Tetrahedron Letters,Vol.23,No.4,pp 373-374,1982 0040-4039/82/040373-02$03.00/0
Printed in Great Britain

CYCLOPENTA(p-PHENYLENE SULFIDE) AND CYCLOTETRA(p-PHENYLENE SULFIDE): EXAMPLES OF A NEW MACROCYCLIC SERIES

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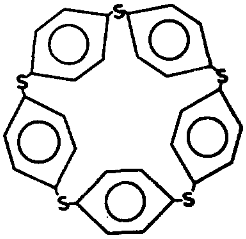
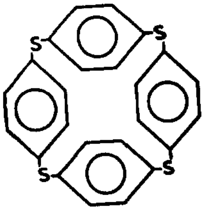
Abstract: Cyclotetrameric and pentameric(p-phenylene sulfides) have been isolated from poly(p-phenylene sulfide) and identified and characterized.

The reaction of p-dichlorobenzene and sodium sulfide in a solvent[1] results in the formation of linear poly(p-phenylene sulfide) (PPS). We have now succeeded in isolating and identifying from the commercial polymer the oligomeric thioethers cyclopenta(p-phenylene sulfide) [I] and cyclotetra(p-phenylene sulfide) [II].



I



II

Extraction of a low molecular weight PPS powder with methylene chloride followed by solvent removal resulted in isolation of 3% of the PPS as an off-white solid. Solid probe mass spectral studies of the solid[2] provided spectra which, in addition to peaks due to open chain oligomers of low molecular weight, exhibited distinct peaks at m/e 432, m/e 540, m/e 648, and m/e 745 together with peaks for the corresponding doubly charged ions. The appearance of each succeedingly larger molecular ion required a higher temperature than that for the previous molecular ion. Similar observations appear to have been incorrectly interpreted.[3] Bruno, et. al. attributed the ions at m/e 432, m/e 540 and m/e 648 to open-chain fragments arising from thermal cleavage of the PPS being examined.

Chromatography (Al_2O_3) of the solid (10g) from the extraction followed by gradient vacuum sublimation (300°->80°) afforded two, white, crystalline products. The first (0.35g), had a molecular ion at m/e 540. Molecular weight determination by vapor phase osmometry[4] gave 571 ± 5%. The second compound (0.05g) had a molecular ion at m/e 432.

The physical data for I and II are summarized below:

	I	II
m.p.	257-259° (corr.)	295-297° (unc.)
IR(cm^{-1}) CsI pellet	3050(w), 1570(m), 1473(s), 1387(m), 1096(s), 1074(m), 1010(s), 825(m), 820(m), 802(s) 745(w), 704(m), 522(m)	3050(w), 1568(m), 1475(s), 1387(m), 1305(w), 1255(w), 1180(w), 1130(w), 1095(m), 1070(m), 1015(s), 834(s), 825(m), 820(m), 805(m), 740(w), 715(m), 704(m), 697(w), 555(m), 510(m)
UV-VIS (nm) (CH_2Cl_2)	271 (42,200) 295(sh) (31,500)	272 (27,700) 294 (24,800)
^{1}H NMR	CS_2 (TMS) singlet 7.13 δ	CS_2 CD_2Cl_2 (TMS) singlet 7.02 δ
^{13}C NMR[5] CD_2Cl_2 CS_2	quaternary C 135.629 ppm protonated C 132.573	138.685 ppm 133.548
ESR Radical Cation	green solution in CH_2Cl_2 with SbF_5. Linewidth 1.08G g = 2.00794	Green solution in Ch_2Cl_2 with SbF_5 g = 2.00805, a_H = 0.25G
Mass Spectrum (strong lines)	540(100), 270(33), 216(12), 184(21),171(17), 153(10) 140(12)	432(100) No other ions greater than 5%

1. J. T. Edmonds, Jr. and H. W. Hill, Jr., U.S. Patent 3,354,129 (1967).
2. A detailed mass spectral analysis of the impurities found in PPS will be reported elsewhere.
3. G. Bruno, S. Foti, P. Maravigna, G. Montando and M. Przybylski, <u>Polymer</u>, <u>18</u>, 1149 (1977).
4. Vapor phase osmometric measurements were performed by L. E. Stillwagon.
5. The help of M. L. M. Schilling in obtaining the ^{13}C spectra is acknowledged.

(Received in USA 18 September 1981)