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Synthesis and Structure of Alkyl-α-arylamino-β-bromo-β-nitroacrylates, New Functionalized β-Nitroenamines

V. M. Berestovitskaya[a], S. V. Makarenko[a], K. S. Kovalenko[a], I. A. Litvinov[b], D. B. Krivolapov[b], and A. D. Shevchenko[a]

[a] *Herzen Russian State Pedagogical University, nab. r. Moiki, 48, St. Petersburg, 191186 Russia*
e-mail: kohrgpu@yandex.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia*

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Abstract—New bromonitroenamine compounds, alkyl-2-arylamino-3-bromo-3-nitroacrylates, were synthesized and characterized using IR, UV, ^{1}H and ^{13}C NMR spectroscopy, and X-ray analysis. Their molecules were found to have the *E*-configuration and to exist as highly conjugated structures. According to the X-ray analysis, in the ethyl-3-bromo-2-(*p*-bromophenylamino)-3-nitroacrylate molecule the bromonitroenamine moiety is almost planar, the ester group is located completely out of the C=C double bond plane, amino hydrogen and nitro oxygen atoms form an intramolecular hydrogen bond.

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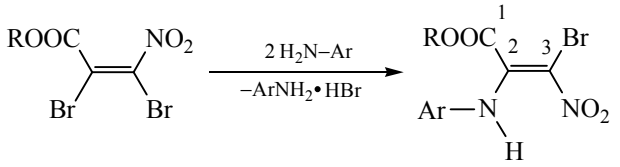
β-Nitroenamines [1] containing β-halogen atom in the geminal position to the nitro group are poorly known [2–6], and the compounds including an additional electron-withdrawing group are unknown at all. However, the structure of a number of halogen-containing nitroenamines are of interest not only from a theoretical point of view (as objects for studying the structure of sterically hindered unsaturated compounds and the transfer of electronic effects in a conjugated systems), but also in the practical aspect (as potential biologically active substances, whose representatives have already been patented as insecticides and pesticides [7, 8]).

Alkyl-α-aryl-β-bromo-β-nitroacrylates can be considered both as halogen-containing nitroenamines and the derivatives of β-nitroacrylic acid ester. The latter is used for the synthesis of some practically important alkaloids and antibiotics [9–12].

The approach to the synthesis of arylaminobromo-nitroacrylates was found to be simple enough. The reaction of α,β-dibromo-β-nitroacrylates **I**, **II** obtained previously [13] with a twofold excess of the primary arylamine proceeds efficiently at room temperature in a solution of anhydrous benzene for 10–45 min to produce brightly colored crystalline α-arylamino-β-bromo-β-nitroacrylates **III–IX** in yields of 54–87%.



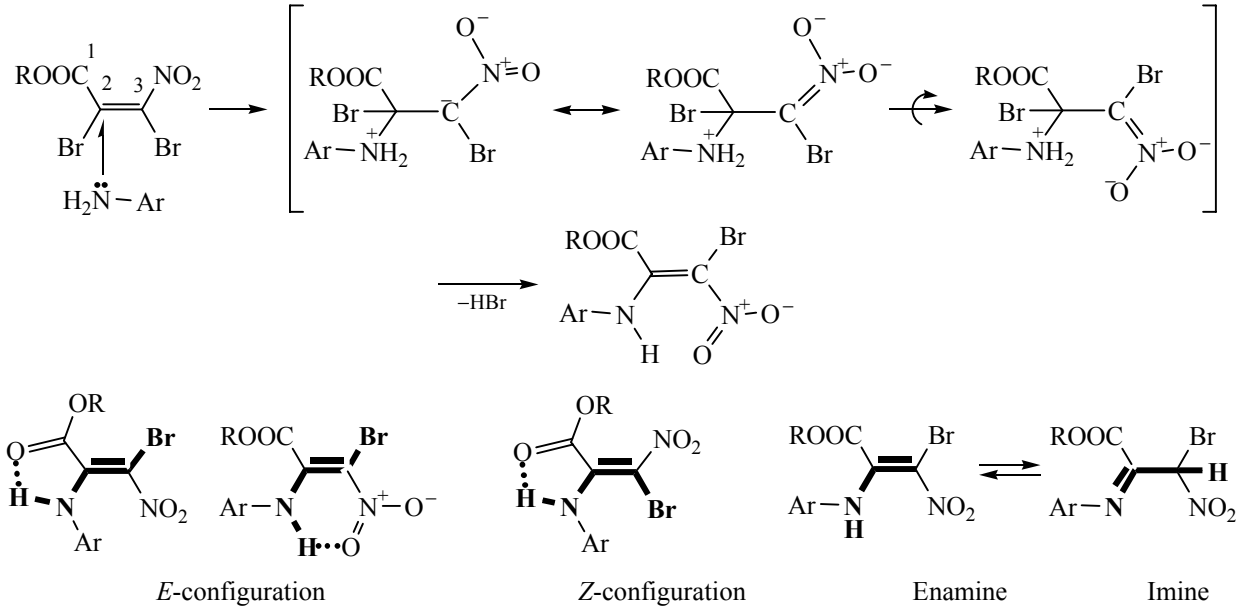
I, II **III–IX**

R = Me (**I**), Et (**II**); R = Me, Ar = *p*-Br-C_6H_4 (**III**), *p*-Me-C_6H_4 (**V**), *p*-EtO-C_6H_4 (**VII**), α-naphthyl (**IX**); R = Et, Ar = *p*-Br-C_6H_4 (**IV**), *p*-Me-C_6H_4 (**VI**), *p*-EtO-C_6H_4 (**VIII**).

Such mild conditions of this reaction are logical, considering activating effect of an additional acceptor, the ester group, on the multiple C=C bond of dihalogen-substituted nitroacrylate. The closest analogs, α,β-dibromo-β-nitrostyrenes, are known to react with the primary arylamines in boiling benzene [5].

The studied reaction occurs apparently by the S_NVin mechanism via the formation of the intermediate bipolar ion, allowing the rotation around the

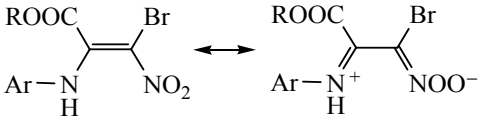
bond C_2-C_3, and the formation of the end-product as *E*- or *Z*-isomer. The formation of not only inter-, but intramolecular hydrogen bond involving the NH-group and the nitro or ester functions is theoretically possible for both configurations. The tautomeric transformation enamine↔imine is not excluded [1].



The structure of the synthesized α-arylamino-β-bromo-β-nitroacrylates **III–IX** was established on the basis of ^{1}H, ^{13}C–{^{1}H} NMR, IR, and UV spectroscopy (Tables 1, 2). The ^{1}H and ^{13}C–{^{1}H} NMR spectra (DMSO-d_6) of compounds **III–IX** contain one set of signals for all structural fragments and suggest the configurational homogeneity of the substances (Table 1). For example, in the spectrum of **III** there is a singlet signal of methoxy protons at 3.63 ppm, doublets of the protons of *p*-substituted aromatic ring at 7.13–7.15 and 7.56–7.58 ppm, as well as a broad signal of the NH-proton at 10.17 ppm.

The ^{13}C–{^{1}H} NMR spectra (Table 1) of compounds **III–IX** contain the signals of carbon atoms of the alkyl substituents of ester groups [53.71–54.15 ppm (CH_3) and 13.73–14.12, 63.20–63.47 ppm (C_2H_5)], the aromatic ring (115.10–158.76 ppm), as well as downfield signals of the carbon of alkoxycarbonyl group (161.04–161.77 ppm). The signals at 148.65–151.07 ppm can be attributed to the carbon atom C_2. The carbon atom C_3 containing the nitro group and bromine atom is observed as a low-intensity broad signal at 100.04–105.99 ppm only in the spectra of compounds **III, IV, VI, VIII, IX**. Their location is consistent with the published data for structurally similar analogs [3, 14]. For example, in the spectrum of 1-bromo-1-nitro-2-phenylaminoethene the signals at 105.2 (=$CBrNO_2$) and 141.8 ppm (=CHN) are assigned [3] to the vinyl carbons, while in the case of 1-nitro-2,2-di-(4-chlorophenylamino)-1-chloroethene they are at 106.4 (=$CClNO_2$) and 149.3 ppm (=CNN) [14].

The infrared and electronic spectra (Table 2) of aminobromonitroacrylates **III–IX** indicate a significant contribution to the electronic structure of the charge separation [1, 15].



Their IR spectra contain vibration bands of C=O bond (1752–1735 cm^{-1}) of the ester group [16] and a set of bands belonging to the vibrations of nitroenamine fragment: a strong band of conjugated multiple bonds C=C and C=N at 1608–1556 cm^{-1} [1], intense overlapping bands originating from the ionized nitro group at 1301–1271, 1253–1203, and 1179–1114 cm^{-1} [17], and broad bands of the free and bound amino groups at 3348–3188 cm^{-1} [16]. Note that the IR spectra in going from the liquid phase (chloroform solution) to the solid (KBr pellets) slightly differ. For example, the amino group appears not as several bands (as in chloroform), but as a single broad band of moderate intensity. Also the position of the vibration band of carbonyl group attracts attention: the band is

Table 1. Yields, melting points, and ^{1}H, ^{13}C NMR spectral data of arylaminobromonitroacrylates **III–IX**

Comp. no.	R	Ar	Yield, %	mp, °C	NMR spectrum, δ, ppm, DMSO-d_6						
					^{1}H[a]			^{13}C[b]			
					OMe (OEt)	Ar	NH	OCH_3 (OC_2H_5)	C^2 (C^3)	Ar	C=O
III	Me	*p*-BrC_6H_4	68	145–146	3.63	7.13–7.15, 7.56–7.58	10.17	54.15	148.65 (105.99)	120.61, 127.27, 132.64, 137.21	161.77
IV	Et	*p*-BrC_6H_4	83	88–89	(1.02, 4.06)	7.14–7.16, 7.56–7.58	10.15	(13.73, 63.46)	149.06 (105.68)	120.71, 127.76, 132.51, 137.15	161.04
V	Me	*p*-MeC_6H_4	54	122–123	3.59	7.06–7.08, 7.17–7.19	10.16	53.95	149.57	125.49, 130.12, 135.03, 137.66	161.75
VI	Et	*p*-MeC_6H_4	81	61–63	(0.99, 4.04)	7.08–7.09, 7.17–7.19	10.10	(13.78, 63.20)	149.84 (104.21)	125.96, 129.99, 134.95, 137.78	161.06
VII	Me	*p*-$EtOC_6H_4$	87	133–135	3.57	6.89–6.91, 7.10–7.12	10.10	53.89	150.05	115.10, 127.52, 129.91, 158.34	161.68
VIII	Et	*p*-$EtOC_6H_4$	68	94–95	(0.98, 3.99)	6.89–6.91, 7.11–7.14	10.07	(14.12, 63.47)	150.73 (103.86)	115.34, 128.31, 130.15, 158.76	161.35
IX	Me	α-Naphthyl	79	139–141	3.38	7.37–7.60, 7.88–7.96	10.43	53.71	151.07 (100.04)	123.67, 125.75, 127.46, 127.60, 128.61, 129.48, 130.30, 133.71, 133.98	161.71

[a] In the ^{1}H NMR spectra of compounds **V** and **VI** the methyl protons of *p*-tolyl moiety appear as singlets at 2.27 and 2.26 ppm, respectively, and ethyl protons of *p*-ethoxyphenylamine fragment (**VII** and **VIII**) are observed as a triplet at 1.28 ppm and a quadruplet at 3.99–4.04 ppm. [b] In the ^{13}C NMR spectra of compounds **V** and **VI** the methyl carbon atoms *p*-tolyl group appear at 21.10 ppm, and the ethyl carbon atoms of *p*-ethoxyphenylamine moiety in the spectra of compounds **VII** and **VIII** are observed as the signals at 9.15–15.37 and 63.86–64.22 ppm.

located in a region characteristic of C=O bond not involved in hydrogen bonding [16].

The electronic spectra of arylaminobromonitroacrylates **III–IX** contain intense long-wave absorption at λ_{max} 380–383 nm (ε 16000–17700). The observed slight red shift compared with the model α-(*p*-bromophenylamino)-β-nitroacrylate of the similar structure (λ_{max} 365 nm, ε 17800 [1, 18]) is apparently due to some contribution of the bromine atom to the electron distribution in the molecules.

Thus, the spectral data obtained confirm nitroenamine structure and show that the synthesized arylaminobromonitroacrylates are highly polarized structures. However, these data do not permit a valid conclusion about the geometry of these compounds and the nature of the hydrogen bonding.

The published data indicate preferential existence of similar structures but without the ester function in the form of nitroenamine with *cis*-arranged arylamino and nitro groups [1]. The latter form quasi-six-membered ring due to the intramolecular hydrogen bonding. As stated above, in the compounds **III–IX** the intra- and intermolecular hydrogen bonds formation involving NH- and NO_2 or NH- and COOR groups also is possible. A convincing conclusion about the fine structure of these compounds was made on the basis of the X-ray analysis of ethyl α-(*p*-bromoaniline)-β-bromo-β-nitroacrylate **IV** (Figs. 1–4, Tables 3, 4).

Compound **IV** forms monoclinic crystals (space group *P*21/*c*) with one independent molecule in the asymmetric part of the unit cell (Fig. 1). By these data, the molecule of compound **IV** in the crystal has *E*-configuration, and the presence of the bulky bromine atom in the *gem*-position to the nitro group hinders significantly the coplanar arrangement of the ester group in the double bond plane [torsion angle

Table 2. IR and electronic spectral data of arylaminobromonitroacrylates **III–IX**

Comp. no.	R	Ar	IR spectrum, ν, cm^{-1}					UV spectrum, DMSO	
			phase	C=O	C=C, C=N	NOO^-	NH	λ_{max}, nm	ε
III	Me	*p*-BrC_6H_4	$CHCl_3$	1752 m	1590 m, 1583 m, 1570 s	1288 m, 1253 m	3348 w, 3238 w. br	382	17700
			KBr	1735 m	1593 m, 1571 s, 1564 s	1285 m, 1271 s, 1234 m, 1210 m	3287 m		
IV	Et	*p*-BrC_6H_4	$CHCl_3$	1748 m	1591 m, 1582 m, 1569 s	1288 m, 1250 m	3347 w, 3236 w. br	380	15950
			KBr	1745 s	1592 m, 1581 m, 1564 s	1283 m, 1249 s	3189 m		
V	Me	*p*-MeC_6H_4	$CHCl_3$	1751 m	1573 s	1290 s	3348 w	381	16200
			KBr	1742 s	1590 m, 1556 s	1298 m, 1252 s, 1230 m, 1207 s	3206 m		
VI	Et	*p*-MeC_6H_4	$CHCl_3$	1749 m	1571 s	1289 m, 1251 m	3348 w, 3230 w. br	380	16100
VII	Me	*p*-$EtOC_6H_4$	KBr	1750 s	1608 m, 1556 s	1301 m, 1248 s, 1209 s	3237 m	383	16300
VIII	Et	*p*-$EtOC_6H_4$	KBr	1748 s	1605 m, 1558 s	1294 s, 1246 s, 1203 s	3216 m	381	16400
IX	Me	α-Naphthyl	$CHCl_3$	1752 m	1578 m, 1570 s	1290 m, 1273 s, 1251 m, 1228 m	3341 w, 3224 w. br	380	17900
			KBr	1751 s	1576 m, 1558 s	1278 s, 1246 s, 1220 s	3188 m		

$C^3C^2C^1O^3$ is 102.8(6)°], whereas the corresponding torsion angle $O^6C^6C^1C^2$ in the model ethyl 2-(*p*-bromoaniline)-3-nitroacrylate is –46.13° (Fig. 1) [18]. The nitroenamine fragment in the molecule of **IV** is almost planar [the torsion angle is –0.2(8)°] that favors the efficient conjugation of the lone electron pair of aniline nitrogen atom with the π-bond and the nitro group. This is seen in the increase in the C^3–C^2 bond length 1.365(7) Å (1.337Å in nitroethylene molecule [19]) and in the decrease in the length of the bonds C^3–N^1 1.435(7), C^2–N^2 1.335(6) Å compared with the usual value (1.45–1.47 Å) in the nitroethene molecules [19–21]. Some geometric parameters are given in Table 4.

In the crystal were found the intra- and intermolecular hydrogen bonds of NH···O type. It should be noted that the hydrogen atom H^2 and the oxygen atom O^{12} are involved into the formation of bifurcated hydrogen bonds. Parameters of the hydrogen bonds are the following: intramolecular N^2–H^2···O^{12}, $d(N^2–H^2)$ 0.83(3), $d(H^2\cdots O^{12})$ 1.93(4), $d(N^2\cdots O^{12})$ 2.615(6) Å, $\angle(N^2–H^2\cdots O^{12})$ 139(5)°; intermolecular, N^2–H^2···$O^{12'}$ (1 – *x*, –*y*, 1 – *z*), $d(N^2–H^2)$ 0.83(3), $d(H^2\cdots O^{12'})$ 2.49(4), $d(N^2\cdots O^{12'})$ 3.222(5) Å, $\angle(N^2–H^2\cdots O^{12'})$ 148(4)°. The intermolecular hydrogen bonding results in the formation of centrosymmetric dimers (Fig. 2).

Thus, the studied reaction can be used as a convenient approach to the new alkyl α-arylamino-β-bromo-β-nitroacrylates, which are of interest as potential biologically active compounds. Both the spectral characteristics (in solution and solid phase) and the X-ray analysis data of the ethyl 3-bromo-2-(*p*-bromophenylamino)-3-nitroacrylate allow the confident conclusion on the *E*-configuration for this series of compounds. Based on the X-ray analysis data we established that the steric hindrances in the molecule of these compounds are overcame mainly by the location of the ester group out of the plane of the double bond, while the relative planarity of nitroenamine fragment is retained.

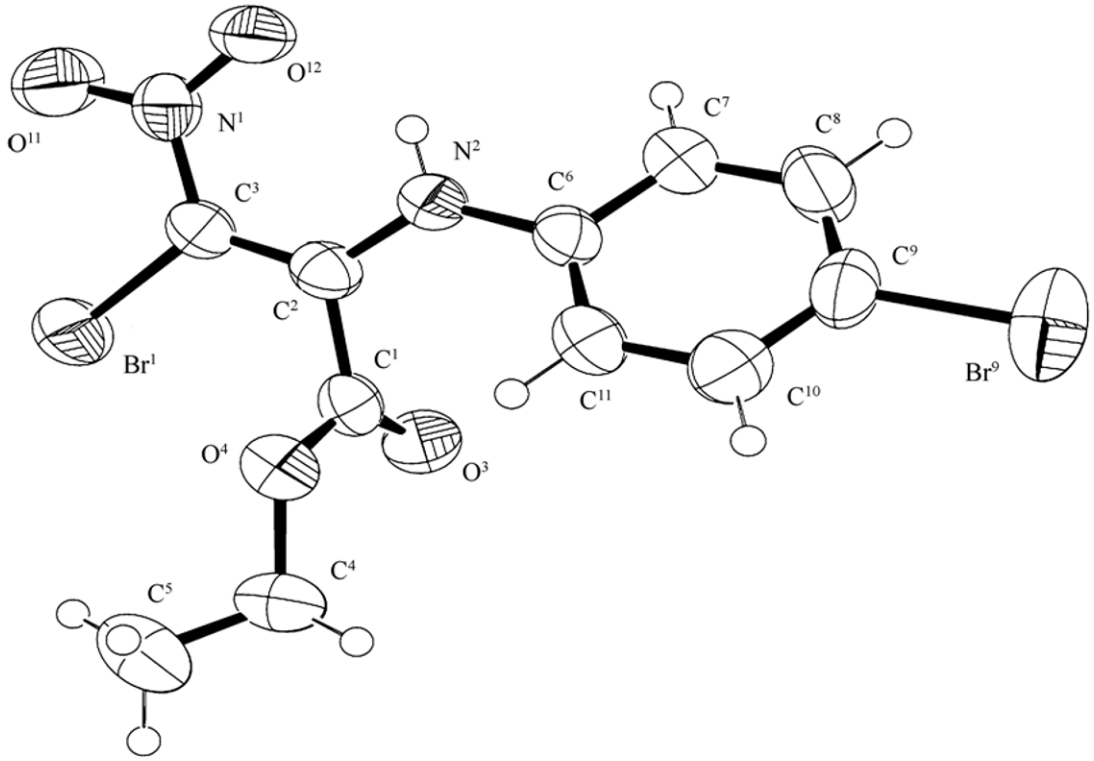


Fig. 1. General view of compound **VI**.

EXPERIMENTAL

The IR spectra were taken on a Shimadzu IRPrestige-21 Fourier-spectrometer from chloroform solutions (*c* 0.1–0.001 M) or pellets with KBr. The ^{1}H, ^{13}C NMR spectra were registered on a Jeol ECX-400A spectrometer operating at 100.525 (^{13}C) and 399.782 MHz (^{1}H) using the signals of the residual protonated solvents as reference signals. The UV spectra were recorded on a Shimadzu UV2401PC spectrophotometer in quartz cell (*l* 0.1 cm) in DMSO. The reaction progress was monitored by TLC method on Silufol UV-254 plates with detecting on a chromatoscope.

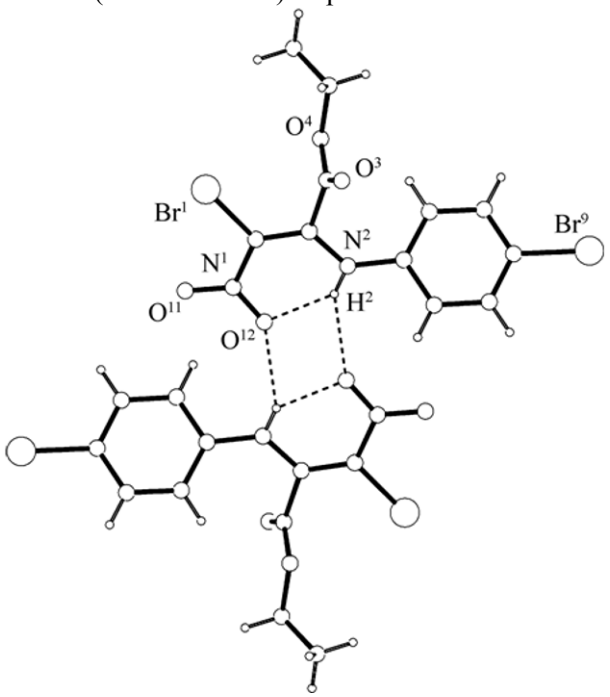


Fig. 2. Hydrogen bonds in the crystal of **IV** (dotted line).

Study of single crystal of **IV** was made in the Laboratory of diffraction analysis methods at the Arbuzov Institute of Organic and Physical Chemistry.

X-Ray diffraction analysis of compound **IV** was performed at 20º on a Bruker Smart APEX2 automated diffractometer (MoK_α irradiation, graphite monochromator, ω-scanning). The extinction was accounted for semiempirically using SADABS program [22]. The structures were solved by the direct method by SIR program [23] and refined first in isotropic and then anisotropic approximation by SHELXL-97 program package [24]. Hydrogen atoms were placed in the calculated position and refined using the *rider* model. The hydrogen atom at the nitrogen atom N^2 was localized from differential Fourier charts and refined in the isotopic approximation. All calculations were

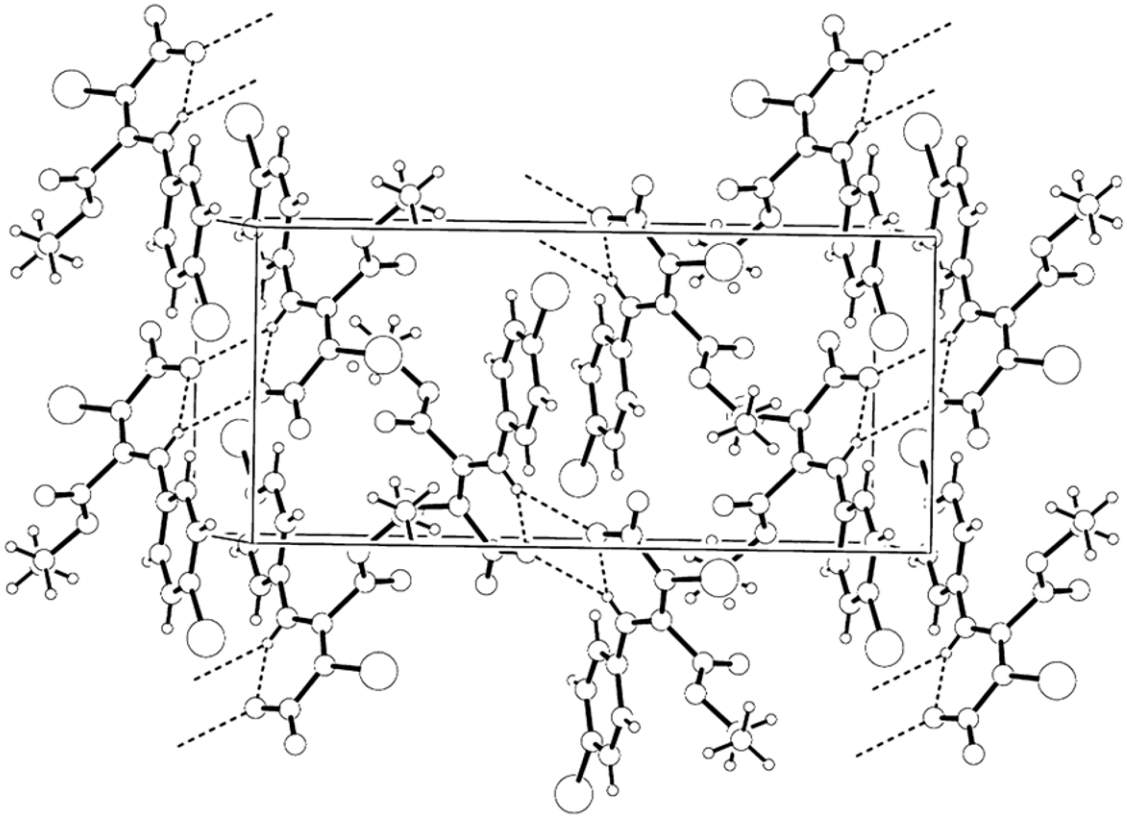


Fig. 3. Molecular organization and hydrogen bonds in the crystal of **IV (**projection of the plane *b*0*c*).

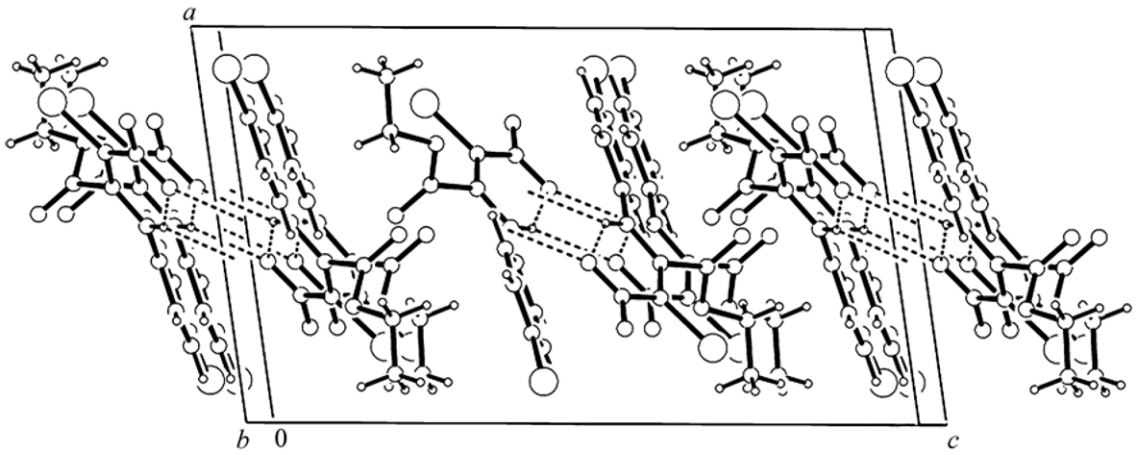


Fig. 4. Molecular arrangement and hydrogen bonds in the crystal of **IV (**projection of the plane *a*0*c*).

performed using WinGX [25] and APEX2 program package [26]. Figure and analysis of hydrogen bonds was made by means of PLATON program [27]. Conditions of the X-ray diffraction studies and crystallographic parameters are given in Table 3. The atomic coordinates and complete structural data are deposited at Cambridge Crystallographic Data Center.

The starting alkyl 2,3-dibromo-3-nitroacrylates **I** and **II** were prepared by the described procedure [13].

Methyl 3-bromo-2-(*p*-bromophenylamino)-3-nitroacrylate (III). To a solution of 0.32 g of methyl 2,3-dibromo-3-nitroacrylate **I** in 8 ml of anhydrous benzene was dropwise added a solution of 0.38 g of *p*-

Table 3. Crystallographic data of the structure **IV**

Parameter	Value
Color, habit	Colorless prisms
Empirical formula	$C_{11}H_{10}Br_2N_2O_4$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell parameters	a 10.2136(18), b 8.0502(14), c 17.278(3) Å; α 90.00°, β 98.240(2)°, γ 90.00°
Volume, Å^3	1405.9(4)
Z	4
Molecular weight	394.03
d_{calc}, g cm^{-3}	1.862
Extinction coefficient, μMo, cm^{-1}	57.76
F(000)	768
Interval θ	$2.01 \le \theta \le 26.00$
R(int)	0.0354
Indices measurement interval	$-12 \le h \le 12$ $-9 \le k \le 9$ $-21 \le l \le 21$
Number of measured reflections/ independent	7652/2687
Number of reflections with $I > 2\sigma(I)$	1649
Final values of divergence factors	R_{ob} 0.0498 R_{wob} 0.1105 R_{all} 0.0935 R_{wall} 0.1308
Fitting parameters	1.028
Δ/σ	0.005
Number of refined parameters	176

bromoaniline in 9 ml of anhydrous benzene. The reaction mixture was maintained for 15 min at vigorous stirring. *p*-Bromoaniline hydrobromide was filtered off, and the solvent was removed. The oily residue was treated with isopropanol. Yield 0.28 g (68%), dark yellow crystals, mp 145–146°C (methanol). Found, %: C 31.60; H 2.39; N 7.08. $C_{10}H_8Br_2N_2O_4$. Calculated, %: C 31.61; H 2.12; N 7.37.

Ethyl 3-bromo-2-(*p*-bromophenylamino)-3-nitroacrylate (**IV**) was prepared similarly from 0.34 g of ethyl 2,3-dibromo-3-nitroacrylate **II** and 0.38 g of *p*-bromoaniline in 13 ml of anhydrous benzene (maintained for 20 min). Yield 0.37 g (83%), dark yellow crystals, mp 88–89°C (methanol). Found, %: C 33.58; H 2.80; N 7.14. $C_{11}H_{10}Br_2N_2O_4$. Calculated, %: C 33.53; H 2.56; N 7.11.

Methyl 3-bromo-3-nitro-2-(*p*-toluidine)acrylate (**V**) was prepared similarly from 0.68 g of methyl 2,3-dibromo-3-nitroacrylate **I** and 0.50 g of *p*-toluidine in 40 ml of anhydrous benzene (maintained for 20). After the solvent removal the oily pale yellow residue was treated with *n*-hexane. Yield 0.40 g (54%), yellow crystals, mp 122–123°C (*n*-hexane). Found, %: N 8.89. $C_{11}H_{11}BrN_2O_4$. Calculated, %: N 8.76.

Ethyl 3-bromo-3-nitro-2-(*p*-toluidine)acrylate (**VI**) was prepared similarly from 0.68 g of ethyl 2,3-dibromo-3-nitroacrylate **II** and 0.48 g of *p*-toluidine in 45 ml of anhydrous benzene (maintained for 20 min). Yield 0.60 g (81%), yellow crystals, mp 61-63°C (*n*-hexane). Found, %: N 8.37. $C_{12}H_{13}BrN_2O_4$. Calculated, %: N 8.51.

Methyl 3-bromo-3-nitro-2-(*p*-ethoxyphenylamine)-acrylate (**VII**) was prepared similarly from 0.48 g of methyl 2,3-dibromo-3-nitroacrylate **I** and 0.43 ml of *p*-ethoxyphenylamine in 25 ml of anhydrous benzene (maintained for 10 min). Yield 0.48 g (87%), mp 133–135°C (methanol). Found, %: C 42.19; H 3.93; N 7.98. $C_{12}H_{13}BrN_2O_5$. Calculated, %: C 41.76; H 3.80; N 8.10.

Ethyl 3-bromo-3-nitro-2-(*p*-ethoxyphenylamine) acrylate (**VIII**) was prepared similarly from 0.49 g of ethyl 2,3-dibromo-3-nitroacrylate **II** and 0.42 ml of *p*-ethoxyphenylamine in 20 ml of anhydrous benzene (maintained for 10 min). After the solvent removal the residue was treated with diethyl ether. Yield 0.38 g (68%), yellow crystals, mp 94–97°C (methanol). Found, %: N 7.73, $C_{13}H_{15}BrN_2O_5$. Calculated, %: N 7.80.

Methyl 3-bromo-2-(α-naphthylamino)-3-nitro-acrylate (IX) was prepared similarly from 0.60 g of methyl 2,3-dibromo-3-nitroacrylate **I** and 0.60 g of α-naphthylamine in 30 ml of anhydrous benzene (maintained for 45 min). After the solvent removal the oily residue was treated with methanol. Yield 0.58 g (79%), yellowish green crystals, mp 139–141°C (methanol). Found, %: N 7.92. $C_{14}H_{11}BrN_2O_4$. Calculated, %: N 7.98.

Table 4. Selected geometrical parameters: bond lengths (*d*, Å), bond angles (ω, deg) and torsion angles (τ, deg) in **IV**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
C^3–C^2	1.365(7)	C^4–O^4	1.485(7)	N^1–O^{11}	1.209(6)
C^3–N^1	1.435(7)	C^6–N^2	1.416(7)	N^1–O^{12}	1.220(5)
C^3–Br^1	1.873(5)	C^9–Br^9	1.904(5)	N^2–H^2	0.828(19)
C^2–N^2	1.335(6)	C^1–O^4	1.308(6)	C^4–C^5	1.422(9)
C^2–C^1	1.534(7)	C^1–O^3	1.197(6)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$C^2C^3N^1$	123.3(4)	$O^3C^1O^4$	128.4(5)	$O^4C^1C^2$	110.5(5)
$C^2C^3Br^1$	121.9(4)	$C^2N^2C^6$	130.0(4)	$O^{11}N^1O^{12}$	124.4(5)
$N^1C^3Br^1$	114.7(4)	$O^3C^1C^2$	121.1(5)	$O^{11}N^1C^3$	118.8(4)
$N^2C^2C^3$	126.2(5)	$C^7C^6N^2$	117.5(5)	$O^{12}N^1C^3$	116.8(4)
$N^2C^2C^1$	116.8(4)	$C^{11}C^6N^2$	123.4(5)	$C^1O^4C^4$	115.9(4)
$C^3C^2C^1$	116.9(4)	$C^{10}C^9Br^9$	120.3(5)	$C^5C^4O^4$	108.9(6)
Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
$N^1C^3C^2N^2$	–0.2(8)	$C^7C^8C^9Br^9$	179.9(4)	$C^2C^3N^1O^{12}$	–0.5(8)
$Br^1C^3C^2N^2$	175.7(4)	$Br^9C^9C^{10}C^{11}$	179.6(4)	$Br^1C^3N^1O^{12}$	–176.6(4)
$N^1C^3C^2C^1$	–175.0(5)	$N^2C^6C^{11}C^{10}$	–176.3(5)	$C^3C^2N^2C^6$	175.0(5)
$Br^1C^3C^2C^1$	0.9(7)	$C^2C^3N^1O^{11}$	179.6(5)	$C^1C^2N^2C^6$	–10.2(8)
$N^2C^2C^1O^3$	–72.5(6)	$Br^1C^3N^1O^{11}$	3.5(7)	$C^7C^6N^2C^2$	149.6(5)
$C^3C^2C^1O^3$	102.8(6)	$N^2C^6C^7C^8$	176.1(5)	$C^{11}C^6N^2C^2$	–34.0(8)
$N^2C^2C^1O^4$	110.3(5)	$C^5C^4O^4C^1$	–146.3(6)	$O^3C^1O^4C^4$	–5.2(8)
$C^3C^2C^1O^4$	–74.4(6)	$C^2C^1O^4C^4$	171.7(4)		

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