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SYNTHESIS OF TRIAZOXYFURAZANES

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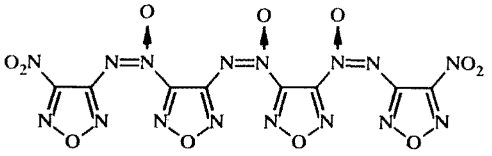
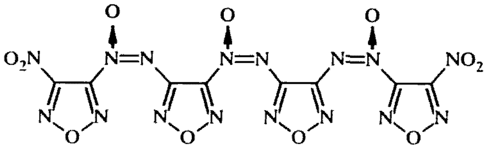
Azo- and zoxyfurazanes containing only two furazane units are described in the literature but they are normally obtained only as a by-products from the oxidation of aminofurazanes [1-3].

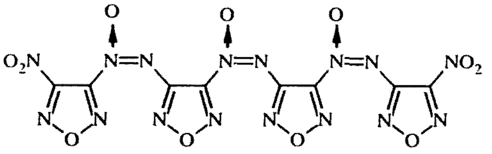
We have synthesized the previously unknown triazoxyfurazanes (Ia-Id) and we have studied their properties.



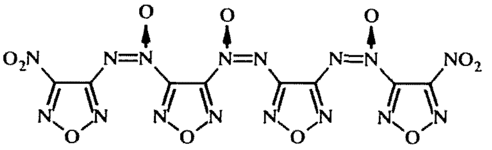
Ia



Ib

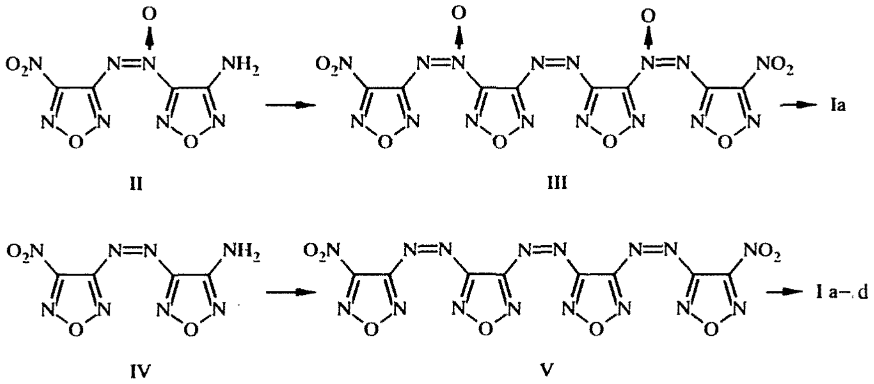


Ic



Id

Azoxybis(nitrofurazanyl-NNO-azoxy)furazane Ia was obtained by oxidative dimerization of 4-amino-4′-nitroazoxyfurazane (II) with subsequent oxidation of the product, azobis(nitrofurazanyl-3-azoxy)furazane (III). Azoxybis(nitrofurazanyl-ONN-azoxy)furazane, Ib, 4-(nitrofurazanayl-ONN-azoxy)-4′-(nitrofurazanyl-NNO-azoxy)azoxyfurazane, Ic, and 4-(nitrofurazanyl-NNO-azoxy)-4′-(nitrofurazanyl-ONN-azoxy)furazane, Id, were synthesized analogously via the azobis(nitrofurazanylazo)furazane (V) starting from 4-amino-4′-nitroazofurane (IV).



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The initial furazanes II and IV were dimerized by addition of 7-10 mole of 0.1-0.3 N $KMnO_4$ solution to a suspension of the furazane in hydrochloric acid. The products (III and V respectively), which were insoluble in the reaction mixture, were filtered off and washed with water. The reagents commonly used to convert azo compounds to the N oxides — Perhydrol or hydrogen peroxide in acids or organic acid anhydrides — were not successful for converting compounds III and V into the triazoxyfurazones Ia to Id. (It is known that the sudceptibility of azo groups to oxidation decreases on introduction of electron acceptor substituents [4]). Successfu oxidation of the azo groups in compounds IV and V was achieved only concentrated hydrogen peroxide in excess acid (5-6 mole H_2SO_4 per mole of H_2O_2). Moreover oxidation occurred only at temperatures above 60°C and extensive decomposition occurred under these conditions. This problem was eliminated by using ammonium peruslfate (30 mole for each azo group) in 104% oleum. In this case self heating did not occur even in the presence of a such a large amount of active oxygen. We used this mixture in later work. The yield of azoxy compounds in both cases was about 80%.

On oxidation of the symmetrical azo compound III only one positional isomer, Ia, with respect to the diazeneoxide oxygen was produced. A mixture of isomers was formed when IV was oxidized. The dependence of the ratio of the isomers with respect to the position of the N-oxide oxygen atom on the orienting influence of substituents has been discussed in detail [4-5]. The nitro group deactivates both nitrogen atoms, but the nearer nitrogen atom to considerably greater extent. Our experiments confirmed this: the ratio of the isomers separated by chromatography was Ia:Ib:Ic:Id = 9:3:4:4.

The structures of compounds Ia-d, III and V were established by elemental analysis coupled with mass spectrometry, IR, ^{13}C NMR and ^{15}N spectroscopy. Structures of the individual triazoxyfurazanes were confirmed by X-ray crystallography. More details of the syntheses and structural characteristics will be given in a full paper.

Compound Ia. $C_8N_{16}O_{11}$. M.p. 148°C. IR Spectrum, cm^{-1}: 1580 w, 1490 w, 1350 s, 1300 w, 1150 s, 1125 m, 1035 m, 950 w, 930 m, 890 m.

Compound Ib. mp 47°C. IR Spectrum, cm^{-1}: 1580 s, 1550 m, 1450 s, 1350 s, 1230 s, 1160 s, 840 s.

Compound Ic. Oil. IR Spectrum, cm^{-1}: 1590 s, 1565 m, 1500 w, 1480 s, 1350 s, 1320 w, 1150 s, 955 s.

Compound Id. mp 124°C. IR Spectrum, cm^{-1}: 1580 s, 1550 m, 1490 s, 1350 s, 1305 w, 1160 s, 890 s.

Compound III. $C_8N_{16}O_{10}$. mp 98°C. IR Spectrum, cm^{-1}: 1580 s, 1530 m, 1495 s, 1350 s, 1200 s, 1150 s, 1030 s, 930 m, 880 m, 800 s.

Compound V. $C_8N_{16}O_8$. mp 83°C. IR Spectrum, cm^{-1}: 1570 s, 1540 s, 1350 s, 1180 s, 1030 w, 1020 s, 950 w, 910 w, 820 s.

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