ELECTRONIC STRUCTURE AND MASS SPECTRA OF SUBSTITUTED HEXAHYDRO-1,3,5-TRIAZINE-2-THIONES

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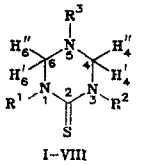
The electron density in the molecules of substituted hexahydro-1,3,5-triazine-2-thiones was calculated by the LCAO-MO SCF method in the MINDO/3 approximation. The mass spectra of substituted 5-methylhexahydro-1,3,5-triazine-2-thiones were studied, and a fragmentation scheme for the compounds is proposed.

The reactivity of substituted hexahydro-1,3,5-triazine-2-thiones, which have found wide use as herbicides [1] and as accelerators for the sulfur and nonsulfur vulcanization of diene rubbers [2], is determined not only by the presence of nucleophilic sulfur atoms in their molecules but also by the nature of the substituents at the nitrogen atoms of the triazine ring [2]. However, in spite of the practical importance of these compounds, published data on their structure are extremely limited. The crystal and molecular structures have been determined only for 1,3,5-trinitrohexahydro-1,3,5-triazine [3] and a compound related to the triazines and containing a thioamide group, i.e., hexahydropyrimidine-2-thione [4]. In addition, the mass spectra of symmetrically substituted hexahydro-1,3,5-triazines have mostly been described in the literature.

In order to determine the effect of the sulfur atom of the thioamide group and also the nature of the substituent at the nitrogen atoms on the distribution of charges and on the nature of dissociation under electron impact we studied the mass spectra of substituted hexahydro-1,3,5-triazine-2-thiones (II, IV-VIII) and undertook a calculation for the model systems (I-IV) by the LCAO-MO SCF method in the MINDO/3 approximation [8].



I-VIII

I, II R^1=H, III, IV, VII R^1=CH_3, V R^1=C_2H_5, VI, VIII R^1=C_6H_5; I—III, VI R^2=H, IV R^2=CH_3, V R^2=C_2H_5, VII, VIII R^2=C_6H_5; I R^3=H, II—VIII R^3=CH_3

Since the molecular and crystal structures were not known for any of the investigated compounds (I-VIII), for the quantum-chemical calculation we used a model constructed on the basis of a comparison of the known structures of related compounds, i.e., 1,3,5-trinitrohexahydro-1,3,5-triazine (IX) [3], hexahydropyrimidine-2-thione (X) [4], and thiourea (XI) [9]. In the molecule of (IX) the triazine ring has a configuration reminiscent of the chair conformation of cyclohexane [3]. The presence of the thioamide group in the molecule of (X) leads to a ring configuration corresponding to a half-chair, since the thioamide group deviates slightly from the plane in which the $C_{(6)}N_{(1)}C_{(2)}N_{(3)}C_{(4)}$, atoms lie. This agrees well with the results from work [9] on the molecular structure of (XI). The idealized model of the saturated triazine ring was therefore selected in the following way. The $C_{(6)}$, $N_{(1)}$, $C_{(2)}$, $N_{(3)}$, $C_{(4)}$, and S atoms lie in one plane, and the $N_{(5)}$ atom projects from it. The model molecules have symmetry described by the C_S point group. The bond lengths and bond angles for the model compounds (I-IV), taken from [3, 4], have the following values:

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TABLE 1. The Distribution of the Charge at the Atoms in the Molecules of (I-IV), au

Atom	I	II	III	IV
S	−0,5700	−0,5633	−0,5731	−0,5818
$N_{(2)}$	0,4699	0,4662	0,4541	0,4426
$N_{(1)}$	−0,1920	−0,1766	−0,1528	−0,1547
$N_{(3)}$	−0,1920	−0,1766	−0,1786	−0,1547
$C_{(4)}$	0,2583	0,2601	0,2581	0,2594
$C_{(6)}$	0,2583	0,2601	0,2617	0,2594
$N_{(5)}$	−0,2388	−0,2253	−0,2270	−0,2286
C_{Me_3}	—	0,1800	0,1790	0,1781
C_{Me_1}	—	—	0,1541	0,1534
C_{Me_2}	—	—	—	0,1534
$H_{(1)}$	0,1248	0,1311	—	—
$H_{(2)}$	0,1248	0,1311	0,1278	—
$H_{(4)}$	−0,0316	−0,0348	−0,0360	−0,0373
$H_{(6)}$	−0,0316	−0,0348	−0,0364	−0,0373
$H_{(4)}$	−0,0383	−0,0666	−0,0679	−0,0696
$H_{(6)}$	−0,0383	−0,0666	−0,0686	−0,0696
$H_{(5)}$	0,0967	—	—	—
H_{Me_3}	—	−0,0458	−0,0469	−0,0479
H_{Me_3}	—	−0,0282	−0,0202	−0,0212
H_{Me_3}	—	−0,0282	−0,0202	−0,0212
H_{Me_1}	—	—	−0,0146	−0,0159
H_{Me_1}	—	—	−0,0258	−0,0273
H_{Me_1}	—	—	0,0332	0,0319
H_{Me_2}	—	—	—	−0,0159
H_{Me_2}	—	—	—	−0,0273
H_{Me_2}	—	—	—	0,0319

$r_{C_2N_1}=1.334$; $r_{C_2S}=1.722$; $r_{C_6N_1}=1.452$; $r_{C_6H_5}=1.454$; $r_{N_5CMe}=1.47$ [10]; $r_{NH}=1.00$; $r_{CH}=1.09$ Å; $\angle SC_2N_1=119.75$; $\angle N_1C_2N_3=120.50$; $\angle C_2N_1C_6=122.40$; $\angle N_1C_6N_5=109.30$; $\angle C_4N_5C_6=114.81$; $\angle C_2N_1H_1=\angle H_1N_1C_6=118.80$; $\angle N_1C_6H'_6=\angle N_1C_6H''_6=109.35$; $\angle H'_6C_6H_5=\angle H''_6C_6N_5=109.35$; $\angle H'_6C_6H''_6=110.12$; $\angle C_6N_5H_5=117.90°$.

For the methyl groups all the angles were taken as tetrahedral. When the hydrogen atoms are substituted by methyl groups, the corresponding bond angles remain unchanged. The calculation was made for the closed electron shells with participation of the s and p orbitals for the C, N, and S atoms and the s orbitals for the H atoms.

As a result of the calculation we obtained the distribution of the charges in compounds (I-IV) (Table 1), the energies of the molecular orbitals, the dipole moments, and the enthalpies of formation (Table 2). (The energies are only given for the last occupied MO.) From Table 1 it is seen that the maximum negative charge in the molecules of (I-IV) is concentrated at the sulfur atom and increases with increase in the number of electron-donating substituents at the nitrogen atoms at positions 1 and 3 of the ring. The last occupied orbital in the molecules of (I-IV) is of the same type as the nonbonding orbitals of the sulfur atom. The first ionization potential of these compounds must therefore be of the n type, and the transition to the ionized state will lead to a decrease in the negative charge at the sulfur atom. An analogous conclusion about the localization of the charge at the sulfur atom of the thiocarbonyl group was reached during study of the photoelectron spectra of thiazolidine-2-thiones [11]. The introduction of substituents at the nitrogen atoms in the molecules of (I) leads to a decrease in the stability of compounds (II-IV), as indicated by the increase in their enthalpies of formation and also by the increase in the antibonding character of the last occupied orbital, which shows up as some decrease in the coefficients at the p_x atomic orbitals of the sulfur atoms in the breakdown of the MO (Table 1). The increase in the antibonding character of the last occupied MO with increase in the number of electron-donating groups at the nitrogen atoms leads to a decrease in the stability of the molecules to electron impact in the transition from (II) to (IV).

According to [5-7], the intensity of the peak for the M^+ ion in the mass spectra of most of the derivatives of hexahydro-1,3,5-triazine, recorded with 70-eV ionizing electrons, is not greater than 3%. In addition, while recording the mass spectra of compounds of this type, Schumacher and Taubenest [5] came up against a number of difficulties due to thermal decomposition of the compounds before the spectra were recorded. The mass spectra of compounds

TABLE 2. The Energy and the Form of the Last Occupied MO, the Dipole Moment, and the Enthalpy of Formation of Compounds (I-IV)

Compound	E, eV	$\Psi_j = \Sigma C_{jk} X_k$*	μ, D	ΔH, kcal/mole
I	−8,252	$0{,}969p_{X_S} - 0{,}092(s_{N_1} - s_{N_3}) + 0{,}091(p_{X_{N_1}} - p_{X_{N_3}}) - 0{,}090(p_{Y_{H_1}} - p_{Y_{H_3}})$	7,302	−15,832
II	−8,323	$-0{,}968p_{X_S} + 0{,}092(s_{N_1} - s_{N_3}) - 0{,}094(p_{X_{N_1}} - p_{X_{N_3}}) + 0{,}091(p_{Y_{H_1}} - p_{Y_{H_3}})$	7,943	1,150
III	−8,074	$-0{,}951p_{X_S} - 0{,}087p_{Z_{C_6}} - 0{,}137p_{Z_{C_4}} + 0{,}104s_{HMe_2}$	7,764	19,644
IV	−7,843	$0{,}941p_{X_S} + 0{,}131(p_{Z_{C_4}} - p_{Z_{C_6}}) - 0{,}103(s_{HMe_2} - s_{HMe_3})$	7,596	32,260

*X_{Ai}/X represents the type of basis AO, A represents the type of atom, and i represents the number of the atom.

TABLE 3. The Mass Spectra of Compounds (II, IV—VIII)*

Compound	m/z values (relative intensity, %)
II	131 (100), 89 (21), 88 (48), 60 (62), 53 (21), 45 (19), 44 (92), 43 (40), 42 (82), 30 (51), 28 (61)
IV	159 (100), 116 (20), 73 (49), 72 (26), 57 (56), 45 (15), 44 (94), 43 (92), 42 (77), 41 (14), 28 (35)
V	187 (100), 144 (45), 129 (35), 103 (28), 87 (67), 72 (24). 59 (27), 58 (77), 57 (93), 44 (25), 42 (76)
VI	207 (56), 164 (24), 135 (79), 119 (75), 118 (91), 105 (32), 91 (82), 77 (100), 64 (63), 51 (49), 42 (73)
VII	221 (17), 136 (16), 135 (100), 105 (13), 103 (10), 77 (74), 51 (28), 50 (11), 43 (33), 42 (59), 41 (12)
VIII	283 (10), 135 (77), 105 (100), 104 (45), 77 (93), 51 (34), 50 (12), 44 (18), 43 (35), 42 (45), 41 (13)

*The M^+ and the 10 strongest ion peaks are given.

(II, IV—VIII) (Table 3) were therefore recorded with 20-eV electrons with the inlet system at room temperature.

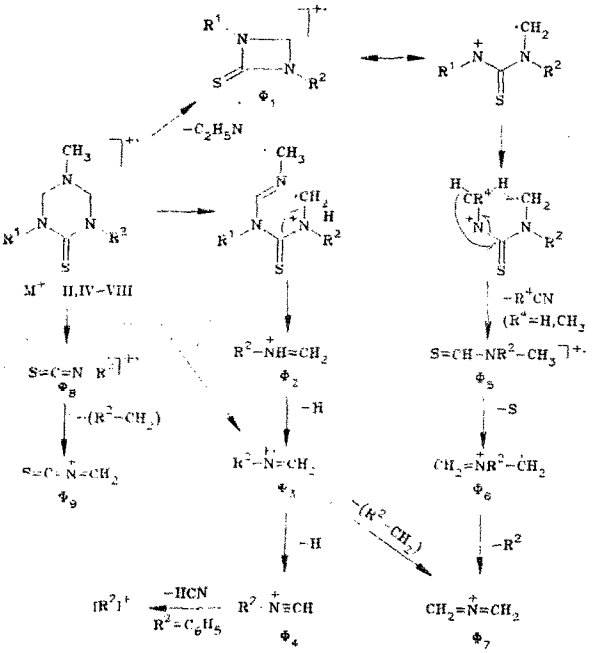
Analysis of the obtained data (Table 4) in comparison with published data [5] shows that the introduction of the thiocarbonyl group into the hexahydrothiazine ring appreciably stabilizes the M^+ ion. Thus, the intensity of the peak for the M^+ ion in the spectrum of 1,3,5-trimethylhexadhydro-1,3,5-thiazine is 9.8% [5], while the peak of the analogous ion in the spectrum of its 2-thioxo derivative (II) has the maximum intensity. The stability of the molecules of compounds (II, IV—VIII) to electron impact decreases with increase in the chain length of the alkyl substituent at the nitrogen atoms and with substitution of the alkyl group by a phenyl group (Table 4).

The dissociation of M^+ ion in compounds (II, IV—VIII) (see the scheme) takes place both in directions independent of the presence of the thiocarbonyl group in the ring and in directions determined by the latter. The Φ_1 fragment [produced by the removal of a neutral molecule containing the $N_{(s)}$ nitrogen atom] and the Φ_2—Φ_4, Φ_7 fragments are removed by the mechanism proposed for the dissociation of the M^+ ion in symmetrically substituted hexahydrotriazines [5]. This is favored by the practically identical intensity of the peaks for the Φ_1—Φ_4, Φ_7 fragments in the spectra of (I) and 1,3,5-trimethyl-hexahydro-1,3,5-triazine [5]. In addition to a cyclic structure the Φ_1 fragment may have an open structure, from which the Φ_5 fragments are formed as a result of migrations of the hydrogen atoms and removal of the nitrogen-containing molecule; the composition of the Φ_5 fragments was established by means of the high-resolution mass spectra of compounds (IV, V). The peak for the analogous ion $[C_3H_9N]^+$ with m/z 59 and a relative intensity of 37% is present in the spectrum of the trimethyl-substituted triazine [5]. Further dissociation of the Φ_5 fragment with the loss of the sulfur atom leads in the spectra of compounds (IV-VI) to the appearance of the peaks for the Φ_6 fragments, which according to the high-resolution mass spectra contain one nitrogen atom. Thus, the fact that the peak for the ion with m/z 57 is absent in the spectrum of

TABLE 4. The Peak Intensities of the Characteristic Fragment Ions in the Mass Spectra of Compounds (II, IV—VIII)

Compound	Peak intensities of ions as percentages of total ion current										
	M^+ (W_M)	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7	Φ_8	Φ_9	$[R^2]^+$
II	18,1	7,0	7,5	2,6	8,9	—	—	12,1	9,1*	—	—
IV	17,9	3,1	14,3	13,9	11,7	1,7	8,4	11,7	7,4	4,0	—
V	13,6	5,3	8,9	10,9	2,0	3,3	0,4	8,9	1,5	2,8	—
VI	6,2	2,5	0,6	3,2	1,6	—	7,7	7,4	8,0	—	10,1
VII	3,7	1,1	0,6	2,6	1,7	—	—	11,9	20,1	0,5	14,8
VIII	1,8	—	1,3	14,8	6,6	—	—	6,6	11,4	—	13,8

*The $[\Phi_8+H]$. fragment



the trimethyl-substituted triazine [5], i.e., the analog of the Φ_6 ion, makes it possible to suppose that the $N_{(5)}$ atom is not involved in the formation of the Φ_6 fragment.

The presence of the thiocarbonyl group in compounds (II, IV—VIII) leads to the appearance in their spectra of peaks for the Φ_8 fragments, which according to the high-resolution mass spectra contain nitrogen and sulfur atoms, and to the absence of peaks for the isobaric $[RNHCH_2NHCH_3]^+$, fragments typical of the spectra of symmetrically substituted hexahydrotriazines [5]. In addition to the peaks shown in the scheme, the spectra of compounds (VI—VIII) contain peaks for phenyl-containing ions with m/z 118 and 77, while the spectrum of (VI) contains peaks for ions with m/z 91, 65, and 64. (According to the high-resolution spectra, the latter is a doublet for $[C_5H_4]^+/[C_4H_2N]^+$, 1:1 , while the ion with m/z 91 contains one nitrogen atom.)

EXPERIMENTAL

The mass spectra were obtained on a Varian MAT-731 instrument with direct injection of the sample into the ion source (accelerating potential 3 kV, cathode emission current 300 μA, ionization potential 20 eV, inlet system temperature 25-35°C). The high-resolution mass spectra were obtained on the same instrument under similar conditions with perfluorokerosene as standard. The resolution was $M/\Delta M = 10\,000$.

The MINDO/3 calculations were carried out on an EC-1960 Computer using the program in [8].

The synthesis of compounds (II, IV—VIII) was described in [1].

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