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Synthesis of Tetrakis(1,2-benzodithio)tetramethyleneethane Dication Salt and Its Two-electron Reduction

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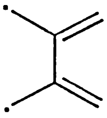
Tetrakis(1,2-benzodithio)tetramethyleneethane dication salt was obtained by two-electron oxidation of a head-to-head dimer of bis(1,2-benzodithio)allene. The dication was two-electron reduced at a comparatively low voltage into the corresponding diradical, whose ESR spectrum seemingly showed a fine structure. The characteristics of the diradical could not be obtained, since the signal intensity did not increase as a result of the preferential intramolecular radical coupling of the diradical into the original allene dimer.

Tetramethyleneethane (1) is one of simple non-Kekulé molecules. The quantitative theory predicts that 1 belongs to a disjoint non-Kekulé class and should have a preference for a singlet ground state to the triplet state.[1)] In contradiction to the theory and more sophisticated quantum calculations,[2)] recent experiments demonstrate that the ground state is triplet irrespectively of planar (D_{2h})[3)] and orthogonal (D_{2d})[4)] conformations of 1. It is worthy to be investigated whether such a disagreement between theory and experiment could be also encountered in more stabilized derivatives of 1. Now we wish to report the synthesis of a two-electron oxidized 1 substituted with four 1,2-benzodithio groups, tetrakis(1,2-benzodithio)tetramethyleneethane dication (2^{2+})[5)] as a stable salt by two-electron oxidation of a head-to-head dimer (8) of bis(1,2-benzodithio)-



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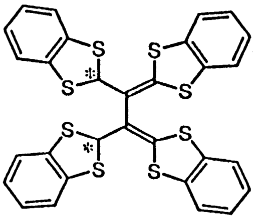
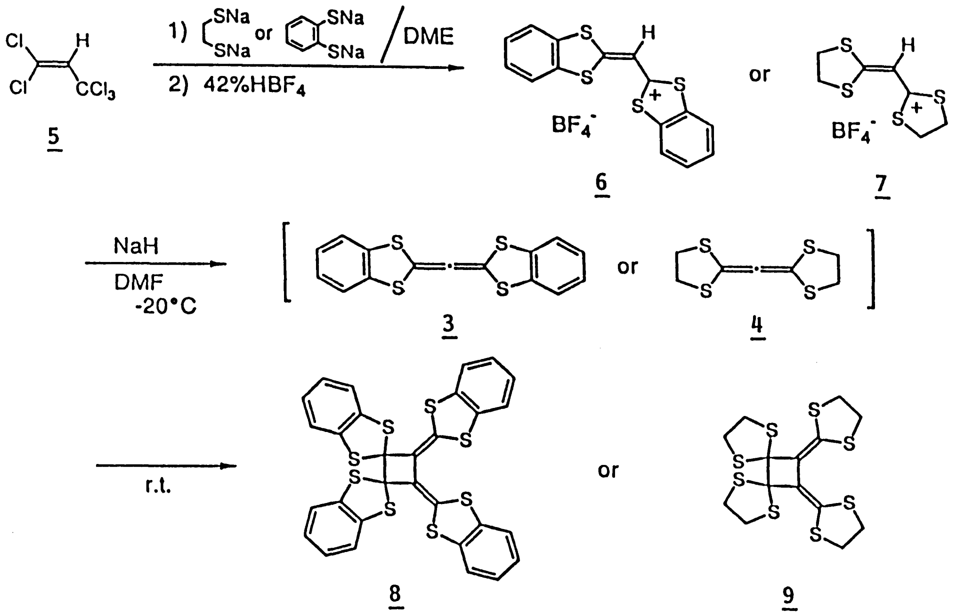


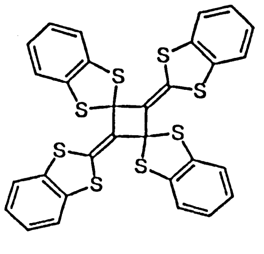
2: * = ·
2^{2+}: * = +

allene (3), and the generation of the corresponding diradical (2).

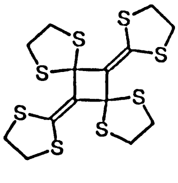
At first the oxidative coupling of 3 and bis(ethylenedithio)allene (4) seemed most convenient for the synthesis of 2^{2+} and its ethylenedithio analogue, respectively.[6)] Now, their synthesis was attempted as shown in Scheme 1. At room temperature 1,1,3,3,3-pentachloropropene (5)[7)] was reacted with disodium 1,2-benzenedithiolate or ethylenedithiolate in DME and then with 42% HBF_4 aq. to give (1,3-benzodithiol-2-ylidene)methyl-1,3-benzodithiolium and (ethylenedithiol-2-ylidene)methylethylenedithiomethylium tetrafluoroborates (6 and 7) in respective yields of 57 and 50%. Subsequently, when these salts were treated with an excess of NaH in dry DMF at -20 °C and kept at room temperature, the expected 3 and 4 were not produced, but their dimers, 8 (a yellow solid, mp 262-264 °C (dec)) and 9 (pale yellow crystals, mp 213-215 °C) were obtained in 95 and 47% yields, respectively. Their structures were assigned to 8 and 9 based on the ^{13}C NMR spectral data, in which there was observed non-equivalence of six benzo carbons in each 1,3-benzodithiol-2-ylidene group and of two methylene carbons in each ethylenedithiol-2-ylidene group, respectively: δ 137.8,



Scheme 1.



8'



9'

137.6, 136.8, 127.4, 125.9, 125.5, 125.1, 121.7, 121.6, 121.4, 117.5, 85.8 for 8 and 129.3, 124.1, 84.2, 40.5, 38.8, 38.5 for 9. The other possible isomers (8' and 9'), which can be produced by dimerization of 3 and 4 in a head-to-tail manner, were not detected at all. Such a selective head-to-head dimerization of 8 and 9 was also observed in the case of tetrakis(methylthio)allene.[8] The similar reactions were carried out in the presence of an excess of silver tetrafluoroborate at -20 °C.[6] The products were only 8 and 9, respectively.

The redox behavior of 8 and 9 was investigated by cyclic voltammetry. The redox cycles at 25 °C were irreversible, in which only oxidation peaks appeared at +0.62 and +0.86 V for 8, and +0.72 and +0.86 V for 9, but at -60 °C the reversibility became better.[9] This result suggests that their dications (8^{2+} and 9^{2+}) might be converted to the expected 2^{2+} and its ethylenedithio analogue through the cyclobutene ring-opening at higher temperature. Indeed, in the former case the bis(tetrafluoroborate) salt of 2^{2+} ($2^{2+}\cdot 2BF_4^-$; a red solid, mp > 300 °C)[10] was isolated quantitatively by the reaction with $NOBF_4$ (10 equiv.) in dry CH_3CN at room temperature.

The redox behavior of the $2^{2+}\cdot 2BF_4^-$ salt was also investigated.[11] The cyclic voltammogram measured at 25 °C was irreversible, in which the reduction peaks only appeared at -0.22 and -0.38 V. However, at -60 °C the reversibility became slightly better, suggesting that the radical cation and 2 remain comparatively stable below -60 °C. Accordingly, the electrochemical reduction was performed at -60 °C in dry DMF and monitored by ESR spectroscopy. A signal began to appear as increasing the reduction voltage gradually, and the maximum in the intensity was achieved at -2.3 V.[12] However, the intensity was rather decreased with continuing the reduction. Unwillingly, the solution was immediately frozen to -102 °C and the ESR

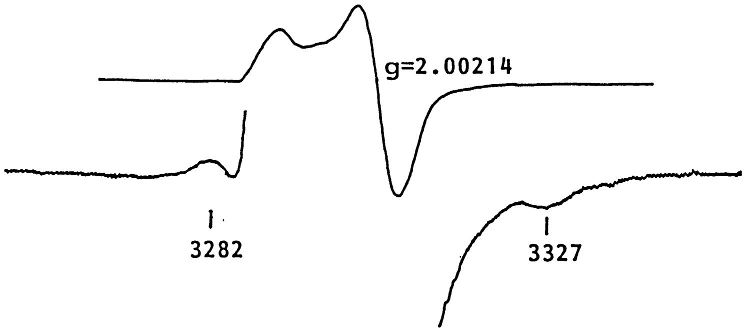


Fig. 1. The ESR spectrum of 2 frozen to -102 °C immediately after electrochemical reduction of $2^{2+}\cdot 2BF_4^-$ at -60 °C in degassed DMF (the microwave frequency used in the measurement: 9.25 GHz).

spectrum was measured. Together with a strong two-overlapped signal at g=2.00214 one pair of weak signals presumably due to the fine structure of 2 was observed (see Fig. 1). Even at this temperature the two unpaired electrons of 2 are not stabilized so enough as to be prevented from intramolecular radical coupling, as evidenced by isolation of 3 from the reaction solution after the ESR measurement. We must wait for discussion on the ground state of 2, till the clear triplet ESR spectrum can be obtained.

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References

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5) This cation salt has already been synthesized in a different method from ours, but the yield is very poor (8%) (R. R. Schmidt and H. Hensen, Chem. Ber., 114, 1723 (1981)).

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9) The measurement was performed in the voltage range of -0.5 - +1.0 V vs. SCE in dry CH_2Cl_2 solution containing (n-Bu)$_4$NClO$_4$. The two pairs of peaks are assumed due to one-electron transfer, respectively.

10) The ^{13}C NMR spectrum of this salt in CF_3CO_2D showed signals at δ 177.0, 135.9, 131.5, 128.4, 127.3, 123.7, 114.6. In the similar manner 9 was also reacted with $NOBF_4$ and an orange solid was obtained, which was however not a bis(tetrafluoroborate) salt of tetrakis(ethylenedithio)tetramethyleneethane dication. The structure and reaction scheme are now under investigation.

11) The measurement was performed in the voltage range of 0 - -0.7 V vs. SCE in dry DMF containing (n-Bu)$_4$NClO$_4$.

12) The voltage is not corrected with a reference electrode.

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