LITERATURE CITED

1. A. S. Nakhmanovich, V. N. Elokhina, I. D. Kalikhman, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2642 (1979).
2. A. S. Nakhmanovich, V. N. Elokhina, I. D. Kalikhman, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 8, 1137 (1977).
3. A. S. Nakhmanovich, V. N. Elokhina, I. D. Kalikhman, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 8, 1041 (1978).
4. V. N. Elokhina, R. V. Karnaukhova, A. S. Nakhmanovich, I. D. Kalikhman, and M. G. Voronkov, Zh. Org. Khim., 15, 57 (1979).
5. V. N. Elokhina, A. S. Nakhmanovich, R. V. Karnaukhova, I. D. Kalikhman, and M. G. Voronkov, Khim. Geterotsikl., Soedin., No. 3, 329 (1981).
6. A. S. Nakhmanovich, V. N. Elokhina, R. V. Karnaukhova, G. G. Skvortsova, and I. D. Kalikhman, Khim. Geterotsikl. Soedin., No. 11, 1489 (1982).
7. F. Kürzer and P. M. Sanderson, J. Chem. Soc., 230 (1982).
8. C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 75, 141 (1953).

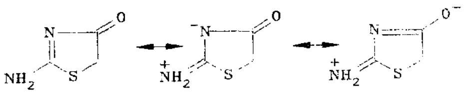
STRUCTURE OF 2-AMINO-4-THIAZOLINONE

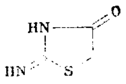
S. M. Ramsh, N. A. Smorygo,
and A. I. Ginak

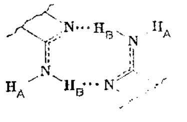
UDC 547.789.1.0:543.25'4:541.623

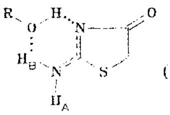
It was shown by the methods of IR and NMR spectroscopy that 2-amino-4-thiazolinone ("pseudothiohydantoin") exists in an amino form in the crystalline state and in solutions in dimethyl sulfoxide, water, and trifluoroacetic acid, and in this amino form all the nitrogen-carbon bonds are partially double. In dimethyl sulfoxide and trifluoroacetic acid there is an autoassociation with the formation of dimers. Inhibited rotation of the amino group around the exocyclic nitrogen-carbon bond was detected. The results of a calculation of the IR spectrum of 2-amino-4-thiazolinone according to the force-field method agrees with the experimental data.

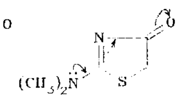
Earlier [1] we showed that in aqueous solution 2-amino-4-thiazolinone (I, "pseudothiohydantoin") exists in the amino form IA. The reports on the predominant tautomeric form of compound I in the crystalline state, based on the results of a study of the IR spectra, are contradictory [1]. A structural peculiarity of the cyclic analogs, 2-aminoazolines and 2-aminoazines, which hinders the interpretation of the data of x-ray crystallographic analysis and IR spectroscopy, is the ability of the molecules of these compounds to dimerize as a result of the formation of short hydrogen contacts N–H...N between the amidine fragments [2-4]. Such contacts enhance the conjugation already present in the monomer molecules, and as a result, the double bonds are delocalized to a substantial degree over the amidine fragments, the N–H bonds are lengthened, and the N...H hydrogen bonds in the contacts N–H...N are shortened, i.e., cyclic dimers IC are mesomeric "hybrids" of the tautomeric forms [5].

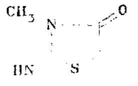

IA


IB


IC


ID


II


III

For such potential tautomeric systems it is insufficient, while knowing the localization of the hydrogen atoms, to establish in which "classic" flow-through tautomeric form the com-

---

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1066-1070, August, 1984. Original article submitted June 22, 1983.

0009-3122/84/2008-0865$08.50

pound exists; the delocalization of the π-electrons in the mesomeric fragment must also be estimated. Without considering the localization of hydrogens and the resonance, the interpretation of the results of the investigation may be incomplete and even incorrect. Thus, the data of IR spectroscopy of crystalline samples [6] and x-ray crystallographic analysis [7, 8] confirm the fact that 2-amino-4-thiazolinone exists in an imino-form IB, while for its 5-phenyl-analog with similar geometry of the molecule, the amino form [3], the polar canonical structure of the amino form [9], and a mixture of resonance hybrids of the amino- and imino-forms [2] have been proposed.

This work presents the results of a study of the structure of 2-amino-4-thiazolinone (I), by experimental methods using NMR and IR spectroscopy and by calculation according to the force-field method.

A comparison of the ^{13}C NMR spectra of compound I and model compounds 2-dimethylamino-4-thiazolinone (II) and 2-imino-3-methyl-4-thiazolidinone (III) convincingly shows (Table 1) that the tautomer IA predominates in DMSO-D_6; moreover, no other tautomeric forms are detected. The most sensitive ("indicative") to a change in the position of the C=N double bond, in the ring or outside it, is the $C_{(2)}$ atom contained in the amidine fragment. An analogous picture is observed for 2-aminothiazines [10].

In the PMR spectra of compounds I and II, the signals of the protons of NH in the amino group and the CH_3 protons of the dimethylamino group are split into doublets as a result of inhibited rotation around the partially double bond $C_{(2)}{=}{=}N_{(2')}$. When the temperature is raised, the components of the doublet coalesce. For compound II the temperature of coalescence and the free energy of activation of rotation, calculated according to the Eyring–Gleichung formula [11], are 353°K and 76.3 kJ/mole, respectively, which is evidence of a large degree of double bonding of the exocyclic $C_{(2)}{=}{=}N_{(2')}$ bond. For compound I the temperature of coalescence cannot be determined exactly on account of the substantial broadening of the signals of the NH protons. They already merge at 338°K, which corresponds to the value of $\Delta G^{\neq} =$ 73.7 kJ/mole, but the true temperature of coalescence, in all probability, lies above that indicated, and the barriers to rotation of compounds I and II cannot be compared. Nonetheless, it is clear that the value of $\Delta G^{\neq}$ of rotation for compound I is no lower than 73.7 kJ/mole, i.e., the exocyclic nitrogen–carbon bond is substantially double in this case also.

The results of a calculation of the frequencies and forms of flat normal vibrations of the molecule of compound I also provide evidence of its mesomerism. According to the calculation of the vibrational spectrum performed earlier [12] without consideration of the actual topography of the molecule, the imino-form IB predominates, with "traces" of the amino-form IA. We calculated the frequencies and forms of the normal vibrations of compound II, simulating the amino-form, and of III, simulating the imino-form [13]. The length of the bonds and values of the valence angles for compound II were taken from [14], and for compound III from [8]. According to the calculation, three bands in the region of 1720-1550 cm^{-1} correspond to the vibrations of the multiple bonds of both forms (Table 1). The high-frequency band is due to the interacting vibrations νC=O, ν of the heterocycle, and for compound III also the vibrations $\nu C_{(2)}{=}N_{(2')}$. It is characteristic that for the model of the amino-form II all three bands lie lower than for the model of the imino-form III.

After replacing the mass of the methyl group by the mass of the hydrogen atom and using the geometrical parameters and the force fields of the model compounds II and III, we calculated the vibrational spectra of the amino- and imino-tautomers. It was found that the IR spectrum of crystalline 2-amino-4-thiazolinone (I) does not coincide with any of the calculated spectra, especially in the region of 1700-1500 cm^{-1}. Coincidence of the calculated spectrum of compound I with the experimental spectrum could be achieved by varying the force constants of the bonds of the model of the amino-form II, which is evidence in support of the aminotautomer IA. While the force constants of the $C_{(2)}{-}{-}N_{(3)}$ bonds are equal, the force constants of the $C_{(2)}{=}{=}N_{(2')}$ and $N_{(3)}{=}{=}C_{(4)}$ bonds in compound I are substantially higher, and of the $C_{(4)}{=}{=}O$ bond lower than in compound II [13]. Moreover, in the molecular fragment $^{\delta+}N_{(2')}{=}{=}C_{(2)}{=}{=}N_{(3)}{=}{=}C_{(4)}{=}{=}O^{\delta-}$ in comparison with compound II the coefficients of interaction of the bonds are increased, which is evidence of a stronger conjugation in this fragment for compound I. The enhancement of mesomerism (increase in the contribution of polar canonical structures) is associated with dimerization of compound I according to the IC type, as well as with the existence of hydrogen bonds N–H...O.

The IR spectra of solutions of model compounds II and III in DMSO and D_2O are similar to the spectra of their solid samples, only the value of νC=O in the IR spectrum of compound II

TABLE 1. NMR and IR spectra of 2-Amino-4-thiazolinone (I), 2-Dimethylamino-4-thiazolinone (II), and 2-Imino-3-methyl-4-thiazolidinone (III)

Compound	NMR spectrum (in DMSO-d_6),						IR spectrum, cm^{-1}				
	^1H			^{13}C			in the crystalline state			in DMSO	in D_2O
	NH	CH_3	CH_2	C_2	C_4	C_5	ω_{exp}	ω_{calc}	type of vibration		
I	8,99*	—	3,97	183,2	187,8	43,5	1688	1685	$\nu C{=}O$	1692	1653
	9,17						1656	1650	ν of ring,	1656	1545
							1648	1630	ν of ring, $\nu C_2{=}N_{2'}$	1648	1535
							1539	1540	$\nu C_2{=}N_{2'}$, δNH_2	1530	
							1506	1500	ν of ring		
II	—	2,91	3,85	188,4	193,0	51,5	1689	1697	$\nu C{=}O$, ν of ring	1715	1667
		2,94					1593	1594	$\nu$of ring, $\nu C{=}N$	1575	1577
							1565	1564	$\nu C{=}N$, ν of ring	1565	1564
III	9,29	3,03	4,03	164,6	179,0	39,3	1710	1709	$\nu C{=}O$, $\nu C{=}N$, ν of ring	1718	1718
							1638	1636	ν of ring, $\nu C{=}O$, $\delta N{-}N$	1635	1620
							1622	1620	$\nu C{=}N$, $\nu C{=}O$, ν of ring		

*Temperature 24°C.

is lowered in D_2O and elevated in DMSO (Table 1). The IR spectrum of the compound I in DMSO is also similar to the spectrum of the solid sample, while its IR spectrum in D_2O resembles the spectrum of compound II in the same solvent. Thus, the IR spectra of the solutions confirm the conclusion that the amino-form of compound I predominates in DMSO and the data of [1] on the predominance of this same form in water. The coincidence of the IR spectra of compound I in the crystalline state and in solution in DMSO is evidence that in DMSO, just as in the solid phase, there is an autoassociation with the formation of dimers of IC. However, NMR spectroscopy on ^1H and ^{13}C nuclei does not reveal the existence of a monomeric equilibrium in DMSO-d_6: the shape of the PMR spectra does not depend on the concentration of compound I, while the ^{13}C nuclei have the same resonances. It can be assumed that in DMSO compound I is entirely dimerized. The formation of dimers does not prevent rotation of the amino group around the $C_{(2)}{=}N_{(2')}$ bond; evidently precisely dimerization permits observation of this rotation by shifting the signals of the H_B protons in the strong-field direction. An analogous picture is observed for duplexes of cytosine and guanine [15]. The strong-field signal 8.99 ppm of the doublet of the amino-protons corresponds to resonance of the H_B protons, participating in the formation of an intermolecular hydrogen bond, while the weak-field signal 9.17 ppm corresponds to resonance of the H_a protons, accessible to the solvent. Such an assignment is explained by shielding of the H_b protons by the π-system of amidine fragments of the dimer IC [16].

The four processes in which the protons of the amino group participate: inhibited rotation (the degenerate exchange), dimerization, hydrogen bonding with the solvent, and exchange with the protons of the water contained in DMSO-d_6, may affect the nature of the temperature dependence of the PMR spectrum of compound I (Fig. 1). It is not surprising that at increased temperatures, all the way up to the temperature of coalescence of the amino-protons, the pictures of the spectra have a not entirely symmetrical form. After coalescence the averaged signal of the amino-protons is monotonically shifted in the strong-field direction with increasing temperature on account of the weakening of the hydrogen bond to the solvent [17].

The nonequivalence of the protons H_a and H_b is also indicated by the PMR spectrum, recorded after the addition of several drops of acetic acid: The weak-field signal of the protons H_a accessible to the solvent disappears, and the signal of the carboxyl protons of the acid, exchanged with the H_a protons and the water protons of the solvent, appears (Fig. 2). With increasing acid concentration the signal of the carboxyl protons is shifted in the weak-field direction. Disappearance of the signal of the H_a protons is due to proton exchange with acetic acid. Since the basic properties of compound I are very weakly expressed [1], it is not protonated by acetic acid. Actually, the signal of the NH protons in the PMR spectrum of 2-amino-4-thiazolinone hydrochloride is a broad peak with intensity greater than 3H (Fig. 2), the position and intensity of which, as a result of acid-catalyzed exchange with the protons of water contained in DMSO-d_6, depend on the water concentration in the solvent and on the temperature of recording. Moreover, the signal of the methylene protons of the hydrochloride

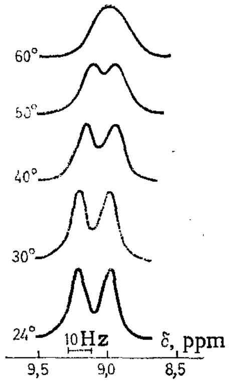


Fig. 1

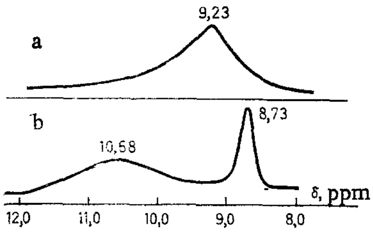


Fig. 2

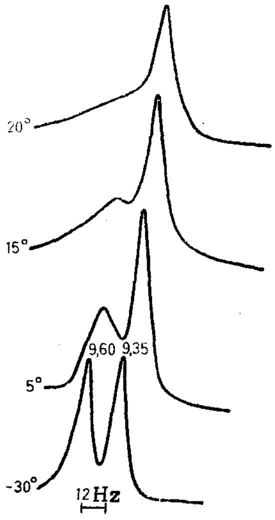


Fig. 3

Fig. 1. Temperature dependence of the signals of the protons of the amino group of 2-amino-4-thiazolinone I in DMSO-d_6.

Fig. 2. Fragments of the PMR spectra in DMSO-d_6: a) 2-amino-4-thiazolinone hydrochloride; b) 2-amino-4-thiazolinone I in the presence of several drops of acetic acid.

Fig. 3. Temperature dependence of the signals of the protons of the amino group of 2-amino-4-thiazolinone I in trifluoroacetic acid.

lies at 4.11 ppm, whereas when acetic acid is added to a solution of compound I in DMSO-d_6 the position of the signal of the methylene protons is unchanged.

Protonation also does not occur in trifluoroacetic acid (Fig. 3). At −30°C a doublet signal of the NH protons, 9.35 and 9.71 ppm, is observed, with intensity 1H each; when the temperature is raised, the weak-field signal is broadened on account of acceleration of exchange with the solvent. Consequently, in this solvent also dimer associates of the amino-form IC predominate.

In aqueous solution the dimers break down, and the IR spectrum of the monomer of compound I virtually coincides with the IR spectrum of the model of the amino-form II (Table 1). It can be assumed that the difference in the energies of the hydrogen bonds formed by compound I with DMSO and water is due to the possibility of existence of solvate complexes of the type of ID in the hydroxyl-containing solvents ROH; they stabilize the monomer form of compound I if R has a small volume.

An alternative explanation of the observed nonequivalence of the H_a and H_b protons of compound I can also be given without enlisting the hypothesis of its dimerization, since even in the monomer form these protons have different magnetic surroundings, and the barrier to rotation around the $C_{(2)}{=}N_{(2')}$ bond is rather high. In this case the higher rate of exchange of hydrogen-bonded H_b protons, the signals of which are shifted in the weak-field direction, is associated with the formation of complexes ID when acetic acid is added. However, all this does not explain why the IR spectra of compound I in the crystalline state and in solution in DMSO resemble one another so strikingly.

EXPERIMENTAL

The calculations of the vibrational spectra were performed on a Minsk-22 computer according to the program of [19]. The IR spectra were recorded on a IKS-29 spectrometer. The crystalline samples were recorded in the form of suspensions in liquid petrolatum and perfluoropetrolatum on KBr plates. The spectra of the solutions were recorded in CaF_2 cuvettes.

The PMR spectra were recorded on RYa-2305 (60 MHz) and Tesla BS-467 (60 MHz) spectrometers; the internal standard was HMDS. The ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer; the standard for the determination of the chemical shifts was TMS. The concentration of the solutions were 0.05-0.20 M.

The production of compounds I-III was described in [1]. 2-Amino-4-thiazolinone hydrochloride was produced by the method of [18].

LITERATURE CITED

1. S. M. Ramsh, A. I. Ginak, N. A. Smorygo, Yu. G. Basova, and E. G. Sochilin, Zh. Org. Khim., 14, 1327 (1978).
2. J. P. Mornon and B. Raveau, Acta Crystallogr., 27B, 95 (1971).
3. J. P. Mornon and R. Bally, Acta Crystallogr., 28B, 2074 (1972).
4. D. Petrovic, B. Ribar, G. Argay, A. Kalman, and W. Nowacki, Acta Crystallogr., 33B, 106 (1977).
5. N. G. Furmanova, Usp. Khim., 50, 1491 (1981).
6. N. N. Khovratovich and I. I. Chizhevskaya, Khim. Geterotsikl. Soedin., No. 4, 637 (1967).
7. R. V. Ananthamurthy, M. R. Udupa, and B. V. R. Murthy, Z. Kristallogr., 137, 316 (1973).
8. V. Amirthalingam and K. V. Muralidharan, Acta Crystallogr., 28B, 2421 (1972).
9. L. A. Plastas and J. M. Stewart, Chem. Commun., 811 (1969).
10. L. M. Jackman and T. Jen, J. Am. Chem. Soc., 97, 2811 (1975).
11. H. Kessler, Angew. Chem., 72, 237 (1970).
12. R. S. Lebedev, V. I. Yakimenko, A. V. Korshunov, N. I. Afanas'eva, and V. E. Volkov, Izv. Vyssh. Uchebn. Zaved., Fizika, 14, No. 9, 76 (1971).
13. Yu. G. Basova, Dissertation for the Degree of Candidate of Chemical Sciences [in Russian], Leningrad (1980).
14. V. Amirthalingam and K. V. Muralidharan, Acta Crystallogr., 28B, 2417 (1972).
15. N. G. Dolinnaya and E. S. Gromova, Usp. Khim., 52, 138 (1983).
16. Ch. F. Howell, W. Fulmor, N. Q. Quinones, and R. A. Hardy, J. Org. Chem., 29, 370 (1964).
17. R. Silverstein, G. Bassler, and T. Morrill, Spectrometric Identification of Organic Compounds, Wiley (1974).
18. N. M. Turkevich, V. M. Vvedenskii, and L. M. Petlichnaya, Ukr. Khim. Zh., 27, 680 (1961).
19. M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich, and V. I. Stepanov, Molecular Vibrations [in Russian], Nauka, Moscow (1972).

MASS SPECTROMETRIC STUDY OF 9-SUBSTITUTED 10-SILA-2-AZAANTHRACENES

A. V. Varlamov, V. K. Shevtsov,
A. M. Klochkov, and N. S. Prostakov

UDC 543.51:547.682

The dissociative ionization of 10 derivatives of 10-sila-2-azaanthracene, containing cyanoethyl (I-III), aminopropyl (IV), amino (V, VI), and amide (VII-X) groups at the $C_{(9)}$ atom, was investigated. It was shown that for all the compounds the general direction of decomposition is elimination of substituents from the silicon and carbon $C_{(9)}$ atoms. The stability of the compounds to electron impact is determined chiefly by the nature of the substituent at the $C_{(9)}$ atoms and depends weakly on the type of substituent at the silicon atom. In the case of amino-derivatives V-X, fragmentation of the molecular ions is determined by the method of localization of the positive charge in the molecular ion. This determines the occurrence of specific decompositions, which permits reliable identification of the compounds studied according to their mass spectra.

An investigation of the dissociative ionization of a new type of heterocyclic compounds, dihydrosilaazaanthracenes and their derivatives, was begun in [1, 2]. It was shown that the main directions of the decomposition of these substances under electron impact are determined primarily by the nature of the substituents in the central hydrogenated ring of the molecule. In this work we studied the mass spectrometric behavior of new derivatives of 10-sila-2-azaanthracene, containing cyanoethyl (I-III), aminopropyl (IV), amino (V, VI), and amide (VII-X)

P. Lumumba Peoples' Friendship University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1071-1076, August, 1984. Original article submitted June 14, 1983; revision submitted October 21, 1983.

0009-3122/84/2008-0869$08.50