1-Aryl-2-nitro-3-trichloromethylaziridines: synthesis and structure

V. M. Berestovitskaya,[a] S. V. Makarenko,[a] I. S. Bushmarinov,[b] K. A. Lyssenko,[b] A. S. Smirnov,[a] and E. V. Stukan´[a]*

[a]*Herzen State Pedagogical University of Russia,*
48 nab. Moika, 191186 St. Petersburg, Russian Federation.
Fax: +7 (812) 571 3800. E-mail: kohrgpu@yandex.ru
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085. E-mail: bush-i@ya.ru

A two-step method was developed for the synthesis of new polyfunctional aziridines involving the addition of aromatic amines to 1-bromo-3,3,3-trichloro-1-nitropropene and the dehydrobromination of the resulting adducts. The ^{1}H and ^{13}C NMR spectroscopic and X-ray diffraction studies showed that 1-aryl-2-nitro-3-trichloromethylaziridines are stereohomogeneous and have the geometry, such that the nitro and aryl substituents are in the *trans* positions with respect to the trichloromethyl group. The chemical bonding in the crystal and the gas phase was investigated based on high-resolution X-ray diffraction analysis of the electron density distribution and quantum chemical calculations.

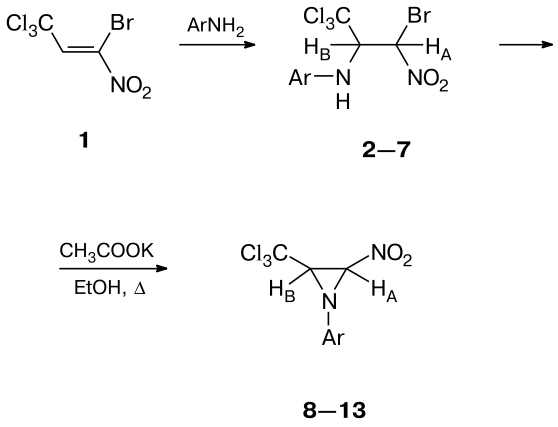
Key words: 1-aryl-2-nitro-3-trichloromethylaziridines, ethyleneimines, 1-bromo-3,3,3-trichloro-1-nitropropene, arylamines.

Due to the ability to readily undergo the cleavage in the presence of nucleophiles, the aziridine (ethyleneimine) ring is a good alkylating agent. This property determines the mutagenic and toxic effects of aziridines.[1] Aziridine is involved in antitumor drugs.[2—4] In particular, triethyleneimine thiophosphoramide[1] is used in the therapy for ovarian and breast cancer. The drug Dipin is recommended for the treatment of lymphatic leukemia and laryngeal cancer.[4] Natural compounds of the aziridine series were also documented. For example, mitomycin C exhibits antibiotic and antitumor activities.[1] Due to all these facts, aziridine derivatives attract considerable interest.[5]

The investigation of the dehydrobromination of nucleophilic addition products of arylamines to the previously unknown 1-bromo-3,3,3-trichloro-1-nitropropene[6] allowed us to synthesize a series of original 1-aryl-2-nitro-3-trichloromethylaziridines.

The reaction of 1-bromo-3,3,3-trichloro-1-nitropropene (**1**) with aromatic amines (aniline, *p*-toluidine, *p*-chloroaniline, *p*-bromoaniline, *m*-nitroaniline, and α-naphthylamine) in anhydrous methanol at room temperature affords *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]anilines (**2**—**7**) in 46—77% yields (Scheme 1). Then compounds **2**—**7** are transformed into 1-aryl-2-nitro-3-trichloromethylaziridines (**8**—**13**) in 19—37% yields under reflux in ethanol in the presence of a one-and-a-half excess of freshly melted potassium acetate.

Scheme 1



1 **2—7** **8—13**

Ar = Ph (**2**,**8**), *p*-MeC_6H_4 (**3**,**9**), *p*-ClC_6H_4 (**4**,**10**), *p*-BrC_6H_4 (**5**,**11**), *m*-$O_2NC_6H_4$ (**6**,**12**), α-naphthyl (**7**,**13**)

The structures of *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]anilines (**2**—**7**) were assigned based on the IR and ^{1}H NMR spectroscopic data (Table 1). The IR spectra of compounds **2**—**7** shows symmetric absorption bands (1350—1340 cm^{-1}) and antisymmetric bands (1575—1570 cm^{-1}) of the unconjugated nitro group with a frequency separation $\Delta\nu$ = 220—230 cm^{-1} characteristic of compounds with the geminal arrangement of the nitro group and the halogen atom.[7,8] The ^{1}H NMR spectra of

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Table 1. Yields and characteristics of *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]anilines **2—7**

Compound	Yield (%)	R_f	Diastereomer[a]	^{1}H NMR ($CDCl_3$, δ, *J*/Hz)				IR ($CHCl_3$), ν/cm^{-1}		
				Ar (m)	H_A (d)	H_B (dd)	NH (d)	Ar	NO_2	NH
2	77	0.64	**A**	—	6.71 (J_{AB} = 3.7)	4.88 (J_{AB} = 3.7, J_{BH} = 10.7)	5.08 (J_{BH} = 10.7)	1600, 1510	1570, 1350	3415
			B	6.79—7.26	6.84 (J_{AB} = 2.7)	5.37 (J_{AB} = 2.7, J_{BH} = 11.1)	4.53 (J_{BH} = 11.1)			
3[b]	71	0.55	**A**	6.73—7.01	6.67 (J_{AB} = 3.3)	4.83 (J_{AB} = 3.3, J_{BH} = 10.3)	4.99 (J_{BH} = 10.3)	1615, 1520	1570, 1350	3430
			B	6.67—6.98	6.83 (J_{AB} = 1.5)	5.29 (J_{AB} = 1.5, J_{BH} = 10.3)	4.48 (J_{BH} = 10.3)			
4	67	0.43	**A**	6.80—7.26	6.75 (J_{AB} = 2.8)	4.78 (J_{AB} = 2.8, J_{BH} = 10.3)	5.09 (J_{BH} = 10.3)	1600, 1505	1575, 1350	3420
			B	6.75—7.20	6.86 (J_{AB} = 1.9)	5.32 (J_{AB} = 1.9, J_{BH} = 10.3)	4.50 (J_{BH} = 10.3)			
5	59	0.55	**A**	6.76—7.37	6.74 (J_{AB} = 3.2)	4.78 (J_{AB} = 3.2, J_{BH} = 10.4)	5.10 (J_{BH} = 10.4)	1600, 1505	1570, 1340	3415
			B	6.71—7.34	6.85 (J_{AB} = 2.5)	5.33 (J_{AB} = 2.5, J_{BH} = 11.0)	4.50 (J_{BH} = 11.0)			
6[c]	52	0.50	**A**	—	6.81 (J_{AB} = 3.5)	4.93 (J_{AB} = 3.5, J_{BH} = 10.6)	5.54 (J_{BH} = 10.6)	1620, 1490	1575, 1350	3415
			B	7.14—7.74	6.88 (J_{AB} = 2.7)	5.44 (J_{AB} = 2.7, J_{BH} = 11.0)	4.91 (J_{BH} = 11.0)			
7	46	0.60	**A**	—	6.89 (J_{AB} = 3.0)	5.14 (J_{AB} = 3.0, J_{BH} = 10.3)	5.98 (J_{BH} = 10.3)	1600, 1490	1570, 1345	3455
			B	6.97—8.03	6.96 (J_{AB} = 2.7)	5.68 (J_{AB} = 2.7, J_{BH} = 10.8)	5.25 (J_{BH} = 10.8)			

[a] The stereoisomers of compounds **2—7** with H_A and H_B at higher field are marked with **A**; the stereoiosmers with H_A and H_B at lower field are marked with **B**. The **A** : **B** ratio for compounds **2—4** is 1 : 2; for compounds **5—7**, 1 : 1.7; 1 : 1.5, and 2 : 3, respectively.
[b] The protons of the methyl group at the *para* position of the benzene ring of compound **3** are observed at δ 2.19 and 2.21 for the diastereomers **A** and **B**, respectively.
[c] The absorption bands of the nitro group in the aromatic ring of compound **6** are observed at 1540 cm^{-1} (ν_{as}) and 1355 cm^{-1} (ν_s).

compounds **2—7** contain a double set of signals, which indicate that *N*-[2-bromo-2-nitro-1-(trichloromethyl)-ethyl]anilines (**2—7**) exist as mixtures of *erythro* and *threo* diastereomers.

The ^{1}H NMR spectra of nitroaziridines **8—13** contain signals for the protons of all structural fragments (Table 2). Thus, the protons of the aromatic ring appear as multiplets at δ 6.91—8.04 and the methine protons of the aziridine ring appear as singlets at δ 5.53—5.91 (H_A) and 4.18—4.45 (H_B). An analysis of the data published in the literature showed that the spin-spin coupling constants $^3J_{H_AH_B}$ in aziridines containing hydrogen atoms in the *trans* positions can vary in a relatively broad range (1—5 Hz) depending on the nature of the substituents. For example, in the spectrum of the related 1-nitro-2-trichloromethyloxirane molecule, the signals for the ring protons H_A ($HCNO_2$) and H_B ($HCCCl_3$) are observed without splitting at δ 5.58 and 4.03, respectively.[9] The *cis* spin-spin coupling constants in aziridines are more conserved and are generally no larger than 4 Hz.[10] Therefore

Table 2. Melting points, yields, and spectral characteristics of 1-aryl-2-nitro-3-(trichloromethyl)aziridines **8—13**

Compound	Yield (%)	M.p./°C	^{1}H NMR ($CDCl_3$, δ)			IR ($CHCl_3$), ν/cm^{-1}		
			Ar (m)	H_A (s)	H_B (s)	NO_2	Ar	CCl_3
8	25	58—59	7.37—7.02	5.58	4.24	1560, 1355	1600, 1495	810
9[a]	30	86—87	7.13, 6.92	5.55	4.21	1565, 1355	1600, 1510	815
10	37	69—71	7.27, 6.93	5.53	4.18	1560, 1350	1610, 1505	820
11	36	106—107	7.46, 6.91	5.56	4.20	1560, 1350	1590, 1490	815
12[b]	19	82—84	7.31—8.04	5.65	4.29	1560, 1350	1590, 1490	815
13	27	116—117	8.04—7.40	5.91	4.45	1570, 1345	1600, 1510	810

[a] The protons of the methyl group at the *para* position of the aromatic ring of compound **9** appear as a singlet at δ 2.31.
[b] The absorption bands of the nitro group in the benzene ring of compound **12** are observed at ν_{as} 1525 and ν_s 1350 cm^{-1}.

the constants $^3J_{H_AH_B}$ provide indirect evidence for the *trans* arrangement of the vicinal protons in the aziridine ring.

The ^{13}C {^{1}H} NMR spectrum of compound **10** shows signals for all carbon atoms (at δ 55.8 (C—CCl_3), 71.2 (C—NO_2), 93.7 (CCl_3), 117.7, 119.7, 132.3, 141.3 (C_6H_4)).

The IR spectra of compounds **8—13** contain stretching bands of the unconjugated nitro group (1570—1560 and 1355—1345 cm^{-1}), the aromatic ring (1600—1590 cm^{-1}), and the CCl_3 groups (820—810 cm^{-1}).

The UV spectra of aziridines **9—11** show intense absorption bands of π→π* transitions of the aromatic rings at λ_{max} 230—233 nm (ε 19100—23600) and weak bands of n→π* transitions at 323—333 nm (ε 1700—1800).

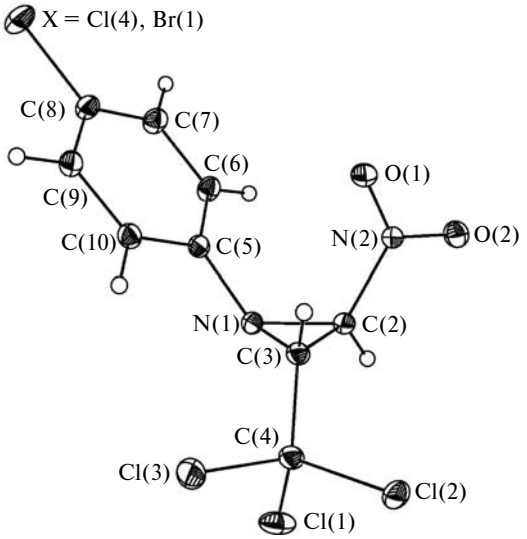

Fig. 2. Molecular structures of compounds **10** and **11** with displacement ellipsoids drawn at p = 50%.

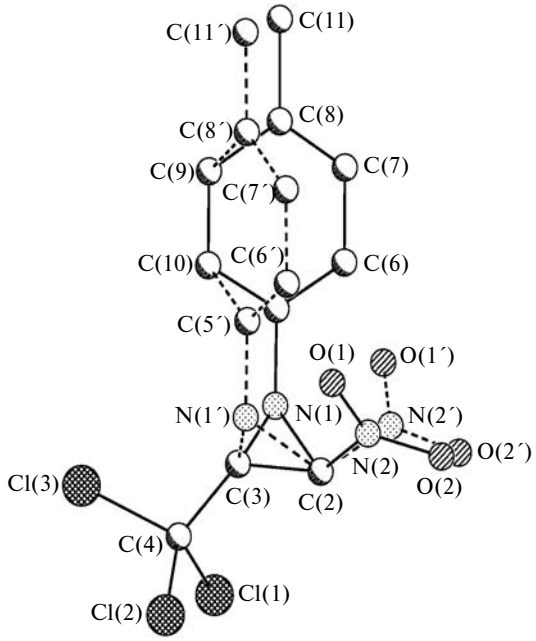

Fig. 1. Molecular structure of compound **9** illustrating the character of disorder.

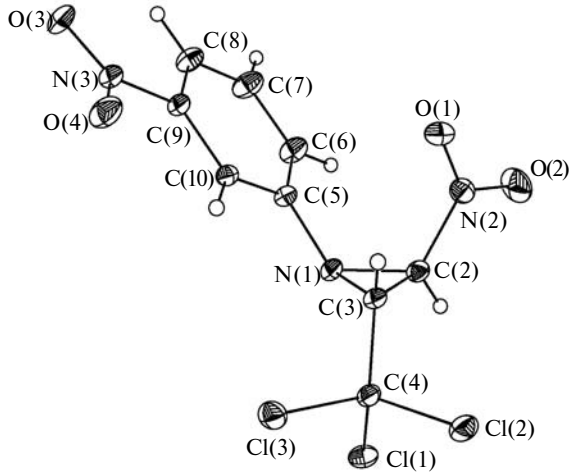

Fig. 3. Molecular structure of compound **12** with displacement ellipsoids drawn at p = 50%.

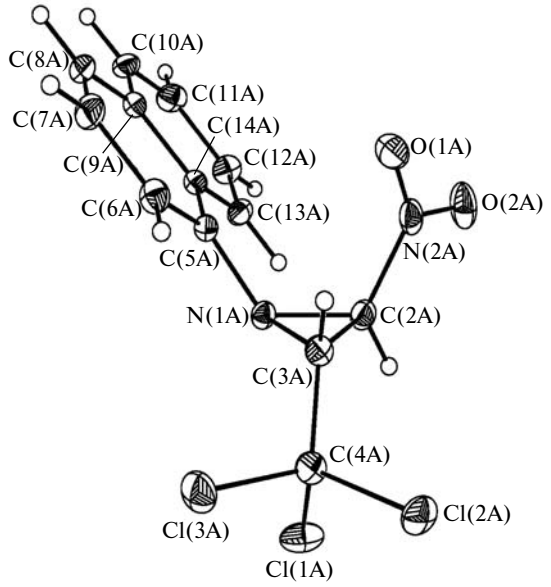

Fig. 4. Molecular structure of compound **13** with displacement ellipsoids drawn at $p = 50\%$.

The structures of trichloromethyl-containing nitroaziridines **8—13** were unequivocally confirmed by the X-ray diffraction study of five compounds **9—13** containing the *p*-methyl, *p*-chloro, *p*-bromo, *m*-nitrophenyl, and α-naphthyl substituents, respectively.

According to the X-ray diffraction data, the nitro group and the aromatic moiety in compounds **9—13** are in the *trans* positions with respect to the trichloromethyl moiety (Figs 1—4).

All compounds crystallize without solvent molecules. Compound **9** and isostructural aziridines **10** and **11** crystallize in the noncentrosymmetric space group $Pna2_1$. Taking into account the fact that compounds **9—11** contain the aromatic ring with electron-donating and electron-withdrawing substituents in the *para* positions, these compounds may be of interest in view of nonlinear optical properties. Compound **13** crystallizes in the centrosymmetric space group $P2_1/n$ with three independent molecules **A—C** per asymmetric unit. Compound **12** crystallizes in the space group $P1$.

Selected geometric parameters of the common fragments and their mutual arrangement in molecules **10—13** are virtually identical (Tables 3 and 4). Unfortunately, the disorder in the crystal structure of **9** (see the Experimental section) makes it impossible to discuss the details of its molecular geometry.

In all the molecules under consideration, the bond lengths in the common fragment are virtually identical. The maximum difference in the bond lengths is 0.019(2) Å for C(4)—Cl(1) and N(1)—C(2) (see Table 3). Therefore, the aromatic ring is not involved in the conjugation with the lone electron pair of the N(1) atom, because the N(1)—C(5) bond length is independent (the maximum change is 0.006(2) Å) of both the nature of the ring and the substituents at the benzene ring. An analysis of the Cambridge Structural Database[11] showed that the N(1)—C(5) bond length (1.420(1) Å) is typical of the bonds between the aziridine nitrogen atom and the benzene ring (see the refcodes COYMOS, COYMOS01, JESKIC, ESIMEY, XEVDOR, IFOKUJ, and KAPBEI), the N—Ph bond length being virtually independent of the angle between the benzene and aziridine fragments (see the refcode KAPBEI), which confirms the suggestion that there is no conjugation between the aziridine nitrogen atom and the aromatic fragment.

Unlike the electronic properties of the aromatic ring, its steric volume leads to a change in the angle of rotation of the aromatic moiety and the nitro group about the N(1)—C(2) bond. Actually, the corresponding torsion angles for the aromatic ring and the NO_2 group are

Table 3. Selected bond lengths in molecules **10—13** in the crystal structures

Bond	*d*/Å					
	10	**11**	**12**	**13A**	**13B**	**13C**
X[a]—C(8)	1.7385(6)	1.9012(19)	—	—	—	—
Cl(1)—C(4)	1.7620(6)	1.7665(19)	1.7700(11)	1.7733(16)	1.7668(16)	1.7615(16)
Cl(2)—C(4)	1.7663(5)	1.7692(17)	1.7684(11)	1.7635(16)	1.7620(15)	1.7640(16)
Cl(3)—C(4)	1.7791(6)	1.7787(19)	1.7733(11)	1.7775(16)	1.7797(16)	1.7836(16)
O(1)—N(2)	1.2216(6)	1.225(2)	1.2276(14)	1.2209(19)	1.2284(17)	1.2234(18)
O(2)—N(2)	1.2246(6)	1.229(2)	1.2246(13)	1.2323(18)	1.2242(17)	1.2228(18)
N(1)—C(5)	1.4198(6)	1.425(2)	1.4213(13)	1.4275(19)	1.4287(19)	1.4264(19)
N(1)—C(3)	1.4401(6)	1.441(2)	1.4422(13)	1.4400(19)	1.4421(19)	1.4433(19)
N(1)—C(2)	1.4406(6)	1.446(2)	1.4506(14)	1.4467(19)	1.4479(19)	1.4549(19)
N(2)—C(2)	1.4908(6)	1.489(2)	1.4923(15)	1.485(2)	1.4853(18)	1.492(2)
C(2)—C(3)	1.4917(7)	1.488(2)	1.4899(14)	1.494(2)	1.488(2)	1.488(2)
C(3)—C(4)	1.5180(7)	1.511(2)	1.5175(15)	1.518(2)	1.518(2)	1.516(2)

[a] X stands for Cl(4) in compound **10** and for Br(1) in compound **11**.

Table 4. Selected bond angles in molecules **9—13** in the crystal structures

Angle	ω/deg					
	9	**10**	**12**	**13A**	**13B**	**13C**
C(5)—N(1)—C(3)	122.51(4)	122.22(14)	123.11(9)	123.41(12)	122.24(12)	122.46(12)
C(5)—N(1)—C(2)	126.19(4)	125.82(14)	123.85(9)	125.12(12)	124.69(12)	124.45(12)
C(3)—N(1)—C(2)	62.37(3)	62.05(11)	62.00(7)	62.35(10)	61.99(10)	61.80(10)
O(2)—N(2)—O(1)	125.41(5)	125.04(16)	125.38(11)	125.18(15)	124.94(13)	125.22(14)
O(2)—N(2)—C(2)	115.98(4)	116.14(14)	115.83(10)	119.12(13)	119.05(12)	116.32(13)
O(1)—N(2)—C(2)	118.61(4)	118.82(14)	118.77(9)	115.64(15)	116.00(12)	118.43(13)
N(1)—C(2)—C(3)	58.80(3)	59.12(11)	58.73(7)	117.60(13)	118.69(12)	58.72(9)
N(1)—C(2)—N(2)	119.64(4)	119.40(14)	118.39(9)	58.61(9)	58.81(9)	117.72(12)
C(3)—C(2)—N(2)	114.68(4)	114.65(14)	114.93(9)	116.42(14)	116.51(12)	115.01(13)
N(1)—C(3)—C(2)	58.83(3)	58.83(11)	59.28(7)	59.04(9)	59.19(9)	59.48(9)
N(1)—C(3)—C(4)	118.83(4)	118.57(15)	118.25(9)	116.19(13)	116.16(12)	117.92(13)
C(2)—C(3)—C(4)	122.39(5)	122.24(15)	121.31(9)	121.69(14)	121.19(13)	123.16(13)
C(3)—C(4)—Cl(1)	112.53(4)	112.65(12)	107.68(7)	109.65(11)	108.93(10)	113.42(11)
C(3)—C(4)—Cl(2)	108.27(3)	108.45(12)	112.49(7)	112.41(11)	112.15(11)	109.24(11)
Cl(1)—C(4)—Cl(2)	109.77(3)	109.33(10)	110.08(6)	108.95(9)	109.45(8)	109.30(8)
C(3)—C(4)—Cl(3)	107.01(4)	107.31(13)	108.58(7)	108.07(11)	107.87(10)	107.01(11)
Cl(1)—C(4)—Cl(3)	109.31(3)	109.20(10)	109.02(6)	109.37(8)	109.77(8)	108.85(8)
Cl(2)—C(4)—Cl(3)	109.89(3)	109.87(9)	108.91(6)	108.34(8)	108.64(8)	108.91(8)

112.7(2)—117(2)° and 40.4(2)—46.6(2)° in the case of the naphthyl substituent and 128.9(1)—130.1(1)° and 31.9(1)—32.9(1)° in the case of the *para*-halophenyl substituent.

Although there are no steric factors, which could fix the conformation of the CCl_3 group, the latter is arranged in all compounds so that the C(4)—Cl(2) and C(4)—Cl(3) bonds are antiperiplanar to the C(2)—C(3) and C(2)—N(1) bonds of the aziridine ring, and the C(4)—Cl(1) bond lies in the bisecting plane of the C(2)—C(3)—N(1) angle (see Figs 1—4). As opposed to the nitro group, the arrangement of the CCl_3 group with respect to the aziridine moiety is independent of the nature of the aromatic substituent. A slight change in the Cl(1)—C(4)—C(3)—N(1) torsion angle (31.6(1)—43.2(1)°) is apparently determined by the crystal packing effects. Interestingly, the C—Cl bonds in the CCl_3 group have different lengths in all the molecules under study. The difference between the longest and shortest C—Cl bonds varies from 0.01 to 0.02 Å depending on the molecule (see Table 3). The ratio between the C(4)—Cl(1), C(4)—Cl(2), and C(4)—Cl(3) bond lengths has a common trend in all the molecules in the crystal structures of **10—13**. In five of the six molecules, the C(4)—Cl(3) bond is the longest one and its length is larger than the other two bonds by 0.01—0.02 Å.

This difference in the bond lengths can be attributed to both the stereoelectronic effects in the molecules and the influence of intermolecular interactions in the crystal structures. To analyze the stereoelectronic effects, we carried out *ab initio* calculations for molecule **10** in the isolated state by the MP2 method with the 6-311G* basis set. The calculations showed that the C—Cl bond lengths in the gas phase increase to 1.786—1.802 Å, but the C—Cl bonds antiperiplanar to the C—C and C—N bonds of the aziridine moiety remain elongated. The orbital population analysis at the NBO level[12,13] (the wave function was obtained from the calculations for compound **10** by the DFT method (B3LYP/6-311G*)) showed that the elongation of the C(4)—Cl(2) and C(4)—Cl(3) bonds is associated with the stereoelectronic interactions between the "banana" bonds of the aziridine ring and the antiperiplanar C—Cl bonds. The energy of the charge transfer from the banana bond to the σ*(C—Cl) bond is 3.67 and 2.44 kcal mol^{-1} for the C(2)—C(3) and C(1)—N(1) bonds, respectively.

In addition to the NBO analysis, the chemical bonding in compound **10** was studied by the Bader theory of Atoms in Molecules.[14] As has been demonstrated previously,[15] this theory makes it possible to reveal finer details compared to the commonly recognized NBO localization procedure.

An analysis of the electron density distribution function (ρ(**r**)) based on the results of MP2 calculations revealed the bond critical points (3,−1) (CP (3,−1)) not only for all expected bonds but also for the intramolecular C(10)—H(10)...Cl(3) contact (H...Cl, 3.105 Å; CHCl, 137.9°). In spite of the low value of ρ(**r**) at CP (3,−1) for the H...Cl contact (0.03 $eÅ^{-3}$), the substantial distance between CP (3,−1) and CP (3,+1) of the attached ring (0.40 Å) indicates that the molecular graph is sufficiently stable. The ellipticity of CP (3,−1) corresponding to the N(1)—C(5) bond is 0.02, which unambiguously indicates that there is no conjugation between the nitrogen lone pair and the benzene ring. The estimation of the energy of

this interaction in terms of the Espinosa correlation scheme[16,17] gave 0.67 kcal mol^{-1}. Therefore, in addition to the steric factors, the invariable mutual arrangement of the aryl substituent and the CCl_3 group is attributed also to the binding interactions between these moieties. The charges on the chlorine atoms of the CCl_3 group, which were evaluated by the integration over the corresponding atomic basins, are −0.152, −0.172, and −0.176 e for the Cl(1), Cl(2), and Cl(3) atoms, respectively. These values are in qualitative agreement with the dependences revealed previously for the stereoelectronic N—C—S interactions.[15] Thus, the Cl(2) and Cl(3) atoms acquire an additional negative charge. It should be noted that the higher charge is observed for the chlorine atom involved in the interaction with the more donor (NBO data) C—C bond of the aziridine moiety. This atom is characterized also by the longer (by 0.005 Å) C—Cl bond. However, the change in the energy for the Cl(2) and Cl(3) atoms estimated by the integration of the local electron energy density ($h_e(\mathbf{r})$) over the atomic basins appeared to be opposite to the change in the charge (+2.4 and +2.8 kcal mol^{-1} with respect to the energy of Cl(1)) for the Cl(2) and Cl(3) atoms, respectively), which is inconsistent with the correlations found for the N—C—S system.[15] This can be attributed to the fact that the stereoelectronic interaction is very weak and, consequently, the relative energies of the Cl(2) and Cl(3) atoms are influenced by other factors, for example, by the polarization of the Cl(1) atom caused by the density of the aziridine ring, as well as to the fact that the interaction with the banana bond can differ in nature from the interaction with the lone pair and, consequently, can have a different effect on the integrated properties of the atoms.

The rotation barrier can serve as another independent estimate of the energy of stereoelectronic interactions. The potential surface scan along the Cl(1)—C(4)—C(3)—N(1) torsion angle coordinate by the density functional theory at the B3LYP/6-311g(d) level gave the rotation barrier of the CCl_3 group equal to 4.1 kcal mol^{-1}. Taking into account the fact that the steric barriers to rotation of the CCl_3 group are virtually absent, this energy can serve as an indirect estimate for the stereoelectronic interaction between the trichloromethyl group and the aziridine ring.

As for the experimental bond lengths, it should be noted that the C(4)—Cl(1) bond, which is not involved in stereoelectronic interactions, is not the shortest bond, at least in molecules **13A** and **13C**. This is apparently attributed to the crystal packing effect. Actually, in all the crystals under study, the CCl_3 groups are involved in the formation of relatively strong Cl...O contacts with the NO_2 groups. The O...Cl distance varies in the range of 2.92—3.25 Å. The Cl—O—N angles are 175.6—100.8°. The geometry of these contacts is typical of Cl...O_2N interactions.[18] Since the shortest Cl...O_2N contacts are characterized by a pronounced directionality (*i.e.*, the C—Cl—O angle is close to 180° and the Cl—N—O angle is virtually equal to 120°), it is reasonable to suggest that these contacts correspond to the charge transfer from the oxygen lone pair of the NO_2 group to the antibonding orbital of the Cl—C bond.

In the crystals, molecules **10** and **11** are arranged in layers through Hal...O_2N interactions, where Hal = Cl or Br (Fig. 5, *a*). These contacts can be considered as structuring interactions, because the CCl_3...NO_2 contacts remain unchanged upon the replacement of the chlorine substituent in the *para* position at the benzene ring (in the crystal of **10**) by the bromine atom (in the crystal of **11**). The only considerable difference is observed for the Br...O_2N contact of the *para* substituent; the elongation of the latter by 0.015 Å compared to the Cl...O_2N contact in the crystal of **10** corresponds to the difference in the van der Waals radii of these halogen atoms. The difference in the X—O—N angles is within experimental error. In the crystal of compound **9**, in which the halogen atom at the benzene ring is replaced by the methyl group, shortened Cl...O_2N contacts (Cl...O, 2.83 Å) are also observed. In the crystal structure, molecules **9** are linked together by these contacts to form chains. In turn, the character of

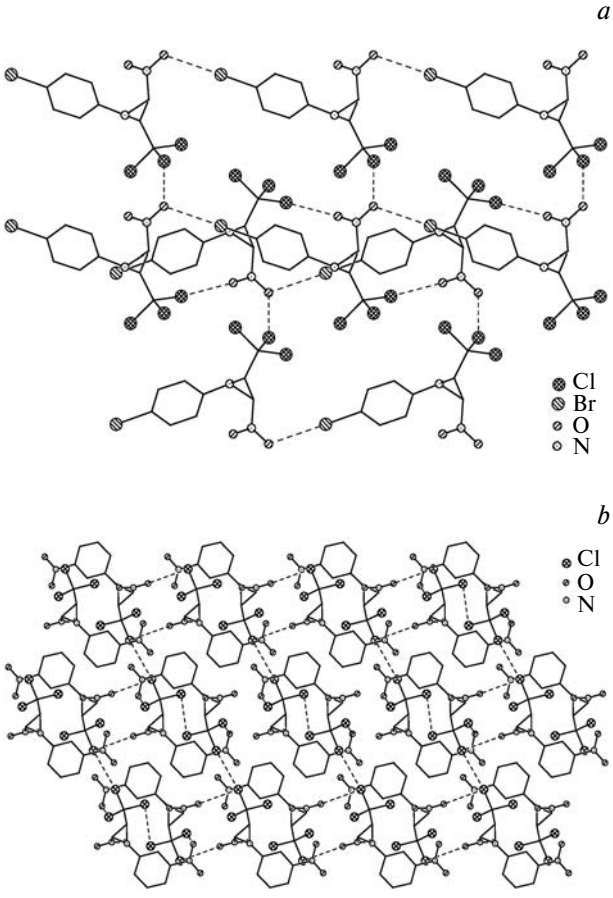

Fig. 5. Fragments of the layers in the crystal structures of compounds **11** (*a*) and **12** (*b*).

the crystal packing changes in the presence of the *meta*-nitrophenyl substituent at the aziridine fragment. In the crystal of **12**, the molecules form layers through Cl...NO_2 and Cl...Cl interactions (Cl...Cl, 3.271(3)—3.444(3) Å) (see Fig. 5, *b*), and the layers are linked only by weak C—H...Cl contacts.

Therefore, the contribution of the X...O_2N interactions (X = Cl or Br) to the stability of the crystals of 1-aryl-2-nitro-3-trichloromethylaziridines is relatively high. Hence, it can be concluded that it is these contacts that determine the preferable crystal packing of the compounds under consideration.

In the crystal structure of **13**, both Cl...O contacts and NO_2...NO_2 interactions are observed. Thus, the O(2B) atom forms a shortened contact with the NO_2 group of **13C** (O(2B)...N(2C), 2.794(5) Å; N(2B)—O(2B)—N(2C), 164.2(2)°), which corresponds to the interaction between the oxygen lone pair and the antibonding orbital of the nitro group.

To study in more detail the nature of intermolecular interactions and the influence of these interactions on the charge distribution, we studied the electron density distribution in the crystal structure of **10** based on high-resolution X-ray diffraction data (Fig. 6). The static function $\rho(\mathbf{r})$ was determined by the multipole refinement (see the Experimental section).

As in the isolated molecule, in the crystal of **10** there is the intramolecular C(10)—H(10)...Cl(3) contact with $\rho(\mathbf{r})$ at CP (3,−1) equal to 0.04 eÅ^{-3} and the energy of the contact E_{cont} equal to 0.72 kcal mol^{-1}. Therefore, even the presence of intermolecular interaction has virtually no effect on this intramolecular contact.

It should be expected that the banana bonds in the three-membered ring would be distorted compared to single covalent bonds in unconjugated structures. Indeed, the maximum in the deformation electron density map for the aziridine ring (Fig. 7) deviates from the bond line. Moreover, an analysis of the topological parameters at CP (3,−1) for the bonds of the aziridine ring showed that they are characterized by unusually high degrees of ellipticity (from 0.64 for the N(1)—C(3) bond to 1.31 for the C(2)—C(3) bond), which is characteristic of banana bonds, π bonds, and three-membered rings in carboranes.[19] An analysis of the bond paths in the aziridine ring in both the crystal and the isolated molecule showed that, unlike cyclopropanes, the deviation of the bond path from the line between the nuclei of the atoms is small and has the maximum value (0.02 Å) for the N(1)—C(2) bond in the crystal.

Based on the deformation electron density distribution in the corresponding planes, it can be concluded that, depending on the geometry of the interaction (to be more precise on the angle at the chlroine atom), the character of Cl...NO_2 interactions can be interpreted as either the transfer of the chlorine lone pair to the antibonding

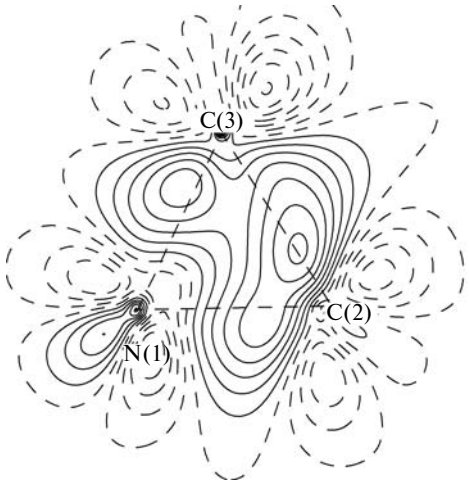

Fig. 6. Deformation electron density map in the plane of the aziridine ring in the crystal structure of **10** contoured at 0.05 eÅ^{-3} intervals; dashed lines indicate the negative values and the zero contour.

orbital of the N—O bond (see Fig. 7, *a*) or the back donation from the oxygen atom to the C—Cl σ*-bond (see Fig. 7, *b*). In this case, such interaction will lead to a substantial charge redistribution predominantly at the chlorine atoms and the NO_2 group compared to the isolated molecule.

Indeed, the ratio of the charges on the chlorine atoms of the CCl_3 group in the crystal structure differs from that

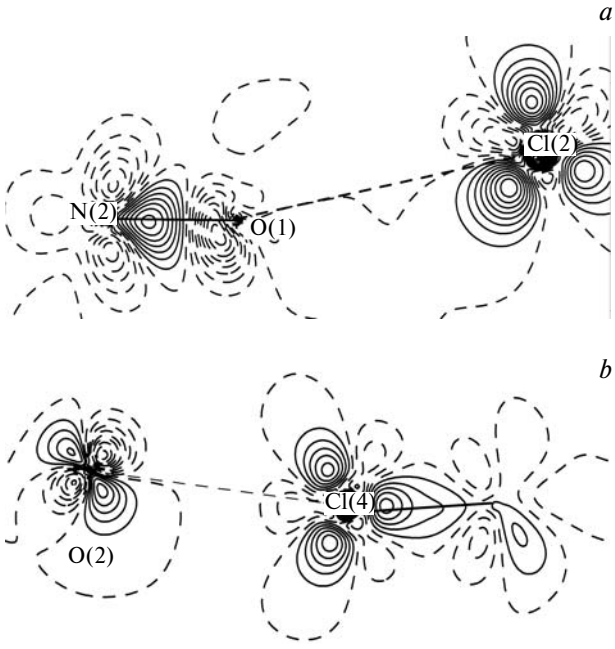

Fig. 7. Deformation electron density distribution in the region of the O(1)...Cl(2) (*a*) and O(2)...Cl(4) (*b*) contacts in the crystal structure of **10** contoured at 0.1 eÅ^{-3} intervals; dashed lines indicate the negative values and the zero contour.

Table 5. Topological parameters* at the critical points (3,−1) for Cl...O_2N interactions in the crystal structure of **10**

Interaction	Symmetry operation	d/Å	$\rho(\mathbf{r})$ /eÅ^{-3}	$\nabla^2\rho(\mathbf{r})$ /eÅ^{-5}	$V(\mathbf{r})$ /a.u.	E_{cont} /kcal mol^{-1}
Cl(2)—O(1)	$2-x, 1-y, -1/2+z$	2.964(1)	0.08	1.13	−0.00716	2.2
Cl(1)—O(2)	$3/2+x, -1/2-y, z$	3.306(1)	0.04	0.56	−0.00292	0.9
Cl(1)—O(1)	$x-1, y, z$	3.408(1)	0.03	0.48	−0.00240	0.8
Cl(1)—O(2)	$x-1, y, z$	3.209(1)	0.05	0.69	−0.00382	1.2
Cl(4)—O(2)	$x, y, z+1$	3.044(1)	0.06	0.85	−0.00505	1.6

* $\nabla^2\rho(\mathbf{r})$ is the Laplacian of the electron density, $V(\mathbf{r})$ is the potential energy density, and E_{cont} is the energy of intermolecular interactions calculated in terms of the Espinosa correlation scheme.

observed in the isolated molecule. Thus, the absolute values of the charges on the Cl(1) (−0.35 e) and Cl(2) (−0.38 e) atoms are substantially higher than the charge on the Cl(3) atom (−0.26 e).

An analysis of the experimental electron density distribution function $\rho(\mathbf{r})$ revealed the presence of the bond critical points (3,−1) for all Cl...O_2N contacts, whose lengths are smaller than the sums of the van der Waals radii of the corresponding atoms, and also for two other Cl...O_2N contacts, whose lengths are only slightly larger than the sum of the van der Waals radii of the Cl and O atoms (Table 5). The positive values of the Laplacian and $h(\mathbf{r})$ at these points indicate that the Cl...O_2N interactions correspond to the closed shells. According to the estimates of the strength of intermolecular contacts in terms of the Espinosa correlation scheme,[16,17] the energies of interactions between the trichloromethyl group and the nitro groups characterized by the Cl...O distances smaller than the sum of the van der Waals radii (Cl(2)...O(1) and Cl(1)...O(2)) are 2.2 and 1.2 kcal mol^{-1}, respectively, which suggests that these interactions play a structure-forming role in the crystal of compound **10**. The Cl...O_2N interaction involving the Cl(4) atom bound to the benzene ring has a comparable energy (1.58 kcal mol^{-1}). It should be noted that of the three chlorine atoms of the CCl_3 group, only the Cl(1) and Cl(2) atoms are linked to the NO_2 groups by intermolecular interactions. As can be seen from Table 5, the total energy of the interactions is comparable and is 2.87 and 2.25 kcal mol^{-1}, respectively. On the contrary, the Cl(3) atom is not involved in the above-mentioned interactions, which is apparently responsible for such a substantial difference of its charge in the crystal.

To sum up, we developed the preparative procedure for the synthesis of 1-aryl-2-nitro-3-trichloromethylaziridines. The structures of these compounds were confirmed by IR, UV, and ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and X-ray diffraction. The X-ray diffraction studies, including the analysis of the electron density distribution in the crystals, and quantum chemical calculations for the molecules in the gas phase revealed the factors stabilizing the observed mutual arrangement of the substituents at the aziridine ring and gave estimates for the stereoelectronic interactions between the banana bond and the σ*(C—Cl) bond and the influence of the crystal packing on the character of charge distribution in the molecules.

Experimental

The IR spectra were recorded on an InfraLyum FT-02 Fourier-transform spectrometer in chloroform (c 0.1—0.001 mol L^{-1}). The electronic absorption spectra were measured in ethanol on a Shimadzu UV2401PC spectrophotometer in quartz cells (l 0.1 cm, c 0.00037—0.00046 mol L^{-1}). The ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-400, Bruker AC-200, and Jeol JNM-ECX400A spectrometers operating at 400.13 MHz (^{1}H), 50.323 MHz (^{13}C) and 399.78 MHz (^{1}H), 100.525 MHz (^{13}C) in $CDCl_3$ and DMSO-d_6 with the use of the residual signal of the nondeuterated solvent as the internal standard. The chemical shifts were measured with an accuracy of ±0.5 Hz on the δ scale. The mass spectra were obtained on a MX 1321 mass spectrometer using a direct inlet system; the ionization voltage was 70 V; the temperature of the ionization chamber was 180 °C.

Crystals of compounds **9**—**13** suitable for the X-ray diffraction study were grown from diethyl ether.

The X-ray diffraction study of compounds **8**—**13** was carried out on a SMART APEX II CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning technique). The structures were solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F^2_{hkl}. An analysis of the temperature factors and difference Fourier maps revealed a superposition of two mirror-symmetric isomers in the crystals of **9**, such that the CCl_3 group and the C(9)—C(10) and C(2)—C(3) bonds are common. The reciprocal space analysis revealed no twinning. In turn, the structure refinement in the monoclinic system on the assumption that the orthorhombic system is determined by the systematic twinning did not eliminate the disorder (BASF 0.0) as well. Based on this fact, the final structure refinement was carried out in the space group $Pna2_1$ and some atoms were refined isotropically. The hydrogen atoms were located in difference Fourier maps and refined isotropically for the structures of **10**—**13** and using a riding model for the structure of **9**. Principal crystallographic data and the X-ray data collection and structure refinement statistics are given in Table 6. All calculations were carried out using the SHELXTL PLUS program package.[20]

Table 6. Principal crystallographic parameters and the X-ray data collection and refinement statistics for compounds **9**—**13**

Parameter	**9**	**10**	**11**	**12**	**13**
Molecular formula	$C_{10}H_9Cl_3N_2O_2$	$C_9H_6Cl_4N_2O_2$	$C_9H_6BrCl_3N_2O_2$	$C_9H_6Cl_3N_3O_4$	$C_{13}H_9Cl_3N_2O_2$
Molecular weight	295.54	315.96	360.42	326.52	331.57
T/K	100	100	100	100	100
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	P-1	$P2_1/n$
Z (Z')	4	4	4	2	12 (3)
a/Å	33.404(4)	7.9594(5)	7.9345(7)	8.6497(3)	8.4810(4)
b/Å	6.1528(7)	14.9116(9)	14.9026(14)	8.8089(4)	16.3054(7)
c/Å	6.1514(6)	10.4502(6)	10.5952(9)	9.2167(5)	30.4277(14)
α/deg	90.00	90.00	90.00	106.2612(9)	90.00
β/deg	90.00	90.00	90.00	94.9897(8)	94.3931(9)
γ/deg	90.00	90.00	90.00	107.9308(6)	90.00
V/Å^3	1264.3(2)	1240.31(13)	1252.83(19)	629.79(5)	4195.4(3)
d_{calc}/g cm^{-3}	1.553	1.692	1.911	1.722	1.575
μ/cm^{-1}	7.15	9.43	39.1	7.40	6.56
F(000)	600	632	704	328	2016
$2\theta_{max}$/deg	54	110	60	65	58
Number of measured reflections	12818	69669	10708	29098	50692
Number of independent reflections	2840	15539	3583	4555	11146
Number of reflections with $I > 2\sigma(I)$	1978	13537	3357	3953	9383
Number of refined parameters	146	179	155	196	542
R_1	0.0594	0.0269	0.0204	0.0286	0.0338
wR_2	0.1327	0.0672	0.0491	0.0711	0.0788
GOOF	1.025	1.016	0.874	1.000	1.034
Residual electron density/eÅ^{-3} (d_{max}/d_{min})	0.550/−0.452	0.747/−0.466	0.278/−0.380	0.593/−0.308	0.556/−0.373

The multipole refinement of compound **10** was carried out in terms of the Hansen—Coppens model[21] with the use of the XD program package.[22] Before the refinement, all C—H distances were normalized to the ideal distance determined by neutron diffraction (1.08 Å).[23] The refinement was performed based on F_{hkl}; the final R factors were R = 0.0194, Rw = 0.0202, GOOF = 0.9227 for 6386 reflections with $I > 2\sigma(I)$. The validity of the refinement was checked from the difference ($\Delta < 0.001$ Å^2) between the mean-square vibration amplitudes for bonded atoms (Hirshfeld rigid-bond test). The topological analysis of the experimental electron density distribution function was carried out with the use of the WinXPRO program package.[24]

The quantum chemical calculations for compound **10** at the B3LYP level of theory were performed using the Gaussian 03 program package.[25] The potential energy surface was scanned along the Cl(1)—C(4)—C(3)—N(1) torsion angle coordinate in the range of 0—360° with a step of 5°. The calculations for compound **10** were performed by the MP2 method with the use of the PC-GAMESS program package.[26] The topological analysis of the wave function was carried out using the AIMAll program package.[27]

The reaction products were purified and separated by recrystallization and column chromatography on Chemapol 100/250 LD silica gel, 100/400 (Czech Republic) with a substance to support weight ratio of 1 : 10 — 1 : 20 using Trappe's eluotropic series of solvents.[28] The course of the reactions was monitored and the individuality of the reaction products was checked by thin-layer chromatography on Silufol UV-254 plates using a hexane—acetone mixture (2 : 1, v/v); the visualization was carried out with iodine vapor and on a chromascope.

The starting 1-bromo-3,3,3-trichloro-1-nitropropene was synthesized according to a known procedure.[6]

***N*-[2-Bromo-2-nitro-1-(trichloromethyl)ethyl]aniline (2).** A solution of freshly distilled aniline (0.323 mL, 0.331 g, 3.55 mmol) in anhydrous methanol (5 mL) was added dropwise to a solution of 1-bromo-3,3,3-trichloro-1-nitropropene (**1**) (0.958 g, 3.55 mmol) in anhydrous methanol (5 mL). The reaction mixture was kept at room temperature for 1 h and then poured into ice crumbs. The resulting emulsion was extracted with diethyl ether (2×30 mL), and the ethereal solution was dried with $MgSO_4$. After removal of the solvent, an oily substance was obtained in a yield of 1.090 g. The substance was chromatographed on a silica gel column. Oily compound **2** was isolated in a yield of 1.00 g (77%), R_f 0.64, from the fractions eluted with hexane and carbon tetrachloride. Found (%): C, 30.08; H, 2.63; N, 7.85. $C_9H_8BrCl_3N_2O_2$. Calculated (%): C, 29.83; H, 2.22; N, 7.73.

***N*-[2-Bromo-2-nitro-1-(trichloromethyl)ethyl]-*p*-toluidine (3)** was synthesized analogously to compound **2** starting from *p*-toluidine (the reaction mixture was kept for 2 h). Oily com-

pound **3** was isolated in 71%, R_f 0.50, from the fraction eluted with *n*-hexane. Found (%): C, 32.03; H, 2.86; N, 7.53. $C_{10}H_{10}BrCl_3N_2O_2$. Calculated (%): C, 31.90; H, 2.68; N, 7.44.

***N*-[2-Bromo-2-nitro-1-(trichloromethyl)ethyl]-4-chloroaniline (4)** was synthesized analogously to compound **2** starting from *p*-chloroaniline (the reaction mixture was kept for 3.5 h). Oily compound **4** was isolated in 67% yield, R_f 0.45, from the fraction eluted with *n*-heptane. Found (%): N, 7.19. $C_9H_7Cl_4BrN_2O_2$. Calculated (%): N, 7.05.

***N*-[2-Bromo-2-nitro-1-(trichloromethyl)ethyl]-4-bromoaniline (5)** was synthesized analogously to compound **2**, starting from *p*-bromoaniline (the reaction mixture was kept for 2 h). Oily compound **5** was isolated in 59% yield, R_f 0.65, from the fraction eluted with *n*-hexane. Found (%): C, 24.87; H, 1.93; N, 6.62. $C_9H_7Br_2Cl_3N_2O_2$. Calculated (%): C, 24.49; H, 1.60; N, 6.35.

***N*-[2-Bromo-2-nitro-1-(trichloromethyl)ethyl]-3-nitroaniline (6)** was synthesized analogously to compound **2** starting from *m*-nitroaniline (the reaction mixture was kept for 2 h). Oily compound **6** was isolated in 52% yield, R_f 0.50, from the fraction eluted with carbon tetrachloride. MS, *m/z*: 407 $[M]^+$.

***N*-[2-Bromo-2-nitro-1-(trichloromethyl)ethyl]-1-naphthylamine (7)** was synthesized analogously to compound **2** starting from 1-naphthylamine (the reaction mixture was kept for 1.5 h). Oily compound **7** was isolated in 46% yield, R_f 0.60, from the fraction eluted with carbon tetrachloride. Found (%): N, 6.73. $C_{13}H_{10}BrCl_3N_2O_2$. Calculated (%): N, 6.79.

2-Nitro-1-phenyl-3-trichloromethylaziridine (8). A hot solution of potassium acetate (0.362 g, 3.69 mmol) was added to a boiling solution of *N*-[2-bromo-2-nitro-1-(trichloromethyl)-ethyl]aniline (**2**) (0.891 g, 2.46 mmol) in ethanol (25 mL). After refluxing for 6 h, the reaction mixture was poured into a beaker with ice crumbs. The resulting emulsion was extracted with diethyl ether (2S30 mL), and the ethereal solution was dried with $MgSO_4$. After removal of the solvent, a dark oily substance was obtained in a yield of 0.546 g. The substance was chromatographed on silica gel. Crystalline compound **8** was isolated in a yield of 0.173 g (25%), m.p. 58—59 °C (from an ethanol—water mixture, 4 : 1), from the fraction eluted with *n*-hexane. Found (%): C, 38.51; H, 2.69; N, 9.86. $C_9H_7Cl_3N_2O_2$. Calculated (%): C, 38.40; H, 2.51; N, 9.95. ^{13}C $\{^1H\}$ NMR ($CDCl_3$), δ: 56.4 ($Cl_3C\underline{C}$), 71.9 ($O_2N\underline{C}$), 94.5 ($Cl_3\underline{C}$), 142.7, 129.8, 125.3, 118.5 (Ar).

2-Nitro-1-(*p*-tolyl)-3-trichloromethylaziridine (9) was synthesized analogously to compound **7** starting from *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]-*p*-toluidine **3** and potassium acetate (the reaction mixture was kept for 2 h). Crystalline compound **9** was isolated in 30% yield, m.p. 86—87 °C (from an ethanol—water mixture, 4 : 3), from the fraction eluted with *n*-hexane. Found (%): C, 40.85; H, 3.36; N, 9.54. $C_{10}H_9Cl_3N_2O_2$. Calculated (%): C, 40.64; H, 3.07; N, 9.47. MS, *m/z*: 294 $[M]^+$. ^{13}C $\{^1H\}$ NMR ($CDCl_3$), δ: 20.8 ($\underline{C}H_3$) 56.4 ($Cl_3C\underline{C}$), 72.0 ($O_2N\underline{C}$), 94.5 ($Cl_3\underline{C}$), 140.2, 135.0, 130.3, 118.3 (Ar).

2-Nitro-1-(*p*-chlorophenyl)-3-trichloromethylaziridine (10) was synthesized analogously to compound **8** starting from *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]-4-chloroaniline **4** and potassium acetate (the reaction mixture was kept for 4 h). Crystalline compound **10** was isolated in 37% yield, m.p. 69—71 °C (from an ethanol—water mixture, 3 : 1), from the fraction eluted with *n*-hexane. Found (%): C, 34.80; H, 2.05; N, 8.95. $C_9H_6Cl_4N_2O_2$. Calculated (%): C, 34.58; H, 1.90; N, 8.86.

1-(*p*-Bromophenyl)-2-nitro-3-trichloromethylaziridine (11) was synthesized analogously to compound **8** starting from *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]-4-bromoaniline **5** and potassium acetate (the reaction mixture was kept for 4 h). Crystalline compound **11** was isolated in 36% yield, m.p. 106—107 °C (from petroleum ether), from the fraction eluted with *n*-hexane. Found (%): C, 30.19; H, 2.06; N, 7.88. $C_9H_6BrCl_3N_2O_2$. Calculated (%): C, 29.99; H, 1.68; N, 7.77. MS, *m/z*: 360 $[M]^+$. ^{13}C NMR ($CDCl_3$), δ: 55.8 (d, $Cl_3C\underline{C}H$, J = 182.3 Hz), 71.2 (d, $O_2N\underline{C}H$, J = 220.5 Hz), 93.7 ($Cl_3\underline{C}$), 141.3, 132.3 (d, J = 167.8 Hz), 119.6 (d, J = 160.4 Hz), 117.7 (Ar). ^1H NMR (DMSO-d_6), δ: 4.92 (d, 1 H, $CHCCl_3$, $^{1,3}J$ = 0.9); 6.03 (d, 1 H, O_2NCH, $^{1,3}J$ = 0.9 Hz); 7.52 and 7.08 (both d, 2 H each, Ar). ^{13}C $\{^1H\}$ NMR ($CDCl_3$), δ: 55.8 ($Cl_3C\underline{C}$), 71.2 ($O_2N\underline{C}$), 93.7 ($Cl_3\underline{C}$), 141.3, 132.3, 119.6, 117.7 (Ar).

2-Nitro-1-(*m*-nitrophenyl)-3-trichloromethylaziridine (12) was synthesized analogously to compound **8** starting from *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]-3-nitroaniline **6** and potassium acetate (the reaction mixture was kept for 4.5 h). Crystalline compound **12** was isolated in 19% yield, m.p. 82—84 °C (from petroleum ether), from the fraction eluted with carbon tetrachloride. MS, *m/z*: 327 $[M]^+$. ^{13}C $\{^1H\}$ NMR ($CDCl_3$), δ: 56.4 ($Cl_3C\underline{C}$), 71.4 ($O_2N\underline{C}$), 93.7 ($Cl_3\underline{C}$), 149.6, 144.0, 130.8, 124.4, 120.1, 113.8 (Ar).

1-Naphthyl-2-nitro-3-trichloromethylaziridine (13) was synthesized analogously to compound **8** starting from *N*-[2-bromo-2-nitro-1-(trichloromethyl)ethyl]-1-naphthylamine **7** and potassium acetate (the reaction mixture was kept for 5 h). Crystalline compound **13** was isolated in 27% yield, m.p. 116—117 °C (from an ethanol—water mixture, 2 : 1), from the fraction eluted with *n*-hexane. Found (%): N, 8.42. $C_{13}H_9Cl_3N_2O_2$. Calculated (%): N, 8.45.

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