5. M. F. Shostakovskii, G. G. Skvortsova, and E. S. Domnina, Usp. Khim., 38, 892 (1969).
6. E. M. Popov and G. A. Kogan, Usp. Khim., 37, 256 (1968).

TETRAHALOTETRAAZAFULVALENES — NEW STRONG ELECTRON ACCEPTORS

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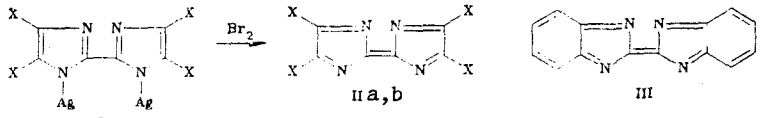
It was deduced in [1] on the basis of quantum chemical calculations that bis(imidazole-2-ylidene) — tetraazafulvalene and its derivatives — which had not so far been reported, should possess high acceptor ability and could be used as a component of organic metals and semiconductors. With the object of studying their electron-acceptor properties we have prepared, for the first time, tetrachloro- and tetrabromotetraazafulvalene (IIa,b) together with the dibenzo-derivative (III) the preparation of which has been described previously [2] but its acceptor properties have not been studied.



I, IIa X=Cl, b X=Br

Tetrachlorotetraazafulvalene (IIa). To a suspension of the silver salt Ia [3] (0.005 mole) in 100 ml CH_2Cl_2 at −30°C was added, with vigorous stirring, a solution of 0.005 mole bromine in 20 ml CH_2Cl_2. The mixture was stirred for 30 min and then warmed to 20°C and filtered. The filtrate was evaporated to a volume of 10 ml and the dark brown needles filtered off in an atmosphere of argon and dried in vacuum. Yield 60%, decomp 145-147°C. UV spectrum (in CH_3CN), λ_{max} nm (log ε): 345 (4.56), 363 (4.63). IR spectrum (nujol mull) (cm^{-1}): 1510, 1465, 1215, 1140, 1120, 1050, 860, 655, 530. Mass spectrum, m/z: 270 (M^+). Compound IIb was prepared in a similar manner in 55% yield, dark brown needles, decomp. 200°C. UV spectrum (in CH_3CN), λ_{max} nm (log ε) 369 (4.58), 387 (4.62). IR spectrum (KBr) (cm^{-1}): 1490, 1455, 1175, 1135, 1120, 1105, 985, 870, 660. Elemental analysis gave results corresponding to the calculated. Compounds IIa and IIb under the action of an equivalent quantity of $NH_2OH \cdot HCl$ in CH_3CN formed 4,4'-5,5'-tetrahalodiimidazolyls; tetraazafulvalene IIa is somewhat unstable to the action of atmospheric oxygen. From cyclic voltammetry data in CH_3CN solution against Ag/AgCl, compound III is a weak electron acceptor comparable in strength to naphthoquinone. Two reversible reduction peaks were observed at potentials $E_1^{red} = -0.65$ V; $E_2^{red} = -1.28$ V; $\Delta E_{1,2} = 0.63$ V which points to the exceptionally high stability of the anion-radical (log K = 10.68). For compounds IIa,b only one quasi-reversible reduction peak was observed at 0.30 and 0.38 V, respectively. Thus the derivatives IIa, b are acceptors similar in strength to tetrafluorotetracyanoquinodimethane. The properties of the ion-radical salts and charge-transfer complexes based on compounds IIa and IIb have been studied.

LITERATURE CITED

1. I. V. Krivoshei, V. E. Umanskii, O. M. Tsyguleva, and A. L. Boiko, Abstracts of papers, VI All-Union Conference on Charge-Transfer Complexes and Ion-Radical Salts, Chernogolovka (1984), p. 63.
2. V. H. M. Hill, J. Org. Chem., 28, 1931 (1963).
3. K. Lehmstedt and H. Rolker, Berichte, 76, 879 (1943).

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