# UV SPECTRA OF SOME DERIVATIVES OF 5,10-DIHYDROPHENARSAZINE AND 5,10-DIHYDROPHENOXARSINE

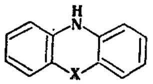
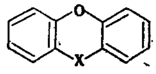
R. R. Shagidullin, A. V. Chernova,
B. D. Chernokal'skii, V. I. Gavrilov,
and G. R. Gavrilova

UDC 543.42.6:547.864'867'242

The long-wave band with a maximum above 300 nm in the UV spectra of substituted 5,10-dihydrophenarsazines is interpreted as a transition with intramolecular charge transfer in which the trivalent arsenic atom acts as an electron acceptor. The unshared pair of electrons of As(III) apparently makes its own contribution to the $\pi \rightarrow \pi^*$ transitions at 240-280 nm.

The UV spectra of arylarsines have been interpreted in a number of papers [1, 2]. However, the spectra and the determination of the nature of the bands become markedly complicated on passing to 10-substituted 5,10-dihydrophenarsazines (5,10-DHPA) [3-5]. We have investigated the UV spectra of a number of 5,10-DHPA and the products of their oxidation and methylation at the arsenic atom (Table 1). The presence in the UV spectra of 5,10-DHPA derivatives of a band at 300-350 nm is characteristic (Fig. 1).

TABLE 1. UV Spectra of 10-Substituted 5,10-Dihydrophenarsazines and 5,10-Dihydrophenoxarsines

| X | $\lambda_{max}$ (log ε), nm (in ethanol) | | | | |
|---|---|---|---|---|---|
| |  | | |  | |
| As-$C_2H_5$ | 246(4,00) | 293(4,11) | 315(3,96)* | 230(4,14)* | 288(3,58) |
| As(O)-$C_2H_5$ | | — | | 242(4,03) | 277(3,59)<br>287(3,68)<br>294(3,69) |
| $As^+(CH_3)C_2H_5I^-$ | 238(3,76)* | 276(4,23) | 316(4,04)<br>340(4,00)* | 243(3,93) | 280(3,53)<br>288(3,59)<br>295(3,60) |
| As-$CH(CH_3)_2$ | 246(3,97) | 294(4,05) | 315(3,93)* | 233(4,12)* | 289(3,60) |
| As(O)-$CH(CH_3)_2$ | 238(3,75)* | 276(4,26) | 310(4,06)<br>325(3,87)*<br>336(3,77)* | — | |
| $As^+(CH_3)CH(CH_3)_2I^-$ | 239(3,65)* | 275(4,21) | 312(4,03)<br>336(3,80)* | — | |
| AsBr | 225(4,54) | 283(4,21) | 308(4,02)<br>353(3,75) | 246(4,13) | 301(3,76) |
| As-$C_6H_5$ | 246(3,96)* | 288(4,06) | 318(3,91) | 236(4,36)* | 289(3,68) |
| As(O)-$C_6H_5$ | 221(4,52)* | 274(4,19) | 309(4,05)<br>328(3,88)*<br>336(3,85)* | 244(4,17)* | 280(3,52)<br>288(3,59)<br>297(3,55) |
| $As^+(CH_3)C_6H_5I^-$ | 218(4,69)* | 273(4,20) | 318(4,06)<br>329(3,99)*<br>339(3,90)* | — | |
| As-$C_6H_4$-$CH_3$-*n* | 235(4,40)* | 292(4,07) | 325(3,97) | 238(4,37)* | 289(3,67) |
| As-$C_6H_4$-Cl-*n* | 238(4,43)* | 290(4,14) | 328(3,99) | 230—<br>238(4,37)* | 288(3,91) |
| As-$C_6H_4$-$OCH_3$-*n* | 240(4,35) | 291(4,05) | 326(3,95)* | 230—<br>240(4,42)* | 284(3,79) |

* Shoulder.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR, Kazan. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 768-770, June, 1974. Original article submitted June 21, 1973.

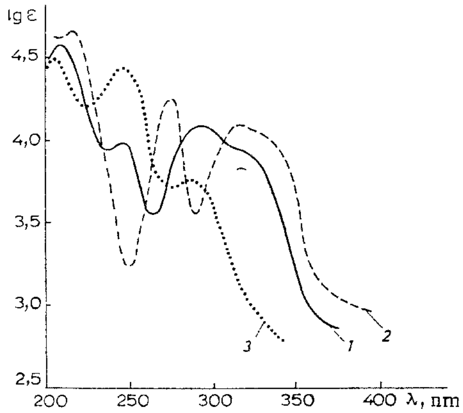


Fig. 1. UV spectra in ethanol: 1) 10-ethyl-5,10-dihydrophenarsazine; 2) 10-ethyl-5,10-dihydrophenarsazine 10-methiodide; 3) 9-chloro-9-arsafluorene.

Its appearance is apparently associated with the presence of two heteroatoms – nitrogen and arsenic – in the molecule [5]. Absorption bands are not observed in the indicated region for model compounds with only one of them (see, for example, the UV spectrum of 9-chloro-9-arsafluorene in Fig. 1).

The exposure of the nature of the long-wave transition in the spectra of 5,10-DHPA derivatives under discussion is facilitated by a comparison of their spectra with the data for the oxides and methiodides (Table 1). If the unshared pair of the electrons of the arsenic atom did participate in the transition, their bonding would lead to a decrease in the absorption at 315 nm. In fact, however, this is not observed in the spectra of the methiodides and oxides of 10-substituted 5,10-DPHA, but, on the contrary, one even notes a bathochromic shift of this band (Fig. 1). In view of the fact that the acceptor properties of the arsenic atom are intensified when it passes to the tetracoordinated state [6, 7], it might have been assumed that the long-wave transition is associated with intramolecular charge transfer to the arsenic atom. There is no doubt that this sort of transition is facilitated to a considerable degree by the presence in the molecule of a nitrogen atom that has electron-donor properties. Replacement of the nitrogen atom by oxygen, which is characterized by a higher ionization potential of the p electrons (I of nitrogen is 9.47 eV, while I of oxygen is 12,81 eV [8]) leads to complete disappearance of the long-wave bands in the spectra of the phenoxarsines (Table 1).

Three intense bands at 200, 240, and 290 nm are observed in addition to the region under consideration in the spectra of 5,10-DHPA derivatives. The parameters of the last two bands are presented in Table 1 (the first band is situated on the boundary of the operating range of the spectrophotometer). The observed transitions are probably transitions of the $\pi \rightarrow \pi^*$ type, inasmuch as a bathochromic shift occurs as the polarity of the solvent increases. In addition, the unshared pair of electron of arsenic apparently also participate in the formation of the bands, inasmuch as the indicated bands are shifted hypsochromically in the spectra of the oxidized and methylated 5,10-DHPA derivatives.

## EXPERIMENTAL

The UV spectra were recorded with SF-8 and Specord UV-Vis spectrophotometers. The solvents were cyclohexane and ethanol. The investigated compounds were recrystallized or distilled directly prior to recording of the spectra. The solution concentrations were $2 \cdot 10^{-3}$-$5 \cdot 10^{-3}$ mole/liter, and the layer thicknesses were 0.002-0.05 cm.

## LITERATURE CITED

1. C. N. Rao, J. Ramachandran, and A. Balasubramanina, Can. J. Chem., 39, 171 (1961).
2. W. R. Cullen, B. R. Green, and R. M. Hochstrasser, J. Inorg. Nucl. Chem., 27, 641 (1965).
3. C. S. Gibson, E. S. Hiscocks, J. D. A. Johnson, and J. L. Jones, J. Chem. Soc., 1622 (1930).
4. H. Moher and J. Sorge, Helv. Chim. Acta, 22, 235 (1939).
5. R. A. Earley and M. J. Gallagher, J. Organomet. Chem., 20, 117 (1969).
6. E. N. Tsvetkov, Author's Abstract of Dissertation [in Russian], 18 (1970).
7. A. S. Gel'fond, V. I. Gavrilov, V. G. Mironova, and B. D. Chernokal'skii, Zh. Obshch. Khim., 42, 2462 (1972).
8. O. P. Charkin, G. V. Bobykina, and M. E. Dyatkina, Molecular Structure and Quantum Chemistry [in Russian], Naukova Dumka, Kiev (1970), p. 155.