PREPARATION, VIBRATIONAL SPECTRA, AND CONFORMATIONS OF 2-SUBSTITUTED 4H,7H-5,6-BENZ-1,3,2-DITHIAARSEPINES

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In the present work, we synthesized a new class of compounds, namely, 2-substituted 4H-7H-5,6-benz-1,3,2-dithiaarsepines and studied their molecular structure using vibrational spectroscopy.



where X = C1 (I), Br (II), Ph (III), p-Br-Ph (IV), pNO₂-Ph (V).

The reactions of o-xylylenedithiol with AsHal, in the cold give the corresponding haloarsenic derivatives:



where Hal = Cl (I), Br (II).

Heating a mixture of o-xylylenedithiol with esters of arylarsonous acids in CCl4 or benzene in a dry inert gas atmosphere gives As-aryl.derivatives:

 $SH + (AlkO)_2AsC_6H_4 - R \rightarrow SAsC_6H_4 - R + 2AlkOH$

where R = H (III), p-Br (IV), p-NO₂ (V); Alk = CH₃ or C₂H₅.

The products are white or lightly colored crystalline compounds, which darken upon storage in the light and decompose upon heating with water, release the corresponding arylarsine oxides or As₂O₃ and starting o-xylylenedithiol. These products dissolve upon heating in CCl₄, CHCl₃, benzene, and cyclohexane but are insoluble in methanol and petroleum ether.

The IR and Raman spectra of (I)-(V) were studied varying the aggregate state, medium, and temperature. Table 1 presents the spectral parameters characterizing the dithiaarsepine ring and the vAs-X bands, where X = C1, Br. In addition, the spectra show benzene fragment bands such as vCH ~ 3020-3060 cm⁻¹ and vC-C ~ 1590, 1568 cm⁻¹ [1-3]. The vAs-S band for the As(SC-)₂ fragment is seen as strong IR bands and especially strong Raman lines at 360-390 cm⁻¹. In previous work [4], we have shown that the oxygen analogs, 5,6-benz-1,3,2-dioxaarsepines with X = Cl and Br are conformationally uniform, while for X = Ph, these analogs are characterized by an equilibrium between the chair (C) and twist (T) forms. More complex conformational behavior is found for (I)-(V). Thus, upon going from the crystalline state to the melt and solutions, the spectra of (III) and (IV) undergo significant changes (Fig. 1): the Raman singlets v_sAsS_2 363, v_sSC 671, $v_{as}SC$ 764 cm⁻¹ are converted in the melt to triplets v_sAsS_2 360, 370, 388, v_sSC 665, 675, 695, $v_{as}SC$ 750, 760, 775 cm⁻¹. The relative intensity of the lines in the triplets underwent redistribution with variation of the medium polarity. Thus, for example, the intensity of the lines at ~670 and ~680 cm⁻¹ increases while the intensity of the line at 695 cm⁻¹ decreases in going from 1,4-dioxane to acetone and acetonitrile. In previous work [4], we found that the Raman frequency ~1220 cm⁻¹ is characteristic for the chair form, while the frequency at -1200 cm⁻¹ is characteristic for the twist form. Subsequently, this criterion was confirmed in the conformational analysis of 5,6-benz-1,3,2-dioxaphosphepines and 1,3dioxa-5,6-benzcycloheptenes [5, 6]. The Raman spectra of crystalline samples of (I)-(V) show

A. E. Arbuzov Institute of Organic Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 182-185, January, 1988. Original article submitted January 21, 1987.

TABLE 1. Frequencies (cm^{-1}) Characteristic for the Dithiaarsepine Ring and vAs-X (X = Cl, Br)*

Compound	v _{as} C–S	v _s C-S	v _s As - S **	v As—Hal **
(I) (II) (III) (IV) (V)	765 v.s 765 v.s 764 v.s 764 v.s 764 v.s	668 \$ 667 v_s 671 m 671 s 670 m	356 v.s 354 v.s 363 v.s 363 v.s 363 v.s 360 v.s	328 s 248 v s

*Frequencies given for crystalline samples. **Raman spectral data, the remaining data are for the IR spec-

tra.

medium-intensity lines at 1235 cm⁻¹ and weak doublet at 1210 and 1220 cm⁻¹. In the liquid state, the shape of the medium intensity line for (III) and (IV) becomes more complex, while the relative intensity of the 1210 cm⁻¹ is approximately doubled. However, these changes are not as pronounced as for dioxaarsepines, i.e., in contrast to their oxygen analogs, the As-(SC)₂ group frequencies are the spectrally "dominant" conformational criterion in the case of the thic compounds, while the region of the vC...C-C band is less informative. This is apparently related to the more characteristic nature of the vC-···C-C band in the case of the thio compounds, in which it is less sensitive to internal rotation. Both the chair and twist forms have similar frequencies. In light of the abovementioned triplet nature of the Raman lines in the liquids and our previous data [4], we may assume that (III) and (IV) and, probably, (V) (the spectrum of the melt of (V) could not be obtained) exist in a three-component equilibrium of the chair forms with equatorial (C-e) and axial (C-a) orientation of the As-X bonds and the twist form. On the other hand, the C-a form is stabilized in the crystals (III)-(V). The spectral alterations of (I) and (II) under analogous conditions are less pronounced. The changes in the region of the vC ... C-C band are insignificant, i.e., these seven-membered rings are less conformationally mobile in the case of exocyclic C1 and Br substituents. It is not excluded that an equilibrium between the C-a form with some twist form exists for (I) and (II) in the liquid and solutions. This may be indicated by the observed doubling of the IR bands at ~670 cm^{-1} (v_sC-S) in going from the crystal to the melt and the absence of such behavior in the region of the vAs-X band (X = C1, Br). The C-a form is apparently found in the crystals of (I) and (II), as in the case of (III)-(V). The difference in the behavior of the oxa- and thiaphosphepines may be due to a weakening of the anomeric effect in the case of thiaphosphepines which extrudes the electronegative substituent into the axial position. We should mention that some of the changes may be also the result of intermolecular interactions. Thus, for example, the broad strong Raman line 328 cm^{-1} (vAs-C1) in the spectra of crystalline (I) is shifted by 20 cm⁻¹ toward higher frequencies upon dissolution in CS₂. Aggregation by means of the X-C1 bond has been noted repeatedly [7]. This is also not excluded in our case.

EXPERIMENTAL

The Raman spectra were taken on a Bruker RT-30 spectrometer with 400 μ m slit width. An ILA-120 Ar⁺ laser (λ 4880 Å) was used as the light source. The spectra of the crystals and melt were taken in a 1.5-mm diameter capillary. The spectra of the solutions were taken in a 0.1 ml cell with 150 mW emission power. The samples were rotated in order to exclude molecular decomposition by the action of laser irradiation. The IR spectra at 400-4000 cm⁻¹ were taken on a UR-20 spectrometer. The spectra of the crystals at 100-400 cm⁻¹ were taken on a Bruker IFS-113 with 1 cm⁻¹ resolution. The samples were prepared by pressing into ~0.1-mm-thick tablets.

<u>3-(p-Bromophenyl-4H,7H-5,6-benz-1,3,2-dithiaarsepine (IV).</u> A mixture of 5.8 g o-xylylenedithiol, 10 g dimethyl p-bromophenylarsonite, and 100 ml CCl₄ was heated for 2 h in a flask equipped with a reflux condenser in a dry, inert gas atmosphere. On the following day, the shiny, white crystalline precipitate was filtered off and dried in a vacuum dessicator to give 11.4 g (83.7%) (IV), mp 144-145°C. Found: C, 42.15; H, 3.40; S, 16.30; Br, 2.07; As, 18.37%. Calculated for $C_{14}H_{12}S_{2}BrAs$: C, 42,12; H, 3.03; S 16.06; Br, 20.02; As, 18.76%. In a similar manner phenylarsenite, p-nitrophenylarsenite, and o-xylylenedithiol were used to synthesize 3phenyl-4H,7H-5,6-benz-1,3,2-dithiaarsepine (III) (mp 110-112°C and 3-(p-nitrophenyl)-4H,7H-5,6-benz-1,3,2-dithiaarsepine (V) (mp 180-181°C). Found: C, 52.38: H 4.62; S, 20.15; As, 23.43%. $C_{14}H_{13}S_{2}As$. Calculated: C, 52.49; H, 4.09; As, 23.4; S, 20.02%. Found: C, 46.06:



Fig. 1. Raman spectra of (III): 1) crystalline, 2) melt.

H 3.29; S, 17.67; N, 3.77; As, 20.25%. C14H12S2O2NAS. Calculated: C, 46.03; H, 3.31; S, 17.55; N, 3.83; As, 20.51%.

<u>3-Chloro-4H,7H-5,6-benz-1,3,2-dithiaarsepine (I)</u>. A solution of 18.13 g AsCl₃ in 15 ml CCl₄ was added dropwise to a solution of 17.03 g o-xylylenedithiol in 60 ml CCl₄ at 22°C in a dry nitrogen atmosphere. A vigorous reaction began immediately with the liberation of HCl. When HCl was no longer given off, the mixture was heated for 15 min. On the following day, the precipitate was filtered off and washed with CCl₄. Drying in a dessicator gave 26.4 g (94.7%) (I) with mp 117-119°C. Found: C, 34.43; H, 2.80; S, 22.87; Cl, 13.15; As, 26.7%. Calculated for C₈H₈S₂ClAs: C, 34.48; H, 2.89; S, 23.01; Cl, 12.72; As, 26.88%. Analogously, o-xylylenedithiol and AsBr₃ gave 3-bromo-4H,7H-5,6-benz-1,3,2-dithiaarsepine (II) with mp 114-116°C. Found: C, 30.41; H, 2.65; S, 19.84; Br, 24.57; As, 23.20%. Calculated for C₈H₈S₂BrAs: C, 29.74; H, 2.49; S, 19.85; Br, 24.75; As, 23.18%.

CONCLUSIONS

1. 4H,7H-5,6-Benz-1,3,2-dithiaarsepines were synthesized and spectrally characterized. The IR and Raman spectra showed changes with variation of the medium, phase state, and temperature, indicating different extents of conformational nonuniformity and intermolecular interactions.

2. Electronegative Cl and Br substituents at the As atom cause reduced conformational mobility, while Ph, p-Br-Ph, and p-NO₂-Ph lead to greater conformational mobility in the liquid state. An equilibrium of the predominant a-type chair and twist form is possible in the case of the former substituents, while a three-component is obtained for the latter with the participation also of the e-type chair. Only the a-type chair is found in the crystals.

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