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CRYSTAL AND MOLECULAR STRUCTURES OF DIPHENYLETHYLARSINE SULFIDE, $C_{14}H_{15}AsS$, AND *p*-TOLYLDIETHYLARSINE SULFIDE, $C_{11}H_{17}AsS$

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Summary

In order to elucidate the influence of aryl or alkyl substituents on the nature of the As=S bond, which controls the complexing properties of the substances $(Alk)_n(Ar)_{3-n}AsS$ (n = 0—3), the X-ray investigation of (p-MeC_6H_4)-Et_2AsS (TDEAS) and Ph_2EtAsS (DPEAS) has been carried out. It was shown that the bond length As=S in these compounds has intermediate values (2.0896 and 2.0812 Å) in respect to those previously found by us in Et_3AsS and Ph_3AsS (2.115 and 2.077 Å). This confirms the conclusion that the increase of the number of aryl substituents in tertiary arsine sulfides leads to a decrease of electron density on the As atom along with simultaneous strengthening of the π-interaction between As and S.

Introduction

The compounds R′R″R‴MX, where M = P or As, X = O or S, R = alkyl or aryl substituents are widely known as very active complexants. The substances with M = P have been investigated thoroughly, but the data about those with M = As are unsufficient. We have determined earlier the structures of two extreme members of the series $(Alk)_n(Ar)_{3-n}AsS$—Ph_3AsS [1] and —Et_3AsS [2], and have shown that during the substitution of alkyl radicals by aryl ones shortening of the As—S bouble bond takes place (2.115 Å in Et_3AsS and 2.077 Å in Ph_3AsS). This was in good agreement with the data on dipole moments and electron-donor properties [3,4]. The structure of Ph_3AsS has been presented independently [5], the results of this work in the limits of experimental error coincide with ours. For a more detailed elucidation of the influence of the substituent on the complexing properties of arsine sulfides we performed an X-ray investigation of two intermediate members of the series: *p*-tolyldiethylarsine sulfide (TDEAS) and diphenylethylarsine sulfide (DPEAS).

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Experimental

X-ray data collection

Single crystals with sizes approximately 0.25 × 0.25 × 0.25 mm were chosen for the experiment. Both crystals are monoclinic with space group $P2_1/b$, $Z = 4$. The unit cell parameters for TDEAS and DPEAS are correspondingly: a 12.284(3) and 12.963(3), b 15.832(4) and 11.283(3), c 6.539(1) and 10.292(2) Å, γ 102.03(1) and 112.17(1)°, D_c 1.37 and 1.38 g cm^{-3}, V 1243.8 and 1393.5 $Å^3$, $F(000)$ 528 and 592. All experimental data were collected using an automatic four-circle diffractometer, SYNTEX $P\bar{1}$, with graphite monochromator, applying Mo-K_α radiation, by the $\theta/2\theta$ scanning method. The sets of experimental intensities were obtained up to $s_{max} = 0.6$ $Å^{-1}$ and made up 1537 (TDEAS) and 1770 (DPEAS) reflections with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization effects but not for absorption (μR less than 0.1).

Structure determination and refinement

Both structures were solved using direct methods and the Fourier technique, where all non-hydrogen atoms coordinates were found. The least squares refine-

TABLE 1

ATOMIC PARAMETERS FOR TDEAS AND DPEAS

Atom	x	y	z
TDEAS			
As(1)	0.35540(3)	0.60496(2)	0.36189(5)
S(1)	0.37932(9)	0.62582(7)	0.67572(14)
C(1)	0.2237(4)	0.5175(3)	0.3048(6)
C(2)	0.1936(4)	0.4949(3)	0.1060(7)
C(3)	0.1008(4)	0.4317(3)	0.0670(8)
C(4)	0.0352(5)	0.3902(4)	0.2236(8)
C(5)	0.0661(4)	0.4139(3)	0.4211(8)
C(6)	0.1600(4)	0.4773(3)	0.4624(8)
C(7)	−0.0667(4)	0.3203(3)	0.1802(7)
C(8)	0.4745(5)	0.5646(4)	0.2247(10)
C(9)	0.5877(4)	0.6185(3)	0.2777(7)
C(10)	0.3378(5)	0.7067(4)	0.2135(11)
C(11)	0.2502(4)	0.7489(3)	0.3030(7)
DPEAS			
As(1)	0.18464(3)	0.13803(4)	0.37453(4)
S(1)	0.1470(1)	−0.0467(1)	0.4447(1)
C(1)	0.3161(4)	0.1927(4)	0.2669(4)
C(2)	0.3336(4)	0.2832(5)	0.1706(5)
C(3)	0.4283(5)	0.3207(6)	0.0954(6)
C(4)	0.5068(5)	0.2684(7)	0.1173(7)
C(5)	0.4885(5)	0.1769(7)	0.2101(7)
C(6)	0.3939(4)	0.1384(5)	0.2849(5)
C(7)	0.2165(4)	0.2624(4)	0.5133(5)
C(8)	0.2716(6)	0.3906(5)	0.4895(6)
C(9)	0.2929(6)	0.4775(6)	0.5902(7)
C(10)	0.2605(5)	0.4373(6)	0.7129(6)
C(11)	0.2059(6)	0.3101(6)	0.7377(5)
C(12)	0.1839(4)	0.2223(5)	0.6377(5)
C(13)	0.0676(4)	0.1583(5)	0.2726(5)
C(14)	0.0397(5)	0.0810(7)	0.1521(6)

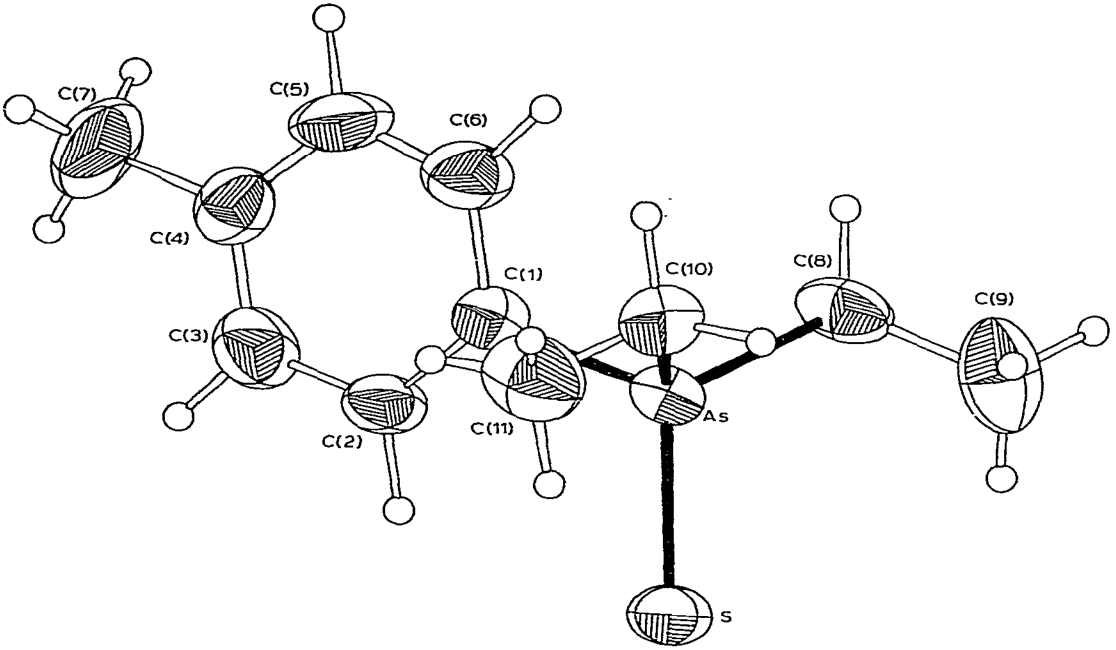

Fig. 1. The ORTEP drawing of TDEAS.

ment using anisotropic thermal parameters was performed with the aid of the XRAY-72 program [6] adapted by us for the EC-1022 computer. The coordinates of H atoms were located by subsequent difference syntheses and were then included in the refinement with isotropic thermal parameters. Atomic

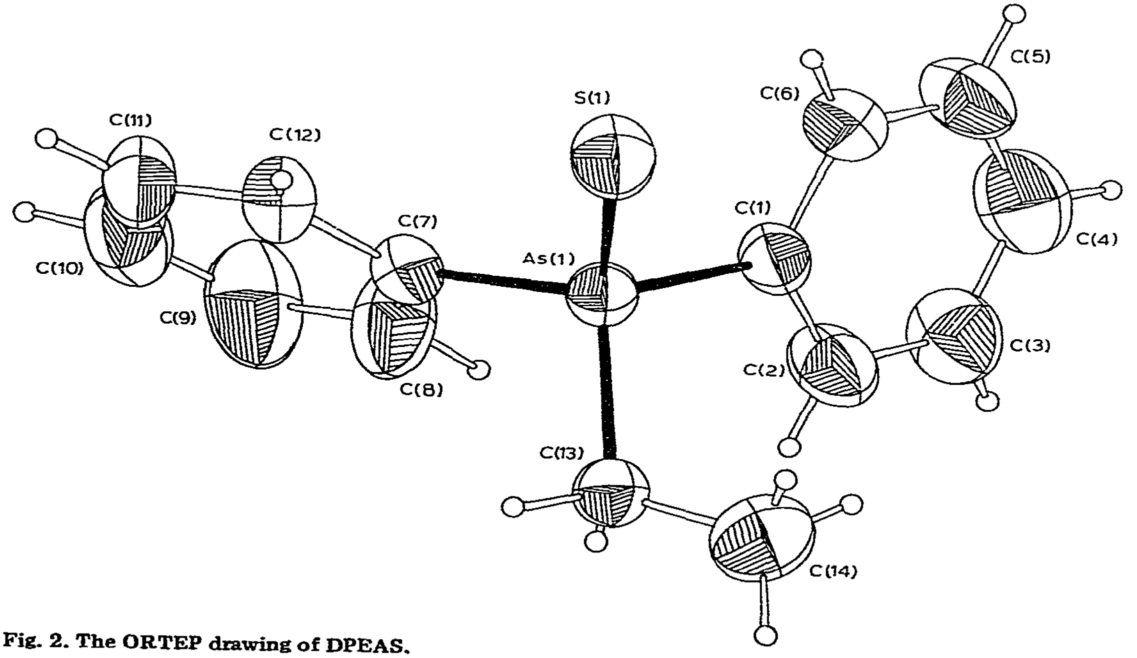

Fig. 2. The ORTEP drawing of DPEAS.

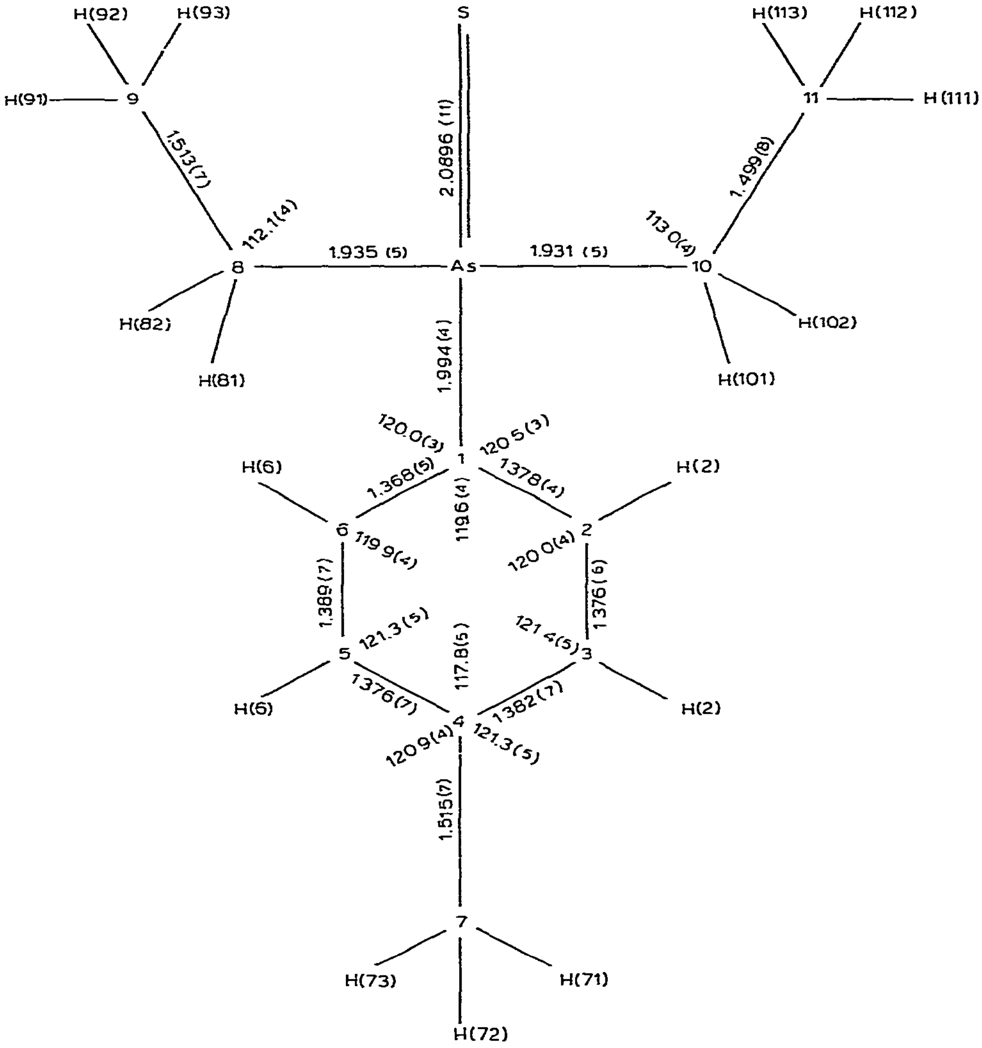

Fig. 3. Interatomic distances and angles in TDEAS.

scattering factors were taken from ref. 7 for As, S and C atoms and from ref. 8 for H atoms. At the final stages of the least squares procedure the refinement of positional and thermal parameters of As and S atoms was carried out using the reflections with $s > 0.4$ Å^{-1} where the relative contribution of the scattering ability of both C and H atoms and valence electrons of As, S atoms is small. The final values of R factors for all reflections are 0.028 for TDEAS and 0.030 for DPEAS. The atomic coordinates with their e.s.d.'s are given in Table 1 *.

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* Tables of F_0 and F_c, anisotropic thermal parameters for As, S and C atoms, positional and isotropic thermal parameters of H atoms may be received upon request from the authors.

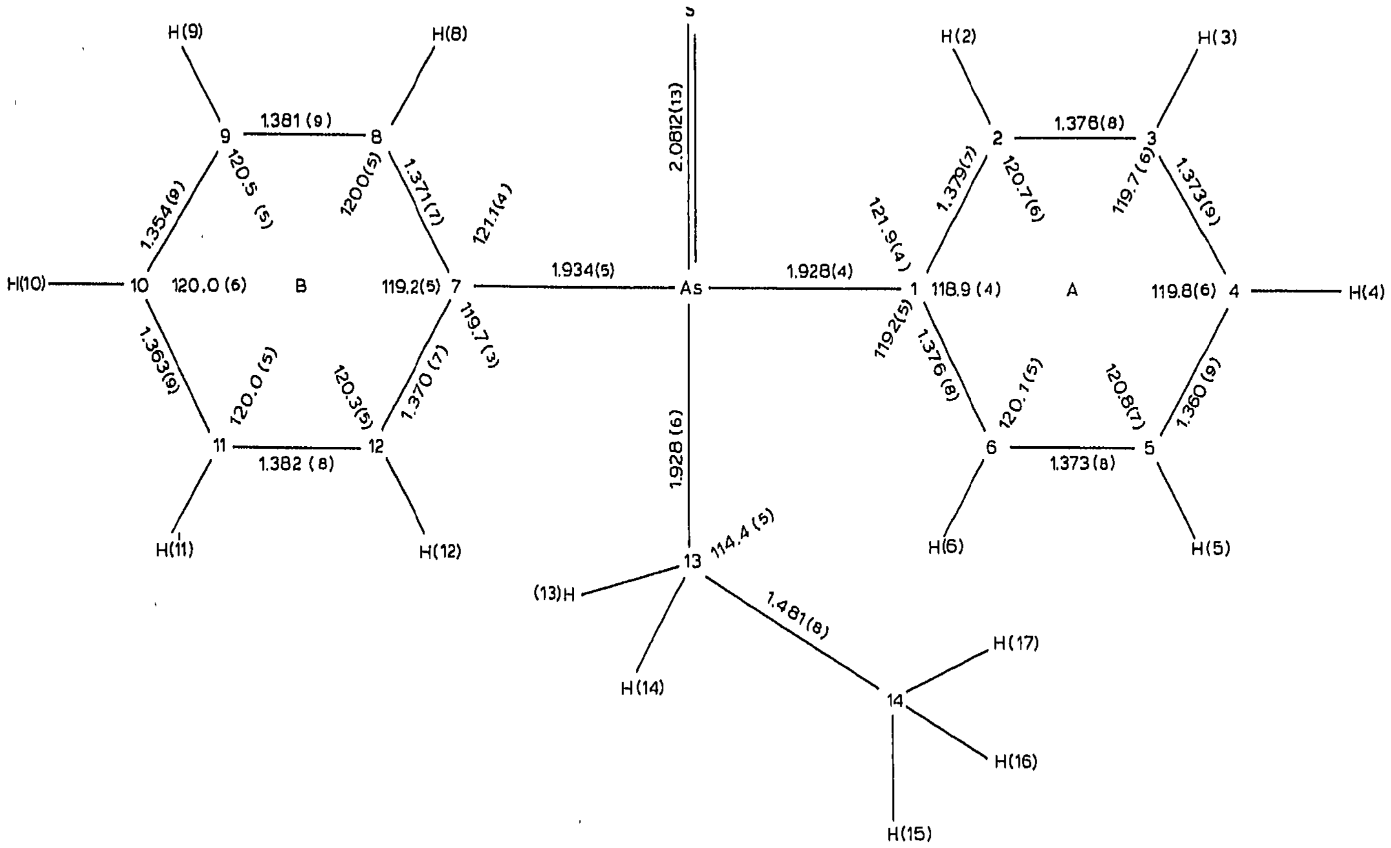

Fig. 4. Interatomic distances and angles in DPEAS.

Discussion

The general view of TDEAS and DPEAS molecules is given in Figs. 1 and 2. Figures 3 and 4 give interatomic distances and bond angles in these structures.

The tetrahedral environment of the As atom in TDEAS is characterized by the angles S—As—C = 111.8(2)° for the tolyl substituent and 114.6(2)° and 113.5(2)° for the ethyl ones. The angles C—As—C are equal to 104.5(2)° and 106.1(2)° for the tolyl—ethyl system and 105.5(3)° between ethyls. The phenyl ring is planar within the limits of 0.003 Å and makes an angle 0.7° with the plane S—As—C(1). The bends of the ethyl group planes relative to the corresponding planes S—As—C are 48.9 and 52.0°. The geometry of this shows some diminishing of the angle at C(4) (117.8°) which is connected with the electron-donor character of the CH_3 group [9]. This value is in good agreement with that of cresole (117.8°) [10] and *p*-nitrotoluene (117.5°) [11]. The problem of *p*-substituents influence on the As=S bond has yet to be investigated and discussed more thoroughly. We shall study this in the near future using also the results of structure investigation of $(p\text{-ClC}_6H_4)_3AsS$ and $(p\text{-CH}_3C_6H_4)_3AsS$. These structures have been solved and will be published soon.

The coordination tetrahedron of the As atom in DPEAS resembles closely that in TDEAS. The phenyl rings A and B are also close to the besecting positions: —25.8° and 17.7°. The torsion angle S—As—C(13)—C(14) is 62.7°. The angles S—As—C are 114.4(2)° for Ph(A), 112.0(2)° for Ph(B) and 114.2(2)° for the ethyl substituent. The angles C—As—C are 106.8° and 106.1° for Et—Ph pairs and 105.7° for the Ph(A)—Ph(B) pair.

The molecular packing in both structures is governed by the usual Van der Waals interactions.

The values of As=S bonds in TDEAS and DPEAS (2.0896(11) and 2.0812(13) Å, respectively) confirm the conclusion [1] that aryl radicals behave in respect to the As=S group as electron-acceptor substituents and that the increase of the number of aryl substituents in molecules of this type leads to shortening of the As=S bond. Along with the previous results [1], considering the values of chemical shifts of ethyl radical protons in NMR spectra, the data on dipole moments and the complexing properties of these compounds, it is evident that the increase of the number of aryl substituents diminishes the electron density on the As atom with simultaneous stengthening of the π-interaction between arsenic and sulfur.

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