Heterocycles with a β-nitroenamine fragment
1. Synthesis of 2-amino-3-nitropyrans from nitroacetonitrile. Crystal and molecular structure of 2-amino-4-(4-fluorophenyl)-3-nitro-7,7-dimethyl-5,6,7,8-tetrahydrochromen-5(4*H*)-one

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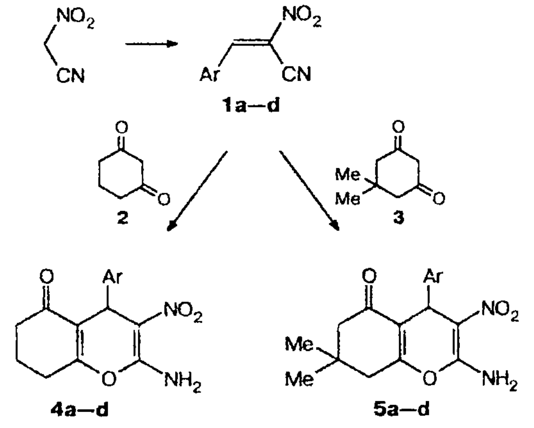
Reactions of dimedone and dihydroresorcinol with arylidenenitroacetonitriles yield fused 2-amino-3-nitropyrans. The crystal and molecular structure of one of the reaction products was determined by X-ray diffraction analysis.

Key words: arylidenenitroacetonitriles, 2-amino-3-nitropyrans, X-ray diffraction analysis.

Earlier,[1] it was reported that arylidenenitroacetonitriles (ANN) react with dimedone to give 2-amino-3-nitropyrans. However, the spectra of the compounds obtained were not presented.

We found that the condensation of the reaction products of nitroacetonitrile with aldehydes,[2] *viz.*, ANN (**1a—d**), with dihydroresorcinol (**2**) or dimedone (**3**) in EtOH in the presence of catalytic amounts of Et_3N results in slightly colored crystalline 2-amino-3-nitropyrans (**4a—d**) or (**5a—d**), respectively (Scheme 1).

Scheme 1



	1a, 4a, 5a	**1b, 4b, 5b**	**1c, 4c, 5c**	**1d, 4d, 5d**
Ar	Ph	4-$MeOC_6H_4$	4-ClC_6H_4	4-FC_6H_4

The structures of the compounds obtained were determined by ^1H NMR and IR spectroscopy (Tables 1 and 2). X-ray diffraction analysis of compound **5d** was carried out to establish the specific features of structures **4** and **5**. The general view of the molecule is shown in Fig. 1. The bond lengths and bond angles are given in Tables 3 and 4, respectively.

The pyran heterocycle in the molecule under study has the conformation of a flattened boat. The O(1) and C(4) atoms deviate from the "boat bottom" plane (the bottom is planar with an accuracy of 0.002 Å) by −0.050 and −0.140 Å, respectively, and the dihedral angles of the ring along the C(2)...C(8A), C(3)...C(4A), and O(1)...C(4) lines are equal to 4.2, 13.4, and 8.9°, respectively. Note that the NO_2 and NH_2 groups also lie in the "boat bottom" plane, which results in the formation of a strong intramolecular N(1)—H(2N)...O(2) hydrogen bond with the following parameters: N(1)...O(2) 2.623(4) Å, N(1)—H(2N) 0.80(2) Å, H(2N)...O(2) 1.99(2) Å, N(1)—H(2N)...O(2) 136(2)°. The planar structure of the N(1)—C(2)=C(3)—N(2)—O(2) fragment (the deviation of the atoms from the average plane does not exceed 0.012 Å) is favorable for conjugation. Thus, the N(1)—C(2) (1.316(3) Å) and C(3)—N(2) distances (1.394(3) Å) are much shorter than the usual ones (the conjugated $C(sp^2)—N(sp^2)$ and $C(sp^2)—NO_2$ bond lengths are equal to 1.336 and 1.468 Å, respectively),[3] while the C(2)=C(3) bond (1.385(3) Å) is significantly longer than the C(4A)=C(8A) bond (1.331(3) Å) and so is the N(2)—O(2) bond (1.242(3) Å) (the standard values[3] of the $C(sp^2)=C(sp^2)$ and $N(sp^2)—O$ (in the NO_2 group) bond lengths are equal to 1.331 and 1.218 Å, respectively). Apparently, the O(1) atom is also involved in conjugation with the C(2)=C(3) double bond, which is

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Table 1. Characteristics of pyrans **4** and **5**

Compound	Yield (%)	M.p. /°C	Found/Calculated (%) C	H	N	Molecular formula	IR, ν/cm^{-1}
4a	62	230—231	62.87 62.93	5.11 4.93	9.81 9.79	$C_{15}H_{14}N_2O_4$	3450—3300 (NH_2), 1670—1630 (CO), 1520 $\nu_{as}(NO_2)$
4b	63	245—246	60.88 60.75	5.81 5.10	8.72 8.86	$C_{16}H_{16}N_2O_5$	3450—3200 (NH_2), 1670—1640 (CO), 1510 $\nu_{as}(NO_2)$
4c	25	185	56.10 56.17	4.32 4.09	8.43 8.73	$C_{15}H_{13}ClN_2O_4$	3400—3100 (NH_2), 1670—1630 (CO), 1505 $\nu_{as}(NO_2)$
4d	30	227	59.71 59.21	4.62 4.31	9.80 9.21	$C_{15}H_{13}FN_2O_4$	3350—3100 (NH_2), 1670—1630 (CO), 1500 $\nu_{as}(NO_2)$
5a	73	221—222	64.49 64.96	6.03 5.77	8.15 8.91	$C_{17}H_{18}N_2O_4$	3450—3300 (NH_2), 1680—1630 (CO), 1490 $\nu_{as}(NO_2)$
5b	65	189—192	62.65 62.78	6.11 5.85	8.40 8.13	$C_{18}H_{20}N_2O_5$	3400—3100 (NH_2), 1670—1640 (CO), 1500 $\nu_{as}(NO_2)$
5c	31	163	58.43 58.54	4.72 4.91	8.14 8.03	$C_{17}H_{17}ClN_2O_4$	3450—3050 (NH_2), 1680—1640, 1505 $\nu_{as}(NO_2)$
5d	42	218	61.12 61.44	5.80 5.16	8.50 8.43	$C_{15}H_{17}FN_2O_4$	3400—3250 (NH_2), 1670—1630 (CO), 1495 $\nu_{as}(NO_2)$

Table 2. ^1H NMR spectra of pyrans **4** and **5**

Compound	2-NH_2 (br.s)	4-H (s)	6-CH_2	7-X*	8-CH_2 (m)	Ar (m)
4a	9.3	4.92	2.3 (m, 2 H)	1.85 (m, 1 H); 2.00 (m, 1 H)	2.7	7.2 (5 H)
4b	9.3	4.9	2.3 (m, 2 H)	1.85 (m, 1 H); 1.95 (m, 1 H)	2.65	6.8—7.15 (4 H)
4c	9.4	4.9	2.3 (m, 2 H)	1.87 (m, 1 H); 1.93 (m, 1 H)	2.7	7.2—7.3 (4 H)
4d	9.4	4.9	2.3 (m, 2 H)	1.87 (m, 1 H); 1.93 (m, 1 H)	2.65	7.0—7.3 (4 H)
5a	9.15	4.91	2.1 (d, 1 H); 2.2 (d, 1 H)	0.91 (s, 3 H); 1.06 (s, 3 H)	2.50	7.2 (5 H)
5b	9.2	4.9	2.1 (d, 1 H); 2.23 (d, 1 H)	0.91 (s, 3 H); 1.06 (s, 3 H)	2.55	6.8—7.2 (4 H)
5s	9.4	4.87	2.1 (d, 1 H); 2.27 (d, 1 H)	0.9 (s, 3 H); 1.05 (s, 3 H)	2.55	7.2—7.4 (4 H)
5d	9.35	4.9	2.1 (d, 1 H); 2.3 (d, 1 H)	0.9 (s, 3 H); 1.05 (s, 3 H)	2.55	7.0—7.3 (4 H)

* CH_2 for **4a—d** and $C(CH_3)_2$ for **5a—d**.

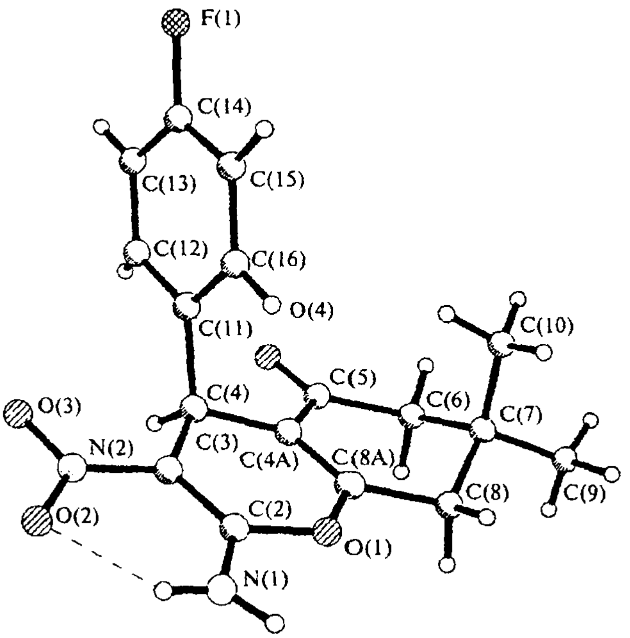


Fig. 1. General view of molecule **5d**. The intramolecular N—H...O hydrogen bond is indicated by the dotted line.

evidenced by shortening of the O(1)—C(2) bond to 1.348(2) Å, as compared to the O(1)—C(8A) bond (1.376(2) Å). The dihedral angle between the two planar fragments considered of the molecule is equal to 4.7°.

It can be seen from Fig. 1 that the cyclohexenone ring exists in the sofa conformation: the C(7) atom deviates from an imaginary plane passing through the C(6), C(5), C(4A), C(8A), and C(8) atoms (the plane is correct to within 0.009 Å) by −0.670 Å, and the dihedral angle between the

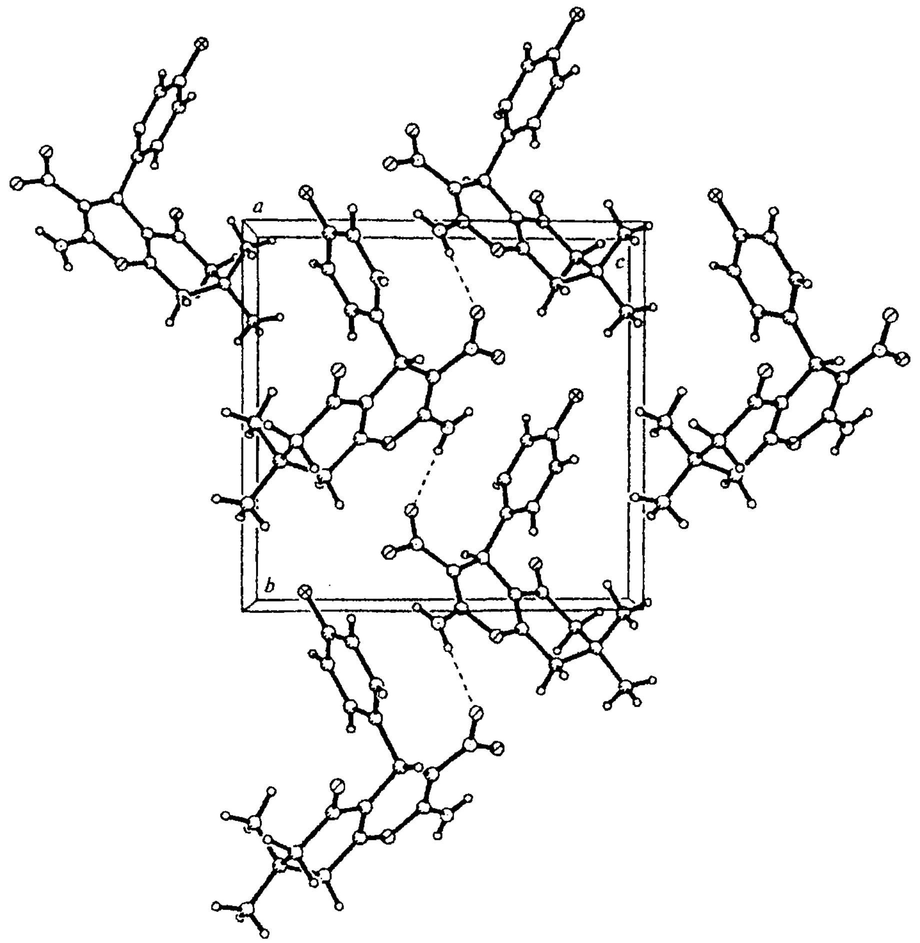


Fig. 2. The *bc* projection of crystal structure **5d**. The intermolecular N—H...O hydrogen bonds are indicated by dotted lines.

Table 3. Bond lengths (*d*) in molecule **5d**

Bond	*d*/Å	Bond	*d*/Å
F(1)—C(14)	1.361(3)	C(4A)—C(5)	1.469(3)
O(1)—C(2)	1.348(2)	C(5)—C(6)	1.507(4)
O(1)—C(8A)	1.376(2)	C(6)—C(7)	1.518(4)
O(2)—N(2)	1.242(3)	C(7)—C(9)	1.525(3)
O(3)—N(2)	1.248(3)	C(7)—C(10)	1.527(4)
O(4)—C(5)	1.208(3)	C(7)—C(8)	1.536(3)
N(1)—C(2)	1.316(3)	C(8)—C(8A)	1.484(3)
N(2)—C(3)	1.394(3)	C(11)—C(16)	1.377(3)
C(2)—C(3)	1.385(3)	C(11)—C(12)	1.386(3)
C(3)—C(4)	1.502(3)	C(12)—C(13)	1.385(4)
C(4)—C(4A)	1.507(3)	C(13)—C(14)	1.347(5)
C(4)—C(11)	1.526(3)	C(14)—C(15)	1.373(4)
C(4A)—C(8A)	1.331(3)	C(15)—C(16)	1.390(3)

heterocycle "bottom" and this plane is equal to 4.3°. Thus, the fragment under discussion of the molecule is markedly flattened. The pseudoaxial C(4)—C(11) bond with the *para*-fluorophenyl substituent is nearly perpendicular to the "boat bottom" of the heterocycle (the dihedral angle is equal to 89.1°).

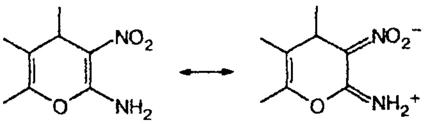
Table 4. Bond angles (ω) in molecule **5d**

Angle	ω/deg	Angle	ω/deg
C(2)—O(1)—C(8A)	120.1(2)	C(6)—C(7)—C(9)	110.6(2)
O(2)—N(2)—O(3)	120.4(2)	C(6)—C(7)—C(10)	110.8(2)
O(2)—N(2)—C(3)	121.8(2)	C(9)—C(7)—C(10)	109.0(2)
O(3)—N(2)—C(3)	117.8(2)	C(6)—C(7)—C(8)	106.9(2)
N(1)—C(2)—O(1)	110.5(2)	C(9)—C(7)—C(8)	109.5(2)
N(1)—C(2)—C(3)	128.7(2)	C(10)—C(7)—C(8)	110.1(2)
O(1)—C(2)—C(3)	120.8(2)	C(8A)—C(8)—C(7)	111.4(2)
C(2)—C(3)—N(2)	119.3(2)	C(4A)—C(8A)—O(1)	122.4(2)
C(2)—C(3)—C(4)	123.5(2)	C(4A)—C(8A)—C(8)	126.6(2)
N(2)—C(3)—C(4)	117.1(2)	O(1)—C(8A)—C(8)	111.0(2)
C(3)—C(4)—C(4A)	108.4(2)	C(16)—C(11)—C(12)	118.4(2)
C(3)—C(4)—C(11)	113.0(2)	C(16)—C(11)—C(4)	119.6(2)
C(4A)—C(4)—C(11)	110.6(2)	C(12)—C(11)—C(4)	122.0(2)
C(8A)—C(4A)—C(5)	117.6(2)	C(13)—C(12)—C(11)	120.9(2)
C(8A)—C(4A)—C(4)	123.6(2)	C(14)—C(13)—C(12)	118.5(2)
C(5)—C(4A)—C(4)	118.8(2)	C(13)—C(14)—F(1)	119.2(3)
O(4)—C(5)—C(4A)	120.2(2)	C(13)—C(14)—C(15)	123.2(2)
O(4)—C(5)—C(6)	121.9(2)	F(1)—C(14)—C(15)	117.6(3)
C(4A)—C(5)—C(6)	118.0(2)	C(14)—C(15)—C(16)	117.4(2)
C(5)—C(6)—C(7)	114.8(2)	C(11)—C(16)—C(15)	121.4(2)

The reciprocal orientation of the substituents observed in the molecule results in an intramolecular H(4)...O(3) nonvalence contact of 2.52(2) Å, which is comparable with the sum of the van der Waals radii of these atoms.[4]

In the crystal, the intermolecular N(1)—H(1N)...O(3) ($-x$, $0.5 + y$, $1 - z$) hydrogen bonds [N(1)...O(3) 3.054(4) Å, N(1)—H(1N) 0.88(2) Å, H(1N)...O(3) 2.18(2) Å, N(1)—H(1N)...O(3) 173(2)°] combine molecules **5d** into infinite chains (Fig. 2).

The features of electron density distribution in the $NH_2—C{=}C—NO_2$ fragment manifest themselves in changes in the bond lengths (X-ray diffraction data) and in the ^1H NMR and IR spectra. In the IR spectra, the absorption band $\nu_{as}(NO_2)$ is shifted to a region of lower frequencies (1510—1490 cm^{-1}) as compared to the usual value (1570—1515 cm^{-1}).[5] The ^1H NMR spectrum exhibits an unusual low-field signal for the NH_2 group (δ 9.0—9.6). All these data suggest that 2-amino-3-nitropyrans can be represented by formula **B** rather than classic formula **A**:



A **B**

Such a significant conjugation was previously observed in the series of acyclic nitroenamines.[6]

Experimental

^1H NMR spectra were recorded on a Bruker WM-250 instrument (250.13 MHz) in DMSO-d_6. IR spectra were recorded on a Perkin—Elmer 457 instrument (KBr).

Synthesis of pyrans (general procedure). A mixture of equimolar amounts of arylidenenitroacetonitriles **1a—d** and diketone (dimedone or dihydroresorcinol) was heated to dissolution in a minimum amount of EtOH. A drop of Et_3N was added, and the reaction mixture was left overnight. The crystals that formed were filtered off, washed with methanol, and dried *in vacuo*.

X-ray diffraction analysis. The crystals of **5d** ($C_{17}H_{17}FN_2O_4$, $M = 332.33$) are monoclinic, $a = 6.117(2)$, $b = 11.311(3)$, $c = 11.804(4)$ Å, $\beta = 93.77(2)°$, $V = 814.9(4)$ Å^3, $d_{calc} = 1.354$ g cm^{-3} (25 °C), $Z = 2$, space group $P2_1$. The unit cell parameters and the intensity data were measured from 2257 reflections on a Siemens P3/PC four-circle automatic diffractometer (λ(Mo-Kα), graphite monochromator, θ/θ scanning until $\theta_{max} = 28°$). The structure was solved by the direct method with location of all nonhydrogen atoms and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms from 2074 independent reflections. All hydrogen atoms were located in an objective manner by differential Fourier syntheses and refined isotropically. The final residuals $R_1 = 0.036$ from 1839 independent reflections with $I > 2\sigma$, $wR_2 = 0.099$ from 2017 reflections. All computations were performed with the SHELXTL PLUS and SHELXTL-93 programs (PC version). Atomic coordinates and isotropic equivalent (isotropic for H atoms) thermal parameters are given in Table 5.

Table 5. Atomic coordinates (×10^4) and isotropic equivalent (isotropic for H atoms) thermal parameters in molecule **5d**

Atom	x	y	z	U_{eq}/Å^2
F(1)	2527(5)	-559(2)	1623(2)	107(1)
O(1)	1040(2)	5702(1)	3638(1)	48(1)
O(2)	634(4)	3509(2)	6357(2)	84(1)
O(3)	3330(4)	2463(2)	5815(2)	70(1)
O(4)	7529(3)	3972(2)	2530(2)	81(1)
N(1)	−829(4)	5295(2)	5108(2)	62(1)
N(2)	2051(4)	3318(2)	5674(2)	58(1)
C(2)	838(3)	4973(2)	4528(2)	45(1)
C(3)	2277(3)	4041(2)	4732(2)	46(1)
C(4)	4054(3)	3726(2)	3965(2)	44(1)
C(4A)	4244(3)	4711(2)	3118(2)	41(1)
C(5)	6104(3)	4708(2)	2391(2)	53(1)
C(6)	6202(4)	5666(3)	1509(2)	63(1)
C(7)	3990(4)	6140(2)	1062(2)	52(1)
C(8)	2777(4)	6528(2)	2099(2)	47(1)
C(8A)	2789(3)	5582(2)	2971(1)	40(1)
C(9)	4273(8)	7199(3)	287(3)	80(1)
C(10)	2677(6)	5185(3)	403(2)	68(1)
C(11)	3655(3)	2547(2)	3357(2)	42(1)
C(12)	5212(4)	1656(2)	3402(2)	60(1)
C(13)	4837(6)	606(2)	2816(2)	73(1)
C(14)	2912(6)	464(2)	2210(2)	66(1)
C(15)	1298(5)	1310(2)	2142(2)	60(1)
C(16)	1718(3)	2365(2)	2719(2)	47(1)
H(1N)	−1648(60)	5889(41)	4862(32)	82(11)
H(2N)	−963(55)	4885(41)	5649(32)	82(11)
H(4)	5323(39)	3674(25)	4419(20)	46(6)
H(61)	6970(55)	5273(37)	882(31)	82(10)
H(62)	7082(56)	6332(38)	1965(28)	77(9)
H(81)	1260(48)	6747(30)	1939(24)	59(7)
H(82)	3381(56)	7238(40)	2477(30)	78(9)
H(91)	4906(107)	7067(66)	−413(53)	149(20)
H(92)	5115(55)	7744(38)	732(31)	74(10)
H(93)	2784(69)	7542(44)	44(36)	97(12)
H(101)	1134(58)	5427(39)	209(29)	83(10)
H(102)	3591(54)	4917(38)	−254(31)	79(9)
H(103)	2495(62)	4419(44)	810(34)	91(11)
H(12)	6532(68)	1811(38)	3572(32)	85(11)
H(13)	5936(50)	8(37)	2827(27)	72(9)
H(15)	−304(48)	1122(33)	1744(25)	67(8)
H(16)	585(47)	2973(31)	2722(25)	62(7)

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