X-RAY DIFFRACTION STUDY OF ARYLSULFONYL-HETARYLUREAS — A NEW GENERATION OF HERBICIDES (REVIEW)*

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Data from an x-ray diffraction study and the conformational behavior in solutions of N-(arylsulfonyl)-N'-(1,3,5-triazin-2-yl)ureas (a comparative description) — a new generation of promising herbicides and plant-growth regulators — are correlated.

Approximately 15 years ago, researchers at DuPont (USA) discovered that some sulfonamides, viz., arylsulfonylhetarylureas o-$XC_6H_4-SO_2-NHCONH$-Het, are capable of having a striking effect on the growth and development of plants. Tested as herbicides, they exhibited unique properties: lower (by two orders of magnitude) norms of consumption as compared with previously known herbicides (5-10 g/ha of the active substance), effective herbicidal selectivity, and comparative technological accessibility [1]. All of this served as a basis for the extremely rapid development of research in a number of countries dealing with the creation of commercial preparations based on them. Among the first to be proposed was the preparation chlorsulfurone (glin) — N-(o-chlorophenylsulfonyl)-N'-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I). The substituents in the 1,3,5-triazine ring were subsequently varied [1-3], the triazine ring was replaced by a pyrimidine ring [1, 2], and the arylsulfonyl radical was replaced by a hetarylsulfonyl radical [1, 2, 4]; in order to decrease the persistence, the chlorine atom in the ortho position of the aryl- or hetarylsulfonyl group was replaced by other groupings such as a methoxycarbonyl group [1, 2, 4], and the hydrogen atom attached to the N^1 atom was replaced by a methyl (alkyl) group [1, 2], etc.

It was found that arylsulfonylhetarylureas, even at very low concentrations, are capable of inhibiting acetolactasynthase — the first specific enzyme in the chain of the biosynthesis of leucine, isoleucine, and valine, which leads to blocking of cell division.

Despite the active study of the chemistry and biological effect of arylsulfonylhetarylureas, until our research [5-8] no x-ray diffraction studies of compounds of this class were actually carried out. At the same time, accurate data on their molecular structures could promote an understanding of the reasons for their high biological activity. See [9, 10] for x-ray diffraction studies of arylsulfonylhetarylureas with somewhat different structures.

Research in solutions showed the existence of two conformations of these compounds that are stabilized by intramolecular bonds.

Two one-proton singlets at 12.95 and 9.77 ppm, respectively, which were assigned to amide hydrogen atoms, are observed in the spectrum of chlorsulfurone (I) in deuteroacetone. The signal at stronger field is shifted slightly to weaker field (up to 0.05 ppm) when the solution is diluted, while the location of the singlet does not change completely. For the unambiguous assignment of these signals we synthesized a sample of chlorsulfurone labeled with the ^{15}N isotope with respect to the nitrogen atom of the sulfonamido group [5]. The ^{15}N—H spin-spin splitting of the signal at 12.95 ppm, which is equal

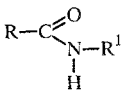
*Dedicated to Professor A. R. Katritzky on his 65th birthday.

K. A. Timiryazeva Moscow Agricultural Academy. A. N. Nesmeyanova Institute of Heteroorganic Compounds, Russian Academy of Sciences. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 969-979, July, 1993. Original article submitted June 23, 1993.

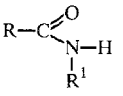
0009-3122/93/2907-0825$12.50

to 88 Hz, made it possible to unambiguously assign precisely this resonance signal to the hydrogen atom of the sulfonamido group; the magnitude of the chemical shift and the behavior when the solution is diluted indicate that this hydrogen atom participates in the formation of an intramolecular hydrogen bond. One might have assumed that the nature of this bond does not change on passing from the solution to the crystalline form.

Among secondary amides, the trans conformer is usually more stable, although bulky substituents stabilize the cis conformer and increase $\Delta G^{\#}$ vis-à-vis rotation relative to the C—N bond [11-13].



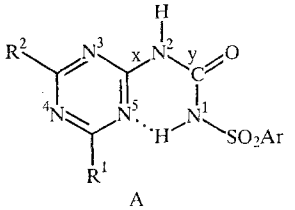
trans-



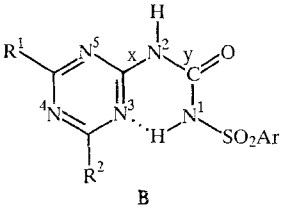
cis-

In arylureas (R^1 = aryl, R = NHR^2) the aryl group is usually turned relative to the N—C=O plane, whereas in tertiary arylureas, in particular, the barrier to rotation relative to the N—Ar bond through the planar transition state may become extremely significant if ortho substituents are introduced into the aryl ring [14].

A study of arylsulfonylureas by means of PMR spectroscopy and x-ray diffraction analysis showed that the result of replacement of the ortho carbon atoms in the aryl ring by nitrogen atoms (1,3,5-triazin-2-yl) is that the equilibrium geometry corresponds only to the planar cis-amide conformations A and B (in solution) or only one of them (in the crystalline state); a large energy barrier develops between these two conformations as a consequence of the realization of an NH···N intramolecular hydrogen bond in these conformations.



A



B

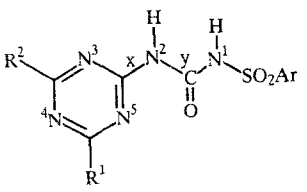
The existence of two conformations of chlorsulfurone (I) in solution in $CDCl_3$ or CD_2Cl_2 (free from acidic impurities, which catalyze intermolecular hydrogen exchange) was proved by Camilleri's group [15].

Fast hydrogen exchange occurs at room temperature, while the signals become broader when the temperature is lowered. At temperatures below 258 K one sees pairs of signals with unequal intensities for the singlets of the methyl and methoxy groups, in addition to two pairs of broad signals of protons of the NH group. Of these, only the weak-field pair of NH signals exhibits a small degree of the dependence on the solvent and temperature that is typical for an intramolecular hydrogen bond [16]; this suggests an equilibrium between the IA and IB conformers.

The assignment of the signals and the confirmation of the structures of the conformers were accomplished using the nuclear Overhauser effect (NOE).

At 210 K additional irradiation of the low-field singlet of protons of the NH group at 13.3 ppm gives an NOE effect only with one of the signals (also weak-field) of the methyl groups, which therefore are related to signals of the IA conformer; irradiation of the NH signal at 12.7 ppm gives a selective NOE only with one of the singlets (weak-field) of the methoxy groups, and these signal are therefore related to the IB conformer.

In principle, the IA ⇄ IB transformation takes place via two pathways: either as a result of rotation relative to the triazinyl-N (x) bond through an orthogonal transition state or via a more complex pathway with initial rotation relative to the amide (y) bond resulting in the formation of the twofold trans-amide conformation C with subsequent rotation relative to the (x) bond and the formation of a second stable conformation that is stabilized by an intramolecular hydrogen bond.



C

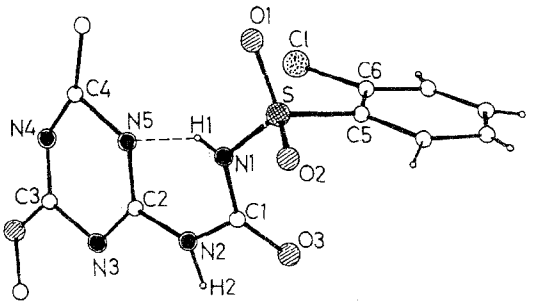


Fig. 1. General form of the chlorsulfurone (I) molecule.

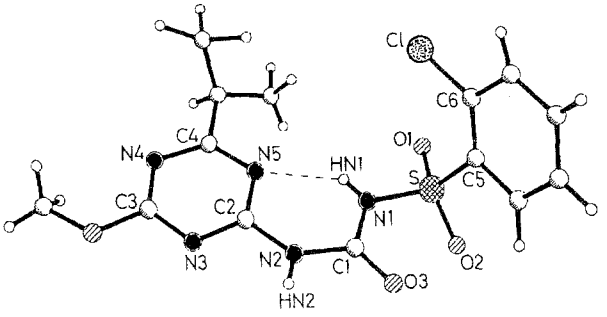


Fig. 2. General form of the arylsulfonylhetarylurea II molecule.

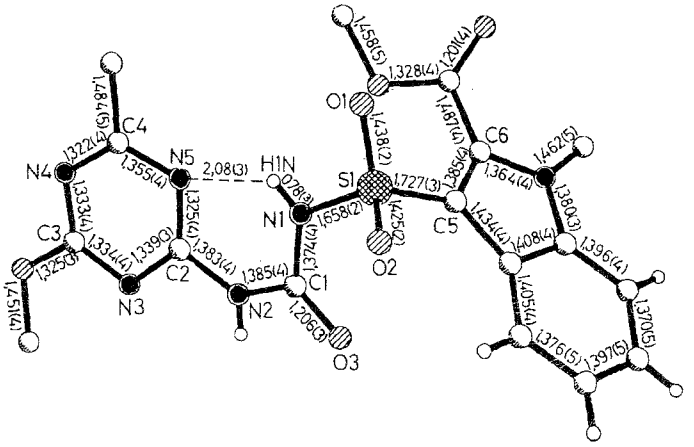


Fig. 3. General form of the V molecule and bond lengths in it.

An analysis of the form of the lines of the methyl and methoxy groups as a function of the temperature (in $CDCl_3$) gave $\Delta G^{\#}$ and $\Delta H^{\#}$ values of ~ 55 and 44 kJ/mole, respectively, for this dynamic process. If one assumes that the enthalpy of the NH···N hydrogen bond is usually equal to 15-20 kJ/mole, the barrier of 24-30 kJ/mole that arises as a result of subtraction corresponds more satisfactorily to rotation relative to the (x) bond rather than the (y) bond, since the latter is a bond of the amide type, and its barrier to rotation is usually significantly greater.

The results obtained do not agree with those found for o-substituted phenylureas, for which the orthogonal conformations are more stable (in order to avoid steric overlapping) and for which the barrier to rotation through the planar transition state has a $\Delta G^{\#}$ value that is significantly higher than 55 kJ/mole [14].

In the light of the data obtained relative to the conformational behavior of arylsulfonylhetarylureas in solutions it was very interesting to carry out a comparative analysis of the x-ray diffraction data from a study of the molecular and crystal structures of these compounds. We studied chlorsulfurone (I) [5], its analogs N-(o-chlorophenylsulfonyl)-N′-(4-methoxy-6-isopropyl-1,3,5-triazin-2-yl)urea (II) [7] and N-(o-chlorophenylsulfonyl)-N^1-(4-dimethylamino-6-methyl-1,3,5-triazin-2-yl)urea (III) [6], the growth regulator N-(o-chlorophenylsulfonyl)-N^1-(4-dimethylamino-6-isopropylideneaminoxy-1,3,5-triazin-2-yl) urea (IV), N-[3-(1-methyl-2-methoxycarbonylindolylsulfonyl)-N^1-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (V), an analog of the herbicide granstar, viz., N-(o-methoxycarbonylphenylsulfonyl)-N^1-ethyl-N^1-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (VI) (as compared with granstar, the N^1-methyl group is replaced by an N^1-ethyl group), and a salt (VII) of chlorsulfurone with 1,4-diazabicyclo[2.2.2]octane [8].

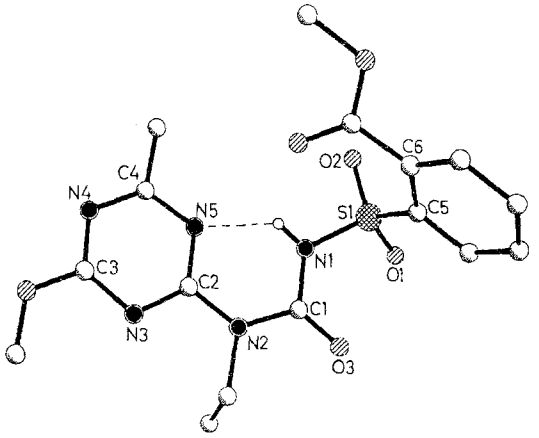
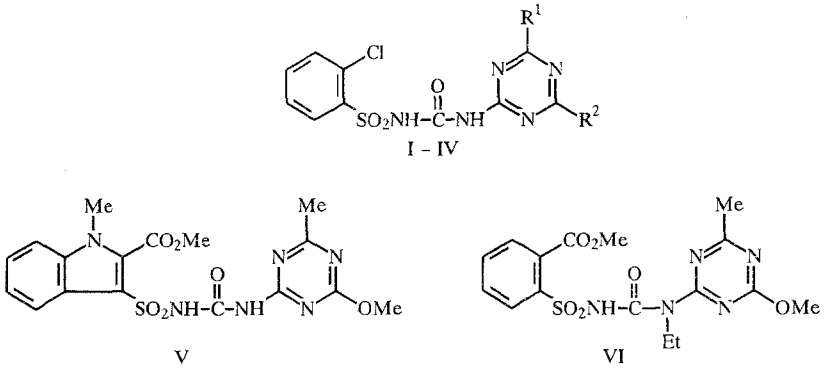


Fig. 4. General form of the VI molecule.



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

A study of chlorsulfurone (I), crystals of which were grown from acetonitrile, showed that in this case the molecule has the IA conformation (Fig. 1) [5]. Attempts to grow a polymorphous crystal modification in which the IB conformation would be realized were unsuccessful.

One might have assumed that the A conformation in the crystal could be destabilized by replacing the methyl group in the triazine ring by bulkier alkyl radicals due to steric repulsion of the substituents. We were able to grow, from cyclohexane—methylene chloride (1:1), a crystal of an analog of chlorsulfurone in which the methyl group was replaced by an isopropyl group (urea II); however, the assumption that we made was not confirmed — the A conformation is realized in the crystal in this case also (Fig. 2) [7]. The same system of intramolecular hydrogen bonds with an analogous conformation of the 4-methoxy-6-methyl-1,3,5-triazin-2-yl radical of A is also observed in crystals of arylsulfonylhetarylureas V-VI grown from acetonitrile (Figs. 3 and 4). Unexpectedly, replacement of the methoxy group of chlorsulfurone by the dimethylamino group, which has greater electron-donor properties and, as we will demonstrate below and as follows from theoretical considerations, increases δ^- on the $N_{(5)}$ atom more markedly as compared with $N_{(3)}$ and $N_{(4)}$, does not lead to strengthening but rather to destabilization of the A conformation: the IIIB conformation is realized in crystals of the corresponding arylsulfonylurea III obtained from acetonitrile (Fig. 5) [6]. The compound in which, as compared with urea III, the methyl group is replaced by —ON=CMe_2 crystallizes from acetonitrile in the form of the IVA conformer (Fig. 6). Probable reasons for this behavior will be discussed below.

The structures of arylsulfonylamides and arylsulfonylimides were thoroughly analyzed by means of x-ray diffraction data in a review [17], and the observed geometries of the I-VI molecules are in good agreement with the data presented. The conformations of the arylsulfonylamido part of the molecules, which is described by torsion angles $N_{(1)}SC_{(5)}C_{(6)}$ (the numbering is arbitrary and was adopted for the I molecule), which are equal to 53.5°, 75.1°, 64.1°, 65.1°, 82.1°, and 74.4°, and $C_{(1)}N_{(1)}SC_{(5)}$, which are equal to 51.3°, 69.0°, 55.1°, 63.5°, 59.3°, and 66.3° for I-VI, respectively, are quite close to one another and are in good agreement with the normal geometry of arylsulfonylamides [17]. The orientation of the o-chlorophenyl

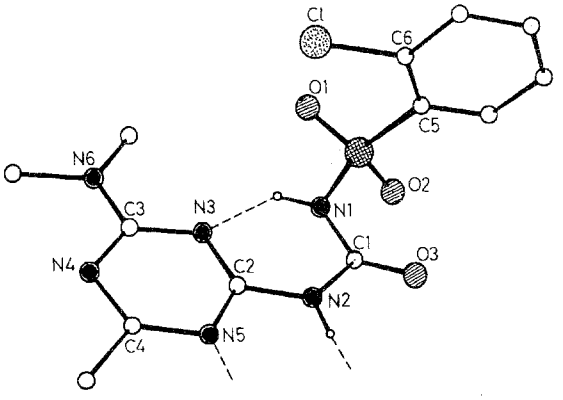


Fig. 5. General form of the III molecule.

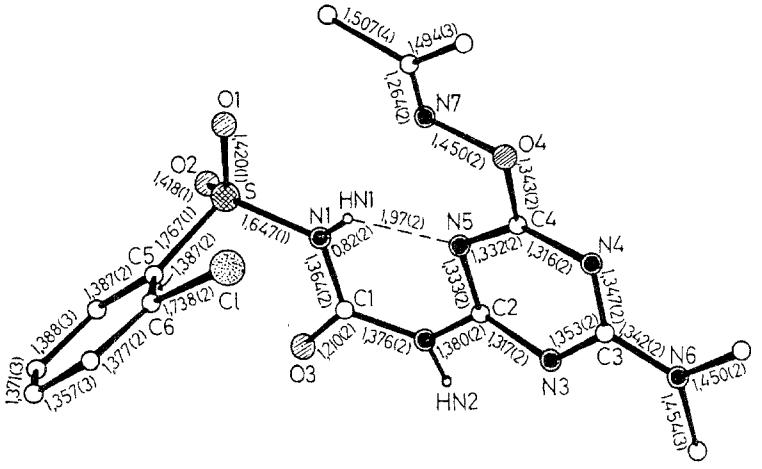


Fig. 6. General form of the IV molecule and bond lengths in it.

ring in the I-V molecules is evidently determined primarily by steric factors and is more favorable for a decrease in the repulsion between the chlorine atom and the O and N atoms bonded with the sulfur atoms. The short intramolecular contacts with the participation of the chlorine atom, however, are retained; this leads to a certain degree of increase in the S—$C_{(5)}$—$C_{(6)}$ bond angle to 122-123° and the $ClC_{(6)}$—$C_{(5)}$ bond angle to 122°. The plane of the methoxycarbonyl group, which is located (in place of the chlorine atom) in the 2 positions of the indole or o-phenyl ring of V and VI, forms angles of 42.9° and 39.8°, respectively, with the plane of the corresponding aromatic system.

The lengths of the S—C and S—N bonds are close to the normal values (1.76-1.78 and 1.63-1.69 Å); the shortened S—C bond of 1.727 Å in V constitutes an exception; this is evidently due to the smaller effective size of the five-membered ring to which the sulfo group is attached as compared with the six-membered ring in I-IV and VI. We also observed inequality of the OSN bond angles; the larger of them is formed with the participation of the synclinal [with respect to the $N_{(1)}$—$C_{(1)}$ bond] $O_{(2)}$ atom and has a value of 108-110° [as compared with angle $O_{(1)}$—S—$N_{(1)}$ (104-105°)], although the magnitude of this angle, as in other sulfonylamides, is usually less than 110°. The remaining bond lengths and bond angles in the arylsulfonylamide fragments have the normal values.

It was also observed that the conformation of the triazinylurea fragment in the I-V molecules is, in fact, the same and is classified as the unusual β type (in accordance with the Dupont classification for pyridylsulfonylureas [18]), which is distinguished by closeness to 0° of torsion angle N(SO_2)—C(O)—N—C [the maximum value of 9.9(6)° is observed for I]. One compound, viz., the preparation "torasemide" (or, to be more precise, one of the independent molecules in its first crystal modification), which is of the same type, has been previously described [19]. As already pointed out above, this unusual β conformation is due to the formation of an N—H...N intramolecular hydrogen bond between the hydrogen atom of the sulfonamido group and one of the nitrogen atoms of the triazine ring [$N_{(1)}$...$N_{(5)}$ 2.61-2.70 Å, $N_{(1)}$—$H_{(1)}$ 0.68-0.76 Å, and $H_{(1)}$...$N_{(5)}$ 1.97-2.08 Å; angle $N_{(1)}$—$H_{(1)}$...$N_{(5)}$ 134-148°]. The resulting planar, six-membered, hydrogen-bond-closed ring is actually coplanar with respect to the triazine ring. The $N_{(1)}$—$C_{(1)}$ bond length of ~1.37 Å is normal for arylsulfonylureas, while the $N_{(2)}$—$C_{(1)}$ bond length of 1.38-1.39 Å is somewhat increased, evidently due to participation of the unshared pair of

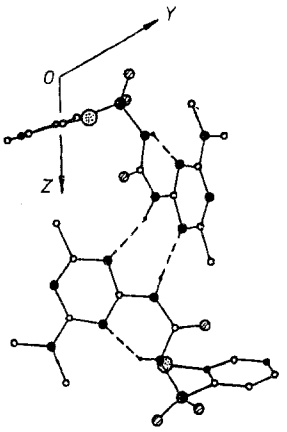


Fig. 7. Projection of the dimer of III (joined together by hydrogen bonds) on the YOZ plane.

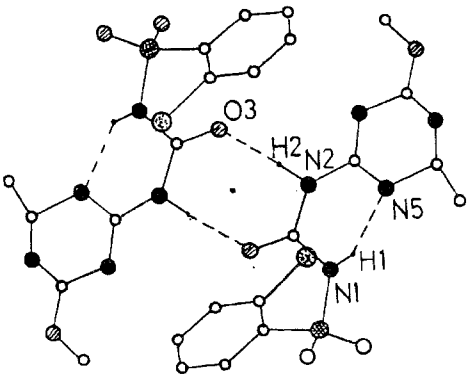
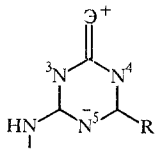


Fig. 8. Projection of the dimer of chlorsulfurone (I) (joined together by hydrogen bonds) on the XOZ plane.

electrons of the $N_{(2)}$ atom in conjugation with the π-electron system of the triazine ring rather than with the carbonyl group. This is probably why the $C_{(1)}—O_{(3)}$ bond (1.20-1.21 Å) in the carbonyl group is also slightly shortened as compared with the values in similar compounds with saturated substituents attached to the $N_{(2)}$ atom [19-21]. The introduction of an alkyl substituent to the $N_{(2)}$ atom of arylsulfonylurea VI led to a small increase in the length of the $N_{(2)}—C_{(1)}$ bond to 1.416(5) Å and, probably as a consequence of this, to the difference in some parameters of the $N_{(1)}—H_{(1)}...N_{(5)}$ intramolecular hydrogen bond [$N_{(1)}...N_{(5)}$ 2.544(7) Å, N—H 0.81(6) Å, H...N 1.90(6) Å, angle N—H...N 137(1)°] from those found for I-V.

An examination of the geometry of the triazine rings of the I-V molecules makes it possible to conclude that the shortening of the ring $C_{(2)}—N_{(3)}$ and $C_{(4)}—N_{(4)}$ bonds is due to the contribution of forms with charge separation to the observed geometry of the molecules:



I - V

I, II, V Э = OMe; III, IV Э = NMe_2

This contribution is naturally greater for structures III and IV than for I and II.

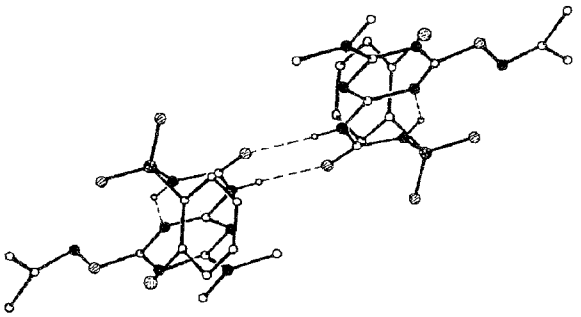


Fig. 9. Dimer of IV joined together by hydrogen bonds.

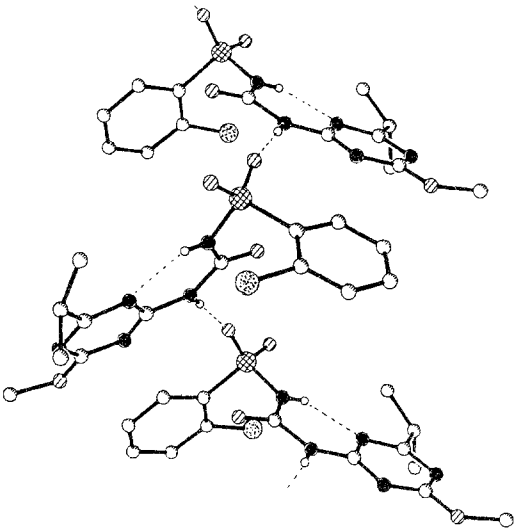


Fig. 10. Projection of a fragment of the chain of II molecules (joined together by hydrogen bonds) on the XOY plane.

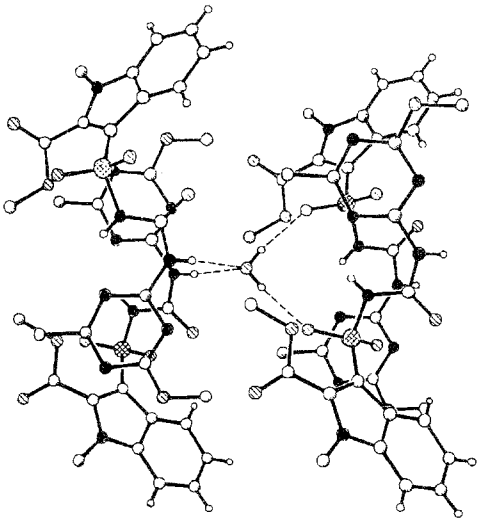


Fig. 11. Intermolecular hydrogen bonds of the V molecule with a molecule of crystallization water.

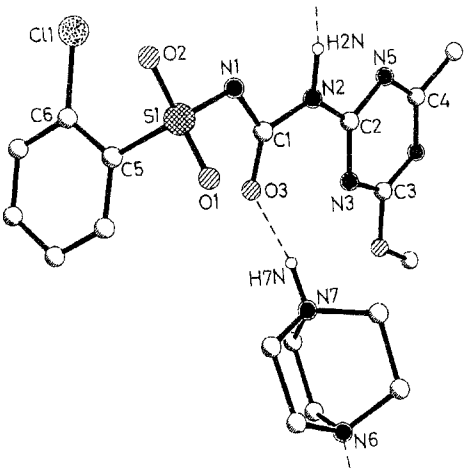


Fig. 12. Ion pair of the salt (VII) of chlorsulfurone (I) with diazabicyclo[2.2.2]octane.

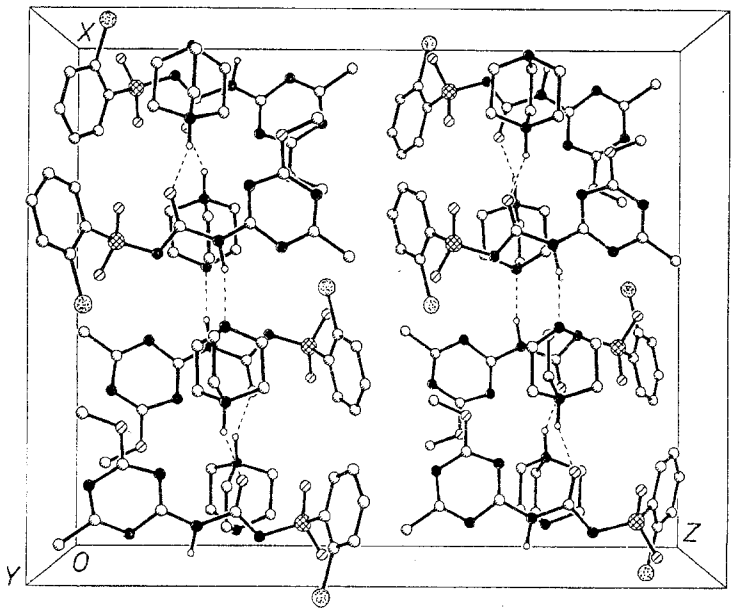


Fig. 13. Cationic-anionic chains formed by hydrogen bonds in the VII structure (form of the structure along the b axis).

Nevertheless, precisely in the case of urea III, in the molecule of which charge δ^- on the $N_{(5)}$ atom is maximal, and for this reason the proton-acceptor properties should also be maximal, the intramolecular hydrogen bond is formed not with the participation of this nitrogen atom but rather with the participation of the $N_{(3)}$ atom. However, this contradiction is easily eliminated, since precisely the $N_{(5)}$ atom participates in the formation of an intermolecular hydrogen bond as a proton acceptor: two intermolecular hydrogen bonds, viz., $N_{(2)}$—H...$N_{(5')}$ and $N_{(2')}$—H...$N_{(5)}$ (N...N 3.05 and 3.025 Å), are formed between two symmetrically independent III molecules (Fig. 7).

In contrast to III, the molecules in I and IV crystals are joined together to form centrosymmetric dimers by means of $N_{(2)}$—H···O(carbonyl) intermolecular hydrogen bonds; however, precisely the heteroring $N_{(5)}$ atom participates in the intramolecular hydrogen bond in both structures (Figs. 8 and 9). It is possible that the realization of the observed geometry for the IV molecule is also due to the weak electrostatic interaction between the $N_{(1)}$—H proton and the nitrogen atom of the N...H dimethylketoxime grouping [2.98(2) Å], the orientation of which is most favorable for the realization of this interaction.

Yet another variation of the formation of intermolecular hydrogen bonds is realized in the II structure: the $O_{(2)}$ atom of the sulfonyl group acts as an acceptor of the proton of the $N_{(2)}$—H grouping [$N_{(2)}$—H...$O_{(2')}$ 2.947(5) Å, $N_{(2)}$—H 0.81(5) Å, H...$O_{(2')}$ 2.14(5) Å, angle $N_{(2)}$—H...$O_{(2')}$ 174.5°], and the molecules are joined together by means of these hydrogen bonds to form infinite chains directed along one of the crystal axes (b) (Fig. 10).

In contrast to I-IV, crystals of sulfonylurea V were obtained in the form of a semihydrate. The presence of water molecules in this structure leads to the development of a new system of intermolecular hydrogen bonds that has not been previously observed for arylsulfonylurea derivatives. In the semihydrate crystal each V molecule participates in the formation of two intermolecular hydrogen bonds: as a proton donor in the $N_{(2)}$—H...OH_2 bond (*a*) and as an acceptor in the HO—H...$O_{(1)}$ bond (b). Thus each water molecule participates in the formation of four intermolecular hydrogen bonds: as a proton donor in two cases of the b type and as an acceptor in two bonds of the *a* type. These intermolecular hydrogen bonds join V and water molecules together to form layers that are parallel to the XOY plane (Fig. 11).

The absence of a second active hydrogen atom attached to the $N_{(2)}$ atom naturally leads to disappearance of the intermolecular hydrogen bonds in the IV structure, and the molecules in the crystal are joined together only by van der Waals interactions.

In a previous paper [21] it was assumed that the deprotonated form of arylsulfonylhetarylureas is biologically active and that dissociation of the acidic hydrogen atom of the sulfonamido group primarily occurs. This should lead to disappearance of the intermolecular hydrogen bond in such ureas and, evidently, to a substantial change in the conformation of the molecule. With this end in mind, we carried out an x-ray diffraction study of a crystal of the salt (VII) of chlorsulfurone (I) and 1,4-diazabicyclo[2.2.2]octane grown from acetonitrile.

This study confirmed unequivocally that transfer of a proton of the sulfonamido group of chlorsulfurone to a nitrogen atom of the diazabicyclooctane occurs in the VII molecule and that the crystal is constructed from chlorsulfurone anions and monoprotonated diazabicyclooctane cations joined together by hydrogen bonds (Fig. 12). Deprotonation of the $N_{(1)}$ atom leads to a significant change in the conformation of the anion as compared with the neutral chlorsulfurone molecule [5]. The triazinylurea chain of the anion has a planar s-trans-zig-zag conformation that differs from that found in the structure of neutral chlorsulfurone by 180° rotation relative to the $N_{(1)}$—$C_{(1)}$ and $N_{(2)}$—$C_{(2)}$ bonds. It must be noted that the anion retains the normal (for arylsulfonylamides) conformation of the $ArSO_2N$ group, which is distinguished by torsion angles $N_{(1)}SC_{(5)}C_{(6)}$ 70.5° and $C_{(1)}N_{(1)}SC_{(5)}$ 62.9°. Unfortunately, because of the strong thermal vibrations of the atoms the accuracy achieved in the determination of the geometrical parameters is insufficient for a detailed discussion of the changes in the bond lengths and bond angles in the anion as compared with the neutral I molecule. One can, however, note a decrease in the length of the S—$N_{(1)}$ bond to 1.539(6) Å and length of the $N_{(1)}$—$C_{(1)}$ bond to 1.333(8) Å (as compared with 1.63-1.69 Å and 1.36-1.38 Å in the neutral arylsulfonylurea), as well as a decrease in bond angle $SN_{(1)}C_{(1)}$ to 117.9(5)° (123.9° in chlorsulfurone). These differences are evidently associated with a change in the hybridization of the $N_{(1)}$ atom and with delocalization of the negative charge of the anion with respect to the $O_2SNC{=}O$ fragment.

In the crystal of salt VII the cations and anions are joined together by $N_{(7)}$—H...$O_{(3)}$ [N....O 2.685(9) Å, N—H 1.02(3) Å, H...O 1.74 Å, angle N—H...O 150(3)°] and $N_{(2)}$—H...N_6 [N...N 2.924(9) Å, N—H 1.00(2), H...N 1.45(2) Å, angle N—H...H 163(3)°] to form infinite chains that are parallel to the *a* axis (Fig. 13).

It is entirely possible that the difference in the biological activity of arylsulfonylhetarylureas as a function of the structure may be determined to a significant extent by the different stabilities and configurations of the hydrogen bonds of specific compounds with enzyme receptors.

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