DETECTION OF 2,5-DIMETHYLENE-2,5-DIHYDROTHIOPHENE AND THIOPHENORADIALENE

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Summary: The reactive species 2,5-dimethylene-2,5-dihydrothiophene and thiophenoradialene have been detected for the first time. The method of HCl elimination has proved to be a generally applicable method for generating heterocyclic xylylenes and radialenes.

Below we report on the generation and spectroscopic detection of the hitherto unknown reactive intermediates 2,5-dimethylene-2,5-dihydrothiophene 1 and tetramethylenetetrahydrothiophene (thiophenoradialene) 2 using the Variable Temperature Photoelectron Spectroscopy (VTPES) and Flash Vacuum Pyrolysis Matrix Isolation Technique (FVP MIT).¹



1 and 2 are quantitatively accessible by pyrolytic elimination of HCl from the precursor systems 3^2 and 4^3 at 600°C or 650°C, respectively and low pressures (≤ 0.02 mbar).⁴ This type of reaction had previously been used to produce dihydrocyclobutabenzenes⁵, 2,3-dimethylene-2,3-dihydrofuran⁶ 5 and 2,3-dimethylene-2,3-dihydrothiophene^{7,8} 6. Note that 5 had been made otherwise before^{5,9} whereas 6 had been unknown prior to our work.⁷ Further note that 2,5-dimethylene-2,5-dihydrofuran 7 and tetramethylenetetrahydrofuran (furanoradialene) 8 are also easily and quantitatively accessible in reactions analogous to reactions a and b shown above.¹⁰ 7^{11,12} and 8^{13,14} had otherwise been generated before.



The structural proof of the new compounds 1 and 2 is based on the following arguments derived from their UV photoelectron spectra¹⁵ (in the gas phase) and UV/VIS¹⁶ and IR absorption spectra¹⁷ (in Ar matrices). Absence of any n_{Cl} ionization bands in the photoelectron spectra as well as of C-Cl vibrational bands in the IR spectra proves the quantitative disappearance of the precursor system and excludes any products still containing one or two chloro-substituents. From our experience^{6,7} with the photoelectron and UV/VIS spectra of 5 and 6 the thermal ring closure reactions of 2 and 8 to the cyclobutafurans 9 or 10 or cyclobutathiophenes 11 and 12 can be excluded, in particular so since the calculated ionization spectra of these systems are not compatible with the measured product spectra.



The photoelectron spectra of the products of reaction a (shown above), of 7 and of 1,4dimethylene-1,4-dihydrobenzene $(p-xylylene)^{18}$ are very similar. The same is true for the UV/ VIS spectra.^{19,20} Likewise the photoelectron spectrum of the products of reaction b (shown above) and of 8 as well as the UV/VIS spectra of both compounds are very similar. In addition, the calculated ionization and excitation spectra of the new systems 1 and 2 are in good agreement with their experimental counterparts (the photoelectron and UV/VIS absorption spectra).²⁰ Finally the photoelectron and absorption spectra of 1 (as well as of 7 by analogy) were perfectly reproduced using the independent generation reaction c (pyrolysis of 13^{11}).



Details about the calculated and measured spectra, the chemical and physical properties of the new systems as well as about some insight gained into the interesting electronic structure of these polyene-like highly reactive species will be given elsewhere.²⁰

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References and Notes

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- 16 Measured vertical electronic transition energies ($\Delta E_{max}/eV$; Ar 15 K); for 1: 3.97, 5.02; for 2: ca. 3.35, ca. 4.20, 4.72, 5.69; for 7: 4.19, 5.98; for 8: 3.63, 4.49, 5.34.
- Measured IR absorption wavenumbers (*ν*/cm⁻¹; År 15 K); for 1:1586.6, 1187.4, 840.8, 831.2, 801.6; for 2: 1585.0, 1405.0, 1182.5, 884.0, 836.0; for 7: 1323.4, 1200.2, 1004.2, 813.6, 804.6; for 8: 1219.2, 1128.4, 1004.4, 882.4, 816.0.
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