Structure of 4-bromophenyl isothiocyanate

ᵃL. ULICKÝ and ᵇJ. SOLDÁNOVÁ

ᵃ*Department of Physical Chemistry, Slovak Technical University,
CS-812 37 Bratislava*

ᵇ*Department of Analytical Chemistry, Faculty of Pharmacy,
Komenský University, CS-832 32 Bratislava*

In this paper we present the results of X-ray structure analysis of 4-bromophenyl isothiocyanate, which provide information about the crystal and molecular structure of the compound. Crystals of 4-bromophenyl isothiocyanate are orthorhombic: $a = 2.0215(50)$ nm, $b = 0.8915(10)$ nm, $c = 0.4301(6)$ nm. Space group is $P2_12_12$, $Z = 4$. The crystal structure was solved by the heavy-atom method and refined by the least-squares method with $R = 0.074$ for 479 observed reflections and for anisotropic thermal parameters for nonhydrogen atoms. Four hydrogen atoms were identified by a difference synthesis.

В работе приводятся результаты рентгеноструктурного анализа 4-бромфенилизотиоцианата, предоставляющие информацию о его кристаллической и молекулярной структуре. Кристаллы 4-бромфенилизотиоцианата орторомбические: $a = 2,0215(50)$, $b = 0,8915(10)$, $c = 0,4301(6)$ нм. Пространственная группа симметрии $P2_12_12$, $Z = 4$. Кристаллическая структура, установленная с помощью метода тяжелого атома и уточненная методом наименьших квадратов, дает $R = 0,074$ для 479 наблюдаемых рефлексов и для анизотропных тепловых параметров для неводородных атомов. Четыре водородных атома были идентифицированы посредством дифференциального синтеза.

To rightly understand the reaction mechanism of substances it is necessary to know their molecular structure and especially in the case of isothiocyanates (ITC), the orientation and structure of the NCS group. While in inorganic solid substances the stereochemistry of this group is sufficiently known from the results of X-ray structure analysis (see *e.g.* the review [1]), in organic ITC its structure was before all investigated in solutions, especially by analyzing IR spectra [2—6], Raman spectra [7—10] and by microwave spectroscopy [11, 12]. There have also been some quantum chemical studies [13—15], which, however, used the experimentally

determined characteristics of structure. The molecular and crystal structure of tetra-B-isothiocyanate-tetra-N-tero-butyl-borazocine (T-ITC) was determined by X-ray analysis by *Clarke* and *Powell* [16]. The molecular structure of methyl isothiocyanate was determined by electron diffraction by *Anderson et al.* [17].

In order to determine the orientation of NCS group with regard to the benzene ring in aromatic ITC, the structure of 4-bromophenyl isothiocyanate (4-BFI) was solved by X-ray analysis from the projections (001) and (010) [18]. It was found that the group lies in one plane with the benzene ring and with respect to the connecting line between bromine and nitrogen it forms a bond angle of 155°. This result has been accepted [19], but considering that the value of the resulting R factor was relatively high, we do not state in our paper, whether the NCS group itself is linear or there is in it a bond ·angle different from 180°.

In this paper we present the results of X-ray analysis of 4-BPI from three--dimensional data.

Experimental

Crystals of 4-BPI were prepared according to [20] by synthesizing 4-bromoaniline with thiophosgene in chloroform.

Crystals are orthorhombic with the following unit cell parameters: $a = 2.0215(50)$ nm, $b = 0.8915(10)$ nm, $c = 0.4301(6)$ nm, $V = 0.7751(25)$ nm^3, space group $P2_12_12$, $Z = 4$. Density was measured pycnometrically, $\varrho_c = 1.7308$ g cm^{-3}, $\varrho_o = 1.734(2)$ g cm^{-3}

Table 1

Final atomic coordinates ($\times 10^4$) of 4-BPI
E.s.d.'s are given in parentheses

Atom	x	y	z
Br	2227(1)	1922(2)	1278(6)
S	5692(3)	3212(8)	12500(20)
N	4701(10)	1957(25)	9143(60)
C(1)	3043(10)	1927(27)	3637(56)
C(2)	3347(11)	594(23)	4371(67)
C(3)	3894(12)	607(24)	6101(73)
C(4)	4156(13)	1950(33)	7246(64)
C(5)	3839(12)	3338(29)	6464(74)
C(6)	3309(12)	3300(24)	4632(76)
C(7)	5130(11)	2536(26)	10523(89)
H(1)	3282(0)	−470(0)	2704(0)
H(2)	4169(0)	−250(0)	6991(0)
H(3)	4130(0)	4307(0)	7189(0)
H(4)	3104(0)	4350(0)	4048(0)

Table 2

Coefficients of anisotropic temperature factors of 4-BPI

E.s.d.'s are given in parentheses. Temperature factor is of the form

$$T = \exp\left[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right]$$

Atom	$B_{11}/10^{-20}$ m^2	$B_{22}/10^{-20}$ m^2	$B_{33}/10^{-20}$ m^2	$B_{12}/10^{-20}$ m^2	$B_{13}/10^{-20}$ m^2	$B_{23}/10^{-20}$ m^2
Br	7.32(15)	3.80(11)	6.09(14)	−0.07(13)	0.16(15)	0.20(15)
S	6.43(37)	4.46(33)	6.51(41)	−0.93(32)	−0.17(39)	−0.20(39)
N	5.19(115)	5.32(117)	6.74(148)	−0.09(117)	1.06(132)	1.73(165)
C(1)	5.42(113)	4.14(118)	3.48(105)	0.26(118)	−1.63(120)	−0.49(152)
C(2)	5.91(131)	2.25(112)	6.03(179)	0.41(112)	0.75(166)	−1.11(134)
C(3)	5.46(125)	2.67(117)	5.62(149)	0.35(115)	−1.02(171)	0.14(146)
C(4)	7.01(153)	4.27(138)	5.64(157)	0.03(159)	0.11(145)	1.79(167)
C(5)	4.25(118)	5.42(160)	5.87(159)	−1.54(118)	−1.08(155)	−0.84(168)
C(6)	5.87(137)	1.96(120)	8.81(219)	−0.68(107)	2.34(168)	0.44(148)
C(7)	4.11(148)	2.79(105)	12.13(281)	0.11(100)	2.61(190)	1.75(157)

A Syntex $P2_1$ diffractometer and $CuK(\alpha)$ radiation ($\lambda = 0.154178$ nm) with a graphite monochromator were used for refinement of the lattice parameters and intensity measurements. The intensities were measured by the $\Theta-2\Theta$ scan technique ($0 < 2\Theta \leqq 100°$) at $T = 213$ K. The scan rate varied from 4.88 to 29.3° min^{-1} in 2Θ. Two standard reflections monitored after every 98 scans showed that no correction for instrument instability or crystal decay was required. The data were corrected for Lorentz and polarization effects. The correction for absorption was not made because the crystal was very small (0.05 mm × 0.07 mm × 0.2 mm). Integral intensities of 535 symmetrically independent reflections were measured and 479 reflections with $I > 1.96 \delta(I)$ were used for the analysis. All computing was performed on a minicomputer Nova 1200 with the Syntex XTL structure determination system.

The crystal structure was solved by the heavy-atom method and refinement by the least-squares method gave $R = 0.074$ for 479 observed reflections and for anisotropic thermal parameters for nonhydrogen atoms. Four hydrogen atoms were identified from a difference synthesis (distance C—H has average value 0.1090 nm). In the final refinement and calculation of structure factors these hydrogen atoms were used with fixed coordinates and with constant isotropic temperature factors $B = 4.0 \times 10^{-20}$ m^2. The residual electron density in the differential Fourier synthesis was 0.88×10^{30} m^{-3}.

Coordinates for all atoms are listed in Tables 1 and 2 and bond distances and angles in Table 3. The packing of structural units in the elementary cell with the atom numbering scheme is shown in Fig. 1.

Table 3

Interatomic distances and angles in the structure unit of 4-BPI
with their estimated standard deviations in parentheses

	d/nm		d/nm
Br—C1	0.193(2)	C4—C5	0.143(4)
C1—C2	0.138(3)	C5—C6	0.133(4)
C1—C6	0.140(3)	C4—N	0.138(3)
C2—C3	0.133(4)	C7—N	0.115(4)
C3—C4	0.140(4)	C7—S	0.154(3)
	φ/°		φ/°
Br—C1—C2	120(2)	C3—C4—N	120(2)
Br—C1—C6	119(2)	C5—C4—N	120(2)
C2—C1—C6	121(2)	C5—C4—C3	120(2)
C1—C2—C3	120(2)	C4—N—C7	153(3)
C2—C3—C4	121(2)	N—C7—S	176(2)

Deviations (nm) of individual atoms from the planes defined by the atoms of the benzene ring are in Table 4.

The least-square plane is described by the equation

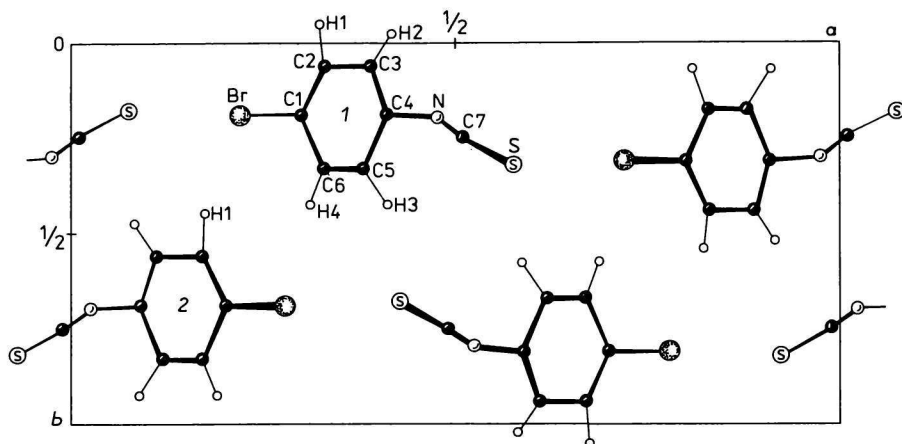$$(0.5698)x + (0.0685)y + (-0.8189)z - (2.3505) = 0$$

Fig. 1. Projection of the structure in the direction of c and numbering scheme of atoms.

Table 4

Deviations of the individual atoms in the structure unit from
the plane of benzene ring

Atom	Deviation/nm	Atom	Deviation/nm
C1	−0.00144	Br	−0.01213
C2	−0.00044	S	−0.00196
C3	−0.00149	N `	−0.00400
C4	−0.00065	H1	0.04464
C5	−0.00122	H2	−0.00350
C6	0.00228	H3	0.01251
C7	−0.00089	H4	0.00563

Discussion

The obtained results gave us the picture of molecular structure of 4-BPI as well as the space arrangement of the molecules of this compound. The NCS group is in one plane with the benzene ring, however, it forms a bond angle of 153° (which is in agreement with [18]) with respect to the connecting line Br—N (Fig. 1). However, we have found, different from paper [18] that the NCS group is not linear but slightly broken with the bond angle N—C7—S 176°. The existence of the bond angle between NCS and the rest of the molecule was found in almost all ITC. Its size is evidently conditioned by the molecular structure. In organic ITC it is the range from 130° to 177° (Table 5). It is necessary to consider that the bond angles

Table 5

Comparison of internuclear distances in organic ITC and ITC acid with our numerical values (nm)

	R—N	N—C	C—S	⊀C—N—C	Ref.
4-BPI	0.138	0.115	0.154	153.63°	This paper
ITC acid		0.121	0.156	130.25°	[21]
Methyl ITC	0.177	0.122	0.156	142°	[22]
	0.148	0.119	0.159	141.6°	[17]
Phenyl ITC	0.14	0.121	0.156	145°	[11]
	0.137	0.121	0.155	148°	[23]
T-ITC	0.143	0.117	0.156	176.42°	[16]

in the molecules of isothiocyanate acid, methyl isothiocyanate, and phenyl isothiocyanate were determined from spectral data [11, 21, 22, 24] or from electron diffraction [17], while in 4-BPI and T-ITC [16] by X-ray analysis of solid substances. In the solid state the position of the molecule is fixed in the space structure, the augmentation of the bond angle R—NCS can, therefore, be in both ITC's conditioned by steric causes.

The existence of the bond angle different from 180° between NCS and the benzene ring in 4-BPI causes a rotating moment of this group. However, in the crystal structure the rotation is impossible.

Between structural units there are mutual interactions by intercession of Br and S atoms in the direction of *a* as well as *c*. This interaction is shown in detail in Fig. 2.

Mutual interactions cause 4-BPI molecules to form in the direction of *a* a broken chain structure (zig-zag). The distances of Br and S between structural units in neighbouring chains are, however, so great (~0.6—0.8 nm), that in the direction of *b* there does not occur an interaction between molecules. This fact is also very
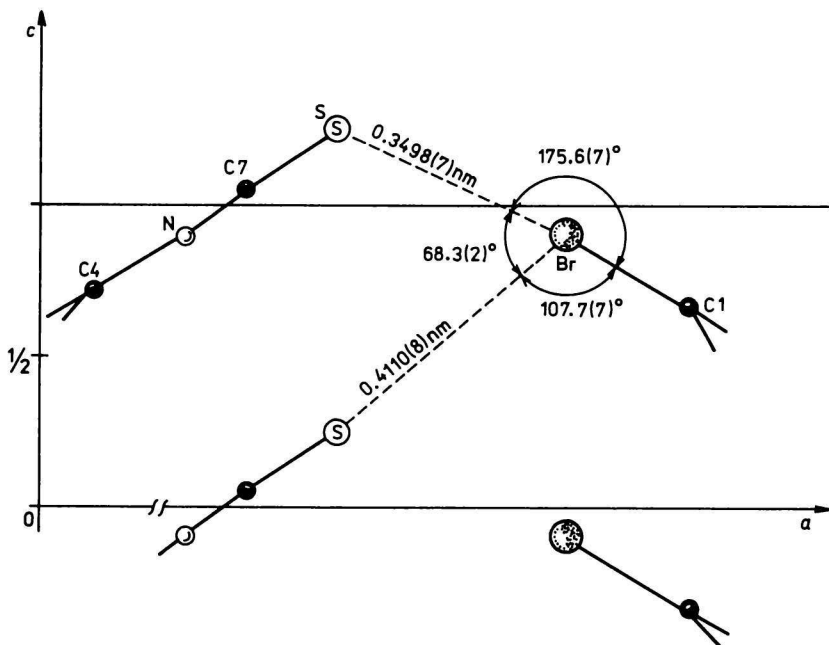
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Fig. 2. Interactions between Br and S atoms.

apparent in crystallization by sublimation, where the crystals grow in thin layers parallel with *c*.

The structural units of individual chains are closest to one another in hydrogens H4 (from structural unit 1, Fig. 1) and H1 (from structural unit 2). Their determined mutual distance is 0.314 nm. In the case both hydrogens (H1 and H4) were lying in the plane of benzene rings, the distance between them would be ~0.2 nm. Such a close approach evidently caused H1 to be by 0.04 nm "protruded" above the plane of the benzene ring (Table 4).

The above-mentioned structure of the substances points to the fact that 4-BPI molecule in the solid state is rather markedly deformed. Molecules, therefore, have tendency to get into an energetically more advantageous state where the NCS group could freely carry out the precessional movement and hydrogen H1 could return into the plane of the benzene ring. This could be the explanation for the uncommonly high pressure of 4-BPI vapours and resulting great volatility.

In many crystal structures the ITC ligand is linear and the bond angle NCS differs only slightly from 180°. We, however, know cases where the deviation from the linearity of this group is considerable. For instance, in [Ni(triam) (—NCS)$_2$] [24] the bond angle is ~170° and in compounds [Cu(en) (—NCS) (—NCS—)] [25] and [Cu(NH$_3$)$_2$(—NCS) (—NCS—)] [26] ~160°.

In organic ITC the NCS group is considered as a rule linear, or only with a slight deviation from 180° [19]. A relatively greater deviation in 4-BPI is probably brought about by steric causes from the setting of molecules in the crystal structure (the influence of the remnants of charges on sulfur, nitrogen, and bromine).

Internuclear distances in the NCS group correspond to the values given for this group [1]. A comparison of internuclear distances in organic ITC and ITC acid with our values is in Table 4 in nm. The distance of Br—benzene ring is greater than the distance of Br—C in 4-dibromobenzene (0.184 nm [27]; 355) as well as in chlorobromobenzene (0.188 nm [27]; 354).

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