Synthesis and structure of 2-amino-5-azolyl-3-cyano-4*H*-pyrans

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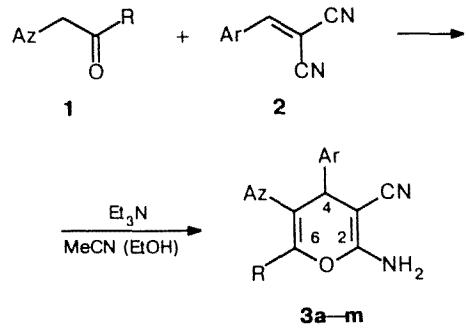
Previously unknown 5-azolylpyrans were obtained by reactions of *N*-acetonyl- and *N*-phenacylimidazoles, -triazoles, and -tetrazoles with arylmethylenemalononitriles. The structure of 2-amino-3-cyano-6-methyl-5-(5-nitrotetrazol-2-yl)-4-phenyl-4*H*-pyran was established by X-ray structural analysis.

Key words: *N*-acetonylazoles, *N*-phenacylazoles, arylmethylenemalononitriles, 2-amino-5-azolyl-3-cyano-4*H*-pyrans, heterocyclization, X-ray structural analysis.

Substituted 2-aminopyrans are of interest from the viewpoint of their possible use as drugs and dyes[1] and as intermediates in the synthesis of condensed heterocycles.[2–4] One of the general methods of preparing these compounds involves the reactions of 1,3-dicarbonyl compounds (β-diketones and β-oxo esters) with α,β-unsaturated nitriles,[1,5,6] while reactions of monocarbonyl compounds with unsaturated nitriles afford various carbocycles and heterocycles. For instance, ω-cyanoacetophenone reacts with arylmethylenemalononitriles to form the corresponding 2-aminopyrans,[7] whereas pyridinium ylides stabilized by the carbonyl group give, depending on the structure of these ylides, cyclopropanes[8] or the products of 1,3-dipolar addition (indolizines).[9]

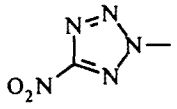
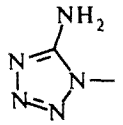
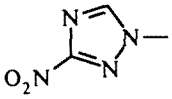
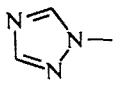
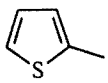
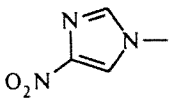
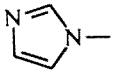
In this work, we studied the reactions of *N*-acetonyl- and *N*-phenacylazoles (**1**) with arylmethylenemalononitriles (**2**) for the first time. It was established that these reactions proceed regioselectively to form azolyl-substituted pyrans (**3**) (Scheme 1, Table 1).

Scheme 1



3a–m

Table 1. Yields of 2-amino-5-azolyl-3-cyano-4*H*-pyrans (**3a–m**)

Az	Compound	R	Ar	Yield of 3 (%)
	**3a**	Me	Ph	55
	3b	Me	3-IC_6H_4	58
	3c	Me	4-FC_6H_4	48
	**3d**	Me	Ph	32
	3e	Me	3-IC_6H_4	29
	3f	Ph	Ph	60
	3g	Ph	3-IC_6H_4	61
	**3h**	Me	Ph	69
	3i	Ph	Ph	58
	**3j**	Ph	Ph	46
	3k	Ph		24
	**3l**	Ph	Ph	62
	**3m**	Ph	Ph	46

2-Acetonyl-5-nitrotetrazole does not react with certain arylmethylenemalononitriles **2** (Ar = 4-$MeOC_6H_4$, 3-$NO_2C_6H_4$, 2-thienyl, or 2-furyl). Benzylidenemalono-

† Deceased.

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Table 2. ^{1}H NMR spectra of compounds **3a—m** (δ, *J*/Hz)

Compound	H(4)	NH_2	Other signals
3a	4.81 (d, *J* = 1.5)	6.48 (br.s)	2.10 (d, *J* = 1.5, 3 H, Me); 7.4—7.5 (m, 5 H, Ph)
3b	4.80 (d, *J* = 1.5)	6.59 (br.s)	2.15 (d, *J* = 1.5, 3 H, Me); 7.14 (t, 1 H); 7.32 (d, 1 H); 7.66 (d, 1 H); 7.70 (s, 1 H) (all aromatic)
3c	4.88 (d, *J* = 1.5)	6.55 (br.s)	2.13 (d, *J* = 1.5, 3 H, Me); 7.07 (t, 2 H, $J_{HH} = J_{HF}$ = 8.7); 7.32 (dd, 2 H, J_{HH} = 8.7, J_{HF} = 5.3) (all aromatic)
3d	4.45 (d, *J* = 1.5)	6.71 (br.s)	1.82 (d, *J* = 1.5, 3 H, Me); 6.48 (br.s, 2 H, NH_2); 7.1—7.3 (m, 5 H, Ph)
3e	4.47 (d, *J* = 1.5)	6.42 (br.s)	1.81 (d, *J* = 1.5, 3 H, Me); 6.20 (br.s, 2 H, NH_2); 7.0—7.2 (m, 2 H, H arom.); 7.6—7.7 (m, 2 H, H arom.)
3f	4.58 (br.s)	6.73 (br.s)	6.3—6.5 (br.s, 2 H, NH_2); 7.2—7.4 (m, 10 H, 2 Ph)
3g	4.65 (br.s)	6.56 (br.s)	5.8—6.2 (br.s, 2 H, NH_2); 7.13 (t, 1 H); 7.2—7.5 (m, 6 H); 7.65 (d, 1 H); 7.78 (d, 1 H) (all aromatic)
3h	4.59 (d, *J* = 1.5)	6.39 (br.s)	1.97 (d, *J* = 1.5, 3 H, Me); 7.3—7.45 (m, 5 H, Ph); 8.35 (s, 1 H, H(5′))
3i	4.80 (s)	6.55 (br.s)	7.2—7.5 (m, 10 H, 2 Ph); 8.09 (s, 1 H, H(5′))
3j	4.72 (s)	6.37 (br.s)	7.2—7.4 (m, 10 H, 2 Ph); 7.63 (s, 1 H, H(5′)); 7.92 (s, 1 H, H(3′))
3k	5.05 (s)	6.51 (br.s)	6.81 (d, *J* = 3.6, 1 H, H(3″)); 6.90 (dd, 1 H, H(4″), *J* = 5.0, 3.6); 7.21 (d, 2 H, *o*-Ph); 7.3—7.4 (m, 4 H, *m*- and *p*-Ph, H(5″)); 7.72 (s, 1 H, H(5′)); 8.00 (s, 1 H, H(3′))
3l	4.73 (s)	6.52 (br.s)	7.27 (d, *J* = 1.3, 1 H, H(2′)); 7.3—7.5 (m, 10 H, 2 Ph); 7.96 (d, *J* = 1.3, 1 H, H(5′))
3m	4.54 (s)	6.42 (br.s)	6.8—6.85 (m, 2 H, H(4′) and H(5′)); 7.03 (s, 1 H, H(2′)); 7.2—7.4 (m, 10 H, 2 Ph); 1.14 (t, 3 H); 3.60 (q, 2 H); 3.45 (br.s, 1 H) (EtOH)

Note. The protons of the azole fragment are primed, in compound **3k**, the protons of the thiophene ring are doubly primed. For the protons of the benzene ring, the assignments and the spin-spin interaction constants are generally omitted.

nitrile does not react with *N*-phenacylsuccinimide, *N*-phenacylphthalimide, and 1-acetonyl-3,5-dinitro-1,2,4-triazole, which is, apparently, associated with the steric hindrance in the initial ketones (double substitution in the heterocycle in the immediate vicinity of the oxo group). Note also that the reaction is reversible to some extent (according to the TLC data, even when reaction was conducted for a long period, complete disappearance of the initial compounds was never observed), and therefore, the yields of **3a—m** were no more than 70 %.

The ^{1}H NMR spectra of products **3** show the signals of the H(4) proton at δ 4.5—5.0 and the signals of the protons of the amino group at δ 6.4—6.7. The signal of the C(3) atom observed in the unusually (for the olefin carbon atoms) high field (~60 ppm), which is caused by the shielding effect of the nitrile group and by a conjugation in the $O(NH_2)C{=}C{-}CN$ fragment, is characteristic of the ^{13}C NMR spectra. The IR spectra show the bands of stretching (3200—3500 cm^{-1}) and deformation (~1650 cm^{-1}) vibrations of the amino group and the narrow intense band of the conjugated nitrile group at 2195—2220 cm^{-1}. All these facts, as well as the data of the NMR spectra (Tables 2 and 3), agree well with the published data.[5,10] In addition, all IR spectra show a medium-intensity band at 1695—1715 cm^{-1}, which is difficult to explain.

The last-mentioned fact necessitated the search for additional supporting evidence for the structures suggested. The structure of compound **3a** was confirmed by

Table 3. ^{13}C NMR spectra of compounds **3a—m** (δ, *J*/Hz)

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	CN	Other C atoms
3a	159.34	60.34	42.61	117.10	150.73	118.93	16.11 (Me); 128.73, 129.02, 129.77, 141.10 (Ph); 166.72 (C(5′))
3b	159.14	58.98	41.86	116.27	150.68	118.06	15.76 (Me); 94.73, 127.90, 131.25, 137.07, 137.57, 143.53 (arom.); 166.47 (C(5′))
3c	159.21	59.32	41.76	116.62	150.39	118.28	15.69 (Me); 116.05 (d, $^2J_{C,F}$ = 21.6); 130.39 (d, $^3J_{C,F}$ = 7.9); 137.13 (d, $^4J_{C,F}$ = 3.0); 162.84 (d, $^1J_{C,F}$ = 244) (arom.); 166.50 (C(5′))
3d	158.81	56.51	41.24	109.74	147.31	119.47	14.85 (Me); 127.36, 127.91, 128.24, 140.96 (Ph); 155.12 (C(5′))
3e	159.81	58.11	42.04	110.46	148.70	119.01	15.03 (Me); 94.57, 128.36, 130.87, 137.18, 137.54, 144.28 (arom.); 156.05 (C(5′))
3f	159.14	56.87	42.01	110.27	147.78	119.39	127.45, 127.67, 128.21, 128.33, 129.82, 130.08, 140.89 (Ph); 154.77 (C(5′))
3g	159.34	56.29	41.69	109.58	148.40	119.47	95.02, 127.84, 128.36, 129.81, 130.31, 130.62, 136.41, 136.77, 143.62 (arom.); 154.85 (C(5′))
3h	159.16	57.98	42.35	114.76	148.31	118.96	14.65 (Me); 128.05, 128.95, 140.99 (Ph); 147.79 (C(5′)); 163.02 (C(3′))
3i	159.74	59.32	43.55	115.92	148.88	118.49	128.40, 128.51, 129.25, 129.41, 130.02, 131.13, 141.18 (Ph); 148.80 (C(5′)); 163.60 (C(3′))
3j	159.97	59.45	43.68	116.64	146.87	118.75	128.09, 128.17, 128.43, 128.92, 129.18, 130.53, 130.93, 142.02 (Ph); 146.01 (C(5′)); 152.81 (C(3′))
3k	160.33	58.50	39.10	116.35	146.51	119.30	128.17, 129.09, 130.76 (Ph); 126.41 (C(3′′) and C(5′′)); 127.51 (C(4′′)); 146.67 (C(2′′)); 146.41 (C(5′)); 153.08 (C(3′))
3l	159.78	59.32	44.49	115.23	147.47	118.73	128.39, 128.69, 129.17, 129.56, 130.52, 130.83, 141.80 (Ph); 121.55 (C(5′)); 146.12 (C(2′)); 148.50 (C(4′))
3m	159.93	57.34	45.11	116.24	145.48	118.93	127.87, 128.22, 128.51, 128.82, 129.30, 130.14, 131.33, 142.80 (Ph); 120.15 (C(5′)); 129.72 (C(4′)); 138.05 (C(2′)); 18.56 (Me); 59.53 (CH_2) (from EtOH)

Note. In some cases, the signals of the aromatic C atoms overlap, and therefore, the number of the signals given in the table for some compounds is less than the number of C atoms in these compounds. For the atomic labelling, see the note in Table 2.

X-ray structural analysis (the overall view of one atropoisomer of **3a** is shown in Fig. 1; the bond lengths and bond angles are given in Tables 4 and 5, respectively). In the molecule studied, the 4*H*-pyran cycle has a flattened boat conformation: the O(1) and C(4) atoms deviate from the plane through the remaining atoms of the "bottom of the boat" (the fragment is planar to within ±0.010 Å) by −0.066 and −0.189 Å, respectively, which corresponds to the folding of the cycle along the C(2)...C(6), C(3)...C(5), and O(1)...C(4) lines by 5.5°, 12.1°, and 11.9°, respectively. Previously,[11,12] analogous conformations of the heterocycle were found in the molecules of 2-amino-3-ethoxycarbonyl-4-(3-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran and 2-amino-3-ethoxycarbonyl-4-(2-fluorophenyl)-4*H*-naphtho[2,1-*b*]pyran.

The dihedral angle between the plane of the pseudoaxial phenyl substituent and the "bottom of the boat" is 85.0°. The absence of shortened nonbonded intramolecular contacts (within the sum of the van der Waals radii[13] of N and C) between the substituted tetrazole and Ph cycles (the C(9)—C(4)—C(5)—N(3) torsion angle is 68.4°) determines rather free rotation of the heterocycle about the C(5)—N(3) bond. Because of this, the heterocycle is disordered between two positions (*i.e.*, the crystal structure contains two atropoisomers of **3a**, which differ in the angle of rotation of the tetrazole fragment about the C(5)—N(3) bond). The dihedral angles between the planes through the N(3), N(4), C(15), N(5), N(6) and N(3), N(4′), C(15), N(5′), N(6′) atoms and between the planes through the N(7), O(2), O(3) and N(7′), O(2′), O(3′) atoms are 59.2 and 60.1°, respectively.

In molecule **3a**, the fragment, which contains the C(2)=C(3) bond and the NH_2 and CN groups attached to this bond, is of interest. Equalization of the N(1)—C(2), C(2)=C(3), and C(3)—C(8) bond lengths (see Table 4) is indicative of a pronounced conjugation between the lone electron pair of the planar-trigonal N(1) atom (the sum of the bond angles is 360°) and the

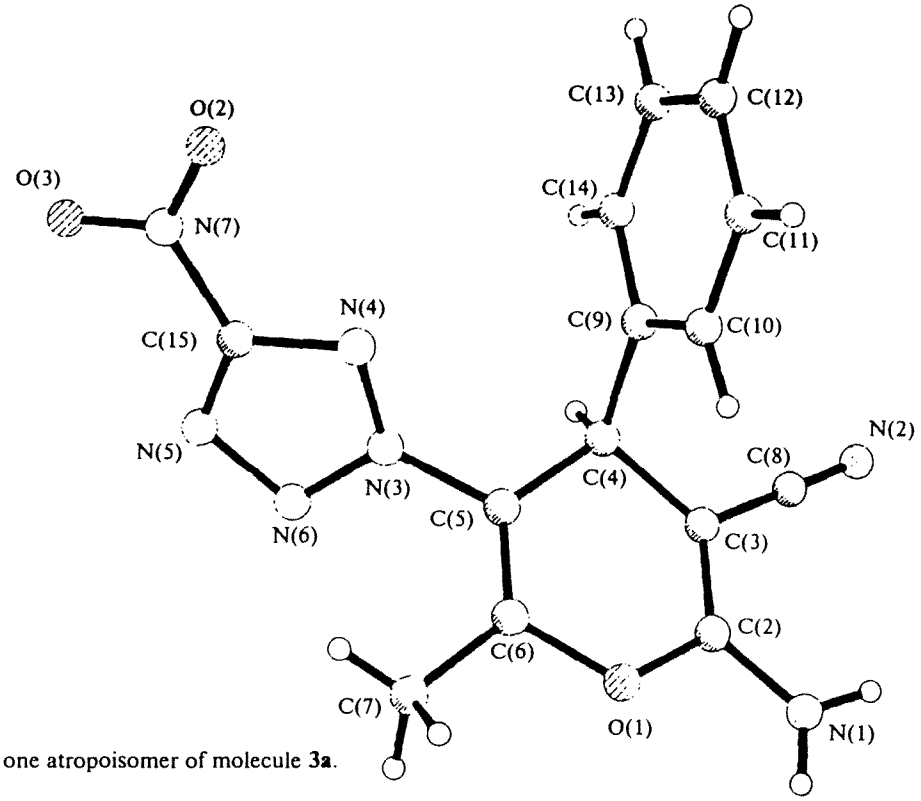

Fig. 1. Overall view of one atropoisomer of molecule **3a**.

Table 4. Bond lengths (d) in molecule **3a**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
O(1)—C(2)	1.369(3)	N(3)—N(4′)	1.241(6)	N(5′)—C(15)	1.370(6)	C(6)—C(7)	1.481(4)
O(1)—C(6)	1.386(3)	N(3)—N(6)	1.320(5)	N(7)—C(15)	1.469(8)	C(9)—C(10)	1.382(4)
O(2)—N(7)	1.197(9)	N(3)—N(6′)	1.467(5)	N(7′)—C(15)	1.441(8)	C(9)—C(14)	1.380(4)
O(2′)—N(7′)	1.211(9)	N(3)—C(5)	1.435(3)	C(2)—C(3)	1.352(3)	C(10)—C(11)	1.370(4)
O(3)—N(7)	1.23(1)	N(4)—C(15)	1.369(6)	C(3)—C(4)	1.515(3)	C(11)—C(12)	1.367(5)
O(3′)—N(7′)	1.16(2)	N(4′)—C(15)	1.284(6)	C(3)—C(8)	1.417(4)	C(12)—C(13)	1.361(5)
N(1)—C(2)	1.336(4)	N(5)—N(6)	1.320(6)	C(4)—C(5)	1.501(3)	C(13)—C(14)	1.374(5)
N(2)—C(8)	1.142(4)	N(5′)—N(6′)	1.315(7)	C(4)—C(9)	1.518(4)		
N(3)—N(4)	1.322(6)	N(5)—C(15)	1.253(6)	C(5)—C(6)	1.321(4)		

Table 5. Bond angles (ω) in molecule **3a**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(2)—O(1)—C(6)	119.0(2)	O(2′)—N(7′)—C(15)	115.3(6)	N(2)—C(8)—C(3)	179.0(3)
N(4)—N(3)—N(6)	114.7(3)	O(3′)—N(7′)—C(15)	120.8(9)	C(4)—C(9)—C(10)	120.0(2)
N(4′)—N(3)—N(6′)	111.0(3)	O(1)—C(2)—N(1)	110.6(2)	C(4)—C(9)—C(14)	122.1(2)
N(4)—N(3)—C(5)	123.1(3)	O(1)—C(2)—C(3)	122.1(2)	C(10)—C(9)—C(14)	117.9(2)
N(4′)—N(3)—C(5)	129.8(3)	N(1)—C(2)—C(3)	127.3(2)	C(9)—C(10)—C(11)	121.3(3)
N(6)—N(3)—C(5)	120.5(3)	C(2)—C(3)—C(4)	123.3(2)	C(10)—C(11)—C(12)	120.0(3)
N(6′)—N(3)—C(5)	117.9(3)	C(2)—C(3)—C(8)	118.7(2)	C(11)—C(12)—C(13)	119.4(3)
N(3)—N(4)—C(15)	96.9(4)	C(4)—C(3)—C(8)	117.8(2)	C(12)—C(13)—C(14)	121.1(3)
N(3)—N(4′)—C(15)	105.9(4)	C(3)—C(4)—C(5)	106.4(2)	C(9)—C(14)—C(13)	120.3(3)
N(6)—N(5)—C(15)	106.3(4)	C(3)—C(4)—C(9)	112.3(2)	N(4)—C(15)—N(5)	116.0(4)
N(6′)—N(5′)—C(15)	104.4(4)	C(5)—C(4)—C(9)	112.0(2)	N(4′)—C(15)—N(5′)	114.6(4)
N(3)—N(6)—N(5)	104.9(4)	N(3)—C(5)—C(4)	115.2(2)	N(4)—C(15)—N(7)	116.3(4)
N(3)—N(6′)—N(5′)	104.0(4)	N(3)—C(5)—C(6)	118.1(2)	N(5)—C(15)—N(7)	127.6(4)
O(2)—N(7)—O(3)	124.8(8)	C(4)—C(5)—C(6)	126.6(2)	N(4′)—C(15)—N(7′)	125.6(4)
O(2′)—N(7′)—O(3′)	123.9(10)	O(1)—C(6)—C(5)	120.4(2)	N(5′)—C(15)—N(7′)	119.3(4)
O(2)—N(7)—C(15)	121.1(6)	O(1)—C(6)—C(7)	110.3(2)		
O(3)—N(7)—C(15)	114.1(7)	C(5)—C(6)—C(7)	129.3(2)		

π-system of the multiple bond. Other bond lengths and bond angles have normal values.[14] In the crystal, molecules **3a** are linked in chains through intermolecular hydrogen bonds N(1)—H(1.2)...N(2) (1 − *x*, 0.5 + *y*, 0.5 − *z*) [N(1)...N(2) 3.047(4) N(1)—H(1.2) 0.82(3), H(1.2)...N(2) 2.27(3) Å, the N(1)—H(1.2)...N(2) angle 157(3)°]. The second hydrogen atom of the NH_2 group is not involved in hydrogen bonding and does not form shortened contacts.

The question of whether free rotation about the C(5)—N bond is possible is of particular interest in the case of compounds **3d—g** (Az = 5-aminotetrazol-1-yl). One would expect that the amino group in the *ortho* position of the tetrazole substituent can substantially hinder the rotation of the tetrazole group about the C(5)—N bond. Actually, certain of the signals in the NMR spectra of compounds **3f,g** in which the aminotetrazole fragment is adjacent to the bulky phenyl substituent at position 6 are substantially broadened. In the ^1H NMR spectra, the signals of the H(4) atom and the protons of the amino group of the tetrazole fragment are broadened; in the ^{13}C NMR spectra the signals of the C(3), C(4), and C(6) atoms and the C atom of the Ar group directly bonded to C(4) are broadened. However, in the NMR spectra of compounds **3d,e** (R^1 = Me), the signals are not broadened, *i.e.*, when the substituent at position 6 is less bulky, free rotation of the aminotetrazole fragment about the C(5)—N bond becomes possible.

The nature of the substituents in the azole cycle has little effect on the course of the reaction; in the case of azoles containing either electron-withdrawing or electron-donating substituents, the reaction occurs in reasonable yields. As mentioned above, only the absence of substantial steric hindrance is necessary. Therefore, taking into account that the initial α-azolylketones are available (from azoles and α-halideketones[15]), the Az, Ar, and R^1 substituents can vary, and pyrans of type **3** can undergo further conversions,[2—4] the reaction considered here is promising in the synthesis of azolyl-substituted heterocycles.

Experimental

The ^1H NMR spectra were recorded on Bruker AC-200 and Bruker AM-300 instruments (200 and 300 MHz, respectively); the ^{13}C NMR spectra were measured on a Bruker AM-300 instrument (75.47 MHz). The IR spectra were recorded on a Specord M-80 instrument (KBr pellets). The ^1H NMR spectra of compounds **3d—g** were obtained in a $(CD_3)_2CO$—$(CD_3)_2SO$ mixture; the ^{13}C NMR spectra of these compounds were measured in $(CD_3)_2SO$. The NMR spectra of all other compounds were recorded in $(CD_3)_2CO$. Ethanol, acetone, and aqueous DMSO were used for recrystallization of compounds **3a—c,h**, **3i—l**, and **3d—g**, respectively. Elemental analysis of compounds **3a—m** gave satisfactory results.

2-Acetonyl-5-nitrotetrazole, 1-acetonyl-5-aminotetrazole, and 1-acetonyl-3-nitro-1,2,4-triazole were synthesized as described previously.[15]

1-Phenacyl-1,2,4-triazole[16] **and 1-phenacylimidazole**[17] were obtained using the known procedures.

1-Phenacyl-3-nitro-1,2,4-triazole and 1-phenacyl-4-nitroimidazole. A solution of phenacyl bromide (2.0 g, 0.01 mol) in acetone (15 mL) was added to a solution of the initial nitroazole (0.01 mol) and KOH (0.56 g, 0.01 mol) in water (5 mL), and then acetone (25 mL) was added to the mixture. The solution was stirred at 20 °C for 5 h and then kept for ~16 h. Then the reaction mixture was filtered off. The filtrate was concentrated to ~10 mL and cooled to 0 °C. The precipitate was filtered off and washed on a filter with ether. **1-Phenacyl-3-nitro-1,2,4-triazole** and **1-phenacyl-4-nitroimidazole** were obtained in the yields of 69 and 64 %, respectively (m.p. 129—130 °C and 156—157 °C, respectively).

5-Amino-1-phenacyltetrazole. A solution of phenacyl bromide (2.0 g, 0.01 mol) in dichloroethane (8 mL) was added to a solution of 5-aminotetrazole dihydrate (1.21 g, 0.01 mol), KOH (0.56 g, 0.01 mol), and tetrabutylammonium bromide (0.25 g) in water (8 mL). The emulsion was stirred at 40—50 °C for 8 h. The precipitate that formed was filtered off and washed with dichloroethane. **5-Amino-1-phenacyltetrazole** was obtained in the yield of 61 %, m.p. 233—234 °C (decomp.).

General procedure for the preparation of pyrans 3a—c,h—m. One drop of Et_3N was added to a slightly warmed (~30 °C) solution of α-azolylketone **1** (1 mmol) and arylmethylenemalononitrile **2** (1.04 mmol) in MeCN (2 mL). The reaction mixture was kept at ~20 °C for ~24 h. Then the solvent was allowed to evaporate (to ~1/3 of the initial volume). The precipitate was filtered off. In the case of **3a,b,k**, the precipitate sometimes did not form; in these cases, the solvent was evaporated to dryness, the oil obtained was diluted with $CHCl_3$. After 1 h, the crystals that formed were filtered off. In the case of **3m**, the oil obtained after evaporation of the solvent was diluted with EtOH, and after 3 h the crystals that formed were filtered off.

A mixture of MeCN (2 mL) and EtOH (2 mL) was used as a solvent in the synthesis of pyrans **3d—g** (the same amounts of the initial reagents and Et_3N were used). The suspension thus formed was stirred at 40—50 °C until the precipitate completely dissolved (1—2 h). Then the stirring was discontinued, the solution was heated for an additional 1 h, and then the reaction mixture was kept at ~20 °C for ~24 h. The precipitate was filtered off.

2-Amino-3-cyano-6-methyl-5-(5-nitrotetrazol-2-yl)-4-phenyl-4*H*-pyran (3a). M.p. 169—170 °C (decomp.). IR, ν/cm^{-1}: 3440, 3325 (νNH_2); 2210 (νCN); 1635 (δNH_2); 1565, 1310 (νNO_2).

2-Amino-3-cyano-4-(3-iodophenyl)-6-methyl-5-(5-nitrotetrazol-2-yl)-4*H*-pyran (3b). M.p. 154—155 °C (decomp.). IR, ν/cm^{-1}: 3435, 3315 (νNH_2); 2210 (νCN); 1650 (δNH_2); 1560, 1310 (νNO_2).

2-Amino-3-cyano-4-(4-fluorophenyl)-6-methyl-5-(5-nitrotetrazol-2-yl)-4*H*-pyran (3c). M.p. 159—160 °C (decomp.). IR, ν/cm^{-1}: 3440, 3345, 3210 (νNH_2); 2205 (νCN); 1660 (δNH_2); 1570, 1315 (νNO_2).

2-Amino-5-(5-aminotetrazol-1-yl)-3-cyano-6-methyl-4-phenyl-4*H*-pyran (3d). Decomposition temperature >190 °C. IR, ν/cm^{-1}: 3450, 3325, 3160 (νNH_2); 2220 (νCN); 1650 (δNH_2).

2-Amino-5-(5-aminotetrazol-1-yl)-3-cyano-4-(3-iodophenyl)-6-methyl-4*H*-pyran (3e). Decomposition temperature >180 °C. IR, ν/cm^{-1}: 3450, 3325, 3180 (νNH_2); 2210 (νCN); 1640 (δNH_2).

2-Amino-5-(5-aminotetrazol-1-yl)-3-cyano-4,6-diphenyl-4*H*-pyran (3f). M.p. 228—230 °C (decomp.). IR, ν/cm^{-1}: 3465, 3320, 3180 (νNH_2); 2220 (νCN); 1645 (δNH_2).

Table 6. Atomic coordinates ($\times 10^4$; $\times 10^3$ for H atoms) in molecule **3a**

Atom	x	y	z
O(1)	3442(1)	7550(1)	421(2)
O(2)	−157(3)	5432(5)	−4652(6)
O(2′)	−380(3)	6958(4)	−4485(6)
O(3)	−1350(8)	5881(11)	−3304(10)
O(3′)	−1356(10)	5994(15)	−3331(17)
N(1)	4708(2)	6951(2)	1676(4)
N(2)	4380(2)	4088(2)	2345(3)
N(3)	1219(1)	6381(2)	−834(3)
N(4)	998(4)	6030(4)	−2264(6)
N(4′)	886(4)	6616(4)	−2148(7)
N(5)	−204(3)	6723(4)	−993(6)
N(5′)	−190(3)	5701(4)	−821(6)
N(6)	544(3)	6894(4)	−107(6)
N(6′)	562(3)	5733(4)	78(6)
N(7)	−507(5)	5816(6)	−3510(9)
N(7′)	−620(5)	6375(5)	−3417(9)
C(2)	3889(2)	6663(2)	1043(3)
C(3)	3510(2)	5657(2)	1003(3)
C(4)	2619(2)	5390(2)	112(3)
C(5)	2159(2)	6457(2)	−257(3)
C(6)	2541(2)	7431(2)	−153(3)
C(7)	2147(3)	8505(3)	−587(4)
C(8)	3997(2)	4789(2)	1738(3)
C(9)	2793(2)	4727(2)	−1363(3)
C(10)	3451(2)	5065(2)	−2425(3)
C(11)	3628(2)	4479(3)	−3760(4)
C(12)	3158(2)	3533(3)	−4054(4)
C(13)	2508(3)	3188(3)	−3020(4)
C(14)	2323(2)	3772(2)	−1681(4)
C(15)	63(2)	6214(2)	−2181(3)
H(1.1)	510(2)	647(3)	205(4)
H(1.2)	485(2)	760(3)	174(3)
H(4)	222(2)	495(2)	75(3)
H(7.1)	208(2)	892(2)	36(4)
H(7.2)	258(3)	892(3)	−118(4)
H(7.3)	161(3)	842(3)	−108(4)
H(10)	381(2)	566(2)	−218(3)
H(11)	407(2)	473(2)	−449(3)
H(12)	325(2)	318(2)	−501(3)
H(13)	216(2)	251(3)	−313(4)
H(14)	189(2)	356(2)	−91(3)

2-Amino-5-(5-aminotetrazol-1-yl)-3-cyano-4-(3-iodophenyl)-6-phenyl-4*H*-pyran (3g). M.p. 247—248 °C (decomp.). IR, ν/cm^{-1}: 3460, 3305 (νNH_2); 2210 (νCN); 1645 (δNH_2).

2-Amino-3-cyano-6-methyl-5-(3-nitro-1,2,4-triazol-1-yl)-4-phenyl-4*H*-pyran (3h). M.p. 244—245 °C (decomp.). IR, ν/cm^{-1}: 3470, 3330 (νNH_2); 2195 (νCN); 1635 (δNH_2); 1550, 1310 (νNO_2).

2-Amino-3-cyano-5-(3-nitro-1,2,4-triazol-1-yl)-4,6-diphenyl-4*H*-pyran (3i). M.p. 161—162 °C (decomp.). IR, ν/cm^{-1}: 3465, 3315 (νNH_2); 2210 (νCN); 1650 (δNH_2); 1555, 1305 (νNO_2).

2-Amino-3-cyano-4,6-diphenyl-5-(1,2,4-triazol-1-yl)-4*H*-pyran (3j). M.p. 198—199 °C. IR, ν/cm^{-1}: 3445, 3330, 3210 (νNH_2); 2205 (νCN); 1660 (δNH_2).

2-Amino-3-cyano-6-phenyl-4-(2-thienyl)-5-(1,2,4-triazol-1-yl)-4*H*-pyran (3k). M.p. 190—191 °C. IR, ν/cm^{-1}: 3330, 3210 (νNH_2); 2200 (νCN); 1650 (δNH_2).

2-Amino-3-cyano-5-(4-nitroimidazol-1-yl)-4,6-diphenyl-4*H*-pyran (3l). M.p. 123—126 °C (decomp.). IR, ν/cm^{-1}: 3315 (νNH_2); 2200 (νCN); 1645 (δNH_2); 1540, 1295 (νNO_2).

2-Amino-3-cyano-5-(imidazol-1-yl)-4,6-diphenyl-4*H*-pyran (3m) was isolated as a crystal solvate with EtOH, m.p. 112—114 °C (with loss of EtOH). IR, ν/cm^{-1}: 3150—3450 (νNH_2, νOH); 2200 (νCN); 1665 (δNH_2).

X-ray structural analysis of compound 3a. Crystals of **3a** are monoclinic, at 20 °C: a = 14.404(2), b = 12.295(3), c = 8.491(4) Å, β = 90.92(2)°, V = 1503(1) Å^3, d_{calc} = 1.441 g cm^{-3}, Z = 4, space group $P2_1/c$. The unit cell parameters and intensities of 2317 independent reflections were measured on a four-circle automated Siemens P3/PC diffractometer (Mo Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique to θ_{max} = 27°). The structure was solved by the direct method, which allowed us to reveal all nonhydrogen atoms, and refined by the full-matrix least-squares method with anisotropic temperature factors for nonhydrogen atoms using 1863 reflections with $I > 3\sigma(I)$. The O(2), O(3), N(4), N(5), N(6), and N(7) atoms are disordered between two positions, which is associated with the rotation of the heterocycle about the C(5)—N(3) bond. According to the refinement, the occupancies of the O(2), O(3), N(4), N(5), N(6), N(7) and O(2′), O(3′), N(4′), N(5′), N(6′), N(7) atoms are 0.50 and 0.50, respectively. All hydrogen atoms were located from the difference Fourier syntheses and refined isotropically. The final values of the R factors were R = 0.043, R_w = 0.043 (S = 0.626). All calculations were carried out using the SHELXTL PLUS program[18] (the PC version). Atomic coordinates are given in Table 6 (thermal parameters may be obtained from the authors).

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