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STRUCTURE OF 2-AMINO-4-THIAZOLINONE AND ITS 2-ARYL DERIVATIVES IN THE CRYSTALLINE STATE

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According to IR spectroscopic analysis, the compounds 2-amino-4-thiazolinone and 2-arylamino-4-thiazolinone exist in the amino form in the crystalline state.

The amino-imino tautomerism of 2-amino-4-thiazolinone (pseudothiohydantoin, Ia) and its 2-aryl derivatives IIa-e has been described in the literature [1-3]. Two independent groups of investigators concluded that in the case of the 2-arylamino-4-thiazolinones (IIa-e), the amount of the amino form A increased as the electron withdrawing nature of the benzene ring substituents was enhanced, and also upon solution of the compounds in hydroxylic solvents [2, 3]. Vibrational spectroscopic analysis of the compounds Ia and IIa-e in the crystalline state led to the opposite conclusion [1, 3-7]. In the present paper we attempt to clarify this contradiction.

X-ray structural analysis (XRA) of the compounds under investigation indicated that the $C=N$ double bonds were extensively delocalized [8-15]. The presence of short hydrogen contacts ($N-H\cdots N$ and $N-H\cdots O$) in the crystalline state enhanced the resonance effect, which is characteristic even of unassociated molecules [1, 2]. It has also been established that in the crystalline state certain cyclic amides exhibit a type B form of dimeric association [11, 12, 15].

Based on the hydrogen atom positions and the $C-N$ bond lengths, the 5-phenyl analog of the pseudothiohydantoin Ib was found to exist in the amino form A with its accompanying resonance forms [10, 11]; these structures are sometimes referred to as "zwitterionic imino structures" [10]. The 5-phenyl analog of 2-phenylamino-4-thiazolinone IIf also exists in the amino form A [14]. With respect to pseudothiohydantoin itself (Ia), the authors [9] assigned it, appar-

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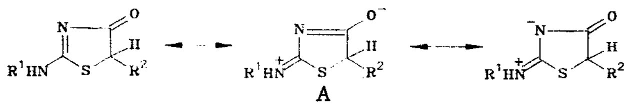
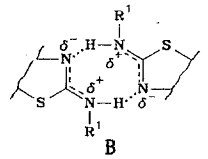
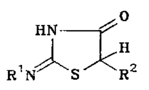


A



B



C

I a, b $R^1=H$; a $R^2=H$; b $R^2=Ph$; II a $R^1=Ph$; b $R^1=p\text{-}CH_3OC_6H_4$; c $R^1=p\text{-}NO_2C_6H_4$; d $R^1=p\text{-}(CH_3)_2NC_6H_4$; e $R^1=p\text{-}BrC_6H_4$; a – e $R^2=H$; f $R^1=R^2=Ph$

ently erroneously, the imino structure C, based on XRA, even though the hydrogen atoms could not be located and the C–N bond lengths were similar to those in the 5-phenyl derivative.

These problems illustrate the ambiguity involved in the assignment of "resonance structures" and "tautomeric forms" in the literature [9, 12]; the inadequacy of these assignments has already been noted [16]. Thus, in [9], the authors discuss the "resonance between the amino and imino forms," although in the crystalline state, from the point of view of the hydrogen atom positions, the compound exists as a resonance hybrid of one tautomeric form. In [12], where the "ratio between the amino and imino structures" is measured, the question really centers on the contributions of various resonance forms, not of different tautomers.

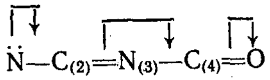
Based on these precedents, a correct interpretation of the IR spectra of the compounds under investigation would be impossible without a study of the resonance form of the $O–C_{(4)}–N_{(3)}–C_{(2)}–N_{(2')}$ fragment. Any decrease in the C=N double bond order, as well as any increase in the C–N single bond order, induced by resonance and augmented by association [12], will manifest itself in the IR spectrum in many different bands which are related to vibrations of the C•••N bonds. Participation by the carbonyl groups in the association of these molecules will decrease the frequency of $\nu_{C=O}$ in comparison with $\nu_{C=O}$ of methyl analogs displaying tautomeric forms, although in the case of the model compounds resonance may be augmented as a result of hyperconjugation involving the methyl groups.

According to our recent calculations of the frequencies and shapes of the normal vibrations, the compound Ia exists in the amino form in the crystalline state [1]. The following more detailed study of the experimental IR spectrum and its changes upon deuteration of the molecule confirms this conclusion regarding the amino structure of pseudothiohydantoin Ia.

The 3600-2000 cm^{-1} Region. The diffuse absorbance between 3220 and 2990 cm^{-1} (Fig. 1a) is assigned to the symmetric and antisymmetric stretches of the N–H bond which is not involved in N–H•••N hydrogen bonding; the band which apears as a shoulder at 3110 cm^{-1}, as well as the band at 2805 cm^{-1}, are assigned to vibrations of the N–H bond which participates in N–H•••N hydrogen bonding. A narrow band at 2930 cm^{-1} is due to the stretching vibrations of the 5-CH_2 group. This band does not shift upon deuteration of the molecule; the PMR spectrum of a deuterated sample of Ia shows a signal arising from the protons of the 5-CH_2 methylene group. Thus, in contrast to the behavior of the 2-thio analog of rhodanine [17], the protons in the methylene group in the pseudothiohydantoin Ia do not undergo exchange upon deuteration. The isotopic shift ratios of the 3220 and 2990 cm^{-1} bands are 1.33 and 1.34, respectively, whereas the isotopic shifts of the 3110 and 2805 cm^{-1} bands are 1.32; as a result, the bands in the deuterated sample appear as shoulders (Fig. 1b). These values for the isotopic shift ratios (less than $\sqrt{2}$) are characteristic of coupled stretching vibrations such as ν_sN–H and ν_{as}N–H.

The IR spectrum of the deuterated analog of Ia contains a new narrow band of medium intensity at 3560 cm^{-1}; this does not appear to be an overtone, since the spectrum does not contain a fundamental vibration at the corresponding requisite frequency. Apparently this band is a combination band arising from the frequencies for νN–D at 2230 cm^{-1} and δN–D at 1325 cm^{-1}.

The 1800-1500 cm^{-1} Region. The IR spectrum of a deuterated sample of Ia contains a band at 1325 cm^{-1} corresponding to the isotopic shift (ratio 1.35) of a weak intensity band at 1785 cm^{-1}. An analogous band at 1780 cm^{-1} in the IR spectrum of rhodanine [17] has been ascribed to Fermi resonance of $\nu_{C=O}$ and the first overtone of the C–H bond stretch. In the case of Ia, the shift of the 1785 cm^{-1} band upon deuteration precludes this type of interpretation. A similar band at 1770 cm^{-1} in the IR spectrum of oxazolines has been attributed to a fundamental transition in [18]. The 1785 cm^{-1} band in Ia has likewise been assigned to a fundamental vibration; the observed isotopic shift does not permit it to be assigned either to an overtone (the IR spectrum does not contain fundamental transitions with frequencies of 890-895 cm^{-1}) or to a combination band of vibrations in the fingerprint region of the spectrum. The band in question is therefore assigned to a deformation of the N—H bond, the frequency of which has been increased due to association.

Two types of hydrogen bonds (N—H•••N and N—H•••O) are present in the crystalline state of pseudothiohydantoin Ia [9]. These formally different modes of association give rise to a series of stretching and deformation vibrations. The IR spectrum of Ia contains, in addition to the band at 1785 cm^{-1}, another δN—H band at 1690 cm^{-1}; this band is very weak and disappears upon deuteration. This band has usually been assigned to the C═O strength [5, 6]; the isotopic shift of 1.37 precludes this interpretation and verifies the assignment of bands at 1660 [4] and 1645 cm^{-1} [19] to νC═O. These bands, as well as that at 1510 cm^{-1}, are very intense and possess a complex character due to interaction with other vibrations in the  $\ddot{N}-C_{(2)}=N_{(3)}-C_{(4)}=O$ conjugated system. They contain contributions of the δN—H vibrations (i.e., $\nu\,C\underline{---}O$ and $\nu\,C\underline{---}N$ interact with δN—H), which explains the appearance of new bands at 1175, 1160, and 1050 cm^{-1} upon deuteration.

Even more difficulties arise in the interpretation of the IR spectra of the compounds IIa-e in the crystalline state. The IR spectrum of 2-phenylamino-4-thiazolinone (IIa) is analyzed below.

The 3600-2700 cm^{-1} Region. The complexity of absorption bands in this region results from the crystal packing characteristics of the molecules of IIa. XRA [14, 20] of 5-phenyl-2-phenylamino-4-thiazolinone indicates that the compound contains at least four crystallographically independent molecules which differ from one another in the interatomic distances of the $O-C_{(4)}-N_{(3)}-C_{(2)}-N_{(2')}$ fragment; two of these molecules contain hydrogen bonds [$N_{(2')}-H\cdots N_{(3)}$ and $N_{(2')}-H\cdots O$] which are absent in the other two molecules (based on the N—N and N—O separations) [20]. It is therefore not surprising that the N—H stretching region of IIa, whose crystallographic parameters are apparently similar to those of the phenyl analog IIf, contains a multiplet of bands at 3290, 3225, 3160, 3105, 3015, 3000, 2960, and 2810 cm^{-1} (Fig. 1c); these bands are shifted to the 2460-2125 cm^{-1} region upon deuteration (isotopic shift 1.33). The high frequency end of this absorption multiplet consists of νN—H bands for the hydrogen bonded N—H•••O groups [21]. The presence of N—H...O hydrogen bonds in the crystalline state of IIa is verified by the magnitude of νC═O in the amino form, which increases when the IR spectrum is taken in a solvent (dioxane and methanol) [2] rather than in the solid phase. The frequencies at 2940, 2935, and 2865 cm^{-1} do not shift upon deuteration (Fig. 1d) and therefore correspond to νC—H stretches. The PMR spectrum of deutero-IIa contains a signal for the methylene group protons, confirming that they do not undergo exchange upon heating in methanol-d_4.

Surprisingly, deuteration also resulted in the disappearance of the band at 1635 cm^{-1} (isotopic shift 1.32), which we [7], as well as others [3, 5], had mistakenly assigned to νC═N of the imino form. The stretching vibration $\nu C\overset{---}{=}N$ should rather be associated with the narrow, medium intensity band at 1560 cm^{-1} and the complex band at ca. 1500 cm^{-1} (broad, very intense); in the latter band the $\nu C\overset{---}{=}N$ absorbance is superimposed on the $\nu C\overset{---}{=}C_{arom}$ vibrations of the phenyl ring. The $\nu C\overset{---}{=}N$ vibration at ca. 1500 cm^{-1} is further mixed with δN—H; as a result, this band moves to 1535 cm^{-1} upon deuteration, and new bands appear at 1150 cm^{-1} (shoulder, isotopic shift 1.30) and 1060 cm^{-1} (isotopic shift 1.41). These assignments contradict the conclusions [3, 5, 7] that compound IIa occurs as a mixture of the amino and imino forms in the crystalline state. On the contrary, comparison of the IR spectra of IIa and methylated derivatives which incorporate both the amino and imino tautomers indicates that the compound IIa exists as the amino structure in the crystalline state.

We were able to prepare two crystalline forms of the compound 2-p-methoxyphenylamino-4-thiazolinone (IIb): IIb-1 was obtained upon recrystallization from acetone, and form IIb-2 was obtained from chloroform. The melting points and solution spectra (in dioxane or methanol-d_4) were identical for these two forms; the solid phase IR spectra of these two forms differed significantly from one another.

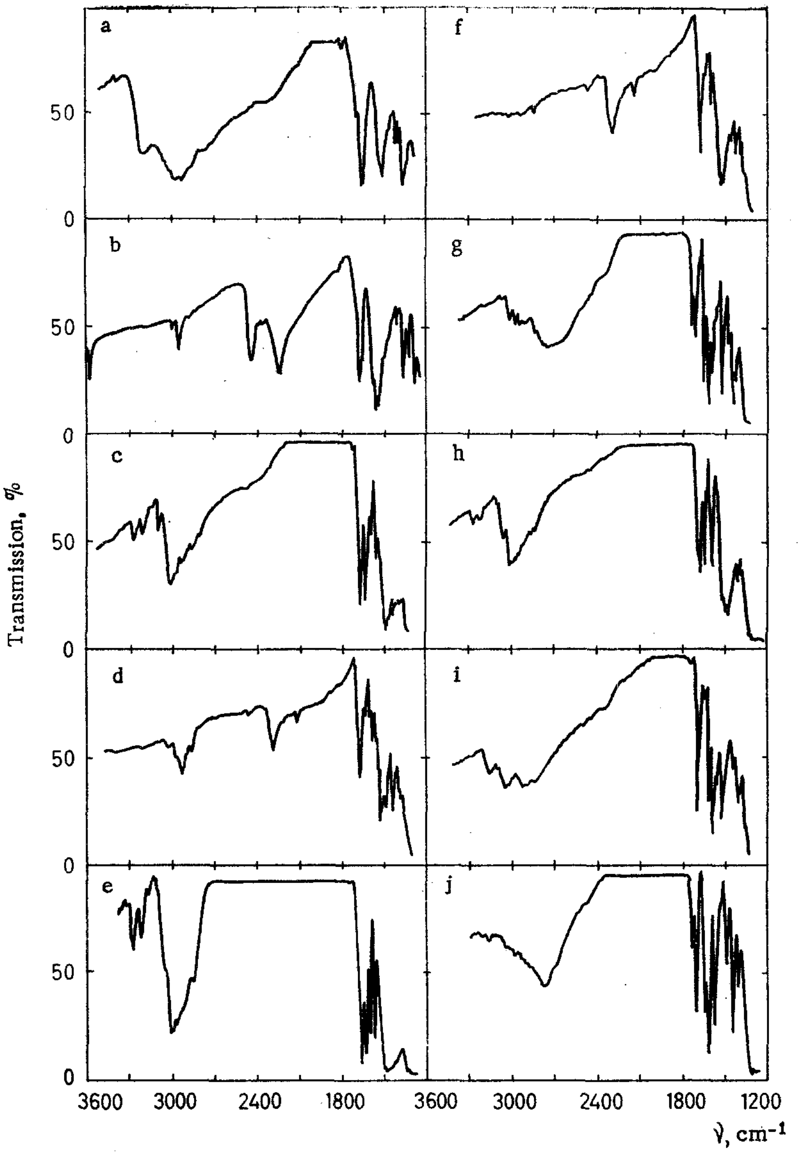


Fig. 1. IR spectra in perfluorovaseline oils. a) 2-Amino-4-thiazolinone (Ia); b) deuterated 2-amino-4-thiazolinone (Ia); c) 2-phenylamino-4-thiazolinone (IIa); d) deuterated 2-phenylamino-4-thiazolinone (IIa); e) 2-p-methoxyphenylamino-4-thiazolinone (IIb-1); f) deuterated 2-p-methoxyphenylamino-4-thiazolinone (IIb); g) 2-p-methoxyphenylamino-4-thiazolinone (IIb-2); h) 2-p-nitrophenylamino-4-thiazolinone (IIc); i) 2-p-dimethylaminophenylamino-4-thiazolinone (IId); j) 2-p-bromophenylamino-4-thiazolinone (IIe).

Form IIb-1. The 3300-2700 cm^{-1} region contains the same set of bands as the IR spectrum of IIa: 3270, 3220, 3160 cm^{-1}, and a diffuse absorbance at 3000 cm^{-1}; the low frequency end of this broad absorbance features several shoulders (Fig. 1e). The bands in the region of double bond stretches are also similar to those found in the IR spectrum of IIa: νC=O at 1665 cm^{-1}, νC═N at 1570 and 1500-1470 cm^{-1} (complex band), and νC═C$_{arom}$ at 1605 cm^{-1}. The δN–H band is also found in this region at 1635 cm^{-1}. The IR spectrum of IIb-1 after deuteration exhibits all of the changes observed for compound IIa, namely, the bands assigned to νN–H disappear, a new multiplet appears at 2460-2130 cm^{-1}, the band at 1635 cm^{-1} disappears, and the band between 1500-1470 cm^{-1} is shifted to 1530 cm^{-1}; new bands also appear at 1245, 1150 (shoulder), and 1060 cm^{-1} (Fig. 1f). The form IIb-1 therefore consists of the amino structure, in analogy with IIa. Deuteration does not alter the crystal structure of this material.

Form IIb-2. The 3300-2700 cm^{-1} region contains two broad, nearly run-together bands at 2745 and 2685 cm^{-1}; a broad complex multiplet of bands appears at the high frequency and between 3060 and 2840 cm^{-1} (Fig. 1g). The double bond stretching region of the spectrum contains bands at 1725, 1700, 1640, 1610, 1575, and 1515 cm^{-1}. Two differences stand out in a comparison of this region of the IR spectrum with that of IIb-1: the absence of absorbances between 1500-1470 cm^{-1}, and the appearance of new bands at 1725 and 1700 cm^{-1}. Based on the preponderance of the imino form C in aprotic solvents [2, 3], one would conclude that compound IIb crystallizes as the imino form out of chloroform. The imino model compound does indeed contain two bands in the region under investigation: $\nu C{=}O$ at 1720 cm^{-1} and $\nu C{=}N$ at 1630 cm^{-1}. A second explanation, however, seems more likely. If the crystalline state of form IIb-1 exists as a linear oligomeric association of the type found in 5-phenyl-2-phenylamino-4-thiazolinone IIf [14], then form IIb-2 consists of a Type B dimeric association. This explanation agrees with our discovery of the dimerization of 2-arylamino-4-thiazolinones in aprotic solvents [2], and with the very low values for the $\nu N{-}H$ vibrational frequencies in the solid spectra of IIb-2. The presence of two carbonyl stretching frequencies for IIb-2 may be rationalized in terms of crystal packing characteristics, i.e., the two molecules of the dimer are crystallographically nonequivalent; the higher frequency (relative to IIb-1) $\nu C{=}O$ stretch indicates the absence of strong intermolecular $N{-}H \cdots O$ hydrogen bonds. The bands at 1640, 1610, 1575, and 1515 cm^{-1} overlap those found in the IR spectrum of IIb-1. Since the two forms differ from one another in the types of N—H hydrogen bonds formed, it is not surprising that IIb-2 does not contain a broad band at 1500-1470 cm^{-1}. After deuteration form IIb-2 does not differ from a deuterated sample of IIb-1.

2-p-Nitrophenylamino-4-thiazolinone (IIc) also exists as the amino form in the crystalline state. The series of $\nu N{-}H$ bands (Fig. 1h) overlaps that of compound IIa and substantiates this conclusion. The double bond stretching regions for compounds IIa and IIc differ from one another only in the intensity of the band at 1590 cm^{-1}, which we have assigned to $\nu C{\equiv}C_{arom}$.

The $\nu N{-}H$ stretching frequencies at 3170, 3045, 2920, and 2835 cm^{-1} in the IR spectrum of 2-p-dimethylaminophenylamino-4-thiazolinone (IId) are lower than those of compounds IIa, IIb-1, and IIc. The double bond stretching region of the IR spectrum of IId is similar to that of IIb-2, if one compares the following sets of bands: 1695 and 1700, 1610 and 1640, 1590 and 1610, 1560 and 1575, 1525 and 1515, 1450 and 1460, and 1410 with 1430 cm^{-1}; the only exception is the absence of the carbonyl band (in IId). Apparently compound IId crystallizes as the centrosymmetric dimer (amino form B), in analogy with IIb-2. Samples of IId obtained via crystallization from benzene or acetone possess identical spectra.

2-p-Bromophenylamino-4-thiazolinone (IIe) likewise crystallizes as the amino structure in the form of a type B dimer. The N—H stretching region contains a broad band between 3240-2550 cm^{-1}; the maximum absorbance occurs at 2790 cm^{-1}. The double bond stretching region of the IR spectrum, like that for IId, is similar to that of form IIb-2 of the methoxy analog: the set of bands at 1730, 1710, 1650, 1620, 1575, 1495, and 1450 cm^{-1} in the IR spectrum of IIe (Fig. 1j) is very similar to the set of bands at 1725, 1700, 1640, 1610, 1575, 1515, and 1430 cm^{-1} in the IR spectrum of IIb-2.

These studies demonstrate that all of the 2-arylamino-4-thiazolinones (IIa-e) under investigation exist as the amino forms in the crystalline state. Compounds IIa and IIc crystallize in the form of a linear association of molecules; compounds IId and IIe crystallize as hydrogen bonded dimers, and compound IIb crystallizes in either form depending upon the nature of the recrystallizing solvent.

EXPERIMENTAL

The preparation of compounds IIa-e is described in [22]. The following solvents were employed for recrystallization: ethanol (compounds IIa and IIc), chloroform (compounds IIb and IIe), benzene (compound IId), and acetone (compounds IIb and IId).

Deuterated samples of IIa and IIb were obtained via threefold recrystallization from methanol-d_4. IR spectra were recorded on an IKS-29 spectrophotometer. Spectral samples were prepared as suspensions in vaseline or perfluorovaseline on KBr plates.

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ELECTRONIC STRUCTURE AND REACTIVITY OF THIONES AND SELENONES IN THE HETEROAROMATIC SERIES

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Quantum mechanical calculations were carried out for a series of thieno- and selenophenodihetero-2-thiones and selenones using the semiempirical SCF MO LCAO method and the CNDO/2 valence approximations with complete optimization of geometric parameters. The data obtained in this way was used to determine the reactivity of the compounds in processes leading to the formation of corresponding heterofulvalenes.

The synthesis of charge transfer complexes (CTC) based on tetrathiafulvalenes and tetraselenafulvalenes [1] constitutes a major achievement of the past few years in the preparation of organic substances displaying electronic conductivity similar to metals (so-called "organic metals"). Several superconductors based on these compounds are known [2-4]. Heterofulvalenes condensed with benzene or, in particular, heteroaromatic rings could also serve as prospective donor compounds in CTC. The introduction of additional heteroatoms of different natures into these systems would permit one to systematically and delicately vary the structural characteristics of the CTC, which, in turn, determine whether their phase transition properties are of the semiconductor—conductor or conductor—superconductor type.

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