Formation of benzofuran and 2*H*-chromene structures in one reaction. A novel synthesis of 2*H*-chromene derivatives

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Heating the morpholinal of nitrosalicylic aldehyde with methyl propiolate in acetonitrile in the presence of CuI affords an equimolar mixture of 2-methoxycarbonylmethyl-3morpholino-5-nitrobenzofuran and 3-methoxycarbonyl-2-morpholino-6-nitro-2*H*-chromene, the structures of which were determined by X-ray analysis. Only the 2*H*-chromene mentioned above was obtained in the absence of CuI and solvent.

Key words: nitrosalicylic aldehydes aminals, methyl propiolate, interaction; 2-methylcarbonylacetylene; 2-methoxycarbonylmethyl-3-morpholino-5-nitrobenzofuran, derivatives of the 2*H*-chromene, X-ray analysis.

Aromatic o-amino-, o-hydroxy-, o-mercaptoaldehydes, and their aminals are widely used in the synthesis of various heterocyclic compounds.¹⁻⁷ This work is devoted to unusual transformations of the morpholinal of 5-nitrosalicylic aldehyde (1) and its analogs in the reactions with carbonyl-containing derivatives of acetylene.

We found that heating aminal 1 with methyl propiolate (2) in acetonitrile in the presence of CuI (Scheme I) leads to the formation of an equimolar mixture (according to ¹H NMR spectra) of two isomers: 2-methoxy-carbonylmethyl-3-morpholino-5-nitrobenzofuran (5) and 3-methoxycarbonylmethyl-2-morpholino-6-nitro-2*H*-chromene (9).

It is likely that the reaction we described previously⁶ proceeds at the first stage of interaction between 1 and 2 and results in the formation of a mixture of E- (3) and Z-(6) isomers of 2-methoxycarbonylmethylene-3-morpholino-5-nitro-2,3-dihydrobenzofuran. According to molecular mechanics calculations the Z-isomer is somewhat more stable ($\Delta E = 1.61$ kcal mol⁻¹) than the *E*-isomer. The *s*-cis-conformation of the exocyclic enone fragment is the most favorable for the *E*-isomer since it favors the prototropic rearrangement of compound 3 into 5 (see Scheme 1, path *a*). The same conformation of the Z-isomer, the morpholyl substituent having pseudoaxial orientation.

The presence of a nitro group in the starting aldehyde might be a necessary condition for the transformations

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Fig. 1. Charge distribution in the model molecule of 2-hydroxycarbonylmethylene-3-morpholino-4-nitro-2,3-di-hydrofuran.

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described above. Calculations of the charges at the atoms of the model compound, 2-hydroxycarbonylmethylene-3morpholino-4-nitro-2,3-dihydrobenzofuran (Fig. 1), showed that the structure of molecule 6 is favorable for an intramolecular nucleophilic attack of the N atom of the morpholine cycle against the C(2) atom of the furan ring; the intermediate compound 7 formed is rearranged with the ring extension to give a 2H-chromene derivative 9 (see Scheme 1, path b).

Additionally, an energetic exothermic reaction result-

ing in the formation of 2*H*-chromene 9 in 80 % yield was found to start after a short induction period upon addition of ether 2 to the crystalline aminal 1 in the absence of solvent and CuI. *trans*-1-Methoxycarbonyl-2-morpholylethylene, the product of the interaction between the morpholine released and the excess of methyl propiolate, was isolated from the reaction mixture; however, no traces of benzofuran 5 were found (TLC on Al_2O_3). That result can be explained by the formation of the only Z-isomer 6 and its further rearrangement into 2*H*-chromene 9.

2-Propylcarbonylacetylene (10) as readily reacts with aminal 1 with the formation of 2H-chromene 11.



Chromenes 13a-d are the products of analogous reactions of compounds 2 and 10 with aminals of 3-nitrosalicylic aldehydes 12a,b.



 $R^{1} = H(a), OMe(b)$



 $R^{1} = H, R^{2} = OMe (a); R^{1} = H, R^{2} = CHMe_{2} (b);$ $R^{1} = R^{2} = OMe (c); R^{1} = OMe, R^{2} = CHMe_{2} (d)$

Previously,⁸ 5-nitrosalicylic aldehyde was shown to interact with highly basic aliphatic secondary amines, yielding salt-like adducts (dimeric in the crystalline state) instead of amines. These compounds also enter into exothermic reactions with carbonyl-containing acetylene deUkhin et al.

rivatives 2 and 10. Thus, corresponding 2H-chromenes 15a,b were obtained from salt 14.



In those cases when the isolation of crystalline adducts of the type 14 is difficult, they can be used *in situ*; however, the yields of 2H-chromenes are reduced (for instance, the yield of 2-N-methylpiperazinochromene (16) is merely 9 %).



The structure of compounds 5 and 9 was proved by Xray analysis. A general view of the molecule 5 is represented in Fig. 2, and bond lengths and bond angles in the molecule are given in Table 1 and 2, respectively. The benzofuran fragment of the molecule 5 is planar; the morpholine cycle has the conformation of a nearly ideal chair (the values of torsion angles lie within the limits of 55.8-59.5(3)°) and is rotated to be almost perpendicular to the bicycle plane: the angle between the root-meansquare planes of the benzofuran fragment and C(12)C(13)C(14)C(15) is 81.4°. The C(6), C(9), C(10), C(11), O(4), and O(5) atoms lie in the same plane with an accuracy of $\leq 3\sigma$; the carbonyl group C(10)=O(4) is rotated with respect to the furan cycle by $-76.3(3)^{\circ}$ (the torsion angle O(1)-C(6)-C(9)-C(10)). The C(11) atom of the methyl group has the synperiplanar conformation relative to the double bond C(10)=O(4). The nitro group is virtually coplanar with the benzene ring plane (the



Fig. 2. General view of molecule 5.

Table 1. Bond lengths (d) in molecule 5

Bond	d/Å	Bond	d/Å
N(1)-O(2)	1.220 (3)	C(1)-C(2)	1.388 (3)
N(1)-O(3)	1.221 (3)	C(1) - C(8)	1.395 (3)
N(1) - C(2)	1.458 (3)	C(2) - C(3)	1.400 (3)
N(2) - C(7)	1.408 (3)	C(3) - C(4)	1.375 (4)
N(2) - C(12)	1.458 (3)	C(4) - C(5)	1.382 (3)
N(2) - C(14)	1.469 (3)	C(5)-C(8)	1.394 (3)
O(1) - C(5)	1.364 (3)	C(6) - C(7)	1.354 (3)
O(1) - C(6)	1.407 (3)	C(6)-C(9)	1.486 (3)
O(4) - C(10)	1.196 (3)	C(7) - C(8)	1.453 (3)
O(5) - C(10)	1.333 (3)	C(9) - C(10)	1.507 (4)
O(5) - C(11)	1.442 (4)	C(12) - C(13)	1.508 (4)
O(6) - C(13)	1.422 (4)	C(14) - C(15)	1.500 (4)
O(6)-C(15)	1.432 (4)	. , . , ,	~ /

torsion angle O(2)—N(1)—C(2)—C(1) is equal to $0.3(3)^{\circ}$) despite the shortened intramolecular contact H(3)...O(3)[2.40(1) Å] (the corresponding sum of van der Waals radii is equal to 2.45 Å).⁹

The substantial distortion of the exocyclic bond angles at the C(6) and C(7) atoms has engaged our attention. The N(2)-C(7)-C(6) [131.2(2)°] and C(7)-C(6)-C(9) angles [136.2(2)°] are much larger than N(2)-C(7)-C(8) [122.4(2)°] and O(1)-C(6)-C(9) [112.9(2)°] angles. Such deformations of bond angles are likely to be due to the shortened intramolecular contacts H(12B)...H(9A) [2.24(1) A], C(12)...H(9A) [2.68(1) A], and C(12)...C(9) [3.29(1) A] (the corresponding sums of van der Waals radii equal 2.32, 2.87, and 3.42 Å, respectively).

Two shortened intermolecular contacts C(5)...C(5)' (-x, -y, 1-z) [3.38(1) Å] and H(15A)...C(5)' (-x, -0.5 + y, 0.5 - z) [2.65(1) Å] were found in the crystal.

A general view of the molecule 9 is represented in Fig. 3; bond lengths and bond angles are listed in Table 3 and 4, respectively. The pyran cycle has the distorted sofa conformation (the puckering parameters¹⁰ S = 0.38, $\theta = 51.1^{\circ}$, $\psi = 28.5^{\circ}$). The O(1), C(5), C(8), and C(9) atoms are in one plane, while the C(6) and C(7) atoms deviate



Fig. 3. General view of molecule 9.

from it by 0.20(1) and 0.45(1) Å, respectively. The morpholine cycle at the C(6) atom has a pseudoaxial orientation (the torsion angle C(8)—C(7)—C(6)—N(2) is equal to 105.6(6)°) and the conformation of a nearly ideal chair (the puckering parameters S = 1.18, $\theta = 0.9^\circ$, $\psi = 17.0^\circ$). The double bonds C(7)=C(8) and C(15)=O(4) have *s*-trans-configuration and are not perfectly coplanar (the torsion angle C(8)—C(7)—C(15)—O(4) is equal to 165.7(6)°) which is due to a shortened intramolecular contact H(8)...O(5) [2.40(1) Å]. The methyl group is in the synperiplanar conformation with respect to the carbonyl group (the torsion angle C(16)—O(5)—C(15)—O(4)

Table 2. Bond angles (ω) in molecule 5

Angle	ω/deg	Angle	ω/deg
$\overline{O(2)-N(1)-O(3)}$	121.7(2)	O(2) - N(1) - C(2)	119.2(2)
O(3) - N(1) - C(2)	119.1(2)	C(7) - N(2) - C(12)	118.9(2)
C(7) - N(2) - C(14)	116.0(2)	C(12) - N(2) - C(14)	111.5(2)
C(5) - O(1) - C(6)	106.4(2)	C(10) - O(5) - C(11)	116.4(2)
C(13)-O(6)-C(15)	110.4(2)	C(2) - C(1) - C(8)	116.6(2)
N(1)-C(2)-C(1)	118.6(2)	N(1) - C(2) - C(3)	118.0(2)
C(1) - C(2) - C(3)	123.4(2)	C(3) - C(4) - C(5)	116.6(2)
C(2)-C(3)-C(4)	120.0(2)	O(1) - C(5) - C(4)	125.4(2)
O(1) - C(5) - C(8)	110.3(2)	C(4) - C(5) - C(8)	124.2(2)
O(1) - C(6) - C(7)	110.9(2)	O(1) - C(6) - C(9)	112.9(2)
C(7) - C(6) - C(9)	136.2(2)	N(2) - C(7) - C(6)	131.2(2)
N(2) - C(7) - C(8)	122.4(2)	C(6) - C(7) - C(8)	106.2(2)
C(1) - C(8) - C(5)	119.2(2)	C(1) - C(8) - C(7)	134.7(2)
C(5) - C(8) - C(7)	106.1(2)	O(4)-C(10)-O(5)	124.4(2)
C(6) - C(9) - C(10)	113.7(2)	O(5) - C(10) - C(9)	109.4(2)
O(4) - C(10) - C(9)	126.2(2)	N(2) - C(12) - C(13)	108.8(2)
O(6) - C(13) - C(12)	111.2(3)	N(2) - C(14) - C(15)	109.4(2)
O(6)-C(15)-C(14)	111.5(2)		

 Bond
 d/Å Bond
 d/Å

 N(1)-O(2)
 1.202(8)
 C(2)-C(3)
 1.399(8)

 N(1)-O(3)
 1.224(9)
 C(3)-C(4)
 1.370(9)

 N(1)-C(2)
 1.463(8)
 C(4)-C(5)
 1.389(9)

N(1)-O(3)	1.224(9)	C(3)-C(4)	1.370(9)
N(1)-C(2)	1.463(8)	C(4)-C(5)	1.389(9)
N(2)-C(6)	1.428(7)	C(5)-C(9)	1.414(7)
N(2)-C(10)	1.449(8)	C(6) - C(7)	1.508(7)
N(2)-C(14)	1.473(7)	C(7)-C(8)	1.331(7)
O(1)-C(5)	1.360(7)	C(7)-C(15)	1.477(9)
O(1)-C(6)	1.473(7)	C(8)-C(9)	1.427(8)
O(4)-C(15)	1.209(8)	C(10)+C(11)	1.498(8)
O(5)-C(15)	1.328(7)	C(11)-O(12)	1.431(7)
O(5)-C(16)	1.430(1)	O(12)-C(13)	1.413(8)
C(1)-C(2)	1.366(9)	C(13)-C(14)	1.496(8)
C(1)—C(9)	1.396(7)		

equals 2.5(9)°), and the nitro group virtually lies in the benzene ring plane (the angle O(2)-N(1)-C(2)-C(1) amounts to 7(1)°) despite a shortened intramolecular contact H(1)...O(2) [2.39(1) Å].

The shortened intermolecular contacts O(12)...H(3)(1 - x, 1 - y, 1 - z) [2.35(1) Å], C(13)...H(3)[2.79(1) Å], H(13B)...H(10B) (0.5 + x, 0.5 - y, 0.5 + z) [2.21(1) Å], and C(13)...H(10B) (0.5 + x, 0.5 - y, 0.5 + z) [2.79(1) Å] were found in the crystal (the corresponding sums of the van der Waals radii equal 2.45, 2.87, 2.32, and 2.87 Å, respectively).

Experimental

IR spectra were recorded on a Specord IR-75 instrument in vaseline oil. ¹H NMR spectra were recorded on a UNITY-300 spectrometer in $CDCl_3$. Morpholinal 1 and the adduct of 5-nitrosalicylic aldehyde with piperidine 15 were obtained according to known procedures.^{6,8} Spectral characteristics of synthesized 2*H*-chromenes are given in Table 5.

2-Methoxycarbonylmethyl-3-morpholino-5-nitrobenzofuran (5) and 3-methoxycarbonyl-2-morpholino-6-nitro-2*H*-chromene (9). A mixture of aminal 1 (0.8 g, 2.5 mmol), methyl propiolate 2 (0.45 mL, 5 mmol), and CuI (0.4 g, 2 mmol) in 8 mL of anhydrous acetonitrile was boiled for 30 min with stirring and filtered hot. The precipitate was washed with hot acetonitrile on the filter; 10 mL of concentrated NH₄OH and 30 mL of water were added to the filtrate after cooling. The precipitated oil was crystallized after rubbing; the crystals were filtered, washed with water and dried. Recrystallization of the crude product (0.77 g, 97 %) from octane gave 0.5 g of the mixture of isomers 5 and 9 (1 : 1). Double recrystallization of the mixture from ethyl acetate affords pyran 9 as colorless crystals, m.p. 185–186 °C.

The filtrates left after recrystallizations were combined, ethyl acetate was removed, and morpholinobenzofuran 5 was obtained by repeated recrystallization of the solid residue from MeOH (control of isolated crystals under the microscope and by TLC on Al₂O₃) as yellow crystals, m.p. 117–118 °C. Found (%): C, 56.51; H, 5.39; N, 8.80. C₁₅H₁₆N₂O₆. Calculated (%): C, 56.25; H, 5.00; N, 8.75. IR, v/cm⁻¹: 1720, 1714 (C=O); 1627, 1614, 1592 (arom. cycle); 1514, 1341 (NO₂). ¹H NMR, δ : 3.28 (m, 4 H, CH₂N); 3.87 (s, 3 H, CH₃); 3.94 (m, 4 H, CH₂O); 4.05 (s, 2 H, CH₂); 7.52 (d, 1 H, C(7)H, J = 9.1 Hz); 8.23 (dd, 1 H, C(6)H, ³J = 9.1 Hz, ⁴J = 2.0 Hz); 8.59 (d, 1 H, C(4)H, ⁴J = 2.0 Hz).

Table 4. Bond angles (ω) in molecule 9

			and the second se
Angle	ω/deg	Angle	ω/deg
$\overline{O(2)-N(1)-O(3)}$	122.9(6)	N(2)-C(6)-C(7)	112.4(5)
O(2) - N(1) - C(2)	118.1(6)	O(1) - C(6) - C(7)	111.5(4)
O(3) - N(1) - C(2)	119.0(6)	C(6) - C(7) - C(8)	121.5(5)
C(6) - N(2) - C(10)	115.9(4)	C(6) - C(7) - C(15)	116.1(4)
C(6) - N(2) - C(14)	113.6(5)	C(8) - C(7) - C(15)	122.4(5)
C(10) - N(2) - C(14)	109.6(4)	C(7) - C(8) - C(9)	121.2(5)
C(5) - O(1) - C(6)	120.3(4)	C(1) - C(9) - C(5)	118.0(5)
C(15)-O(5)-C(16)	116.7(5)	C(1) - C(9) - C(8)	123.2(5)
C(2) - C(1) - C(9)	119.8(5)	C(5) - C(9) - C(8)	118.7(5)
N(1)-C(2)-C(1)	118.7(5)	N(2) - C(10) - C(11)	111.0(4)
N(1)-C(2)-C(3)	119.0(6)	C(10) - C(11) - O(12)	110.7(6)
C(1) - C(2) - C(3)	122.1(5)	C(11) - O(12) - C(13)	109.7(4)
C(2) - C(3) - C(4)	118.9(6)	O(12) - C(13) - C(14)	112.2(5)
C(3) - C(4) - C(5)	119.9(5)	N(2) - C(14) - C(13)	109.0(5)
O(1) - C(5) - C(4)	118.3(5)	O(4)-C(15)-O(5)	123.3(6)
O(1) - C(5) - C(9)	120.4(5)	O(4)-C(15)-C(7)	124.1(5)
C(4) - C(5) - C(9)	121.2(5)	O(5)-C(15)-C(7)	112.5(5)
N(2)-C(6)-O(1)	111.2(5)		

Morpholinal of 3-nitrosalicylic aldehyde (12a). 3-Nitrosalicylic aldehyde (3.4 g, 20 mmol) was dissolved upon heating in 10 mL of isopropyl alcohol. Morpholine (4 mL, 45 mmol) was added in small portions (boiling up) to the hot solution with stirring; the mixture was cooled and allowed to stand for ~24 h. The isolated crystalline precipitate was filtered, washed with cold isopropyl alcohol and petroleum ether, dried in air, and used in syntheses without further purification. Yield 4.5 g (68 %), m.p. 121-126 °C. IR, v/cm⁻¹: 1607, 1594 (arom. cycle); 1514, 1354 (NO₂); 1114 (C-O-C).

Morpholinal of 5-methoxy-3-nitrosalicylic aldehyde (12b). 5-Methoxy-3-nitrosalicylic aldehyde (1.5 g, 10 mmol) was dissolved with heating in 30 mL of isopropyl alcohol. Morpholine (2 mL, 22 mmol) was added to the hot solution with stirring; the mixture was cooled with ice, and 30 mL of ether were added, while the flask walls were rubbed with a glass rod. An abundant yellow crystalline precipitate was filtered, washed with ether and petroleum ether, dried in air, and used in syntheses without further purification. Yield 2.45 g (91 %), m.p. 145–152 °C. IR, v/cm^{-1} : 3220 (OH); 1614 sh, 1581 (arom. cycle); 1534, 1314–1381* (NO₂); 1250, 1141 (C–O); 1114 (C–O–C).

2H-Chromenes 9, 11, 13a-d, 15a,b (general procedure). The crystalline morpholinal (1, 12a,b) or adduct 14 was placed into a small round-bottomed flask or test-tube and moistened with a two- or three-fold excess of carbonyl-containing acety-lene derivative (2, 10). After an energetic exothermic reaction had been completed, several milliliters of MeOH or EtOH were added. The reaction mixture was cooled with ice and rubbed. The crystalline precipitate was filtered and washed with cold alcohol and pentane.

3-Methoxycarbonyl-2-morpholino-6-nitro-2*H*-chromene (9). Yield 77 %, colorless crystals, m.p. 185–186 °C (from ethyl acetate). Found (%): C, 56.31; H, 5.43; N, 9.24. $C_{15}H_{16}N_{2}O_{6}$. Calculated (%): C, 56.25; H, 5.00; N, 8.75.

3-(2-Propyl)carbonyl-2-morpholino-6-nitro-2*H***-chromene (11). Yield 49 %, colorless crystals, m.p. 160–164 °C (from MeOH). Found (%): C, 60.87; H, 6.22; N, 8.21. C_{17}H_{20}N_2O_5. Calculated (%): C, 61.45; H, 6.02; N, 8.43.**

^{*}Correct assignment is difficult since seven bands of approximately equal intensity are observed in this region.

Compound (molecular formula)	IR, ν/cm^{-1}	¹ H NMR, δ (J/Hz)
9	1707 (C=O); 1647, 1614,	2.53 (m, 2 H, CH ₂ N): 2.87 (m, 2 H, CH ₂ N): 3.59 (t, 4 H, CH ₂ O, $J = 4.7$)
$(C_{15}H_{16}N_{2}O_{6})$	1574 (C=C arom.);	3.87 (s, 3 H, CH ₂); 6.02 (s, 1 H, C(2)H); 7.03 (d, 1 H, C(8)H, $J = 9$);
10 10 2 0	1521, 1341 (NO ₂); 1114	7.73 (s, 1 H, C(4)H); 8.15 (d, 1 H, C(5)H, $J = 2.6$); 8.20 (dd, 1 H,
	(C-O-C)	$C(7)H, {}^{3}J = 9, {}^{4}J = 2.6)$
11	1654 (C=O); 1627, 1607,	1.19 (m, 6 H, CH ₂); 2.54 (m, 2 H, CH ₂ N); 3.33 (m, 1 H, CH, $J = 6.7$);
$(C_{17}H_{20}N_{2}O_{5})$	1574 (C=C arom.);	3.57 (t, 4 H, CH ₂ O, $J = 4.7$); 6.13 (s, 1 [°] H, C(2)H); 7.03 (d, 1 H, C(8)H,
·· +	1514, 1334 (NO ₂); 1114	$J = 8.5$; 7.56 (s, 1 H, C(4)H); 8.18 (dd, 1 H, C(7)H, ${}^{3}J = 8.8$, ${}^{4}J = 2.6$);
	(C-O-C)	8.22 (d, 1 H, C(5)H, ${}^{4}J = 2.6$)
13a	1720 (C=O); 1654, 1614,	2.56 (m, 2 H, CH ₂ N); 2.93 (m, 2 H, CH ₂ N); 3.59 (m, 4 H, CH ₂ O);
$(C_{15}H_{16}N_{2}O_{6})$	1581 (C=C arom.);	3.86 (s, 3 H, CH ₃); 6.07 (s, 1 H, C(2)H); 7.01 (t, 1 H, C(6)H, $J = 7.9$);
	1527, 1360 (NO ₂); 1121	7.44 (dd, 1 H, C(5)H, ${}^{3}J = 7.3$, ${}^{4}J = 1.5$); 7.74 (s, 1 H, C(4)H); 7.93
	(C-O-C)	$(dd, 1 H, C(7)H, {}^{3}J = 8.2, {}^{4}J = 1.5)$
13b	1673 (C=O); 1641, 1607,	1.18 (m, 6 H, CH_3 , $J = 3.5$); 2.57 (m, 2 H, CH_2N); 2.80 (m, 2 H, CH_2N);
$(C_{17}H_{20}N_2O_5)$	1567 (C=C arom.);	3.31 (m, 1 H, CH, $J = 6.7$); 3.53 (t, 4 H, CH ₂ O, $J = 4.7$); 6.17 (s, 1 H,
	1514, 1347 (NO ₂); 1121	$C(2)H$; 7.02 (t, 1 H, $C(6)H$, $J = 7.9$); 7.46 (dd, 1 H, $C(5)H$, ${}^{3}J = 7.5$,
	(C-O-C)	${}^{4}J = 1.5$; 7.57 (s, 1 H, C(4)H); 7.94 (dd, 1 H, C(7)H, ${}^{3}J = 8.2$, ${}^{4}J = 1.5$)
13c	1714, 1687 sh (C=O);	2.55 (m, 2 H, CH_2N); 2.90 (m, 2 H, CH_2N); 3.58 (m, 4 H, CH_2O);
$(C_{16}H_{18}N_2O_7)$	1661, 1634, 1581 (C=C	3.84 (s, 3 H, $CH_3O-C(4)H$); 3.86 (s, 1 H, CH_3O); 5.99 (s, 1 H, $C(2)H$);
	arom.); 1541, 1327 (NO ₂);	7.02 (d, 1 H, C(5)H, ${}^{4}J = 3$); 7.49 (d, 1 H, C(7)H, ${}^{4}J = 3.2$); 7.68 (s, 1 H,
	1127 (C-O-C)	C(4)H)
13d	1672 (C=O); 1654, 1621,	1.18 (m, 6 H, CH ₃ , $J = 3.8$); 2.55 (m, 2 H, CH ₂ N); 2.87 (m, 2 H, CH ₂ N);
$(C_{18}H_{22}N_2O_6)$	1567 (C=C arom.);	2.87 (m, 2 H, CH_2N); 3.29 (m, 1 H, CH); 3.56 (t, 4 H, CH_2O , $J = 4.7$);
	1541, 1327 (NO ₂); 1127	3.84 (s, 3 H, CH_3O); 6.10 (s, 1 H, $C(2)H$); 7.04 (d, 1 H, $C(5)H$, $^4J = 3$);
	(C-0-C)	7.49 (d, 1 H, C(7)H, ${}^{4}J = 3$); 7.51 (s, 1 H, C(4)H)
15a	1727 (C=O); 1647, 1621,	1.44 (m, 6 H, CH); 2.47 (m, 2 H, CH_2N); 2.80 (m, 2 H, CH_2N); 3.85
$(C_{16}H_{18}N_2O_5)$	1581 (C=C arom.);	(s, 3 H, CH ₃); 6.03 (s, 1 H, C(2)H); 7.00 (d, 1 H, C(8)H, $J = 9$); 7.70
	1521, 1347 (NO ₂)	(s, 1 H, C(4)H); 8.14 (d, 1 H, C(5)H, J = 2.6);
		8.18 (dd, 1 H, C(7)H, $J = 9$, $J = 2.6$)
156	1667 (C=O); 1647, 1607,	1.18 (q, 6 H, CH_3); 1.40 (m, 6 H, CH_2); 2.50 (m, 2 H, CH_2 N); 2.79 (m, 2 H,
$(C_{18}H_{22}N_2O_4)$	15/4 (C=C arom.);	CH_2N ; 3.29 (m, 1 H, CH, $J = 6.7$); 6.14 (s, 1 H, C(2)H); 6.99 (d, 1 H,
• 4	$1507, 1334 (NO_2)$	C(8)H, J = 8.5); 7.52 (s, 1 H, C(4)H); 8.18 (m, 2 H, C(5)H, C(7)H)
	1661 (C=0); 1634, 1607,	1.18 (q, 6 H, CH ₃ , $J = 3.2$); 2.22 (s, 3 H, NCH ₃); 2.30 (m, 4 H, CH ₂ N);
$(C_{18}H_{23}N_{3}U_{4})$	1507 (C=C arom.);	2.59 (m, 2 H, CH_2N); 2.90 (m, 2 H, CH_2N); 3.51 (m, 1 H, $CH, J = 6.7$);
	$1507, 1334 (NO_2)$	0.10 (S, I H, $C(2)H$); 0.9/ (d, I H, $C(8)H$, $J = 10$); 7.54 (S, I H, $C(4)H$);
		$\delta_{1,1,2}$ (a, 1 H, C(3)H, $J = 2.0$); $\delta_{1,1}$ (aa, 1 H, C(7)H, $J = 10$, $J = 2.0$)

Table 5. Cpectral parameters of 2H-chromenes 9, 11, 13a-d, 15a, b, and 16

3-Methoxycarbonyl-2-morpholino-8-nitro-2H-chromene (13a). Yield 86 %, colorless crystals, m.p. 185–189 °C (from isopropyl alcohol). Found (%): C, 56.88; H, 5.01; N, 8.73. $C_{15}H_{16}N_2O_6$. Calculated (%): C, 56.28; H, 5.00; N, 8.75.

3-(2-Propyl)carbonyl-2-morpholino-8-nitro-2*H*-chromene (13b) was obtained from morpholinal 12a (1.6 g, 5 mmol) and 2-propylcarbonylacetylene 10 (0.8 mL); MeOH (5 mL) was added; to start crystallization a seed crystal was required. A small portion of the solution was placed in a test-tube; it was cooled with ice, its walls were rubbed with a glass rod, and several drops of water were added; the crystals formed were transferred into the solution cooled with ice. The precipitate was recrystallized from isopropyl alcohol (30 mL). Yield 0.7 g (43 %), colorless crystals, m.p. 154–160 °C. Found (%): C, 61.64; H, 5.49; N, 8.38. $C_{17}H_{20}N_2O_5$. Calculated (%): C, 61.63; H, 5.74; N, 8.46.

6-Methoxy-3-methoxycarbonyl-2-morpholino-8-nitro-2*H***chromene (13c).** Yield 53 %, yellow crystals, m.p. 194–197 °C (from isopropyl alcohol). Found (%): C, 54.99; H, 5.44; N, 7.85. $C_{16}H_{18}N_2O_7$. Calculated (%): C, 54.86; H, 5.14; N, 8.00.

3-(2-Propyl)carbonyl-6-methoxy-2-morpholino-8-nitro-2*H*chromene (13d). Yield 41 %, yellow crystals, m.p. 133–134 °C (from isopropyl alcohol—petroleum ether (2 : 1) mixture). Found (%): C, 59.44; H, 5.72; N, 7.55. $C_{18}H_{22}N_2O_6$. Calculated (%): C, 59.67; H, 6.08; N, 7.73. **3-Methoxycarbonyl-6-nitro-2-piperidino-2***H***-chromene** (15a). Yield 43 %, colorless crystals, m.p. 175–178 °C (from EtOH). Found (%): C, 60.01; H, 5.48; N, 9.18. $C_{16}H_{18}N_2O_5$. Calculated (%): C, 60.38; H, 5.66; N, 8.81.

3-(2-Propyl)carbonyl-6-nitro-2-piperidino-2*H*-chromene (15b). Yield 14 %, colorless crystals, m.p. 159–160 °C (from EtOH). Found (%): C, 64.74; H, 5.98; N, 8.10. $C_{18}H_{22}N_2O_4$. Calculated (%): C, 65.45; H, 6.67; N, 8.48.

3-(2-Propyl)carbonyl-2-N-methylpiperazino-6-nitro-2Hchromene (16). A mixture of 5-nitrosalicylic aldehyde (0.84 g, 5 mmol) and N-methylpiperazine (0.5 mL) was warmed up to 130-140 °C upon rubbing with a glass rod; then it was cooled, carbonylacetylene 10 (0.6 mL) was added, and the reaction mixture temperature was again raised to 100 °C. After the nixture had been cooled, EtOH (3 mL) was added, and the mixture was warmed up to reach homogenization. The mixture was cooled with ice, and the precipitate was filtered and washed with cold EtOH and pentane. Yield 0.15 g (9 %), colorless crystals, m.p. 174-178 °C (from EtOH). Found (%): C, 62.30; H, 7.17; N, 11.74. $C_{18}H_{23}N_3O_4$. Calculated (%): C, 62.61; H, 6.66; N, 12.17.

X-ray study of compounds 5 and 9. The crystals of both compounds (isomers of $C_{15}H_{16}N_2O_6$) are monoclinic. For 5: at 20 °C a = 10.397(4) Å, b = 9.321(4) Å, c = 15.599(4) Å, $\beta =$

Table 6. Coordinates of the nonhydrogen atoms $(\times 10^4)$ in structure of 5

Atom	x	У	z
N(1)	-3726(2)	-516(2)	3545(1)
N(2)	1388(2)	463(2)	2655(1)
O(1)	692(2)	2112(2)	4726(1)
O(2)	-3693(2)	-1127(2)	2855(1)
O(3)	-4689(2)	-527(3)	3988(1)
O(4)	1972(2)	4838(2)	3848(1)
O(5)	4067(2)	4548(2)	4145(1)
O(6)	2501(2)	-261(2)	1072(1)
C(1)	-1472(2)	169(2)	3369(1)
C(2)	-2572(2)	201(2)	3866(1)
C(3)	-2634(3)	890(3)	4661(2)
C(4)	-1564(2)	1564(3)	4995(2)
C(5)	-466(2)	1526(2)	4503(1)
C(6)	1521(2)	1852(3)	4036(1)
C(7)	920(2)	1082(2)	3415(1)
C(8)	-389(2)	862(2)	3704(1)
C(9)	2820(2)	2483(3)	4169(2)
C(10)	2864(2)	4084(3)	4033(1)
C(11)	4268(3)	6072(3)	4058(3)
C(12)	2756(2)	134(3)	2597(2)
C(13)	2957(3)	-873(3)	1853(2)
C(14)	883(3)	1068(3)	1850(1)
C(15)	1156(3)	55(3)	1127(2)

90.55(2)°, V = 1511(1) Å³, $d_{calc} = 1.407$ g cm⁻³, space group $P2_1/c$, Z = 4. The unit cell parameters and intensities of 1732 reflections with $F > 4\sigma(F)$ were measured on an automatic fourcircle Siemens P3/PC diffractometer (λ (Mo-K α), graphite monochromator, $\theta/2\theta$ -scanning technique, $2\theta_{max} = 50^{\circ}$). For 9: at 20 °C a = 8.422(2) Å, b = 16.825(4) Å, c = 11.087(3) Å, $\beta = 106.31(2)^{\circ}$, V = 1508(1) Å³, $d_{calc} = 1.327$ g cm⁻³, space group $P2_1/n$, Z = 4. The unit cell parameters and intensities of 1197 reflections with $F > 6\sigma(F)$ were measured on an automatic Siemens P3/PC diffractometer (λ (Mo-K α), graphite monochromator, $\theta/2\theta$ -scanning technique, $2\theta_{max} = 60^{\circ}$). Both structures were solved by the direct method using the

Both structures were solved by the direct method using the SHELXTL PLUS¹¹ program package. Positions of the hydrogen atoms in structure 5 were located from the difference electron density synthesis. The refinement was carried out by the full-matrix least-squares method (LSM) in anisotropic approximation (isotropic for the hydrogen atoms) to R = 0.041 ($R_w = 0.051$, S = 1.88). The coordinates of nonhydrogen atoms in structure 5 are given in Table 6. Positions of the hydrogen atoms in structure 9 were calculated from geometry and refined using the riding model with a fixed $U_{iso} = 0.08 \text{ Å}^2$. The full-matrix LSM refinement in anisotropic approximation for nonhydrogen atoms was conducted to R = 0.067 ($R_w = 0.067$, S = 1.19). The coordinates of nonhydrogen atoms in structure 9 are given in Table 7.

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Atom	x	у	z
N(1)	-802(7)	4850(4)	1473(5)
N(2)	4289(5)	3115(3)	7107(4)
O(1)	2550(5)	4253(3)	6467(4)
O(2)	-1693(7)	4344(4)	877(5)
O(3)	-701(7)	5517(4)	1061(5)
O(4)	1516(5)	2134(3)	8137(4)
O(5)	-23(5)	1696(3)	6274(4)
C(1)	-106(6)	3953(4)	3268(5)
C(2)	170(7)	4660(4)	2755(5)
C(3)	1259(7)	5231(4)	3447(7)
C(4)	2094(7)	5071(4)	4673(7)
C(5)	1821(6)	4359(4)	5217(6)
C(6)	2701(6)	3449(4)	7016(5)
C(7)	1305(6)	2917(4)	6316(5)
C(8)	416(6)	3082(4)	5148(5)
C(9)	717(6)	3783(4)	4520(5)
C(10)	4663(6)	2975(4)	5927(5)
C(11)	6265(7)	2537(4)	6133(6)
O(12)	7589(4)	2968(3)	6968(4)
C(13)	7231(7)	3094(4)	8124(6)
C(14)	5664(6)	3552(4)	7968(5)
C(15)	953(6)	2224(4)	7016(6)
C(16)	-455(10)	1007(5)	6870(9)

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