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CRYSTAL AND MOLECULAR STRUCTURE OF N-(o-CHLOROPHENYLSULFONYL)-N′-(4-DIMETHYLAMINO-6-ISOPROPYLIDENEAMINOXY-1,3,5-TRIAZIN-2-YL)UREA: PLANT GROWTH REGULATOR OF THE SULFONYLUREA CLASS

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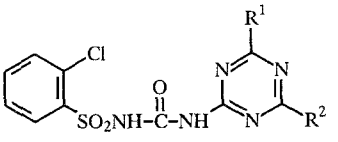
We synthesized and conducted an x-ray diffraction investigation of an effective plant growth regulator of the sulfonylurea class: N(o-chlorophenylsulfonyl)-N′-(4-dimethylamino-6-isopropylideneaminoxy-1,3,5-triazin-2-yl)urea. We discuss the hydrogen bond system in the crystal of the studied compound.

For the past 20 years, interest has steadily increased in derivatives of arylsulfonylheterylureas in connection with their unique herbicidal and growth-regulatory activity [1]. Among such compounds, derivatives containing an oxime group in the 1,3,6-triazinyl ring of the urea have stimulated definite interest [2]. Continuing a study of the molecular structure of arylsulfonylheterylurea and hydrogen bond systems in their structures, we have carried out an x-ray diffraction investigation of N-(o-chlorophenylsulfonyl)-N′-(4-dimethylamino-6-isopropylideneaminoxy-1,3,5-triazin-2-yl)urea I, a promising plant growth regulator which was briefly reported in the review [3].



I-IV

I R^1 = O—N=CMe_2, R^2 = NMe_2; II R^1 = Me, R^2 = OMe; III R^1 = Me, R^2 = NMe_2; IV R^1 = *i*-Pr, R^2 = OMe

The sulfonylurea I was synthesized by condensation of o-chlorophenylsulfonylisocyanate with 2-amino-4-dimethylamino-6-isopropylideneaminoxy-1,3,5-triazine with heating up to 70-80°C in acetonitrile [2].

Earlier an x-ray diffraction investigation was carried out on N-(o-chlorophenylsulfonyl)-N′-(1,3,5-triazin-2-yl)ureas II-IV [3-6], which are structurally similar to compound I. The conformations of molecules II-IV proved to be quite close, but the intermolecular hydrogen bond systems in these structures are quite different. Thus in the crystal of II, the carbonyl oxygen atom takes part in formation of the intermolecular hydrogen bond as the acceptor; this role is played by the sulfonyl oxygen atom in IV and by one of the atoms of the triazine ring in II. Such a difference in the hydrogen bonds of structures II and III is explained by the introduction of the strong electron-donor substituent NMe_2 into the heterocycle of molecule III, which leads to an increase in electron density and consequently to enhancement of the proton–acceptor properties of the nitrogen atom opposite to the donor substituent, due to the substantial contribution from the form with charge separation.

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TABLE 1. Basic Bond Lengths d (Å) in Molecule I

Bond	d	Bond	d	Bond	d
Cl—$C_{(15)}$	1,738(2)	$N_{(2)}$—$C_{(2)}$	1,380(2)	$N_{(7)}$—$C_{(7)}$	1,264(2)
S—$O_{(1)}$	1,420(1)	$N_{(3)}$—$C_{(2)}$	1,317(2)	$C_{(7)}$—$C_{(8)}$	1,494(3)
S—$O_{(2)}$	1,418(1)	$N_{(3)}$—$C_{(3)}$	1,353(2)	$C_{(7)}$—$C_{(9)}$	1,507(4)
S—$N_{(1)}$	1,647(1)	$N_{(4)}$—$C_{(3)}$	1,347(2)	$C_{(10)}$—$C_{(11)}$	1,387(2)
S—$C_{(10)}$	1,767(1)	$N_{(4)}$—$C_{(4)}$	1,316(2)	$C_{(10)}$—$C_{(15)}$	1,387(2)
$O_{(3)}$—$C_{(1)}$	1,210(2)	$N_{(5)}$—$C_{(2)}$	1,333(2)	$C_{(11)}$—$C_{(12)}$	1,388(3)
$O_{(4)}$—$N_{(7)}$	1,450(2)	$N_{(5)}$—$C_{(4)}$	1,332(2)	$C_{(12)}$—$C_{(13)}$	1,371(3)
$O_{(4)}$—$C_{(4)}$	1,343(2)	$N_{(6)}$—$C_{(3)}$	1,342(2)	$C_{(13)}$—$C_{(14)}$	1,357(3)
$N_{(1)}$—$C_{(1)}$	1,364(2)	$N_{(6)}$—$C_{(5)}$	1,454(3)	$C_{(14)}$—$C_{(15)}$	1,377(2)
$N_{(2)}$—$C_{(1)}$	1,376(2)	$N_{(6)}$—$C_{(6)}$	1,450(2)		

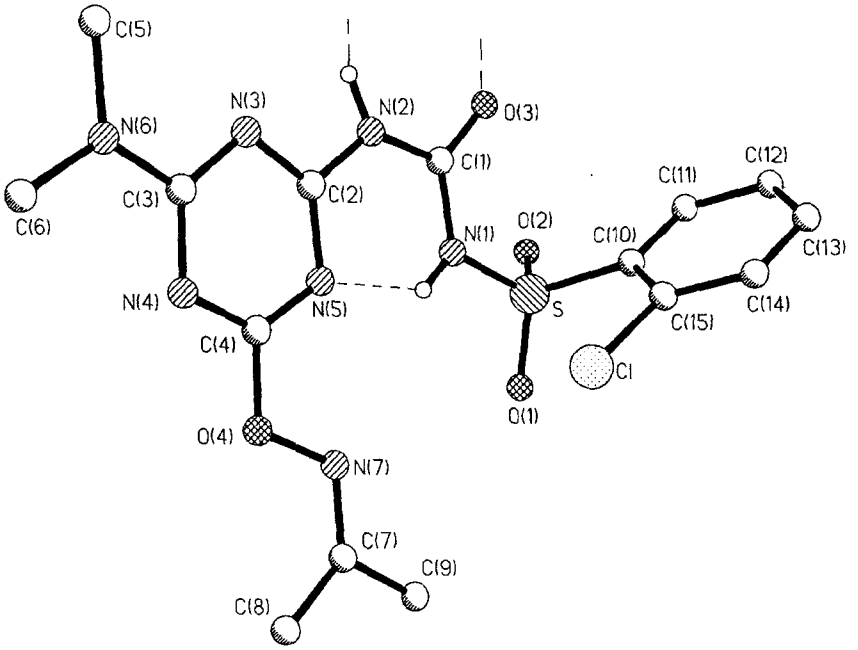

Fig. 1. General form of molecule I (only the hydrogen atoms participating in hydrogen bond formation are shown).

The general form and numbering scheme for the atoms in the investigated molecule I are shown in Fig. 1; the bond lengths and bond angles are presented in Tables 1 and 2.

The conformation of molecule I, characterized by the torsional angles $C_{(15)}C_{(10)}SN_{(1)}$ 65.1(2)°, $C_{(10)}SN_{(1)}C_{(1)}$ 63.5(2)°, $SN_{(1)}C_{(1)}N_{(2)}$ −175.7(2)°, $N_{(1)}C_{(1)}N_{(2)}C_{(2)}$ 4.9(2)° and $C_{(1)}N_{(2)}C_{(2)}N_{(5)}$ −2.6(2)°, is very close to that found in molecules II-IV. The basic geometric features of the structure of the arylsulfonylurea moiety of molecule I, specifically the inequality of the bond angles NSO (109.85(8) and 104.70(7)°) and the increase in the exocyclic angles $SC_{(10)}C_{(15)}$ 122.7(1)° and $C1C_{(15)}C_{(10)}$ 121.8(1)°, also coincide with those found in II-IV. As in the compounds II-IV we studied earlier, the planar conformation of the triazinylurea moiety is due to formation of an intramolecular hydrogen bond $N_{(1)}$—$H_{(N1)}$...$N_{(5)}$, the parameters of which ($N_{(1)}$—$N_{(5)}$ 2.606(2), $H_{(N1)}$...$N_{(5)}$ 1.97(2) Å, angle $N_{(1)}$—$H_{(N1)}$...$N_{(5)}$ 134.6(9)°) are close in all four compounds. In the triazine ring of molecule I, we observe significant inequality of the C—N bond lengths: the $N_{(3)}$—$C_{(2)}$ and $N_{(4)}$—$C_{(4)}$ are shortened to 1.317(2) and 1.316(2) Å, and the $N_{(3)}$—$C_{(3)}$ and $N_{(4)}$—$C_{(3)}$ are lengthened to 1.353(2) and 1.347(2) Å. Such a distribution of bond lengths in the heterocycle allows us to conclude that a substantial contribution to the observed geometry of molecule I comes from the quinoidal form with charge separation and increased multiplicity of the exocyclic bond $N_{(6)}$—$C_{(3)}$, analogous to that suggested for compound III in [5]. Replacement of the methyl substituent in molecule III by the more electron—acceptor isopropylideneaminoxy group in I probably leads to a decrease in the contribution from the form with charge separation, which in particular is apparent in some increase in the $N_{(6)}$—$C_{(3)}$ bond length, equal in I to 1.342(2) Å (in

TABLE 2. Basic Bond Angles, ω (degrees)

Angle	ω	Angle	ω
$O_{(1)}SO_{(2)}$	119,89(8)	$N_{(3)}C_{(2)}N_{(5)}$	127,6(1)
$O_{(1)}SN_{(1)}$	104,70(7)	$N_{(3)}C_{(3)}N_{(4)}$	125,1(1)
$O_{(1)}SC_{(10)}$	109,45(7)	$N_{(3)}C_{(3)}N_{(6)}$	116,5(1)
$O_{(2)}SN_{(1)}$	109,85(8)	$N_{(4)}C_{(3)}N_{(6)}$	118,4(1)
$O_{(2)}SC_{(10)}$	106,95(7)	$O_{(4)}C_{(4)}N_{(4)}$	113,4(1)
$N_{(1)}SC_{(10)}$	105,09(7)	$O_{(4)}C_{(4)}N_{(5)}$	119,2(1)
$N_{(7)}O_{(4)}C_{(4)}$	112,1(1)	$N_{(4)}C_{(4)}N_{(5)}$	127,4(1)
$SN_{(1)}C_{(1)}$	122,8(1)	$N_{(7)}C_{(7)}C_{(8)}$	127,2(2)
$C_{(1)}N_{(2)}C_{(2)}$	130,4(1)	$N_{(7)}C_{(7)}C_{(9)}$	113,8(2)
$C_{(2)}N_{(3)}C_{(3)}$	113,4(1)	$C_{(8)}C_{(7)}C_{(9)}$	119,0(2)
$C_{(3)}N_{(4)}C_{(4)}$	113,8(1)	$SC_{(10)}C_{(11)}$	117,4(1)
$C_{(2)}N_{(5)}C_{(4)}$	112,7(1)	$SC_{(10)}C_{(15)}$	122,7(1)
$C_{(3)}N_{(6)}C_{(5)}$	121,3(2)	$C_{(11)}C_{(10)}C_{(15)}$	119,8(1)
$C_{(3)}N_{(6)}C_{(6)}$	121,1(2)	$C_{(10)}C_{(11)}C_{(12)}$	119,3(2)
$C_{(5)}N_{(6)}C_{(6)}$	117,6(2)	$C_{(11)}C_{(12)}C_{(13)}$	119,7(2)
$O_{(4)}N_{(7)}C_{(7)}$	109,3(1)	$C_{(12)}C_{(13)}C_{(14)}$	121,2(2)
$O_{(3)}C_{(1)}N_{(1)}$	122,8(1)	$C_{(13)}C_{(14)}C_{(15)}$	120,0(2)
$O_{(3)}C_{(1)}N_{(2)}$	120,8(2)	$ClC_{(15)}C_{(10)}$	121,8(1)
$N_{(1)}C_{(1)}N_{(2)}$	116,5(1)	$ClC_{(15)}C_{(14)}$	118,3(1)
$N_{(2)}C_{(2)}N_{(3)}$	114,9(1)	$C_{(10)}C_{(15)}C_{(14)}$	119,9(2)
$N_{(2)}C_{(2)}N_{(5)}$	117,5(1)		

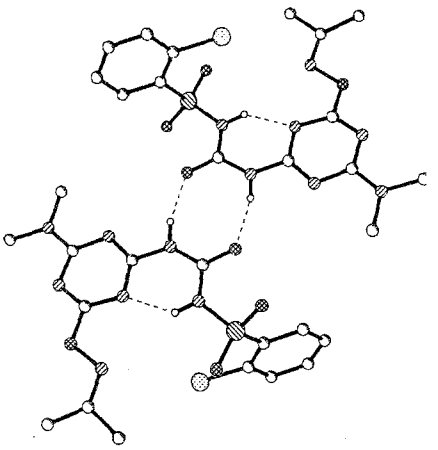

Fig. 2. Dimer formed as a result of intermolecular hydrogen bonds of molecule I.

the two independent molecules of compound III, 1.326 and 1.333 Å). The partial decrease (compared with III) in the negative charge on the $N_{(5)}$ atom does not make it possible for this atom to compete any longer with the carbonyl group as a proton acceptor in formation of an intermolecular hydrogen bond, which is observed in III; and it is specifically the $N_{(5)}$ atom which takes part in the intramolecular hydrogen bond. Probably one more factor promoting formation of an intramolecular hydrogen bond with participation of the $N_{(5)}$ atom is possible weak electrostatic interaction between the $N_{(7)}$ atom of the isopropylideneaminoxy group and $H_{(N1)}$: the $H_{(7)}...H_{(N1)}$ distance is rather short and is 2.98(2) Å, while the orientation of this group, in fact lying in the plane of the heterocycle (torsional angle $N_{(5)}C_{(4)}O_{(4)}N_{(7)}$ 2.7(1)°) and turned by the $N_{(7)}$ atom toward the $N_{(1)}$ atom, is most optimal for such an interaction.

The packing of molecules in the crystal of I is quite similar with that found for II in [4]: the molecules are interconnected into centrosymmetric dimers by hydrogen bonds between the nitrogen $N_{(2)}$ atoms and the carbonyl oxygen atoms $O_{(3)}N_{(2)}...O_{(3)}$ 2.839(2) Å, $H_{(N2)}...O_{(3)}$ 1.98(2) Å, angle $N_{(2)}-H_{(N2)}...O_{(3)}$ 170.5(9)°). The general form of the dimer formed as a result of the hydrogen bonds is shown in Fig. 2.

TABLE 3. Coordinates ($\times 10^4$; $\times 10^5$ for Cl and S atoms) and Isotropic Equivalent Temperature Factors B_{eq} ($Å^2$) of Nonhydrogen Atoms

Atom	x	y	z	Beq	Atom	x	y	z	Beq
Cl	67049(8)	16438(2)	83828(8)	5,30(1)	$C_{(2)}$	6982(3)	505(1)	11663(2)	3,21(4)
S	110107(8)	14418(2)	98329(6)	3,56(1)	$C_{(3)}$	4504(3)	295(1)	12786(2)	3,68(4)
$O_{(1)}$	10432(2)	1847(1)	10349(2)	4,72(4)	$C_{(4)}$	5243(3)	994(1)	12667(2)	3,16(4)
$O_{(2)}$	12947(2)	1316(1)	10063(2)	5,35(4)	$C_{(5)}$	3806(4)	-474(1)	12911(3)	6,04(7)
$O_{(3)}$	10920(2)	497(1)	9575(2)	5,61(4)	$C_{(6)}$	1840(4)	66(1)	14049(3)	6,25(7)
$O_{(4)}$	4832(2)	1400(1)	13027(2)	3,80(3)	$C_{(7)}$	5456(4)	2088(1)	12629(3)	5,20(6)
$N_{(1)}$	9762(2)	1085(1)	10559(2)	3,69(4)	$C_{(8)}$	3666(5)	2209(1)	13249(4)	8,17(9)
$N_{(2)}$	8482(3)	396(1)	10902(2)	4,11(4)	$C_{(9)}$	6688(6)	2440(1)	12109(4)	9,1(1)
$N_{(3)}$	5968(3)	176(1)	12050(2)	3,89(4)	$C_{(10)}$	10336(3)	1407(1)	7969(2)	3,12(4)
$N_{(4)}$	4097(3)	704(1)	13139(2)	3,85(4)	$C_{(11)}$	11720(3)	1284(1)	7105(2)	4,21(5)
$N_{(5)}$	6726(2)	923(1)	11928(2)	3,18(3)	$C_{(12)}$	11289(4)	1280(1)	5627(3)	5,81(6)
$N_{(6)}$	3410(3)	-24(1)	13213(2)	4,97(5)	$C_{(13)}$	9514(4)	1403(1)	5041(3)	6,04(7)
$N_{(7)}$	6092(3)	1712(1)	12465(2)	4,34(4)	$C_{(14)}$	8148(4)	1520(1)	5880(3)	5,27(6)
$C_{(1)}$	9774(3)	653(1)	10300(2)	3,81(4)	$C_{(15)}$	8535(3)	1519(1)	7350(2)	3,66(5)

TABLE 4. Coordinates of Hydrogen Atoms ($\times 10^3$) and Their Isotropic Temperature Factors B_{iso} ($Å^2$)

Atom	x	y	z	B iso
H(N1)	880(3)	118(1)	1097(2)	4,8(5)
H(N2)	863(3)	12(1)	1085(2)	3,9(5)
H(5.1)	267(4)	-60(1)	1272(4)	10,2(9)
H(5.2)	456(5)	-51(1)	1222(3)	9,7(9)
H(5.3)	415(5)	-62(1)	1370(4)	11(1)
H(6.1)	234(6)	0(2)	1493(4)	11(1)
H(6.2)	92(4)	-7(1)	1360(3)	7,8(8)
H(6.3)	119(4)	31(1)	1360(3)	7,8(8)
H(8.1)	379(4)	243(1)	1374(3)	9,9(9)
H(8.2)	283(5)	203(1)	1344(3)	9,2(9)
H(8.3)	425(7)	208(2)	1463(5)	23(2)
H(9.1)	712(5)	265(1)	1281(4)	11(1)
H(9.2)	741(5)	234(1)	1147(3)	11(1)
H(9.3)	609(5)	267(1)	1151(4)	12(1)
H(11)	1295(3)	120(1)	753(2)	4,5(5)
H(12)	1219(3)	119(1)	516(2)	5,3(6)
H(13)	931(4)	139(1)	406(3)	7,6(8)
H(14)	680(4)	161(9)	549(3)	6,9(7)

EXPERIMENTAL

The IR spectrum was recorded on the UR-20 (in KCl). The PMR spectrum was recorded on the VXR Varian 400 in CD_3CN, internal standard TMS. TLC was carried out on Silufol UV-254 plates in the system CCl_4 – EtOAc – AcOH, 1:1:0.04.

Compound I was obtained as in [2], yield 85%, T_{mp} 203-204°C (with decomposition, from acetonitrile), R_f 0.41. IR spectrum: 3300(NH), 1703(C=O), 1355 and 1165(SO_2). PMR spectrum: 2.05 and 2.07 (6H, two s, $=CMe_2$), 3.14 (6H, s, NMe_2), 7.57 (1H, t.d. 5-H), 7.60 (1H, d.d. 6-H), 7.62 (1H, t.d. 4-H), 8.19 (1H, d.d. 6-H), $J_o \sim 8$ Hz, $J_M \sim 1.5$ Hz, 8.23 (1H, br.s. CONH), 13.40 (1H, br.s. SO_2NH).

The elemental analysis data for C and H correspond to the calculated values.

Crystals of Compound I, $C_{15}H_{18}ClN_7O_4S$ are monoclinic (from acetonitrile), at 20°C $a = 7.068(2)$, $b = 30.968(4)$, $c = 9.376(1)$ Å, $\beta = 95.93(2)°$, $Z = 4$, space group $P2_{1/n}$. The cell parameters and the intensities of 2712 reflections with $I > 3\sigma$ were measured on the Nonius CAD-4 automatic four-circle diffractometer ($\lambda MoK\alpha$, graphite monochromator, ratio of scanning rates ω: $\theta = 1.2$: 1, $\theta < 28°$). The structure was deciphered by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all the nonhydrogen atoms. All the hydrogen atoms, determined from a difference series, were refined isotropically. In the final stages, the refinement was carried out using 2611 reflections with $I > 5\sigma$. The final values of the reliability factors were $R = 0.035$, $R_w = 0.52$. All the calculations were done on the PDP-11/23 PLUS computer using the SDP PLUS program [7]. The coordinates of the nonhydrogen atoms are presented in Table 3; the coordinates of the hydrogen atoms are presented in Table 4.

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