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SYNTHESIS AND PROPERTIES OF 1,3-DITHIOLE-[3]- AND [4]-DENDRALENES, ACYCLIC SYSTEMS OF THE CORRESPONDING [3]- AND [4]-RADIALENES

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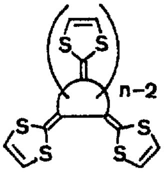
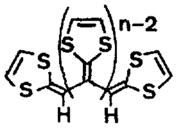
Abstract: 1,3-Dithiole-[3]- and [4]-dendralenes (2 and 3) have successfully been synthesized by using Vilsmeyer reactions on 2,2'-(ethanediylidene)bis(1,3-dithiole) (5) and 2 and the following Wittig reaction. Their electrochemical properties are discussed in comparison with those of 5 and 1,3-dithiole[4]radialene (4). Furthermore, conversion of 2 and 3 to 1,3-dithiole-[3]radialene and 4, respectively, was attempted by using zero-valent nickel complexes.

[n]Radialenes substituted with 1,3-dithioles (1,3-dithiole[n]radialenes)[1-3] are of particular interest as both a multi-stage redox system and a promising donor component for preparation of organic conductors[4] and/or organic ferromagnets.[5] In order to much more understand their characteristic redox behavior involving a remarkable structural change in their central rings, there is need for investigating electrochemical properties of the corresponding acyclic systems, [n]dendralenes[6] substituted with 1,3-dithioles (1,3-dithiole[n]dendralenes). In addition, such a [3]dendralene can be also expected as a plausible precursor for the synthesis of our target 1,3-dithiole[3]radialene[7] (1), which continues to receive considerable interest as a donor component for preparation of new organic materials mentioned above because of its highly planar structure and strongly electron-donating property. In this communication we wish to report the synthesis of 1,3-dithiole-[3]- and [4]-dendralenes, tris(1,3-dithiol-2-ylidene)propane (2) and tetrakis(1,3-dithiol-2-ylidene)butane (3), conversion of 3 to 1,3-dithiole[4]radialene (4), and their electrochemical properties.



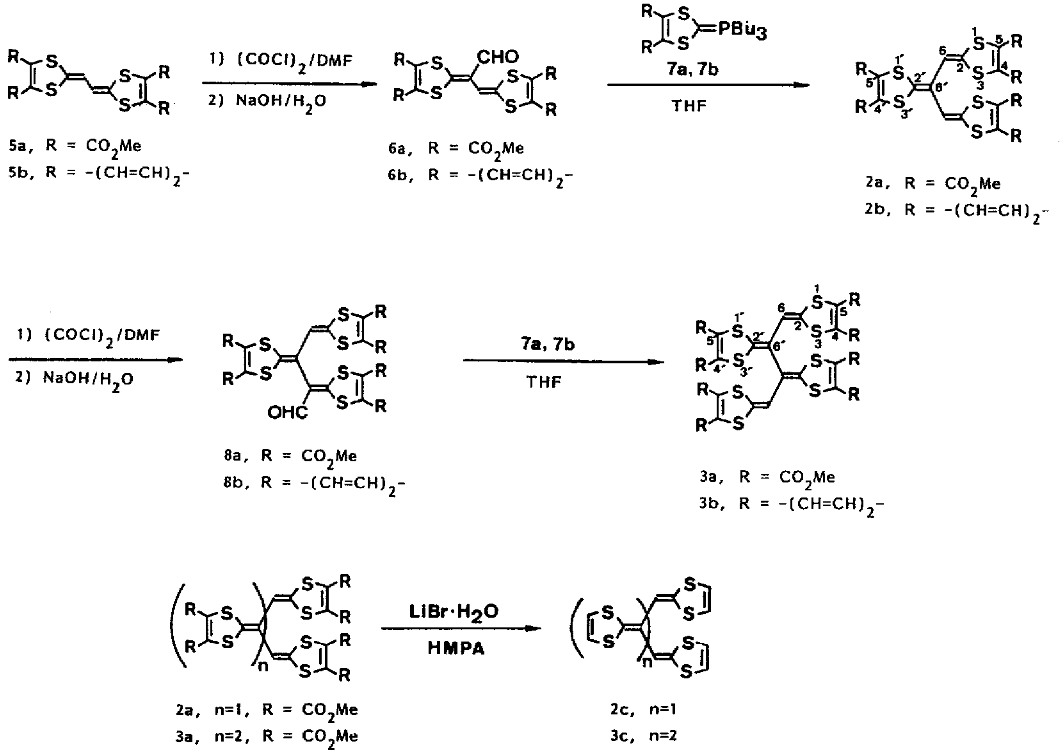
1,3-dithiole[n]radialene



1,3-dithiole[n]dendralene

The synthesis of 2 and 3 was achieved as shown in Scheme I. Thus, treatment of tetracarbomethoxy- and dibenzo-derivatives of 2,2'-(ethanediylidene)bis(1,3-dithiole) (5a and 5b)[8] with oxalyl chloride (2 equiv.) in DMF at 0 °C, and subsequent hydrolysis of the reaction mixture with 1N NaOHaq in CH_2Cl_2 gave the corresponding 1-formyl derivatives (6a and 6b) in 75 and 74% yields, respectively.[9,10] The reaction of 6a and 6b with 1,3-dithiol-2-ylidene-tri-n-butylphosphorane's (7a and 7b), which were generated in situ by treatment of the corresponding (1,3-dithiol-2-yl)tri-n-butylphosphonium tetrafluoroborate with n-BuLi (1 equiv.) in

Scheme I

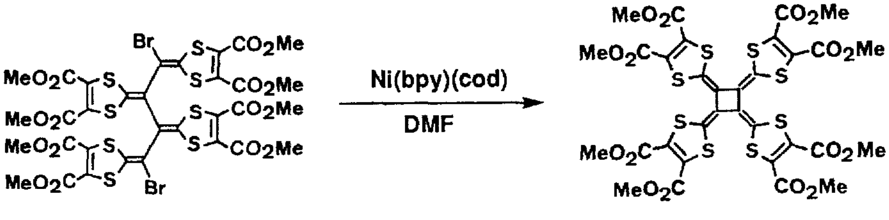


THF at -70 °C,[8,11] afforded hexacarbomethoxy- and tribenzo-2 (2a and 2b) in respective yields of 83 and 92%.[9] The similar method was applied for the synthesis of 3. By the reaction of 2a and 2b with oxalyl chloride (2 equiv.) in DMF were obtained 1-formyl-tris(1,3-dithiol-2-ylidene)propane's (8a and 8b) in 86 and 85% yields, respectively,[9,10] which were successively allowed to react with the corresponding 7 in THF at -70 °C to afford octacarbomethoxy- and tetrabenzo-derivatives of 3 (3a and 3b) in 89 and 73% yields, respectively.[9] The unsubstituted systems of 2 and 3 (2c and 3c) were obtained by the reaction of 2a and 3a with an excess of LiBr·H$_2$O in HMPA at 95-155 °C in both 80% yields.[9,12] In comparison of electronic spectra between 2, 3 and 5 there is no significant bathochromic shift of the absorption maxima due to π-conjugation extention. In the ^{13}C NMR spectra the C-2' carbons appeared at δ ca. 118-120, which shifted to the higher field by 9-13 ppm compared with those of the C-2 carbons. In correspondence with this the C-6' carbon signals appeared at relatively lower field of δ 134-140 compared with their C-6 carbon signals (δ 108-110). The chemical shifts of C-2 and C-6 carbons were comparable to those of the corresponding 5's.

When 2a, 2b and 3a were allowed to react with NBS (2 equiv.) in CH$_2$Cl$_2$ at room temperature, the corresponding 1,3- and 1,4-dibromo derivatives (9a, 9b and 10a) were obtained quantitatively. Successive intramolecular reductive coupling reactions were carried out by using various zero-valent nickel complexes. The reaction of 10a with Ni(bpy)(cod) (1 equiv.)

(bpy: 2,2'-bipyridine; cod: 1,5-cyclooctadiene) in DMF at room temperature gave an octacarbomethoxy derivative of 4 albeit in very low yield (3%) (see Scheme II). In a similar manner the conversion of 2a and 2b to the corresponding [3]radialene was attempted, but a fruitful result was not so far obtained.

Scheme II



10a

4a

Electrochemical behavior of 2 and 3 was investigated by cyclic voltammetry.[13] For all 2's two pairs of electrochemically reversible waves and one pair of irreversible waves were observed, each of which corresponds to one-electron transfer. Their redox potentials are as follows: 2a, +0.70, +0.79, +1.75 V vs. SCE in PhCN; 2b, +0.50, +0.62, +1.53 V; 2c, +0.26, +0.40, +1.32 V. Also, 3c exhibited three pairs of redox waves at +0.25, +0.37 and +0.72 V, in which the first and second pairs of waves correspond to reversible one-electron transfer processes, respectively, and the third pair involves irreversible two-electron transfer. On the other hand, the cyclic voltammograms of 3a and 3b were composed of only two pairs of redox waves at +0.73 and +1.14 V for 3a, and +0.54 and +0.97 V for 3b, respectively, as a result of apparent overlap of the first- and second-electron transfer processes. The second (E_2) redox potentials of 2 and 3 are more negative by 90-170 mV compared with those of the corresponding 5's,[8] while the first (E_1) potentials are nearly equal. The smaller (E_2-E_1) values (90-140 mV for 2 and 0-120 mV for 3) than those of 5 (190-210 mV) indicate much more decreasing on-site Coulomb repulsion in 2^{2+} and 3^{2+} than in 5^{2+}.[14] Comparison of the fourth (E_4) redox potentials between 3 and the corresponding 4 is of much interest in examining the influence of a cyclobutadiene structure on the redox of 4. The E_4 values of 4's[1] are much more positive by 680-740 mV than those of corresponding 3's, indicating a remarkable instability of the tetracation of 4, in which an antiaromatic cyclobutadiene structure appears in the central four-membered ring. The electrochromic property of these dendralenes was also investigated by chemical oxidation of 2b and 3b with $NOBF_4$. The stepwise spectral change between 2b (399 nm), $2b^{+\cdot}$(589 and 734 nm) and $2b^{2+}$ (507 and 673 nm) was observed, which were colored yellow, dark blue and bluish green in CH_2Cl_2, respectively.[15] In the oxidation of 3b there was concomitant formation of $3b^{+\cdot}$ (577, 674 and 768 nm) and $3b^{2+}$ (595 and 733 nm).[15] It is noteworthy that the absorption maxima at the longest wavelength of $2b^{2+}$ and $3b^{2+}$ largely shift by ca. 270 and 330 nm to the longer wavelength than that of the dication (404 nm) of 2,2'-(ethanediylidene)bis(1,3-dithiole) ($5c^{2+}$), while there is no significant difference of the absorption maxima between $2b^{+\cdot}$, $3b^{+\cdot}$ and $5c^{+\cdot}$ (760 nm).[16]

References and Notes

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(9) Satisfactory elemental analyses and spectral data were obtained for all new compounds.

(10) In all cases 1,2- and 1,3-diformyl derivatives were not obtained even by using a large excess of oxalyl chloride.

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(13) The cyclic voltammetry was performed by using Pt working and counter electrodes and $(n\text{-Bu})_4NClO_4$ as an electrolyte at 25 °C (scan rate, 100 mV/s).

(14) It is a most probable cause that two positive charges can delocalize over three or four 1,3-dithiole rings for 2^{2+} and 3^{2+}, while two positive charges must localize in each 1,3-ditihole ring for 5^{2+}.

(15) Both $2b^{2+}$ and $3b^{2+}$ were also isolated as stable bis(tetrafluoroborate) salts by the reaction of 2b and 3b with $NOBF_4$ (2 equiv.) in 70 and 76% yields, respectively.[9] The 1 equiv. use of $NOBF_4$ gave the corresponding radical cation salts, but they were not so pure because of contamination with an unreacted 2b or 3b, and $2b^{2+}$ or $3b^{2+}$.

(16) We are now considering a cause of such a remarkable bathochromic shift in absorption maxima at the longest wavelength of $2b^{2+}$ and $3b^{2+}$.

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