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cis-DISULFIDES

PHOTOELECTRON SPECTRUM OF A 6,7-DITHIABICYCLO[3.2.1]OCTANE

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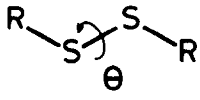
Summary: The photoelectron spectrum of 2,4-dichloro-6,7-dithiabicyclo[3.2.1]octane (2) shows the largest sulfur lone pair energy gap ever observed as a consequence of the *cis*-disulfide conformation, which has been further studied by molecular mechanics (MM1) and molecular orbital (CNDO/S) calculations of the parent compound, 6,7-dithiabicyclo[3.2.1]octane (3).

Photoelectron (PE) spectroscopy provides a powerful method for conformational analysis of organic compounds, particularly those with vicinal lone pairs (hydrazines, peroxides, disulfides etc.),[1] but previous studies[2] of disulfides (1) have been limited by the availability only of compounds with torsional angles about the S-S bond, Θ(CSSC), in the range of 30-110°.

Incorporation of a disulfide moiety in the relatively rigid bicyclo[3.2.1]-octane framework offers an ideal possibility for achieving the *cis*-disulfide conformation, and this paper reports the PE spectrum, of 2,4-dichloro-6,7-dithiabicyclo[3.2.1]octane (2),[3] the first simple *cis*-disulfide studied by PE spectroscopy.



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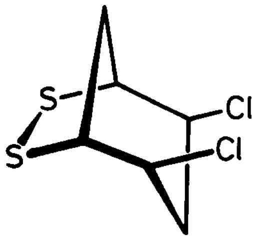

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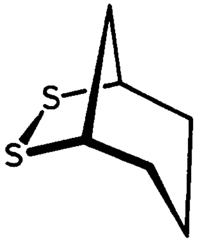

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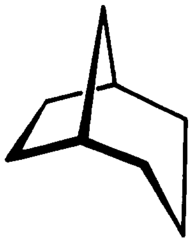

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Molecular mechanics (Allinger's MM1, 1973 version[4]) optimized structures of 6,7-dithiabicyclo[3.2.1]octane (3) and bicyclo[3.2.1]octane (4) (cf. Figure 1) reveal that replacement of CH_2-CH_2 by S-S (4 → 3) has several structural effects. The bicyclic framework in 3 forces as expected the C-S-S-C unit to be *cis*, despite the known preference of disulfides to assume a *gauche* ($\theta \sim 90^\circ$) arrangement;[5] the bridgehead-bridgehead distance increases from 2.34 Å (4) to 2.48 Å (3) as a function of the longer S-S and C-S bonds in 3, and the puckering of the six-membered ring increases. Another consequence is a diminution of the C-S-S bond angles by 6.5° relative to the values in CH_3SSCH_3 (MM1: 103.7°).[6]

To gain insight into the electronic structure of the 6,7-dithiabicyclo-[3.2.1]octane system, a CNDO/S molecular orbital calculation[7] of 3 based on the MM1 fully optimized structure has been performed. The highest occupied molecular orbital (HOMO, $\varepsilon = -9.71$ eV) is the out-of-phase combination of the sulfur lone pairs (n_{SS}^-) and is completely localized on the sulfur atoms (97 %). Contrary to this, the following orbital (H-1, $\varepsilon = -12.14$ eV), the n_{SS}^+ combination, is diluted by mixing with the σ orbitals of the carbon framework (78 % localized on the sulfur atoms). Thus, the difference between the two sulfur lone pair combinations, which is calculated to be $\Delta\varepsilon = 2.43$ eV for 3, is primarily dependent on the dihedral angle about the S-S bond, but also interaction with lower lying σ orbitals may influence its value. The following orbitals (H-2, $\varepsilon = -12.63$ eV and H-3, $\varepsilon = -12.96$ eV) correspond to antisymmetric and symmetric combinations of the σ_{CS} orbitals, respectively.

The photoelectron spectrum of 2,4-dichloro-6,7-dithiabicyclo[3.2.1]octane (2) (see Figure 2) contains a single low-energy ionization at 8.20 eV from the n_{SS}^- sulfur lone pair combination, the other sulfur lone pair combination (n_{SS}^+) being assigned to the second ionization energy at 10.31 eV. Thus, the energy gap of 2.11 eV between the first two ionizations is the largest ever observed for a simple, non-aromatic disulfide[8] and confirms the presence of the

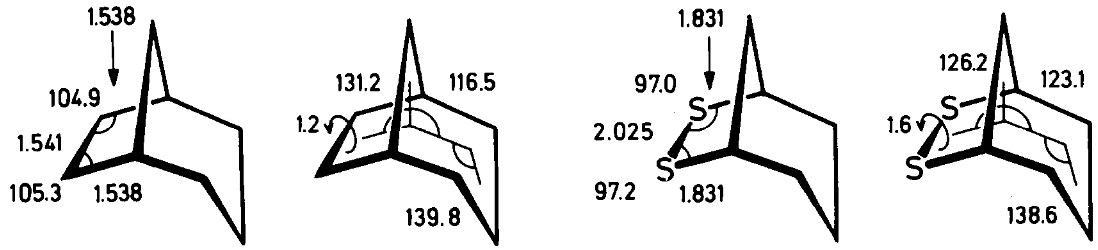

Figure 1. Molecular mechanics (MM1) calculated structural data for bicyclo-[3.2.1]octane (4) and 6,7-dithiabicyclo[3.2.1]octane (3), (bond lengths in Å and bond angles in degrees).

cis conformation of the disulfide moiety.[9] It also allows us to determine the resonance integral for the interaction of the parallel sulfur 3p lone pairs, $\beta_{SS} \sim -2.1$ eV, a value previously available only by extrapolation.[10] The higher intensity of the 10.31 eV peak indicates coincidence of the n^{+}_{SS} and σ^{-}_{CS} combinations, the σ^{+}_{CS} combination being assigned to the ionization energy at 10.83 eV. The chlorine 3p lone pairs are responsible for the intense peak at 11.28 eV.[11]

Determination of the sulfur lone pair energy gap, $\Delta E(n^{+}_{SS}-n^{-}_{SS})$, for 2, a disulfide with a *cis* conformation, allows previously established correlations of Θ(CSSC) *versus* $\Delta E(n^{+}_{SS}-n^{-}_{SS})$[2c,5b,8,12] to be extended from the range $30^{\circ} < \Theta < 110^{\circ}$ to $\Theta = 0^{\circ}$ and makes conformational analysis by PE spectroscopy of disulfides with small torsional angles possible. Further elaboration of a reliable $\Theta(\mathrm{CSSC})/\Delta E(n^{+}_{SS}-n^{-}_{SS})$ correlation is necessary, since the recently suggested relationship $\Delta E_{obs} = 1.78\ |\cos \Theta| + 0.13$ eV[12] implies $\Delta E_{cis} = \Delta E_{trans}$ in contrast to results derived from a recent experimental study of bulky disulfides.[5b]

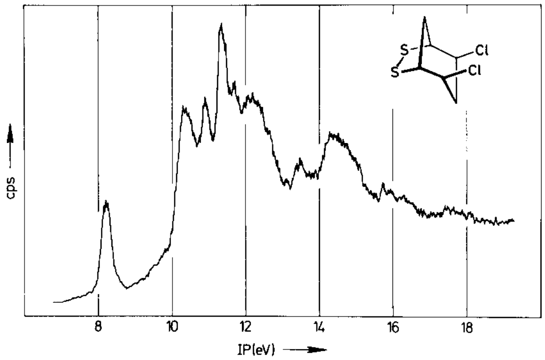

Figure 2. Photoelectron spectrum of 2,4-dichloro-6,7-dithiabicyclo[3.2.1]-octane (2) recorded on a Perkin-Elmer PS-18 spectrometer at 45° with a resolution of 35 meV, using Ar and Xe as internal calibrants.

Experimental

7-Thiabicyclo[4.1.0]heptane[3] (56 mg, 0.5 mmol) and SCl_2 (51.5 mg, 0.5 mmol), each dissolved in CH_2Cl_2 (25 mL), were simultaneously added dropwise, over 30 min., to CH_2Cl_2 (200 mL) which was stirred at -50 °C. The solution was maintained at this temperature for 15 min. after the additions, allowed to warm to room temperature, washed with aq. $NaHCO_3$, brine, water and dried. Removal of the solvent gave a yellow semi-solid (105 mg). Recrystallization from ethyl acetate-hexane furnished yellow, microcrystalline prisms of 2,4-dichloro-6,7-dithiabicyclo[3.2.1]octane (2) (45 mg, 42 %) mp. 134-137 °C. Anal. calc. for $C_6H_8Cl_2S_2$: C 33.50, H 3.75 %. Found: C 33.74, H 3.50 %.[9]

Acknowledgement

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References and Notes

1. a) M. Klessinger and P. Rademacher, Angew. Chem., 91, 885 (1979), Angew. Chem. Int. Ed., 18, 826 (1979); b) R. S. Brown and F. S. Jørgensen in "Electron Spectroscopy. Theory, Techniques and Applications", (eds. C. R. Brundle and A. D. Baker), Vol. 5, Academic Press, 1982, in press.
2. a) H. Bock and G. Wagner, Angew. Chem., 84, 119 (1972), Angew. Chem. Int. Ed., 11, 150 (1972); b) G. Wagner and H. Bock, Chem. Ber., 107, 68 (1974); c) M. F. Guimon, C. Guimon and G. Pfister-Guillouzo, Tetrahedron Lett., 441 (1975).
3. P. H. McCabe and A. Stewart, J. Chem. Soc. Chem. Commun., 100 (1980).
4. Quantum Chemistry Program Exchange, QCPE, 11, 318 (1976).
5. a) F. S. Jørgensen and J. P. Snyder, J. Org. Chem., 45, 1015 (1980); b) G. Rindorf, F. S. Jørgensen and J. P. Snyder, J. Org. Chem., 45, 5343 (1980) and references therein.
6. F. S. Jørgensen and J. P. Snyder, Tetrahedron, 35, 1399 (1979).
7. C. Guimon, D. Gonbeau and G. Pfister-Guillouzo, Tetrahedron, 29, 3399, 3599 (1973), M. Arbelot, C. Guimon, D. Gonbeau and G. Pfister-Guillouzo, J. Mol. Struct., 20, 487 (1974).
8. R. Gleiter and J. Spanget-Larsen, Top. Curr. Chem., 86, 139 (1979).
9. The structure of 2 has been established by spectroscopic methods (ref. 3 and P. H. McCabe, unpublished results). A maximum at 361 nm in the UV spectrum of 2 indicates the presence of the *cis*-disulfide moiety (cf. G. Bergson and B. Sjöberg, Acta Chem. Scand., 14, 222 (1960)). By mass spectrometry the disulfide 2 has been shown to vaporise unchanged.
10. The $\beta_{SS} \sim -2.1$ eV is in fact identical to the value derived by extrapolation (ref. 8), although it must be considered as a lower limit due to the mixing of the n_{SS}^{+} combination with lower lying σ orbitals (cf. the CNDO/S calculations above).
11. Ionization energies corresponding to chlorine 3p lone pairs are normally found in the range 11.2 - 11.7 eV. See for example B. Ruscič, L. Klasinc, A. Wolf and J. V. Knop, J. Phys. Chem., 85, 1486, 1490, 1495 (1981).
12. H. Bock, U. Stein and A. Semkow, Chem. Ber., 113, 3208 (1980).

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