a refrigerator for 1 d) only the 2-substituted benzopyrano[4,3-*c*]pyrazol-4-ones **5h-m** were obtained. The ^{1}H NMR spectra of all the compounds synthesized (Table 2) contained signals of the protons of all the structural units of the arylhydrazones **3** and the pyrazolocoumarins **4** and **5**.

With the objective of determining the structure of isomers **4** and **5** we obtained X-ray crystallographic data for compounds **4a** and **5m** which were compared with the ^{1}H NMR spectra of a pair of isomers in $CDCl_3$ and DMSO-d_6 (Table 3). The ^{1}H NMR spectra of 1- and 2-substituted benzopyranopyrazolones in $CDCl_3$ were practically indistinguishable. On changing the solvent to DMSO-d_6, the more low polarity resonance signal of the C(3)-H proton of one of the isomers underwent a greater shift to lower field ($\Delta\delta$ 0.63-1.07 ppm) than that of the other isomer ($\Delta\delta$ 0.11-0.22 ppm). Such a strong dependence of the resonance of this proton on the solvent permitted us to propose that the greatest of the solvent should be on the C(3)–H proton of the N(2)-substituted isomer, because of the closeness of the substituent in this case, the change in solvent may be accompanied by a notable change in the effect of the magnetic anisotropy of the aromatic substituent on the resonance of the C(3)–H proton.

The anomalously small change in the chemical shift of C(3)–H on changing from DMSO-d_6 to $CDCl_3$ in compound **5m** is explained by the deshielding effect of the lone electron pair of the nitrogen atom immediately close to this proton (Fig. 1b).

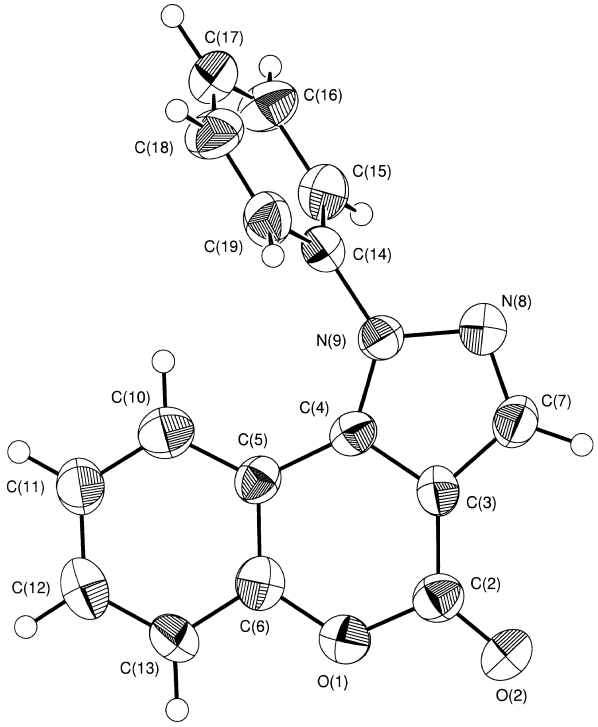
The ^{1}H NMR spectra in DMSO-d_6 and $CDCl_3$ of the isomeric mixtures **4d**, **5d** and **4g**, **5g**, which could not be separated by fractional crystallization, contained C(3)–H signals for both isomers, from which it was determined that the ratios of isomers were 50:50 (**4d** : **5d**) and 86:14 (**4g** : **5g**).

TABLE 1. Characteristics of Compounds **2-5**

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yield, %
		C	H	N	Hal		
2	$C_{10}H_5ClO_3$	57.40 / 57.58	2.35 / 2.42		16.80 / 17.00	120-122	67
3a	$C_{16}H_{11}ClN_2O_2$	64.19 / 64.33	3.60 / 3.71	9.31 / 9.39	11.70 / 11.87	181-182	62
3b	$C_{16}H_{10}BrClN_2O_2$	50.98 / 50.89	2.58 / 2.67	7.33 / 7.42		207-209	77
3d	$C_{16}H_{10}Cl_2N_2O_2$	57.50 / 57.68	3.11 / 3.03	8.30 / 8.41	21.50 / 21.28	220-221	76
3e	$C_{16}H_{10}Cl_2N_2O_2$	57.55 / 57.68	3.05 / 3.03	8.44 / 8.41	21.50 / 21.28	263–265	74
3f	$C_{16}H_{10}ClFN_2O_2$	60.51 / 60.68	3.09 / 3.18	8.60 / 8.84		175-177	73
3h	$C_{16}H_9Cl_3N_2O_2$	52.11 / 52.28	2.37 / 2.47	7.59 / 7.62	28.70 / 28.93	228-230	80
3i	$C_{16}H_9ClF_2N_2O_2$	57.60 / 57.41	2.61 / 2.71	8.18 / 8.37		191-192	82
3j	$C_{17}H_{11}ClN_2O_4$	59.51 / 59.57	3.12 / 3.24	8.16 / 8.17	10.10 / 10.34	240-242	59
3k	$C_{16}H_{10}ClN_3O_4$	55.96 / 55.91	2.90 / 2.93	12.11 / 12.23	10.20 / 10.31	267-268	88
3l	$C_{18}H_9ClF_6N_2O_2$	49.60 / 49.73	2.02 / 2.09	6.50 / 6.44		261-264	55
4a	$C_{16}H_{10}N_2O_2$	73.11 / 73.27	3.83 / 3.84	10.55 / 10.68		183-185	23
4b	$C_{16}H_9BrN_2O_2$	56.12 / 56.33	2.49 / 2.66	8.10 / 8.21	23.20 / 23.42	173-176	16
4e	$C_{16}H_9ClN_2O_2$	64.63 / 64.77	3.00 / 3.06	9.49 / 9.44	11.80 / 11.95	149-152	16
5a	$C_{16}H_{10}N_2O_2$	73.08 / 73.27	3.81 / 3.84	10.50 / 10.68		201-203	62
5b	$C_{16}H_9BrN_2O_2$	56.10 / 56.33	2.61 / 2.66	8.18 / 8.21	23.30 / 23.42	240 (subl.)	55
5c	$C_{16}H_9ClN_2O_2$	64.67 / 64.77	3.01 / 3.06	9.29 / 9.44	11.80 / 11.95	178-170	38
5d	$C_{16}H_9ClN_2O_2$	64.60 / 64.77	3.13 / 3.06	9.31 / 9.44	11.80 / 11.95	208-210	67
5e	$C_{16}H_9ClN_2O_2$	64.82 / 64.77	3.05 / 3.06	9.22 / 9.44	11.80 / 11.95	220 (subl.)	50
5f	$C_{16}H_9FN_2O_2$	68.44 / 68.57	3.11 / 3.24	10.10 / 10.00		190 (subl.)	48
5h	$C_{16}H_8Cl_2N_2O_2$	58.19 / 58.03	2.40 / 3.43	8.41 / 8.46	21.30 / 21.41	198-200	47
5i	$C_{16}H_8F_2N_2O_2$	64.55 / 64.43	2.68 / 2.70	9.30 / 9.39		222-224	62
5j	$C_{17}H_{10}N_2O_4$	66.56 / 66.67	3.11 / 3.29	9.10 / 9.15		258-260	67
5k	$C_{16}H_9N_3O_4$	62.45 / 62.54	2.96 / 2.95	13.60 / 13.68		240 (subl.)	67
5l	$C_{18}H_8F_6N_2O_2$	54.10 / 54.28	2.00 / 2.02	7.07 / 7.03		190 (subl.)	38
5m	$C_{15}H_9N_3O_2$	68.32 / 68.44	3.41 / 3.45	15.99 / 15.96		215 (subl.)	69
5n	$C_{18}H_{10}N_4O_2$	68.88 / 68.79	3.10 / 3.21	17.80 / 17.83		200 (subl.)	64

To place their structures on a firm basis monocrystals of compounds **4a** and **5m** were prepared and X-ray crystal analysis was then carried out (Fig. 1, Tables 4 and 5).

a



b

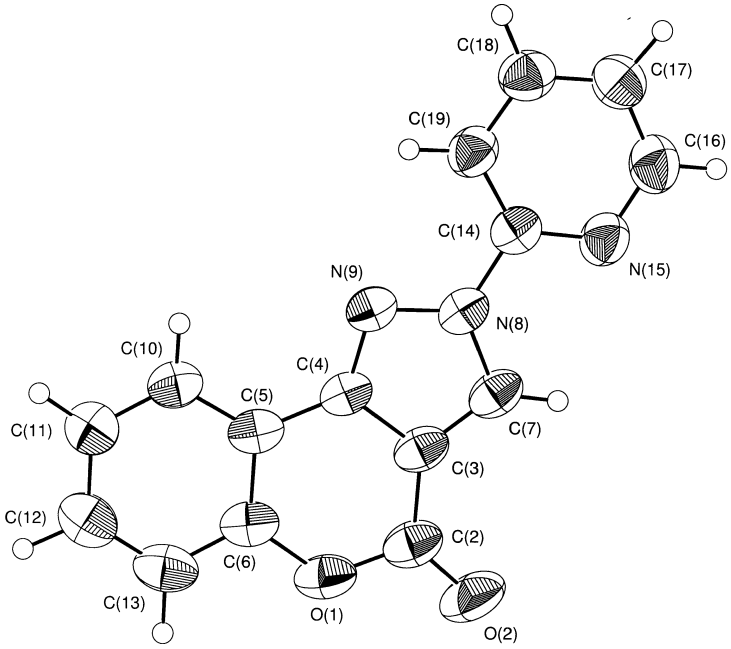


Fig. 1. Molecular structures of compounds **4a** (*a*) and **5m** (*b*) with numbering of atoms and thermal vibration ellipsoids.

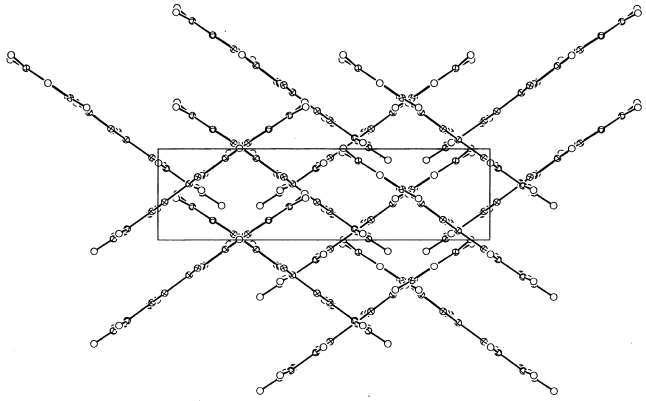


Fig. 2. Projection of the unit cell of crystals of **5m** along (1 0 0).

TABLE 2. ^{1}H NMR Spectra of Compounds **3-5**

Com-pound	Chemical shifts, δ, ppm (*J*, Hz)*	Com-pound	Chemical shifts, δ, ppm (*J*, Hz)*
3a	6.84-8.01 (9H, m, Ar); 8.04 (1H, s, =CH); 10.96 (1H, br. s, NH)	**5a**	7.37-8.16 (9H, m, Ar); 9.54 (1H, s, =CH–)
3b	7.02-8.04 (8H, m, Ar); 8.12 (1H, s, =CH); 11.02 (1H, br. s, NH)	**5b**	7.38-8.18 (8H, m, Ar); 9.65 (1H, s, =CH–)
3d	6.78-8.02 (8H, m, Ar); 8.09 (1H, s, =CH); 11.04 (1H, br. s, NH)	**5c**	7.45-8.12 (8H, m, Ar); 9.27 (1H, s, =CH–)
3e	7.04-8.11 (8H, m, Ar); 8.11 (1H, s, =CH); 10.02 (1H, br. s, NH)	**5d**	7.41-8.13 (8H, m, Ar); 9.65 (1H, s, =CH–)
3f	7.08-8.05 (8H, m, Ar); 8.07 (1H, s, =CH); 10.96 (1H, br. s, NH)	**5e**	7.34-8.08 (8H, m, Ar); 9.65 (1H, s, =CH–)
3h	7.39-7.48 (6H, m, Ar, =CH–); 7.94 (1H, dd, ^3J = 8, ^4J = 2, Ar); 8.54 (1H, d, ^4J = 2, Ar); 10.94 (1H, br. s, NH)	**5f**	7.49-8.09 (8H, m, Ar); 9.48 (1H, s, =CH–)
3i	7.01-7.96 (7H, m, Ar); 8.36 (1H, s, =CH); 10.82 (1H, br. s, NH)	**5h**	7.43-8.17 (7H, m, Ar); 9.29 (1H, s, =CH–)
3j	6.85 (1H, m, Ar); 7.34-7.97 (7H, m, Ar); 8.22 (1H, s, =CH); 11.61 (1H, br. s, NH); 12.82 (1H, br. s, COOH)	**5i**	7.36-7.91 (7H, m, Ar); 9.26 (1H, s, =CH–)
3k	7.18 (2H, m, ^3J = 8, Ar); 7.47-8.09 (4H, m, Ar); 8.21 (2H, m, ^3J = 8, Ar); 8.29 (1H, s, =CH–); 11.67 (1H, br. s, NH)	**5j**	7.36-8.01 (8H, m, Ar); 9.27 (1H, s, =CH–); 12.72 (1H, br. s, COOH)
3l	7.28-8.07 (7H, m, Ar); 8.07 (1H, s, =CH); 11.02 (1H, br. s, NH)	**5k**	7.36-8.42 (8H, m, Ar); 9.73 (1H, s, =CH–)
4a	6.89-7.72 (9H, m, Ar); 8.47 (1H, s, =CH)	**5l**	7.42-8.76 (7H, m, Ar); 9.92 (1H, s, =CH–)
4b	6.96-8.15 (8H, m, Ar); 8.53 (1H, s, =CH)	**5m**	7.54-8.67 (8H, m, Ar); 9.47 (1H, s, =CH–)
4e	7.08-8.30 (8H, m, Ar); 8.51 (1H, s, =CH)	**5n**	7.26-8.26 (8H, m, Ar); 9.55 (1H, s, =CH–); 9.87 (1H, s, =CH)
4g*[2]	3.94 (3H, s, CH_3); 7.23-7.54 (8H, m, Ar); 8.32 (1H, s, =CH)		

* ^{1}H NMR spectra were recorded in $CDCl_3$ (compounds **4g** and **5n**) or DMSO-d_6 (the remaining compounds).

*[2] Compound **4g** consisted of 86% of the **4g**,**5g** mixture.

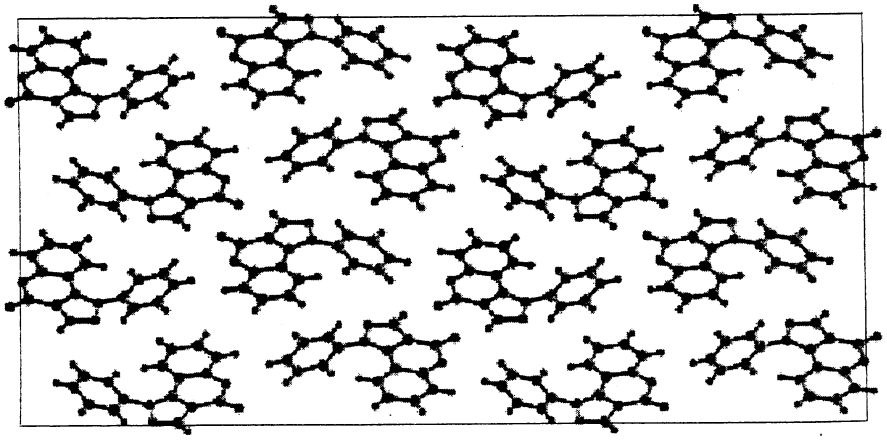


Fig. 3. Projection of the crystal structure of compound **4a** on the (0 0 1) plane.

Although molecules of **5m** are found in both positions in the crystal lattice, all the atoms of the molecules lie in a single plane within the limits of experimental error. As a result of this coplanarity, conjugation extends over the whole molecule. Consequently all of the single bonds in the molecule of **5m** are shortened and all the double bonds (except the carbonyl bond) are lengthened. It is clear that the bond orders of the corresponding bonds in molecule **4a** and C(2)–O(2) in **5m** are different, consequently differences in the values of the bond lengths and bond angles are observed (see Tables 4 and 5). Because molecule **4a** is sterically hindered (hydrogen atoms H(10) and H(19) repel one another) it cannot be coplanar; therefore the torsion angle N(8)–N(9)–C(14)–C(15) is large -73.1(6)°.

Molecules in the crystal structure of **5m** (Fig. 2) are parallel to one another, forming two systems of columns, one of which is parallel to the crystallographic plane (0 3 1) and the other to the plane (0 $\bar{3}$ 1). A characteristic of the crystal structure **4a** is the quite unusual type of crystal lattice (space group (*F dd*2). The mean plane of the molecule of **4a** is approximately perpendicular to the 2 axis in the crystal (Fig.3). For all atoms in both crystal structures intermolecular contacts are at distances not less than the sums of the van der Waals radii [15].

TABLE 3. Chemical Shifts of the C(3)–H Protons in Compounds **4** and **5**

Com-pound*	Chemical shifts, δ, ppm			Com-pound*	Chemical shifts, δ, ppm		
	DMSO-d_6	$CDCl_3$	Δ(δDMSO-d_6 – δ$CDCl_3$)		DMSO-d_6	$CDCl_3$	Δ(δDMSO-d_6 – δ$CDCl_3$)
4a	8.47	8.36	0.11	**5h**	9.29	8.65	0.64
4b	8.53	8.36	0.17	**5i**	9.26	8.62	0.64
4e	8.51	8.35	0.16	**5j**	9.27	8.51	0.76
5a	9.54	8.65	0.89	**5k**	9.73	8.85	0.88
5b	9.65	8.66	0.99	**5l**	9.92	8.85	1.07
5c	9.27	8.64	0.63	**5m**	9.47	9.38	0.09
5e	9.65	8.87	0.78	**4d-5d**	9.65 (8.54)	8.67 (8.36)	0.98 0.18
5f	9.48	8.61	0.87	**4g-5g**	9.45 (8.45)	8.54 (8.32)	0.91 0.13

* For the mixtures of compounds **4d**, **5d** and **4g**, **5g**, the chemical shifts of the 2-aryl isomers (**5d**, **5g**) are cited together with those of the 1-aryl isomers (**4d**, **4g**) (in brackets), recorded in DMSO-d_6 and $CDCl_3$.

TABLE 4. Bond Lengths (*l*) in the Molecules **4a** and **5m**

Bond	*l*, Å		Bond	*l*, Å	
	4a	**5m**		**4a**	**5m**
O(1)–C(2)	1.395(3)	1.382(6)	N(8)–C(14)	—	1.431(5)
C(2)–O(2)	1.197(3)	1.200(5)	N(9)–C(14)	1.427(3)	—
C(2)–C(3)	1.432(3)	1.439(5)	C(10)–C(11)	1.371(4)	1.384(7)
C(3)–C(4)	1.381(3)	1.414(5)	C(11)–C(12)	1.368(4)	1.386(6)
C(3)–C(7)	1.410(3)	1.373(7)	C(12)–C(13)	1.376(4)	1.382(7)
C(4)–C(5)	1.452(3)	1.436(6)	C(14)–N(15)	—	1.317(5)
C(4)–N(9)	1.344(3)	1.335(5)	C(14)–C(15)	1.394(4)	—
C(5)–C(6)	1.385(3)	1.403(5)	C(14)–C(19)	1.370(5)	1.380(6)
C(5)–C(10)	1.397(3)	1.396(6)	N(15)–C(16)	—	1.343(7)
C(6)–O(1)	1.378(3)	1.392(5)	C(15)–C(16)	1.383(4)	—
C(6)–C(13)	1.384(3)	1.383(7)	C(16)–C(17)	1.372(5)	1.373(8)
C(7)–N(8)	1.312(3)	1.352(5)	C(17)–C(18)	1.381(5)	1.370(7)
N(8)–N(9)	1.388(3)	1.367(5)	C(18)–C(19)	1.354(5)	1.383(7)
N(8)–C(14)	—	1.431(5)			

TABLE 5. Bond Angles (ω) in Molecules **4a** and **5m**

Angle	ω, deg.		Angle	ω, deg.	
	Molecule **4a**	Molecule **5m**		Molecule **4a**	Molecule **5m**
C(6)–O(1)–C(2)	123.3(2)	123.7(3)	C(7)–N(8)–N(9)	104.6(2)	113.1(3)
O(6)–C(2)–O(2)	116.6(2)	117.5(4)	C(7)–N(8)–C(14)	—	126.8(4)
O(1)–C(2)–C(3)	114.0(2)	114.8(3)	N(9)–N(8)–C(14)	—	120.0(3)
O(2)–C(2)–C(3)	129.4(2)	127.7(5)	C(4)–N(9)–N(8)	111.5(2)	103.8(3)
C(4)–C(3)–C(2)	123.4(2)	122.7(4)	C(4)–N(9)–C(14)	129.6(2)	—
C(4)–C(3)–C(7)	104.8(2)	105.5(3)	N(8)–N(9)–C(14)	118.8(2)	—
C(2)–C(3)–C(7)	131.7(2)	131.8(4)	C(5)–C(10)–C(11)	120.3(2)	120.9(4)
C(3)–C(4)–C(50)	120.8(2)	120.1(3)	C(10)–C(11)–C(12)	119.5(2)	119.8(5)
C(3)–C(4)–N(9)	107.0(2)	111.4(4)	C(13)–C(12)–C(11)	121.1(2)	120.6(5)
C(5)–C(4)–N(9)	132.1(2)	128.4(3)	C(6)–C(13)–C(12)	119.1(2)	119.3(4)
C(4)–C(5)–C(6)	114.5(2)	116.0(4)	N(15)–C(14)–C(19)	—	125.4(4)
C(4)–C(5)–C(10)	127.7(2)	126.0(3)	C(15)–C(14)–C(19)	119.8(3)	—
C(6)–C(5)–C(10)	117.8(2)	118.0(4)	C(16)–N(15)–C(14)	—	115.8(4)
O(1)–C(6)–C(13)	114.9(2)	116.1(3)	C(16)–C(15)–C(14)	119.5(2)	—
O(1)–C(6)–C(5)	123.9(2)	122.5(4)	C(16)–C(17)–C(18)	120.0(3)	118.7(5)
C(13)–C(6)–C(5)	121.2(2)	121.3(4)	C(19)–C(18)–C(17)	120.6(3)	119.1(4)
C(3)–C(7)–N(8)	112.0(3)	106.1(4)	C(14)–C(19)–C(18)	120.3(3)	117.2(4)

EXPERIMENTAL

^{1}H NMR spectra were recorded with Bruker WH 90/DS (90 MHz) and Varian-Mercury BB (200 MHz) spectrometers with TMS as internal standard. IR spectra of nujol mulls (1800-1500 cm^{-1}) and hexachlorobutadiene mulls (3600-2000 cm^{-1}) were obtained with Specord IR-75 apparatus. The arylhydrazines and their hydrochlorides used in this work were obtained from Acros, Maybridge, and Lancaster.

Physicochemical and spectroscopic characteristics are cited in Tables 1-3.

TABLE 6. Crystallographic Data of Compounds **4a** and **5m**

Characteristic	**4a**	**5m**
Molecular formula	$C_{16}H_{10}N_2O_2$	$C_{16}H_9N_3O_2$
Molecular mass	262.27	263.26
Crystal color	Colorless	Colorless
Crystal size, mm	0.04 × 0.06 × 0.52	0.05 × 0.18 × 0.50
Crystal class	Rhombic	Rhombic
Parameters of the unit cell, Å		
a	20.5064(7)	18.911(1)
b	43.111(3)	14.9116(8)
c	5.624(2)	4.1991(2)
Volume of the unit cell, *V*, Å^3	4972.0(15)	1184.1(1)
Space group	*F dd*2	*P na*2$_1$
Number of molecules per unit cell, *Z*	16	4
Density, *d*, g/cm^3	1.402	1.477
Absorption coefficient, μ, mm^{-1}	0.09	0.10
Number of independent reflexions	948	1584
Number of reflexions with $I > 3\sigma(I)$	735	1096
Number of parameters refined	181	208
Final residual factor, *R*	0.0467	0.0386

X-ray Crystallographic Investigations. Monocrystals of compounds **4a** and **5m** were grown from DMF. Diffraction data were collected at 20° on a Nonius Kappa CCD automatic diffractometer (MoKα, $2\theta_{max}$ = 55 (**4a**), $2\theta_{max}$ = 45° (**5m**)). The structures were solved by direct methods and refined by full matrix least squares in the anisotropic approximation. The basic crystallographic characteristics and the parameters of the refined crystal structures are cited in Table 6. Calculations were carried out using the programs [16,17].

4-Chloro-3-formylcoumarin (2). Phosphorus oxychloride (10.8 ml, 120 mmol) was added dropwise and with stirring to dry DMF (40 ml) at 0°C (cooled in ice). The prepared reagent, cooled in ice, was added dropwise and with stirring to a solution of 4-hydroxycoumarin (6.50 g, 40 mmol) in dry DMF (30 ml). After all the formylating agent had been added the reaction mixture had reached 55-65°C. It was then cooled and poured onto crushed ice. The yellow precipitate was filtered off and recrystallized from 2:1 acetone–water to give yellow crystals (5.60 g, 67%), mp 120-122°C (mp 120-122 [1, 5], 124-126 [5], 125-127 [4], 130°C [2]). IR spectrum, ν, cm^{-1}: 1720 (O–C=O), 1690 (–C=O). Found, %: C 57.66; H 2.40; Cl 22.80. $C_{10}H_5ClO_3$. Calculated, %: C 57.57; H 2.42; Cl 23.01.

4-Chloro-3-hydrazonomethylcoumarins (3a,d,e,h,i,j,k,l). 4-Chloro-3-formylcoumarin (0.41 g, 2 mmol) dissolved on heating in ethanol (15 ml). An arylhydrazine hydrochloride (2 mmol) and anhydrous sodium acetate (2 mmol) were dissolved in 85% ethanol (10 ml) on heating. The two solutions were rapidly mixed with stirring. A precipitate began to form immediately. The reaction mixture was kept at 50-60°C for 5-10 min, cooled, and after 1 h was filtered and the precipitate recrystallized from DMF.

1-Phenyl[1]benzopyrano[4,3-*c*]pyrazol-4(1H)-one (4a). The aldehyde **2** (0.41 g, 2 mmol) dissolved on boiling in ethanol (10 ml) and was then cooled to 15-20°C. A solution prepared from phenylhydrazine hydrochloride (0.29 g, 2 mmol) and triethylamine (4 mmol) in 60%) ethanol (10 ml) was slowly added dropwise so that the temperature of the reaction mixture did not exceed 25°C. After addition of the reagent was complete a yellowish precipitate formed rapidly. The precipitate was filtered off and recrystallized from ethanol and then twice more from DMF to give fine colorless crystals (0.1 g, 19%); mp 183-185°C, which, according to X-ray crystallography (Fig. 1a), was the 1-substituted benzopyranopyrazolone **4a**.

1-(4-Bromophenyl)[1]benzopyrano[4,3-*c*]pyrazol-4(1H)-one (4b) and 1-(4-Chlorophenyl)[1]-benzopyrano[4,3-*c*]pyrazol-4(1H)-one (4e) were prepared analogously to **4a** from the chlorovinyl aldehyde **2**, the corresponding hydrazine hydrochloride, and triethylamine.

2-Phenyl[1]benzopyrano[4,3-*c*]pyrazol-4(2H)-ne (5a). A mixture of aldehyde **2** (0.41 g, 2 mmol), phenylhydrazine (2 mmol), and triethylamine (2 mmol) was boiled for 5 h in ethanol (15 ml). The mixture was kept in the refrigerator for 1 d, the precipitate was filtered off and recrystallized twice from DMF to give yellowish crystals (0.32 g, 62%); mp 201-203°C.

2-(4-Bromophenyl)- (5b) and 2-(4-Chlorophenyl)[1]benzopyrano[4,3-*c*]pyrazol-2H-one (5e) were prepared analogously to the 2-aryl[1]benzopyrano[4,3-*c*]pyrazol-4(2H)-ones **5h-n.**

2-(2-Chlorophenyl)- (5c), 2-(3-Chlorophenyl)- (5d), 2-(4-Fluorophenyl)- (5f), 2-(2,4-Dichlorophenyl)- (5h), 2-(2,4-Difluorophenyl)- (5i), 2-(2-Hydroxycarbonylphenyl)- (5j), 2-(4-Nitrophenyl)- (5k), 2-[3,5-Di(trifluoromethyl)phenyl]- (5l), 2-(2-Pyridyl)- (5m), 2-(2-Quinoxalyl)- (5n) [1]benzopyrano[4,3-*c*]-pyrazol-4(2H)-ones. The formylderivative **2** (0.41 g, 2 mmol) was dissolved on heating in ethanol (15 ml). A hot solution of the corresponding hydrazine hydrochloride (2 mmol) and triethylamine (4 mmol), in ethanol (20 ml) was rapidly poured into the hot solution with stirring. The reaction mixture was boiled for 5 h, then kept in the refrigerator for 24 h, the precipitate was filtered off and recrystallized from DMF.

The Reactions of 4-Chloro-3-formylcoumarin (2) with 3-Chlorophenylhydrazine and 4-Methoxyphenylhydrazine were carried by the method used to synthesize compounds **4a** and **5a**, **5h-n**. In both cases multiple crystallizations from ethanol and DMF gave solid substances containing, in the first case, a mixture of **4d** and **5d**, and in the second case, a mixture of **4g** and **5g** according to TLC and ^{1}H NMR spectra (Table 3).

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