STRUCTURES AND PROPERTIES OF MOLECULAR COMPLEXES OF IODINE WITH AZOLES

V. N. Sheinker, L. G. Tishchenko, A. D. Garnovskii, and O. A. Osipov

UDC 541.49:547.781:546.15

We have found that the reaction of iodine with azoles, regardless of the basicity and aromatic character of the latter, gives n–σ complexes through the pyridine nitrogen atom; primarily 1:1 complexes are obtained.

The complexes of azoles with extensively varied basicities (pK_a values presented in parentheses) — 1-methylimidazole (I, 7.33), 1-methylbenzimidazole (II, 5.57), 1,3,5-trimethylpyrazole (III, 4.38), thiazole (IV, 2.53), 1-methyl-1,2,4-triazole (V, 2.30), benzothiazole (VI, 1.41), 2-methylbenzoxazole (VII, 0.99), benzoxazole (0.5), and 3,5-dimethylisoxazole (VIII, -2) — were studied by dielcometry and electronic spectroscopy.

The stability constants of the complexes (K_s in liter/mole, λ_{max} in nm) in CCl_4 (dielectric permeability 2.23) and CH_2Cl_2 (dielectric permeability 9.08) were calculated from the Drago equation [1]: I K_s 375 (λ 395), K_s 435 (λ 370); II K_s 208 (λ 410), K_s 173 (λ 380); III K_s 72.2 (λ 420); K_s 29.4 (λ 400); IV K_s 9.6 (λ 430), K_s 8.8 (λ 415); V K_s 14.0 (λ 430), K_s 5.9 (λ 415); VI K_s 11.3 (λ 430), K_s 8.7 (λ 420); VII K_s 14.0 (λ 432), K_s 7.7 (λ 420); VIII K_s 1.7 (—), K_s 2.01 (—). The symbatic relationship between the stability constants of the complexes in solvents of different polarity and the pK_a values of the azoles indicates the formation of complexes with iodine at the nitrogen atom of the pyridine type. Correspondingly, the vectorially calculated increases in the dipole moments during complexing increase as the basicity of the azoles increases. The contribution of the structure with charge transfer from 1 (for VIII) to 30% (for I) increases in the same direction.

The oscillator forces [2] (f_{opt}) of the complexes of azoles with iodine were calculated from the blue-shift band. The observed linear relationship between the square of the dipole moments and f_{opt} also confirms coordination of iodine at the same reaction center — the pyridine nitrogen atom of the azole ring.

LITERATURE CITED

1. N. J. Rose and R. S. Drago, J. Amer. Chem. Soc., 81, 6138 (1959).
2. G. Briegleb and J. Czekalla, Z. phys. Chem. (Frankfurt), 24, 37 (1960).

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, p. 571, April, 1975. Original submitted November 11, 1974.