Molecular and crystal structures of 5,7-dichloro-4-nitro-2,1,3-benzoxadiazole and products of its reactions with secondary amines

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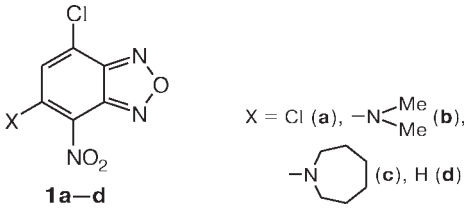
The molecular and crystal structures of 5,7-dichloro-4-nitro-2,1,3-benzoxadiazole and products of its reactions with hexamethyleneimine and dimethylamine were established by X-ray diffraction analysis. The molecular structures and the systems of hydrogen bonds in the crystals of these compounds are discussed.

Key words: 5,7-dichloro-4-nitro-2,1,3-benzoxadiazole, 7-chloro-5-dimethylamino-4-nitro-2,1,3-benzoxadiazole, 7-chloro-5-hexamethyleneimino-4-nitro-2,1,3-benzoxadiazole.

5,7-Dichloro-4-nitro-2,1,3-benzoxadiazole (**1a**) is a poorly studied electrophile. The only data on the relative mobilities of the chlorine atoms were obtained when using compound **1a** in the synthesis of a 5-azido-7-chloro-4-nitro derivative.[1] We found that both chlorine atoms in **1a** can be replaced in its reactions with amines. Depending on the reaction conditions, compounds containing either identical or different fragments of aromatic or aliphatic amines at positions 5 and 7 can be synthesized. It is reasonable that the replacement of the chlorine atom at position 5 by an arylamino or alkylamino group leads to a decrease in mobility of the intact chlorine atom. The introduction of alkylamino or dialkylamino groups possessing strong donor properties has the most pronounced effect on the mobility of the Cl atom and, what is very important, this effect is different in different cases. For example, the reaction of 5-dimethylamino-substituted compound **1b** with piperazine hexahydrate (DMF, ~20 °C, two equivalents of the nucleophile) was completed in 75 min, whereas the reactions of related 5-X-substituted derivatives (where X is diethylamino, piperidino, morpholino, or hexamethyleneimino groups) performed under the same conditions were completed in ~360 min. The duration of the reaction was determined by TLC from the disappearance of the starting compound in the reaction mixture.

The present study was aimed at revealing the reasons for the above-mentioned changes based on the three-dimensional molecular structures of compound **1a** and the newly synthesized 7-chloro-5-dimethylamino-4-nitro-2,1,3-benzoxadiazole (**1b**) and 7-chloro-5-hexamethyleneimino-4-nitro-2,1,3-benzoxadiazole (**1c**), which are products of the reactions of **1a** with dimethylamine and hexamethyleneimine, respectively.



1a—d

Results and Discussion

The structures of compounds **1a—c** were established by X-ray diffraction analysis, which allowed us to reveal the order in which the chlorine atoms in substrate **1a** are replaced. It is a matter of common knowledge that the nitro group in aromatic and heterocyclic systems located in the *ortho* or *para* position with respect to the halogen atom activates the latter. The most pronounced effect is generally accounted for by the virtually planar arrangement of the nitrophenyl fragment.

To our knowledge, the structures of about two tens of 2,1,3-benzoxadiazole derivatives were established by X-ray diffraction analysis among which only 7-chloro-4-nitro-2,1,3-benzoxadiazole (**1d**)[2] is similar to the compounds under study in the type of replacement. Under the conditions described, the reaction of electrophile **1d**,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 101—106, January, 2002.

1066-5285/02/5101-105 $27.00

whose nitro group is virtually coplanar with the benzene fragment, with piperazine hexahydrate was completed in 20 min.

Let us consider the molecular structures of compounds **1a—c** and compare them with the data for compound **1d**. There is one molecule per asymmetric unit in the crystal structures of **1a—c**. The molecular structures of **1a—c** in the crystals are shown in Fig. 1. The bond length, bond angles, and torsion angles in compounds **1a—c** are typical of 2,1,3-benzoxadiazoles[2–6] (Tables 1—3). In compounds **1a—c**, the oxadiazole ring together with the fused benzene ring comprise the nine-membered fragment (the maximum deviations of the atoms from the mean plane of this fragment are 0.017(3), 0.073(3), and 0.070(3) Å, re-

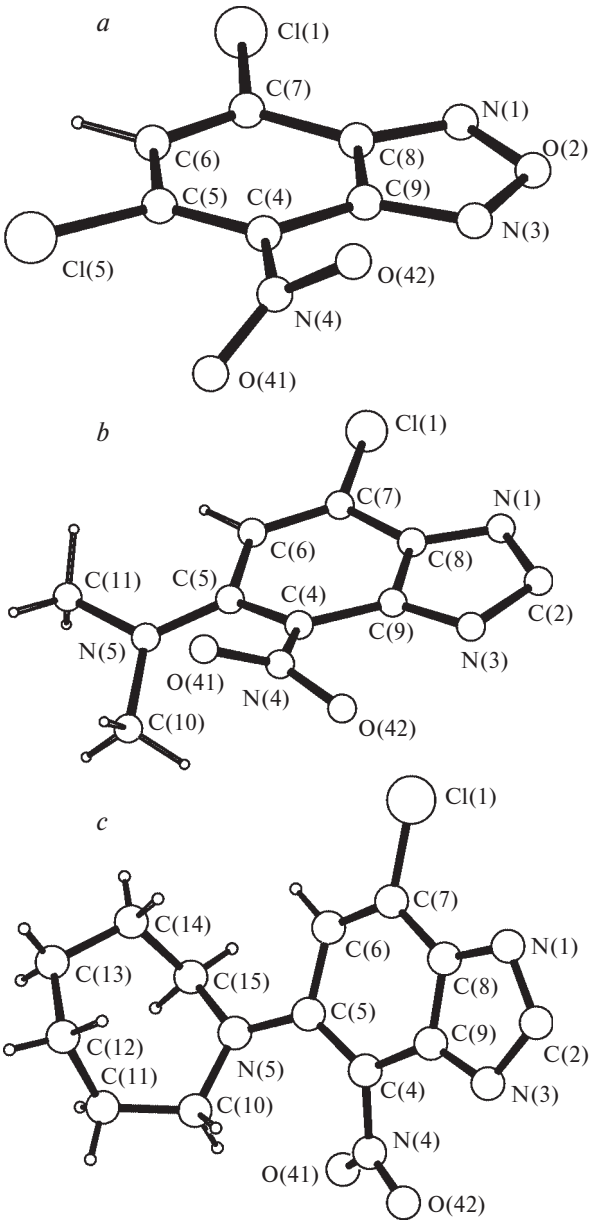


Fig. 1. Molecular structures of 5,7-dichloro-4-nitro-2,1,3-benzoxadiazole (**1a**) (*a*), 7-chloro-5-dimethylamino-4-nitro-2,1,3-benzoxadiazole (**1b**) (*b*), and 7-chloro-5-hexamethyleneimino-4-nitro-2,1,3-benzoxadiazole (**1c**) (*c*) in the crystals.

Table 1. Selected bond lengths (*d*) in compounds **1a—c**

Bond	*d*/Å		
	1a	**1b**	**1c**
Cl(1)—C(7)	1.705(4)	1.718(3)	1.719(3)
O(41)—N(4)	1.211(4)	1.247(3)	1.242(3)
O(42)—N(4)	1.224(3)	1.241(3)	1.229(3)
O(2)—N(1)	1.369(4)	1.374(4)	1.378(4)
O(2)—N(3)	1.383(4)	1.404(3)	1.402(3)
N(1)—C(8)	1.310(4)	1.307(3)	1.295(4)
N(3)—C(9)	1.316(4)	1.315(4)	1.318(4)
N(4)—C(4)	1.464(4)	1.412(4)	1.429(4)
N(5)—C(5)	—	1.338(3)	1.388(3)
N(5)—C(10)	—	1.455(4)	1.481(4)
N(5)—C(11)(C(15))	—	1.471(4)	1.467(4)
C(8)—C(7)	1.422(4)	1.422(4)	1.439(4)
C(8)—C(9)	1.422(5)	1.418(4)	1.429(4)
C(6)—C(7)	1.337(5)	1.348(3)	1.335(4)
C(6)—C(5)	1.429(5)	1.462(4)	1.474(4)
C(5)—C(4)	1.363(4)	1.400(4)	1.410(4)
C(4)—C(9)	1.404(5)	1.426(3)	1.422(4)
C(6)—H(6)	0.94(3)	0.96(3)	0.97(3)

Table 2. Selected bond angles (ω) in compounds **1a—c**

Angle	ω/deg		
	1a	**1b**	**1c**
N(1)—O(2)—N(3)	112.9(2)	112.2(2)	112.3(2)
O(41)—N(4)—O(42)	124.1(3)	121.8(2)	122.6(3)
O(41)—N(4)—C(4)	120.0(2)	119.5(2)	119.0(2)
O(42)—N(4)—C(4)	115.9(3)	118.6(2)	118.3(2)
O(2)—N(1)—C(8)	104.4(3)	104.0(2)	104.1(2)
O(2)—N(3)—C(9)	103.9(3)	104.2(2)	104.1(2)
N(1)—C(8)—C(7)	130.0(3)	128.1(3)	129.5(3)
N(1)—C(8)—C(9)	109.5(3)	110.9(3)	111.1(2)
C(7)—C(6)—C(5)	122.2(2)	121.9(3)	122.6(2)
Cl(1)—C(7)—C(8)	119.1(3)	119.3(2)	117.9(2)
Cl(1)—C(7)—C(6)	123.0(3)	121.0(2)	122.4(2)
C(8)—C(7)—C(6)	117.9(2)	118.8(2)	119.7(3)
C(7)—C(8)—C(9)	120.5(3)	121.0(2)	119.4(2)
C(6)—C(5)—C(4)	120.9(3)	118.7(2)	117.5(2)
C(5)—C(4)—C(9)	118.6(3)	118.7(2)	119.5(2)
C(7)—C(6)—H(6)	121.0(2)	118.0(1)	119.0(2)
C(5)—C(6)—H(6)	116.0(2)	120.0(1)	118.0(2)
N(3)—C(9)—C(8)	109.3(3)	108.7(2)	108.3(2)
N(3)—C(9)—C(4)	130.8(3)	131.8(3)	131.3(3)
C(8)—C(9)—C(4)	119.9(3)	119.5(3)	120.4(2)
N(4)—C(4)—C(5)	122.8(3)	123.2(2)	123.1(2)
N(4)—C(4)—C(9)	118.7(2)	117.9(3)	116.4(2)
C(5)—N(5)—C(5)	—	120.8(2)	121.6(2)
C(5)—N(5)—C(10)	—	121.0(2)	123.5(2)
C(5)—N(5)—C(11)(C(15))	—	118.2(2)	114.6(2)

Table 3. Selected torsion angles (φ) in compounds **1a—c**

Angle	φ/deg		
	1a	**1b**	**1c**
N(1)—O(2)—N(3)—C(9)	−0.7(3)	1.1(4)	0.8(4)
C(5)—C(4)—N(4)—O(41)	41.4(5)	−24.6(4)	23.4(5)
C(5)—C(4)—N(4)—O(42)	−140.7(3)	159.5(3)	−160.2(3)
C(9)—C(4)—N(4)—O(41)	−139.0(3)	149.2(3)	−145.2(3)
C(9)—C(4)—N(4)—O(42)	38.9(4)	−26.7(4)	31.2(5)
N(4)—C(4)—C(5)—C(6)	177.9(3)	159.3(3)	−157.1(3)
C(9)—C(4)—C(5)—C(6)	−1.7(5)	−14.5(4)	11.1(4)
N(4)—C(4)—C(5)— N(5)	—	−26.0(5)	28.9(5)
N(4)—C(4)—C(9)—N(3)	2.4(5)	15.1(5)	−15.9(5)
N(4)—C(4)—C(9)—C(8)	−178.4(3)	−163.6(3)	162.4(3)
C(4)—C(5)—N(5)—C(10)	—	−21.8(5)	20.8(5)
C(4)—C(5)—N(5)—C(11)	—	165.5(3)	−160.3(3)
C(4)—C(5)—N(5)—C(15)	—	165.5(3)	−160.3(3)
C(6)—C(5)—N(5)—C(10)	—	152.9(3)	−153.1(3)
C(6)—C(5)—N(5)—C(11)	—	−19.8(5)	25.8(4)
C(6)—C(5)—N(5)—C(15)	—	−19.8(5)	25.8(4)
N(1)—C(8)—C(9)—N(3)	0.4(4)	−0.4(4)	0.3(3)
Cl(1)—C(7)—C(8)—C(9)	177.9(3)	179.1(3)	−178.9(2)

spectively); the five- and six-membered rings are approximately coplanar (the dihedral angles between the rings are 1.1(2)°, 0.9(2)°, and 3.0(1)°, respectively). Compared to compound **1d**, compound **1a** contains the additional chlorine atom in the *ortho* position with respect to the nitro group giving rise to steric hindrances due to which the nitro group is rotated about the C(4)—N(4) bond by 40.2(2)°. The atoms of the substituents directly bound to the benzene fragment are located in the plane of this ring. The maximum deviations of the Cl(1), Cl(5), and N(4) atoms from this plane are 0.059(1), 0.032(1), and 0.050(3) Å, respectively.

In compounds **1b** and **1c** (see Fig. 1, *b* and *c*), the chlorine atom at position 5 is replaced by the residues of secondary amines, with a consequent increase in steric hindrances. In these compounds, the rotation of the nitro group about the C(4)—N(4) bond is somewhat smaller (32.5(3)° and −31.0(4)°, respectively), but the N(4) and N(5) atoms deviate substantially from the plane of the ring in opposite directions (by −0.455(3) and 0.348(3) Å, respectively, in **1b**; and by −0.431(3) and 0.379(3) Å, respectively, in **1c**). The direction of rotation of the nitro group about the C(4)—N(4) bond in molecule **1b** differs from that in compounds **1a** and **1c**, whereas the direction of rotation of the dialkylamino groups in molecule **1b** is identical with than in **1c**. The Cl(1) atom in **1b** deviates from the plane of the benzene fragment by −0.046(3) Å, whereas the Cl(1) atom in **1c** is located in the plane of this ring. The dihedral angles between the plane of the benzene ring and the planes of the dimethylamino [N(5)C(10)C(11)] and hexamethyleneimino [C(5)N(10)C(15)] fragments are 27.8(3)°. In spite of this fact, the sums of the bond angles at the N(5) atom in compounds **1b** and **1c** are close to 360° and the degree of the pyramidality of N(5) is equal to zero, which is indicative of essential interactions between the lone electron pairs and the π-system of the benzoxadiazole fragment.

From a comparison of the structures of compound **1b** and *N,N*-dimethyl-2,4-dinitroaniline (φ_{NO_2} = 32°, φ_{NMe_2} = 14.4°),[7] it can be concluded that the fused oxadiazole ring produces insignificant steric hindrances to the nitro group. This is also evidenced by the angle φ_{NO_2} = 1.7° in molecule **1d**.[2] Interestingly, the presence of the dimethylamino or hexamethyleneimino fragment (in compounds **1b** and **1c**, respectively) adjacent to the nitro group leads to elongation of the C(4)—C(5) bond, which approaches the length of the single bond, whereas the C(6)—C(7) bond remains virtually unchanged. This is also typical of 4-*R*-5,7-dinitro-2,1,3-benzoxadiazoles bearing a substituent at position 4 adjacent to the nitro group.[4,5] Compound **1d** has the longest C(6)—C(5) bond in the benzoxadiazole system. It should be noted that this bond length remains unchanged (to within the experimental error) after introduction of the chlorine atom at position 5 (*cf.* the corresponding bond in **1a**), whereas the presence of the donor substituents leads to its elongation by 0.03—0.04 Å (**1b** and **1c**).

The molecules of the compounds under study are not involved in hydrogen bonding of the classical type. In molecule **1a**, there are also no interactions of the C—H...O or C—H...Cl type. Apparently, the crystal packing of molecules **1a** is to a large extent determined by π-π electron interactions between the benzoxadiazole systems. As a result, the molecules are packed in tilted stacks along the crystallographic axis 0*y*. In these stacks, the adjacent molecules are arranged in a head-to-tail fashion. The occurrence of the stacking effect is evidenced by the following parameters: the distances between the planes of the initial molecule **1a** and two adjacent molecules generated from the initial molecule by the symmetry operations (−*x*, 1 − *y*, −*z*) and (−*x*, 2 − *y*, −*z*) are 3.463 and 2.934 Å, respectively. The dihedral angle between the planes of the molecules is equal to zero.

The intermolecular D—H...A contacts (D and A are the donor and acceptor, respectively) were analyzed based on the standard criteria for hydrogen bonding (d(D...A) < R(D) + R(A) + 0.50 Å, d(H...A) < R(H) + R(A) − 0.12 Å, the D—H...A angle is larger than 100.0°, where R are the van der Waals radii of the atoms) with the use of the PLATON program,[9] which revealed the presence of hydrogen bonds in the crystal structures of compounds **1b** and **1c** (Table 4). In these crystal structures, intra- and intermolecular C—H...O hydrogen bonds are observed, which formally satisfy the above-mentioned criteria. In the crystals of both compounds, the molecules are linked in dimers, but their mutual arrangements are substantially different.

Table 4. Parameters of hydrogen bonds in compounds **1b** and **1c**

Compound	Bond type[a]	Triad DH...A	H...A	D...A	D—H—A angle /deg
			Å		
1b	InterHB[b]	C(6)—H(6)...O(41)	2.34(3)	3.237(4)	156(2)
	IntraHB	C(10)—H(101...)...O(42)	2.16(3)	2.714(4)	110.6(2)
	InterHB[c]	C(11)—H(111)...O(42)	2.56(3)	3.555(4)	173(2)
1c	InterHB[d]	C(6)—H(6...)...O(41)	2.36(3)	3.260(3)	155(2)
	IntraHB	C(10)—H(101)...O(41)	2.09(3)	2.776(5)	119.9(2)
	InterHB[c]	C(12)—H(121)...O(2)	2.56(2)	3.577(4)	160(2)

[a] IntraHB and InterHB are intra- and intermolecular hydrogen bonds, respectively. The molecules are related by the following symmetry operations:
[b] $1/2 - x$, $1/2 + y$, $-z$;
[c] $-x$, $1 - y$, $-z$;
[d] $-1/2 - x$, $1/2 + y$, $1/2 - z$.

In the crystal of compound **1b**, the molecules are linked in dimers *via* two hydrogen bonds between the corresponding O(42) atoms of the nitro groups and the H(111) atoms of the methyl groups of two molecules related by a center of symmetry. It should be noted that the O(42) atom is involved also in an intramolecular contact with the methyl H(101) atom. These dimers are linked in infinite planar layers through intermolecular contacts between the H(6) proton of the benzene ring of molecule **1b** and the O(41′) atom of the nitro group of the symmetrically related molecule ($1/2 - x$, $1/2 + y$, $1/2 - z$). As a result, the crystal packing can be described as the parallel arrangement of the infinite planar layers along the crystallographic axis $0z$ (Fig. 2).

A somewhat different situation is observed in the case of compound **1c**. In the crystal of the latter, the molecules are linked in centrosymmetrical dimers through pairs of interactions between the O(2) atoms and the methylene

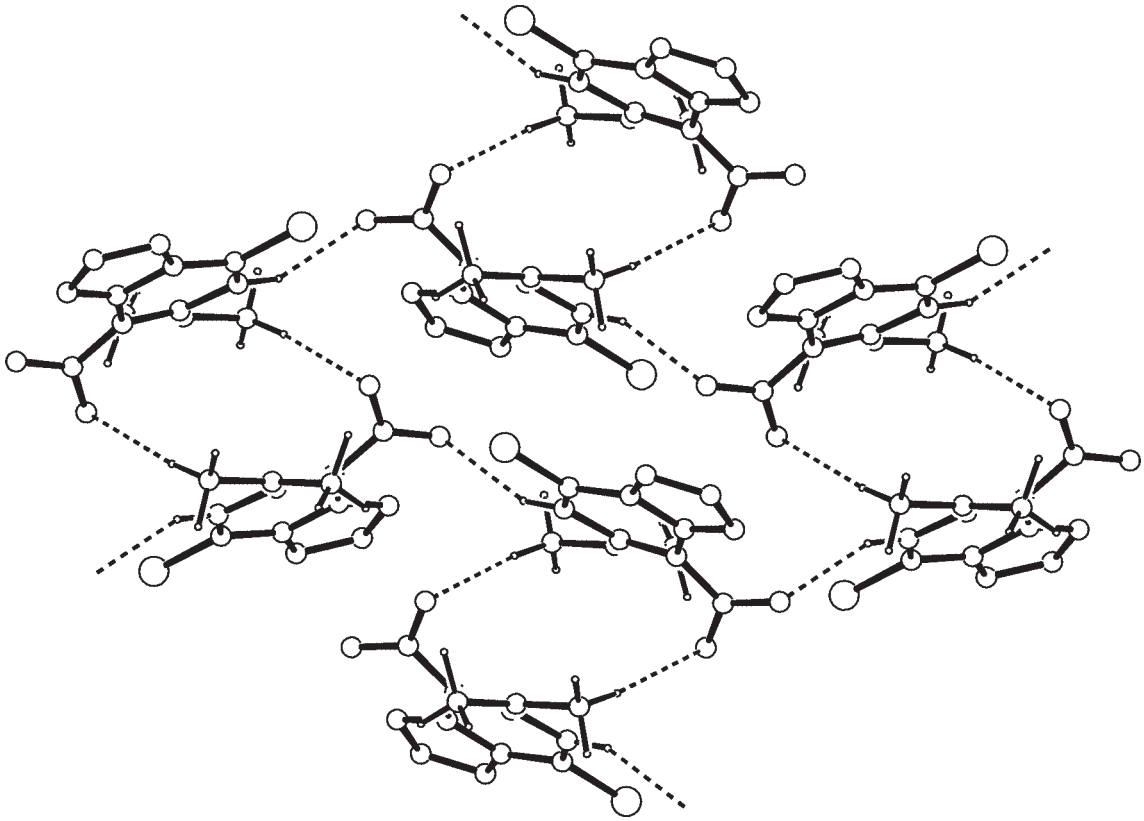


Fig. 2. Formation of infinite planar layers of the hydrogen-bonded molecules in the crystal of **1b**. The intermolecular hydrogen bonds are indicated by dashed lines. The projection along the crystallographic axis $0z$.

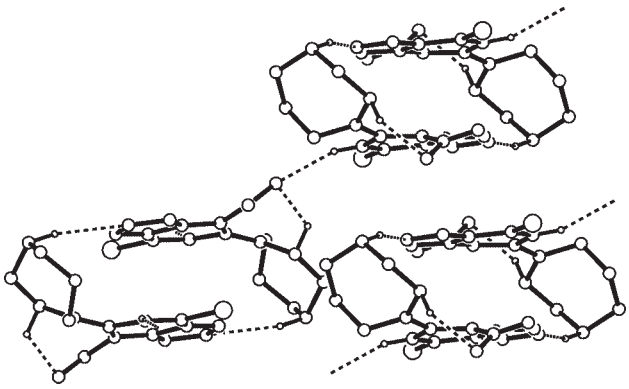


Fig. 3. Fragment of the stacks formed by molecular dimers in the crystal of **1c**. Only protons involved in hydrogen bonding (dashed lines) are shown. The projection along the crystallographic axis 0*y*.

H(121) atoms, which is favored by the inclined arrangement of the seven-membered ring (adopting a twist-chair conformation) with respect to the plane of the benzene ring (the dihedral angle is 57.7(2)°) (Fig. 3). The O(41) atom of the nitro group is involved both in inter- and intramolecular contacts. In **1c**, the intramolecular hydrogen bond is formed by the methylene H(101) atom and the O(41) atom. In the crystal of **1c**, the O(41) atom of the nitro group and the H(6) atom of the phenyl ring of each molecule are involved in hydrogen bonding with the corresponding atoms of the adjacent symmetrically related molecules (each molecule is involved in two intermolecular interactions as the donor and acceptor) to link dimers in an infinite three-dimensional framework of the hydrogen-bonded molecules. In addition to the hydrogen bonds, strong π-π interactions between the benzoxadiazole electron systems make a substantial contribution to the molecular packing in the crystal resulting in the formation of the molecular stacks along the crystallographic axis 0*x*. Both molecules in the hydrogen-bonded dimers are involved in such interactions either with each other or with the adjacent molecules in the stacks. The distance between the planes of the molecules in the dimer is 3.291 Å and the dihedral angle is 0°. The distance between one molecule of the dimer and the adjacent molecule in the stack (the symmetry operation $-1 - x$, $1 - y$, $-z$) is 3.207 Å and the dihedral angle is 0.93°. The supramolecular structure in the crystal of **1c** can be described as a system of hydrogen-bonded molecular stacks.

Hence, the presence of a substituent at position 5 (independently of its nature) leads to changes only in the adjacent positions. The other geometric parameters of the molecules (see Tables 1—3) remain unchanged. Consequently, molecules **1a—c** as a whole adopt virtually identical conformations. Hence, the observed difference in the reactivity of compounds **1b** and **1c** cannot be explained from the viewpoint of their three-dimensional structures. Apparently, these differences were to be looked for in the characteristic features of solvation of the mol-

Table 5. Crystallographic characteristics of compounds **1a—c** and details of X-ray diffraction studies

Parameter	**1a**	**1b**	**1c**
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$	$P2_1/n$
a/Å	8.782(2)	8.669(3)	6.683(3)
b/Å	7.1474(8)	13.951(3)	13.255(5)
c/Å	13.778(3)	9.203(2)	14.691(5)
β/deg	105.47(2)	117.87	94.07(3)
V/Å^3	834.1(3)	983.9(5)	1297.7(9)
Z	4	4	4
M	234.00	242.62	296.71
d_{calc}/g cm^{-3}	1.86	1.64	1.52
Absorption coefficient/cm^{-1}	7.58	3.82	3.04
Radiation μ/Å	λ = Mo-Kα, 0.71073 Å		
θ Scanning range/deg	$2.12 \le \theta \le 26.3$		
Scanning technique	ω/2θ		
Scan angle	0.68 + 0.4 tgθ		
Standard reflections	Two control reflections for orientation and three control reflections for intensity after every 200 reflections		
Ranges for measured indices	$-10 \le h \le 0$ $-8 \le k \le 0$ $-16 \le l \le 17$	$-10 \le h \le 9$ $-17 \le k \le 0$ $0 \le l \le 18$	$-8 \le h \le 0$ $0 \le k \le 0$ $-18 \le l \le 18$
Number of measured reflections	1947	2221	2998
Number of observed reflections with $I > 3\sigma(I)$	1040	985	2045
Conditions for the determination and refinement of hydrogen atoms	Revealed from the difference electron density map, refined isotropically		
Final R and R_w factors	$R = 0.0384$ $R_w = 0.0467$	$R = 0.03609$ $R_w = 0.03894$	$R = 0.05310$ $R_w = 0.06641$
Figure of merit	1.411	1.169	2.329
Δ/σ_{max}	0	0	0.02
Ratio of the number of reflections to the number of refinable parameters	8.16	5.85	6.66

Note. Empirical absorption corrections were applied; the intensities of standard reflections showed no decrease in the course of data collection and, hence, no corrections were applied; calculations were carried out on an Alpha Station 200 using the MolEN program[8] and the SIR program (direct methods for the structure solution).[9] The structures were refined by the full-matrix least-squares method; the $\sum_{\omega}\left(|F_0|-|F_c|\right)^2$ function was minimized; extinction was ignored; the weighting scheme $4F_0^2/[\sigma(I)^2 + (0.04F_0^2)]^2$ was used.

ecules by the solvent as indicated also by the differences in the intermolecular contacts and molecular packing in the crystals of these compounds. Depending on the nature of the substituent at position 5, the supramolecular structures of the compounds under study are characterized by the formation of molecular stacks exclusively through π-π interactions (in the crystal of **1a**), the formation of infinite planar layers of the molecules linked only *via* C—H...O interactions (in the crystal of compound **1b**), or the presence both of π-π and C—H...O interactions giving rise to a three-dimensional framework of parallel molecular stacks (in the crystal of compound **1c**).

Experimental

5,7-Dichloro-4-nitro-2,1,3-benzoxadiazole (1a) was synthesized according to a known procedure,[1] m.p. 89 °C (*cf.* lit. data: 87—88 °C).

Compounds 1b and 1c were synthesized as described below. A solution of the corresponding amine (0.01 mol) in Pr^iOH (3 mL) was added dropwise to a suspension of compound **1a** (1.17 g, 0.005 mol) in Pr^iOH (10 mL) at 10—15 °C. The course of the reaction was monitored by chromatography on Silufol UV-254 plates. After completion of the reaction, the precipitate that formed was filtered off, washed with water, dried, and crystallized from the appropriate solvent.

7-Chloro-5-dimethylamino-4-nitro-2,1,3-benzoxadiazole (1b). The yield was 93%, m.p. 175 °C, R_f 0.23 (toluene—AcOEt, 2 : 1).

7-Chloro-5-hexamethyleneimino-4-nitro-2,1,3-benzoxadiazole (1c). The yield was 95%, m.p. 140—141 °C, R_f 0.51 (toluene—AcOEt, 2 : 1).

X-ray diffraction analysis. The X-ray diffraction data for compounds **1a—c** were collected on an automated four-circle Enraf-Nonius CAD-4 diffractometer. The crystallographic characteristics of compounds **1a—c** and details of the X-ray diffraction studies are given in Table 5.

The crystals of compounds **1a** ($C_6HCl_2N_3O_3$), **1b** ($C_{12}H_{13}ClN_4O_3$), and **1c** ($C_8H_7ClN_4O_3$) were grown from Pr^iOH, a 2 : 1 DMF—Pr^iOH mixture, and a 1 : 1 Pr^iOH—acetone mixture, respectively.

References

1. A. J. Boulton, A. C. J. Gray, and A. R. Katritzky, *J. Chem. Soc. B*, 1967, **9**, 909.
2. H. Suzuki, T. Kurihara, T. Kaino, and F. Ebisawa, *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.*, 1988, **44**, 484.
3. M. Mathew and G. J. Palenik, *Acta Crystallogr., Sect. B, Struct. Sci.*, 1971, **27**, 1388.
4. H.-J. Niclas, B. Gohrmann, M. Ramm, and B. Schulz, *J. Prakt. Chem.*, 1990, **332**, 1005.
5. M. Ramm, J. Kind, and H.-J. Niclas, *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.*, 1993, **49**, 1779.
6. A. Altomare, G. Cascarano, C. Giacovazzo, and D. Viterbo, *Acta Crystallogr., Sect. A, Fund. Crystallogr.*, 1991, **47**, 744.
7. J. N. Law, M. S. V. Daidge-Harrisson, and J. Colo, *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.*, 1996, **52**, 964.
8. L. H. Straver and A. J. Schierbeek, *MolEN, Structure Determination System, Program Description*, Nonius B. V., Delft, 1994, **1**, 180.
9. A. L. Spek, *Acta Crystallogr., Sect. A, Fund. Crystallogr.*, 1990, **46**, 34.

Received December 26, 2000;
in revised form June 4, 2001