Chemistry of Heterocyclic Compounds, Vol. 30, No. 3, 1994

SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF N(1-METHYL-2-CARBOMETHOXYINDOLYL-3-SULFONYL)-N'-HETARYLUREAS

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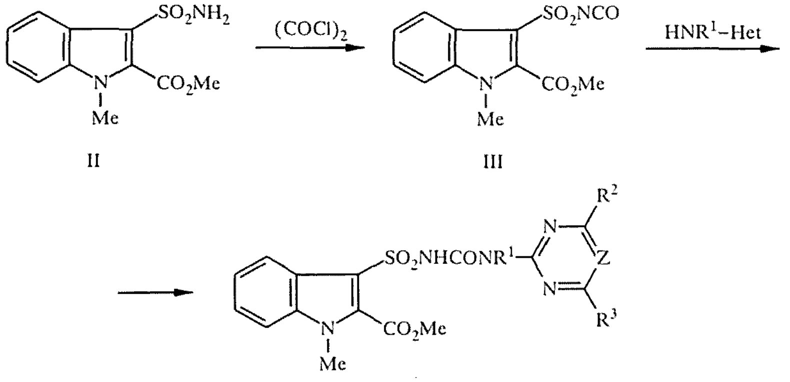
We have carried out synthetic and physicochemical investigations of N-(1-methyl-2-carbomethoxyindolyl-3-sulfonyl)-N'-hetarylureas which are a new generation of potential herbicides and plant growth regulators.

The preparation of a unique, new class of herbicides (arylsulfonylhetarylureas of general formula $2\text{-}XC_6H_4-SO_2-NHCONH-Het$) which exceed in activity all existing compounds by two orders of magnitude marks the appearance of a third generation of herbicides [1]. It was found that small structural changes in the molecule lead to significant changes in their spectrum of activity. In particular, the nature of the hetaryl radical (1,3,5-triazine, pyrimidine) and its associated substitutents were altered. Thus the $2\text{-}XC_6H_4$ radical was replaced by hetaryl (3-carbomethoxy-2-thienyl in the product "Harmony"). A change of the substitutent X = Cl to CO_2CH_3 and of NCH_3 for NH decreased the persistence of the products etc. [1, 2].

The aim of this work was the synthesis and physicochemical investigation of N-(1-methyl-2-carbomethoxyindolyl-3-sulfonyl)-N'-heterylureas Ia-n from 1-methyl-2-carbomethoxy-3-indolylsulfonamide (II) in order to study their herbicide and plant growth regulatory activities and to uncover any structure-activity relationship.



II

III

Ia-n

Ia-e Z = CH, f-n Z = N; a-*l* R^1 = H, m, n R^1 = Me; a R^2 = Me, b-g, m R^2 = OMe, h R^2 = NHMe, i-*l*, n R^2 = NMe_2; a, b, f, h, i, m R^3 = Me, c R^3 = F, d R^3 = Cl, e, j, n R^3 = OMe, g R^3 = CCl_3, k R^3 = $O-N{=}C(C(CH_2)_5$, *l* R^3 = $O-N{=}CMe_2$

Sulfonylureas Ia-n were synthesized by the most common general method for obtaining similar compounds using the sulfonamide II. The latter was obtained from 1-methyl-2-carbomethoxyindole [3] and converted to the corresponding isocyanate III (using oxalyl chloride in reflexing o-xylene or toluene). The unpurified isocyanate was condensed with 2-aminopyrimidines of 2-amino-1,3,5-triazine by gently heating in benzene with triethylenediamine catalyst. After cooling, the sulfonylureas Ia-n

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0009-3122/94/3003-0317$12.50

TABLE 1. Parameters for Sulfonylureas Ia-n

Compound	Empirical formula	Mp (decomp.), °C	Mp (with rapid heating), °C	R_f	Yield, %
Ia	$C_{18}H_{19}N_5O_5S$	185...188*	224...225	0,39	78
Ib	$C_{18}H_{19}N_5O_6S$	179...181*2	212...215	0,38	83
Ic	$C_{17}H_{16}FN_5O_6S \cdot CH_3CN$	202...203	208...210	0,55	93
Id	$C_{17}H_{16}ClN_5O_6S$	185...190	216...218	0,55	79
Ie	$C_{18}H_{19}N_5O_7S$	175...178	197...198	0,48	92
If	$C_{17}H_{18}N_6O_6S$	188...190	202...204	0,31	96
Ig	$C_{17}H_{15}Cl_3N_6O_6S$	159...162	192...195*3 125...128	0,54	45
Ih	$C_{17}H_{19}N_7O_5S$	188...190	242...245	0,06	95
Ii	$C_{18}H_{21}N_7O_5S$	172...176	228...230	0,21	93
Ij	$C_{18}H_{21}N_7O_6S$	165...173	207...208	0,34	96
Ik	$C_{23}H_{28}N_8O_6S$	155...160	195...197	0,33	50
Il	$C_{20}H_{24}N_8O_6S$	175...177	205...208*3 158...160	0,24	57
Im	$C_{18}H_{20}N_6O_6S$	173...177	195...197	0,51	91
In	$C_{19}H_{23}N_7O_6S$	179...184	205...207	0,82	81

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*1Lit. data [4]: 212-215°C (decomp.).

*2Lit. data [4]: 200-203°C (decomp.).

*3Two crystalline modifications, the lower melting was converted to the higher on melting.

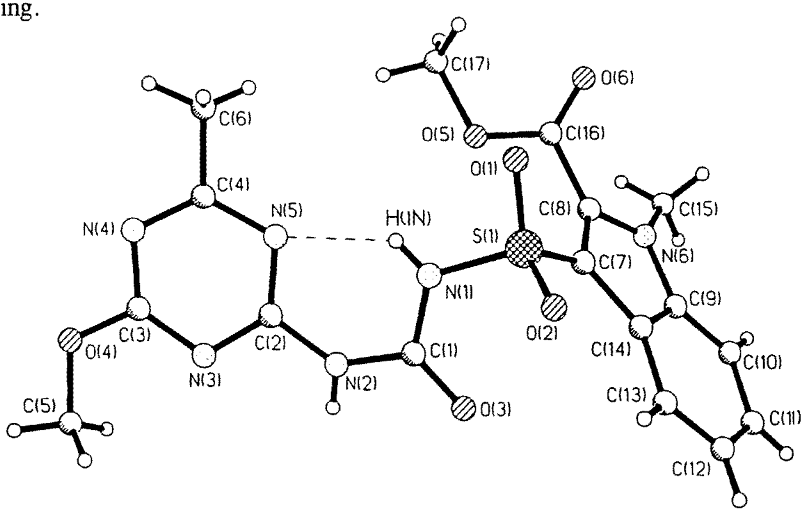


Fig. 1. General view of molecule If.

were separated by filtration. As a contaminant, they contained small amounts of the poorly soluble 4-methyl-4H-isothiazolo[4,5-b]indol-3(2H)-one-1,1-dioxide (IV) [3], being formed in the reaction of sulfonamide II to isocyanate III. It could be removed by crystallization from absolute acetonitrile.

Some of the compounds obtained by us have been reported in a patent [4] but they had been synthesized by an alternative method via Friedel–Crafts condensation of 1-methyl-2-carbomethoxyindole with the carboxamidosulfamoyl chlorides $ClSO_2NHCONRHet$ (which had been prepared without purification by treating the amines HNRHet with chlorosulfonylisocyanate).

X-ray structural investigation of some N-arylsulfonyl-N'-1,3,5-triazin-2-ylureas have shown that for all examples the triazinylurea fragment is planar, being stabilized by an intramolecular hydrogen bond between the sulfonamide NH and one of the heterocyclic nitrogen atoms [5]. Depending on the structure of the particular compound there are also possible a number of intermolecular hydrogen bonds involving the second urea nitrogen NH proton and acceptors both at the oxygen of the C═O or SO_2 groups and the nitrogen atom of the triazine ring [5].

TABLE 2. Bond Lengths d (Å) in If

Bond	d	Bond	d	Bond	d
S(1)—O(1)	1,438(2)	N(2)—C(1)	1,385(4)	C(4)—C(6)	1,484(5)
S(1)—O(2)	1,425(2)	N(2)—C(2)	1,383(4)	C(7)—C(8)	1,385(4)
S(1)—N(1)	1,658(2)	N(3)—C(2)	1,339(3)	C(7)—C(14)	1,434(4)
S(1)—C(7)	1,727(3)	N(3)—C(3)	1,334(4)	C(8)—C(16)	1,487(4)
O(3)—C(1)	1,206(3)	N(4)—C(3)	1,333(4)	C(9)—C(10)	1,396(4)
O(4)—C(3)	1,325(3)	N(4)—C(4)	1,322(4)	C(9)—C(14)	1,408(4)
O(4)—C(5)	1,451(4)	N(5)—C(2)	1,325(4)	C(10)—C(11)	1,370(5)
O(5)—C(16)	1,328(4)	N(5)—C(4)	1,355(4)	C(11)—C(12)	1,397(5)
O(5)—C(17)	1,458(5)	N(6)—C(8)	1,364(4)	C(12)—C(13)	1,376(5)
O(6)—C(16)	1,201(4)	N(6)—C(9)	1,380(3)	C(13)—C(14)	1,405(4)
N(1)—C(1)	1,374(4)	N(6)—C(15)	1,462(5)		

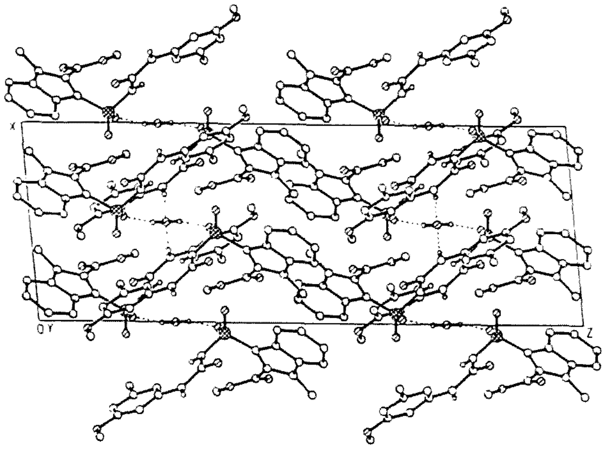


Fig. 2. Crystal packing of molecule If.

The conformational and geometric parameters for the sulfonylurea part of molecule If was essentially the same as found by us earlier for an analogous structure (the overall view of If is given in Fig. 1 and bond lengths and valence angles in Tables 2 and 4). The torsional angles of 59.3° for (C(1)N(1)S(1)C(7) and 82.1°C for N(1)S(1)C (7)C(8) are typical for the sulfonyl group orientation and the S(1)−N(1) bond length of 1.658(2) Å occurs in the normal range for arylsufononamides (1.658 Å) [6]. A small difference in the S−O bond lengths is attributed to the participation of one of the oxygen atoms in formation of intermolecular hydrogen bonds (see below). The shortening of the S(1)−(7) bond length to 1.727(3) Å, when compared with a mean values for arylsulfonamides of 1.761 Å [6], is evidently due to the effectively smaller size of the five membered pyrrole ring in indole If compared with a six membered ring, data for which has been discussed in [6]. The N-methylindole fragment has an unexceptional geometry and the carbomethoxy group plane is at a dihedral angle of 42.9° to it. As discussed by us previously for arylsulfonylhterylueras, in If the urea group (planar within 0.05 Å) occurs in a six membered ring closed by an intramolecular hydrogen bond (N(1)−H...N(5)) (N...N 2.698(4) Å, N−H...N angle 136°). The involved triazine nitrogen atom N(5) is the one situated opposite the more electron donating (methoxy) substituent). The C−N distance in the triazine ring varies widely (1.322-1.355 Å). The remaining geometric parameters for If are normal.

Crystalline If was obtained as a hemihydrate. The presence of water of solvation leads to a new system of intermolecular hydrogen bonds not previously reported for arylsulfonylhetarylureas. In the crystalline hemihydrate each molecule of If takes part in the formation of two intermolecular hydrogen bonds as a proton donor in the bond N(2)−H...OH_2 (A) (parameters given in Table 5) and as an acceptor in the bond HO−H...O(1) (B). The water molecules, found at specific positions on axis 2, take part in four intermolecular hydrogen bonds, two of type B as donor and two of type A as acceptor. These bonds combine molecule If and water in a layer parallel to the XOY plane (Fig. 2).

The IR spectra of the sulfonylureas Ia-n show characteristic absorptions for NH at 3300-3100 cm^{-1}, one or two strong carbonyl absorption bands at 1730-1710 cm^{-1}, and antisymmetric (1360-1340) and symmetric (1150 cm^{-1}) sulfonyl absorptions.

TABLE 3. PMR Spectra for Sulfonylureas Ia-n

Compound	Chemical, δ, ppm										
	CMe, s	NMe_2, s	1-Me, CO_2Me, other OMe, s	Z, s	6-H[*1], t	5-H[*1], т	7-H[*1], d	4-H[*1], d	CONH, s	SO_2NH, s	other protons
Ia	2,43[*2]		3,90; 3,92	7,03	7,36	7,46	7,73	8,14	10,47	13,06	
Ib	2,48		3,96; 3,99; 4,00	6,46	7,42	7,52	7,64	8,26			
Ic			4,00; 4,01; 4,12	6,25	7,35	7,44	7,84	8,32	9,52	12,03	
Id			3,98; 4,03; 4,08	6,69	7,44	7,53	7,65	8,27			
Ie			3,96; 4,00; 4,01[*2]	5,94	7,43	7,52	7,64	8,26	8,24	12,67[*3]	
If	2,52		3,99; 4,01; 4,03		7,34	7,44	7,62	8,30	10,27[*3]	12,64[*3]	
Ig			4,00; 4,02; 4,18		7,35	7,46	7,65	8,29	10,25	12,03	
Ih	2,28		3,91; 3,93		7,36	7,46	7,73	8,12	10,46	13,24	2,85 (s, NHMe)
Ii	2,36	3,15; 3,21	3,94; 3,96		7,30	7,35	7,58	8,24	8,11[*3]	13,21[*3]	
Ij		3,22; 3,24	3,96; 4,00; 4,01		7,42	7,51	7,64	8,24	8,22	12,97	
Ik		3,10; 3,12	3,89; 3,92		7,26	7,38	7,57	8,25	9,10	13,05	1,8...2,5 [m $(CH_2)_5$]
I*l*		3,12; 3,19	3,95; 3,97		7,40	7,51	7,63	8,24	8,22	13,16	2,13; 2,14 (two s, $=CMe_2$)
Im	2,62		3,97; 4,02; 4,10		7,44	7,52	7,65	8,26		13,95	3,36 (s, N'Me)
In		3,24; 3,25	3,97; 3,98; 4,08		7,37	7,47	7,71	8,25		11,84	3,26 (s, N'Me)

[*1] J_{ortho} ~8 Hz.

[*2] Two equivalent groups.

[*3] Broad singlet.

TABLE 4. Valence Anlges ω (deg) in If

Angle	ω	Angle	ω
O(1)—S(1)—O(2)	119,2(1)	N(3)—C(3)—N(4)	126,7(2)
O(1)—S(1)—N(1)	103,1(1)	N(4)—C(4)—N(5)	124,4(3)
O(2)—S(1)—N(1)	108,8(1)	N(4)—C(4)—C(6)	118,2(3)
O(1)—S(1)—C(7)	109,9(1)	N(5)—C(4)—C(6)	117,4(3)
O(2)—S(1)—C(7)	108,2(1)	S(1)—C(7)—C(8)	126,0(2)
N(1)—S(1)—C(7)	107,0(1)	S(1)—C(7)—C(14)	125,9(2)
C(3)—O(4)—C(5)	117,9(2)	C(8)—C(7)—C(14)	107,7(2)
C(16)—O(5)—C(17)	114,9(3)	N(6)—C(8)—C(7)	109,0(2)
S(1)—N(1)—C(1)	121,6(2)	N(6)—C(8)—C(16)	120,5(2)
C(1)—N(2)—C(2)	130,9(3)	C(7)—C(8)—C(16)	130,3(3)
C(2)—N(3)—C(3)	112,7(2)	N(6)—C(9)—C(10)	128,4(3)
C(3)—N(4)—C(4)	115,0(2)	N(6)—C(9)—C(14)	108,8(2)
C(2)—N(5)—C(4)	114,4(2)	C(10)—C(9)—C(14)	122,8(3)
C(8)—N(6)—C(9)	108,9(2)	C(9)—C(10)—C(11)	116,6(3)
C(8)—N(6)—C(15)	127,2(3)	C(10)—C(11)—C(12)	121,8(3)
C(9)—N(6)—C(15)	123,7(3)	C(11)—C(12)—C(13)	121,8(3)
O(3)—C(1)—N(1)	123,5(3)	C(12)—C(13)—C(14)	118,0(3)
O(3)—C(1)—N(2)	121,1(3)	C(7)—C(14)—C(9)	105,6(2)
N(1)—C(1)—N(2)	115,4(2)	C(7)—C(14)—C(13)	135,5(3)
N(2)—C(2)—N(3)	113,2(2)	C(9)—C(14)—C(13)	119,0(3)
N(2)—C(2)—N(5)	120,1(2)	O(5)—C(16)—O(6)	125,0(3)
N(3)—C(2)—N(5)	126,7(2)	O(5)—C(16)—C(8)	111,6(2)
O(4)—C(3)—N(3)	119,4(3)	O(6)—C(16)—C(8)	123,4(3)
O(4)—C(3)—N(4)	113,9(2)		

TABLE 5. Intermolecular Hydrogen Bond Parameters for If

Bond	D...A, Å	D—H, Å	H...A, Å	D—H...A, degrees
N(2)—H...OH_2	3,001 (4)	0,80 (3)	2,21 (3)	167,3 (4)
N(2*)—H...OH_2	3,001 (4)	0,80 (3)	2,21 (3)	167,3 (4)
HO—H...O(1)	2,930 (4)	0,81 (4)	2,13 (4)	167,7 (4)
HO—H...O(1)*	2,930 (4)	0,81 (4)	2,13 (4)	167,7 (4)

TABLE 6. I_{rel} (%) for Characteristic Ions of I obtained under Electron Impact

Compound	Ions								
	M	Φ_1	Φ_2	Φ_5	Φ_6	Φ_7	Φ_3	Φ_4	$NHR^1Het^{+\cdot}$
Ia	0,5	88	32	59	87	54	22	35	100
Ib	—	12	5	45	75	—	10	21	86
Id	0,8	100	35	50	81	57	20	31	52
Ie	—	100	36	70	99	68	20	41	97
In	—	100	32	56	78	47	8	27	75
Ih	—	100	34	64	98	66	16	33	99
Ij	—	94	30	39	63	5	22	23	100

The PMR spectra (Table 3) show signals for the protons of the substituents, a typical aromatic region multiplet for the four protons in the indole ring, and a pyrimidine 5′-H singlet in ureas Ia-e. The low field region shows two singlets for the amide (8-10) and sulfonamide (12-14 ppm) groups (DMSO-d_6, acetone-d_6). On plotting the spectra in acetonitrile-d_3, the signals are broadened and sometimes (Ib, d) not observed at all. In Im, n with the CONMe group the first singlet is naturally not observed. It was interesting to find that the spectra of Ii-ℓ, n showed the triazine NMe_2 as a pair of close singlets at 3.1-3.2 ppm, evidently due to hindered rotation for this group.

Electron impact mass spectrometry showed that the molecular ions $M^{+\cdot}$ for I are unstable and virtually unobserved. They undergo furtherdissociative ionization to form ions corresponding to both azine and indole fragments (Table 6). Theprimary route leads to formation of strong ions for $[HNR'Het]^{+\cdot}$ and $[IndSO_2NCO]^{+\cdot}$ (Φ_1, 294, here and later Ind represents 1-methyl-2-carbomethoxy-3-indolyl); Φ_2, 252, I_{rel} ~ 30-56%) through loss of NCO. A further route for dissociation

TABLE 7. I^{rel} (%) for Characteristic Ions of obtained under Electron Impact

Compound	Ions						
	MH^+	Φ_4	Φ_2	Φ_8	Φ_9	Φ_{10}	$NH_2R^1Het^+$
Ia	4	12	20	8	4	12	58
Ib	4	8	20		5	8	38
Id	14	34	90	24	30	38	30
Ie	34	30	78	20	18	24	40
In	4	10	20	8	8	10	100
Ih	38	25	48	8	5	20	100
Ii	38	13	28	10			100
Ij	40	10	26	6	5	6	100
Ik	32	16	56	15		18	100
I*l*	44	10	20	14	12	44	100

TABLE 8. I_{rel} (%) for Negative Ions of I under Fast Atom Bombardment

Compound	Ions					
	$[M - H]^-$	Φ_{12}	Φ_{13}	Φ_{11}	Φ_{14}	NHR^1Het^-
Ia	5	12	100	24	38	8
Ib	25	12	100	30	38	27
Id	8	10	100	26	23	11
Ie	38	15	100	36	32	32
In	45	5	70	15	10	9
Ih	40	5	100	13	25	75
Ii	5	3	100	6	24	23
Ij	36	15	100	34	26	55
Ik	16	10	56	24	16	8
I*l*	0	8	90	36	34	34

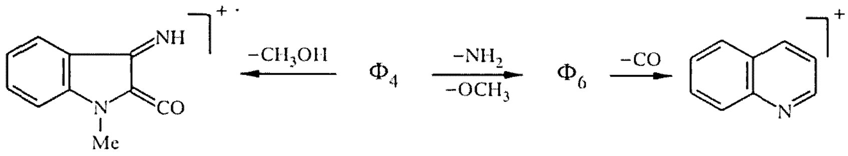
TABLE 9. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors U ($A^2 \times 10^3$) for Non-Hydrogen Atoms in If

Atom	*x*	*y*	*z*	*U*
S(1)	512(1)	4633(1)	1605(1)	37(1)
O(1)	255(2)	3750(1)	1715(1)	49(1)
O(2)	-623(2)	5221(2)	1564(1)	52(1)
O(3)	1964(3)	6273(1)	1787(1)	53(1)
O(4)	5359(2)	5724(1)	4137(1)	49(1)
O(5)	3123(2)	3346(1)	1602(1)	48(1)
O(6)	2742(3)	2622(1)	867(1)	67(1)
N(1)	1651(3)	4928(2)	2086(1)	38(1)
N(2)	3236(3)	5872(2)	2514(1)	40(1)
N(3)	4336(3)	5831(2)	3316(1)	39(1)
N(4)	4305(3)	4553(2)	3807(1)	42(1)
N(5)	3255(2)	4570(1)	2957(1)	35(1)
N(6)	2549(2)	4340(1)	410(1)	36(1)
C(1)	2249(3)	5727(2)	2104(1)	38(1)
C(2)	3609(3)	5388(2)	2945(1)	35(1)
C(3)	4645(3)	5368(2)	3737(1)	37(1)
C(4)	3611(3)	4180(2)	3410(1)	39(1)
C(5)	5758(4)	6615(2)	4099(2)	54(1)
C(6)	3176(4)	3276(2)	3461(2)	52(1)
C(7)	1347(3)	4710(2)	1058(1)	32(1)
C(8)	2230(3)	4104(2)	882(1)	33(1)
C(9)	1900(3)	5107(2)	280(1)	35(1)
C(10)	1959(4)	5588(2)	-163(1)	46(1)
C(11)	1199(4)	6330(2)	-199(1)	55(1)
C(12)	398(4)	6591(2)	185(1)	56(1)
C(13)	347(3)	6123(2)	624(1)	45(1)
C(14)	1118(3)	5360(2)	676(1)	34(1)
C(15)	3518(5)	3915(3)	101(2)	54(1)
C(16)	2727(3)	3274(2)	1107(1)	40(1)
C(17)	3404(5)	2537(3)	1868(2)	67(2)
O(H_2O)	5000	7451(2)	2500	52(1)

TABLE 10. Coordinates ($\times 10^3$) and Isotropic Temperature Factors U $A^2 \times 10^2$) for Hydrogen Atoms in If

Atom	*x*	*y*	*z*	*U*
H(1N)	195(3)	458(2)	228(1)	4(1)
H(2N)	359(3)	633(2)	249(1)	4(1)
H(51)	488(4)	698(3)	404(1)	9(1)
H(52)	639(4)	669(3)	382(2)	9(1)
H(53)	628(4)	672(3)	443(2)	10(1)
H(61)	359(4)	304(3)	379(2)	9(1)
H(62)	321(5)	302(3)	317(2)	11(2)
H(63)	226(5)	324(3)	353(2)	12(2)
H(10)	254(3)	542(2)	-41(1)	4(1)
H(11)	124(4)	666(2)	-48(1)	7(1)
H(12)	-10(3)	710(2)	15(1)	7(1)
H(13)	-22(3)	628(2)	87(1)	5(1)
H(151)	396(5)	430(3)	-11(2)	13(2)
H(152)	307(4)	355(3)	-13(2)	10(2)
H(153)	425(5)	365(3)	31(2)	13(2)
H(171)	261(4)	219(3)	182(1)	8(1)
H(172)	416(5)	222(3)	175(2)	12(2)
H(173)	363(5)	272(3)	220(2)	11(2)
H(H_2O)	503(4)	777(2)	274(1)	7(1)

of $M^{+\cdot}$ involves formation of the ion $[IndSO_2NH_2]^{+\cdot}$ (Φ_3, 268) which loses SO_2 through a known intramolecular rearrangement [7, 8] to give the $[IndNH_2]^{+\cdot}$ ion (Φ_4, 204). Ortho effect type fragmentation [9] leads to formation of ions Φ_5 (172) and Φ_6 (157), ion Φ_6 loses CO to give the quinoline radical cation Φ_7, 129·*



Φ_5 Φ_7

The absence of a significant molecular ion limits possible methods, particularly for analytical problems. Hence it was of interest to study the behavior of these compounds under milder ionization conditions, i.e., fast atom bombardment. We examined first fast atom bombardment with recording of positive ions (Table 7). Protonated ions for MH^+ (I_{rel} ~ 4-44%) were observed in all cases. It is likely that protonation occurs on the pyrimidine pyrimidine fragment of I. Under these conditions degradation of the molecule gives the protonated fragment $[H_2NR^1Het]^+$, previously observed as ions Φ_2 and Φ_4 in the electron impact spectra as well as an ion Φ_8, 236, which most likely has a cyclic imide radical cation structure IV. Quite intense ions were also observed for Φ_9, 188 and Φ_{10}, 158.

For a wider study of the fragmentation mechanism in fast atom bombardment conditions we also recorded the negative ions spectra (Table 8). In this case, the deprotonated molecular ions $[M - H]^-$ (I_{rel} ~ 5-45%) were observed together with ions corresponding to [NR'Het]⁻. Degradation of the $[M - H]^-$ ion begins with fission of the N–C or S–N bonds in the sulfonylurea fragment to form the ions $[IndSO_2NH_2]^-$ (Φ_{11}, 267), $[IndSO_2]^-$ (Φ_{12}, 252), one of the most intense peaks in the spectrum (I_{rel} ~ 50-100%) Φ_{13}, 235 most likely being the deprotonated cyclic imide IV, and Φ_{14}, 209.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 577 instrument for KCl tablets. PMR spectra were taken on a Bruker WM-250 instrument, Ia, h in DMSO-d_6, Ic f, g in acetone-d_6, In in a mixture of DMSO-d_6 and acetone-d_6, and the remainder in acetonitrile-d_3. The internal standard was TMS.

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*These atoms occur in the molecular with the reference parameters 1–x,y,1/2–z; 1/2+x,1/2+y,z, and 1/2–x,1/2+y,1/2–z respectively.

Mass spectra were recorded on a Finningan MAT-8200 mass spectrometer (FRG-USA). For electron impact: ionization energy 70 eV, cathode emission current 1 mA, accelerating potential 3 eV, ion source temperature 250°C (direct sampleintroduction). For fast atom bombardment (positive and negative ions): the same conditions but using glycerin matrix, gas reagent xenon, and beam intensity 4 watts.

General Method for Synthesis of Indolylsulfonylhetarylureas Ia-n. Oxalyl chloride (2 ml) was added with stirring to a suspension of sulfonamide II (1.34 g, 5 mmole) in absolute o-xylene or toluene (25 ml). Upon heating to reflux the suspension dissolved and a precipitate again formed. After 1 h solvent and excess oxalyl chloride (15 ml) were distilled off. The product was cooled and there were added with stirring absolute benzene (15 ml), a crystal of triethylenediamine, and the corresponding 2-aminopyrimidine or 2-amino-1,3,5-triazine (5 mmole) as a finely divided powder. The product was stirred with gentle heating for 2-4 h not allowing the temperature to each reflux. Next day after cooling, the precipitate was washed with benzene, dried, and crystallized from absolute acetonitrile or free from cyclic imide IV contamination by extraction of the sulfonylurea using absolute acetonitrile in a Soxhlet apparatus. In the case of Ig, which was relative soluble in the original solution, the reaction mixture was taken to reflux, filtered hot, and placed in a fridge. Next day, the crystalline precipitate was filtered.

In the preparation of sulfonylurea I*l*, the reaction was carried out and the target product separated by filtration. The mother liquor was placed in a fridge for a short time to give a low melting crystalline modification of I*l* (about 5%). This was gradually converted to the higher melting form on standing.

X-Ray Structural Investigation. Crystals of If ($C_{17}H_{18}N_6O_6 \cdot 0.5H_2O$) were monoclinic (from acetonitrile). At 20°C, $a = 9.643(2)$, $b = 15.633\ (3)$, $c = 26.411\ (7)$ Å, $\beta = 95.84(2)°$, $Z = 8$, space group = C2/c. Cell parameters and intensities of 3282 independent reflections were measured on a Siemens R3m/PC (λMoKα, graphite monochromator, $\theta/2\theta$ scan, $\theta << 30°$), 2700 reflections with $I \geq 4\ \sigma\ (I)$ were used for interpretation and refinement of the structure. It was solved by a direct method and refined by a full matrix least squares analysis in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms revealed by difference Fourier series were refined isotropically. Final values of the difference factors were $R = 0.038$, $R_w = 0.039$. All calculations were carried out on an IBM PC AT using the SHELX PLUS program. Coordinates of non-hydrogen atoms are given in table 9 and of hydrogen atoms in Table 10.

This work was carried out with financial support from the Russian Fund for Research Investigations, project code 93-03-04290.

REFERENCES

1. V. K. Promonenkov, V. I. Sorokin, L. M. Nesterova, O. N. Fedorova, and T. E. Granina, Sulfonylhetarylureas [in Russian], Scientific Research Institute for Technical Chemistry, Moscow (1985).
2. N. N. Mel'nikov, Pesticides [in Russian], Khimiya, Moscow (1987), pp. 584, 640.
3. J. Szmuszkovicz, J. Org. Chem., **29**, 178 (1964).
4. D. F. Zimmerman, Eur. Patent Appl. 70698; Chem. Abstr., **99**, 5650r (1983).
5. V. I. Sorokin, S. N. Golosov, A. N. Kornilov, D. S. Yufit, Yu. T. Struchkov, and V. N. Drozd, Khim. Geterotsikl. Soedin., No. 7, 969 (1993).
6. A. Kalman, M. Czulger, and G. Agray, Acta Crystallogr., **37**, 868 (1981).
7. A. Albasini, M. Melegari, G. Vampa, M. Rinaldu, and A. Pastelli, Bull. Chim. Farm., **117**, 664 (1978).
8. N. S. Vul'fson, V. G. Zaikin, and A. I. Mikaya, Mass-Spectrometry of Organic Compounds [in Russian], Khimiya, Moscow (1986), p. 283.
9. H. Schwarz, Top. Curr. Chem., **73**, 231 (1978).