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Abstract

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ON THE COLORATION OF ARSENO COMPOUNDS AND THE ORIGIN OF COLOR IN POLYMERIZATION

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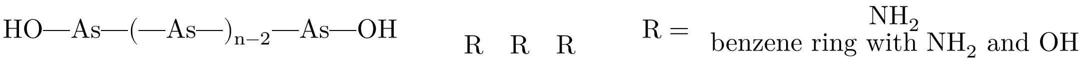
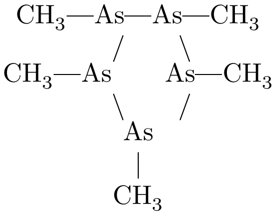
The intense yellow color of salvarsan was previously explained (¹) by the presence in its structure of the groups —As = As—, by analogy with the coloration of azo compounds; and it was even believed that its coloration served as confirmation of the structural formula accepted earlier. However, since it was shown that salvarsan is a polymeric compound (²) of the structure



$$HO—As—(—As—)_{n-2}—As—OH \qquad R \quad R \quad R \qquad R = \overset{NH_2}{\text{benzene ring with } NH_2 \text{ and } OH}$$

(I)

this explanation of the coloration has, naturally, fallen away. The true cause of the coloration of salvarsan, its chromophoric group, is the chain of unsaturated arsenic atoms: of the 5 valence electrons of As, 3 are used to form the bonds shown in formula (I), while the remaining pair of electrons brings about that interaction of the electronic systems of atoms which, in the case of a chain of unsaturated carbon atoms, we call “bond conjugation.” From this point of view, the molecule of salvarsan is a peculiar polyene, colored in exactly the same way as compounds having a sufficiently long chain of conjugated bonds (unsaturated carbon atoms). This point of view is confirmed by the following facts: arsenomethane, which is an almost colorless liquid with b.p. 190°/15 mm, forms intensely colored polymers upon polymerization. As is known, arsenomethane is a cyclic compound (II), whereas the polymers have a linear structure (³) $(I, R = CH_3)$



(II)

In this case, scarcely any other explanation of the coloration of the arsenomethane polymers is possible, since, apart from the chain of unsaturated arsenic atoms, there are no chromophoric groups in the polymer molecule. Further, A. Michaelis (4) also observed that arsenobenzene very readily resinifies (polymerizes). In this process a sticky yellow resin is obtained (5). In this case as well, another explanation of the color of the polymer is difficult. In addition, it is known that the formation of chains of unsaturated atoms of other elements also leads to the formation of colored compounds. Thus, H_2S is colorless, whereas polysulfides (for example, HS—S—S—S—S—H) are yellow. All that has been set forth convincingly indicates that the chromophore of salvarsan is the chain of unsaturated As atoms. Establishment

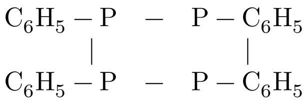
···the true cause of the coloration of salvarsan is, we believe, of great importance for elucidating the structure of other organoarsenic compounds. After the discovery of the chemotherapeutic action of salvarsan by P. Ehrlich and A. Bertheim (1), a large number of investigators undertook syntheses of "organoarsenic compounds" in various series (all the isomers of salvarsan, its homologues and analogues both among heterocyclic and polycyclic compounds, were obtained). As a result, descriptions of various organoarsenic compounds appeared in the literature; these, however, were not subjected to study. We are not able to investigate all the organoarsenic compounds described in the literature, especially since such investigations are far from simple: the study of the structure of salvarsan required many years of persistent work from us. In the coloration of organoarsenic compounds, however, we have a good criterion for establishing their structure: if an organoarsenic compound is colored, it contains a chain of unsaturated As atoms and, consequently, is a polymer; colorless organoarsenic compounds, especially if they crystallize, are cyclic compounds with six-membered (as in the case of arsenobenzene (5)) or five-membered rings formed by arsenic atoms.

Let us cite several examples from among the most thoroughly studied organoarsenic compounds: 4,4 -diaminoarsenobenzene was described by P. Ehrlich and A. Bertheim (6) as a yellow powder dissolving in dilute acids with the formation of yellow solutions.

According to the above, this compound is a polymer, the chromophore of which, as in the case of salvarsan, is a chain of unsaturated, trivalent arsenic atoms (formula I, $R = -C_6H_4 - NH_2$). The polymeric character of this compound is also indicated by the data of P. Ehrlich and A. Bertheim, according to which, in its iodometric determination, the results obtained are too low, as in the case of salvarsan; this is explained by the presence of terminal groups in the polymer molecule (2).

Novarsenol (neosalvarsan) is likewise a yellow powder, dissolving in water with the formation of a yellow solution, which indicates its polymeric structure [formula I, $R = -C_6H_3(OH)(NHCH_2SO_2Na)$]. We had already earlier (7) assigned a polymeric structure to novarsenol, on the grounds that it is obtained under very mild conditions by the action of rongalite ($HOCH_2SO_2Na$) on a polymeric compound (salvarsan), and also on the basis of data (8) on the diffusion of its solutions. The yellow coloration of novarsenol serves as convincing confirmation of its polymeric structure.

Organoarsenic compounds such as arsenobenzene, arsenotoluene, and arsenoanisole, which are colorless and crystallize well, are cyclic compounds in which the six-membered ring is formed by As atoms (5). Apparently, the development of color during polymerization is also observed in other cases, when chains of unsaturated atoms are formed. Thus, W. Kuchen and H. Buchwald (9) observed that almost colorless phosphobenzene, to which, on the basis of a cryoscopic determination of molecular weight, they assigned a cyclic structure:



melts at 150.5°, forming a substance colored an intense yellow. The same is observed on melting arsenobenzene, which in the process polymerizes with formation of a sticky yellow resin. It is highly probable that the same occurs on melting "phosphobenzene" ; in any case, the yellow color of the melt convincingly indicates the formation of a chain of unsaturated, trivalent phosphorus atoms. Further, in one of our previous works (10) we showed that the so-called Schenck phosphorus, which is obtained by heating a solution of yellow phosphorus in PBr_3, is in fact a polymer built from P atoms, containing terminal groups = P—Br, and not an adsorbate of PBr_3 on red phosphorus, as had been assumed. The color of Schenck' s phosphorus (orange-red), in our opinion, well confirms the structure we have proposed.

Indeed, in accordance with all that has been set forth, the color of Schenck' s phosphorus—and probably of other varieties of red phosphorus—can be explained by the formation, evidently, not of a chain of trivalent P atoms, but of a network of these same atoms. The same situation is found in graphite, in which each carbon atom is firmly bound only to its three nearest atoms (C—C = 1.42 Å), while the bond with the fourth atom is incomparably weaker (C—C = 3.35 Å). Thus, the "molecule" of graphite is a plane composed of hexagons formed by unsaturated carbon atoms, which naturally leads to the possibility of "conjugation of bonds" in two dimensions; this explains the absorption by graphite of all visible rays. The crystalline structure of diamond, however, shows that all four valence electrons of the carbon atoms are used to form identical bonds (the C—C distance in all cases is 1.54 Å), which is why it is colorless. Thus, the color of true polyenes (for example, carotene), of salvarsan and other polymeric organoarsenic compounds, as well as of polymeric phosphorus compounds and graphite, is due to one and the same general cause—the formation of a chain or network of unsaturated atoms.

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