CHEMISTRY

M. Ya. Kraft, G. M. Borodina, I. N. Streltsova, and Yu. T. Struchkov

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

M. Ya. Kraft, G. M. Borodina, I. N. Streltsova, and Yu. T. Struchkov

STRUCTURE OF MONOMERIC ARSENO COMPOUNDS

(Presented by Academician A. N. Nesmeyanov, October 12, 1959)

All arseno compounds described in the literature may be divided into two groups. Compounds of the first group are colored, amorphous, do not crystallize, and cannot be distilled. Some compounds of this group are insoluble in any solvents (for example, polymers of arsenomethane), while others dissolve in suitable solvents, forming more or less viscous solutions (for example, salvarsan). According to recent data (^{1}), the structure of compounds of this group is expressed by the formula:

$$\text{(I)} \qquad x - \underset{R}{\mathrm{As}} - \left(-\underset{R}{\mathrm{As}}- \right)_{n-2} - \underset{R}{\mathrm{As}} - x, \qquad x = \mathrm{HO,\ J,\ Cl;}$$

$$R = \mathrm{CH_3}\text{—polymers of arsenomethane;}$$

$$R = -\mathrm{C_6H_3(OH)(NH_2)}\text{—salvarsan.}$$

The value of n, depending on the conditions of preparation, may vary within the limits from 7-8 to 40-50; therefore some polymeric arseno compounds form comparatively low-viscosity solutions (for example, at $n = 8$ and $R = -\mathrm{C_6H_3(OH)(NH_2)}$. The molecular weight of the polymer is ≈ 1500). In the case where $x = \mathrm{OH}$, the polymers, even in aqueous solutions, may undergo dehydration, which leads to an increase in the molecular weight and, naturally, in the viscosity of the solution:

$$m\,\mathrm{HO}\left(-\underset{R}{\mathrm{As}}-\right)_n -\mathrm{OH} \rightleftarrows \mathrm{HO}\left(-\underset{R}{\mathrm{As}}-\right)_n \left[-\mathrm{O} - \left(-\underset{R}{\mathrm{As}}-\right)_n\right]_{m-2} -\mathrm{O}-\left(-\underset{R}{\mathrm{As}}-\right)_n -\mathrm{OH} + \frac{m-2}{2}\mathrm{H_2O}.$$

The reaction is reversible, and it explains the variable viscosity of salvarsan solutions. The molecular weight of salvarsan, at sufficiently large n, may, with appropriate treatment, reach a value on the order of 1,000,000 (^{2}). Polymers of arsenomethane, as is known (^{3}), are insoluble and can be obtained only under conditions in which terminal groups can form (^{4}).

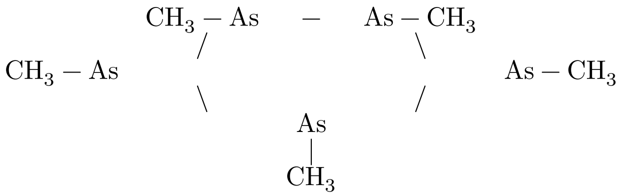
Arseno compounds of the second group are colorless, crystallize well (for example, arsenobenzene, *p*-arsenoanisole, etc.), or can be distilled (arsenomethane). Whereas compounds of the first group are polymers, compounds of the second group clearly have the character of monomeric compounds. For a time, chiefly by analogy with azo compounds, the structure of true "arseno compounds" was assigned to them:

$$\text{(II)} \qquad R - \mathrm{As} = \mathrm{As} - R, \qquad R = \mathrm{CH_3}\text{—arsenomethane } (^5);$$

$$R = \mathrm{C_6H_5}\text{—arsenobenzene } (^6).$$

However, a careful determination of the molecular weight, carried out by V. Steinkopf (^{7}), led to the establishment of a cyclic structure for arsenomethane:

(III)



These data were subsequently confirmed by other investigators (^{8}). Thus, the structure of arsenomethane gives rise to no doubt. The situation is more complicated with the structure of arsenobenzene: determination of its molecular weight by different investigators gave inconsistent results. Thus, for example, A. Michaelis, ebullioscopically in benzene, found 399.8 (^{9}); S. Palmer, under the same conditions, found 402, and cryoscopically, in naphthalene, 642 (^{8}). A precision determination of the molecular weight of arsenobenzene, carried out by F. Blake and Smith (^{10}), gave values of 895 and 915. Apparently it was precisely this diversity that led to the fact that, up to the present time, the structural formula (II) has been generally accepted for arsenobenzene, although it seems almost incredible that a compound of this structure should be colorless. It seemed to us very probable that the above diversity of results obtained in determining the molecular weight of arsenobenzene should be explained by its lability. Indeed, A. Michaelis (^{9}) had already noted that arsenobenzene very readily resinifies (polymerizes), and according to our observations these polymers (a sticky yellow resin) are exceptionally readily oxidized by atmospheric oxygen to $\mathrm{C_6H_5AsO}$. Since arsenomethane polymerizes with greater difficulty, and this is easy to notice, because its polymers are insoluble in everything, determination of its molecular weight gives correct results. The resinification (polymerization) products of arsenobenzene, however, are very readily soluble

Fig. 1. Projection of the electron density of arsenobenzene onto the face ac. Contour lines in relative units

Figure 1: Fig. 1. Projection of the electron density of arsenobenzene onto the face ac. Contour lines in relative units

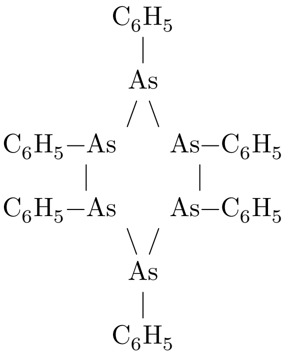
in benzene and other solvents, just like the oxidation products of the polymers; therefore these reactions escape observation and, as a result, determinations of the molecular weight of arsenobenzene give unreliable data. All that has been set forth led us to the conviction that reliable data on the structure of arsenobenzene can be obtained only by X-ray structural analysis. Arsenobenzene was obtained by us by reduction of C_6H_5AsO with hypophosphorous acid and, after recrystallization from toluene, was isolated in the form of almost colorless crystals with m.p. 210—212°, which corresponds to the literature data (10).

Fig. 1. Projection of the electron density of arsenobenzene onto the *ac* face. Contour lines in relative units

The crystals of arsenobenzene belong to the monoclinic system and are thin needles of yellowish color. The long direction of the needle is the b axis; the simple forms are pinacoids $\{100\}$ and $\{001\}$; the end faces are not expressed. The monoclinic angle β, according to goniometric measurements, is $110°09' \pm 0°12'$. Determination of the identity periods from oscillation X-ray photographs gives the following values: $a = 11.93 \pm 0.05$ Å; $b = 6.11 \pm 0.03$ Å; $c = 23.57 \pm 0.12$ Å. Hence the cell volume is $v = 1632$ Å^3, which, at a density of 1.758 g/cm^3, gives 11.3, i.e. 12 residues C_6H_5—As = per cell. Systematic extinctions indicate the space group $C_{2h}^5 = P2_1/c$, and consequently the cell contains 3 crystallographically nonequivalent As atoms.

The elucidation of the structure was carried out from the projection *ac*; the coordinates y' were determined by geometrical analysis. First, from the projection of the interatomic function, the x and z coordinates of the As atoms were found, which served to determine the signs of F_{hol}. The electron-density projection was then calculated, revealing the general contours of the benzene rings. Unfortunately, because of their steep inclination to the plane of projection, not all carbon atoms are resolved in it: instead of 18 atoms we have 10 maxima. A second approximation of the electron-density projection brought the reliability factor to $R = 14.5\%$, which leaves no doubt as to the correctness of the structure found.

As the electron-density projection shows (Fig. 1), the molecule of arsenobenzene is a cyclic system of As atoms, to each of which one phenyl group is attached. The number of members in the ring is 6:



(IV)

In the crystal, such cyclic molecules occupy positions at centers of symmetry. The ring is not planar, but has a chair configuration with valence angle As—As—As = 93° ± 2°. The external valence angles As—As—C are 99 ± 3°. Bond lengths: As—As = 2.44 Å; C—As = 1.96 Å.

The data obtained by us show that, of all the earlier determinations of the molecular weight of arsenobenzene, only the data of F. Blicke and F. Smith [10] are correct; all the others are distorted by the reactions mentioned above. Since the results obtained by F. Blicke and F. Smith for arsenobenzene are correct, their determinations of the molecular weights of *p*-arsenotoluene and *p*-arsenoanisole also deserve confidence. For these compounds the above-mentioned investigators found values of 832 and 1080, 1270, respectively. The values calculated for the corresponding six-membered rings are 996 and 1092. Thus, one must conclude that arseno compounds of the structure R—As = As—R do not exist at all. In reality they are either polymers, whose structure is represented by formulas (I) and (II), or cyclic compounds (III) and (IV). The entire history of arseno compounds once again shows how risky it is to judge the structure of compounds by analogy, for it was precisely by analogy that A. Michaelis ascribed to arsenobenzene the structure C_6H_5—As = As—C_6H_5 [6], and P. Ehrlich and A. Bertheim to salvarsan the structure of 3,3′-diamino-4,4′-dioxyarsenobenzene. In both cases the authors had at their disposal only elemental-analysis data and an analogy with azo compounds.

All-Union Scientific-Research
Chemical-Pharmaceutical Institute
named after S. Ordzhonikidze

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
6 X 1959

CITED LITERATURE

1. M. Ya. Kraft, I. A. Bashuk, DAN, **65**, 509 (1949); M. Ya. Kraft, E. B. Agracheva, DAN, **100**, 279 (1955).
2. M. Ya. Kraft, E. N. Sytina, DAN, **116**, 89 (1957).
3. V. Auger, C. R., **138**, 1706 (1904).
4. M. Ya. Kraft, V. V. Katyshkina, DAN, **66**, 207 (1949).
5. A. Bertheim, Ber., **47**, 273 (1914).
6. A. Michaelis, C. Schulte, Ber., **14**, 912 (1881).
7. W. Steinkopf, S. Schmidt, P. Smie, Ber., **59**, 1468 (1926).
8. C. S. Palmer, A. B. Scott, J. Am. Chem. Soc., **50**, 536 (1928).
9. A. Michaelis, A. Schäfer, Ber., **46**, 1742 (1913).
10. F. F. Blicke, F. Smith, J. Am. Chem. Soc., **52**, 2946 (1930).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.