Tetrahedron Vol. 37, No 16, pp 2743 to 2747, 1981
Printed in Great Britain

0040-4020/81/162743-05$02 00/0
Pergamon Press Ltd.

CONFORMATIONAL ANALYSIS OF MESOCYCLIC POLYTHIOETHERS

GAS PHASE CONFORMATIONAL ANALYSIS OF FIVE MESOCYCLIC POLYTHIOETHERS USING PHOTOELECTRON SPECTROSCOPY

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(*Received in U.S.A.* 7 *August* 1980)

Abstract—The helium I photoelectron spectra of the mesocyclic polythioethers 1,4-dithiacycloheptane (1,4-DTCH), 1,5-dithiacyclooctane (1,5-DTCO), 1,5-dithiacyclononane (1,5-DTCN), 1,4,7-trithiacyclononane (1,4,7-TTCN), and 1,6-dithiacyclodecane (1,6-DTCD) are reported. The conformations of these molecules in the gas phase are deduced from correlations of the observed spectra with semi-empirical MO calculations, as well as molecular mechanics analysis.

Neighboring group facilitation of oxidation of dialkyl sulfides has been proposed[1] in which an electron donating group stabilizes an incipient S cation radical and subsequently dication. Such facilitation has been demonstrated in certain 2-*endo*-substituted 6-*endo*-methylthiobicyclo[2.2.1]heptane derivatives[2] and some mesocyclic† dithioethers.[4] Stabilization of electron deficient sulfides by lone pair donation has been much studied. Simple dialkyl sulfide cation radicals generally readily react with a dialkyl sulfide to form a two-center three-electron bond.[5] Such interactions occur not only intermolecularly but intramolecularly as well. Cation radicals[5e,g,h,6] and dications[6c,7] stabilized by intramolecular bond formation with divalent sulfur as well as trivalent nitrogen[8] are known. Halide ion stabilization of S cation radicals[4e,g] and multicenter interactions in nonpolar solvents have also been reported.[9]

To gain insight into the details of facilitated oxidation of mesocyclic dithioethers conformational analysis of some of these compounds was undertaken. In the preceding paper[10] the conformations of 1,4-dithiacycloheptane (1,4-DTCH), 1,5-dithiacyclononane (1,5-DTCN), and 1,6-dithiacyclodecane (1,6-DTCD) in the solid state were determined by X-ray crystallographic techniques. The solid state conformation of 1,4,7-trithiacyclononane (1,4,7-TTCN) was determined similarly.[11] In this paper, the conformation in the gas phase of five mesocyclic polythioethers are determined by a combination of photoelectron spectroscopy, semi-empirical molecular orbital calculations, and molecular mechanics analysis.

Photoelectron spectroscopy has been widely used for quantitatively assessing the degree of interaction of equivalent orbitals both through bonds and through space.[12] For mesocyclic polythioethers, the positions and magnitudes of splittings of the S lone pair orbitals should reflect the spatial and geometrical positioning, which determines the angle between interacting orbitals, of the S atoms with respect to each other.[13] Assuming Koopman's theorem,[14] each ionization potential, obtained from the photoelectron spectrum, is equal in magnitude to the energy of the orbital from which the electron is ejected. A comparison of the observed photoelectron spectrum with the orbital energies calculated using semi-empirical molecular orbital techniques of the conformational possibilities[15] could, then, lead to assignment of the lowest energy conformation based upon the best fit.[16]

EXPERIMENTAL

The mesocyclic polythioethers were prepared by a modification of published procedures.[17] The photoelectron spectra were measured using a McPherson 36 spectrometer fitted with a He(I) source chamber. All spectra were measured using argon (15.76 eV) as a single internal standard. The resolution was less than 30 meV FWHM. Calibration with MeI showed the energy scale to deviate less than 10 meV from linearity over a range of binding energies from 9 to 17 eV. Instrument drift was controlled at less than 10 meV. Only 1,4,7-trithiacyclononane required heating (60°) to obtain a satisfactory spectrum. The spectra represent a time-averaged sum of the individual scans through a binding energy range of 10 eV, stored in 500 data channels.

Computational details. The general procedure used in this study was to determine the relative energies of all of the conformational possibilities for each compound. The conformational possibilities were derived from the conformers of the corresponding cycloalkane. The relative energies were calculated using the molecular mechanics MMI program[18] with Allinger's 1973 force field[19] and additional parameters for sulfur.[20] For those conformations with $E_{rel} \leq 3.0$ kcal/mole, the resulting optimized geometries (local minima) from these empirical force field calculations were then used in both the extended Hückel (EH)[21] and SCF-CNDO/2[22] semi-empirical molecular orbital methods. This provided a relatively inexpensive way for preliminary examination of the molecular orbital energy levels for the conformations. For those conformations of lowest calculated energy and/or best fit with the observed photoelectron spectra, MINDO/3 calculations[23] with full geometry optimization were carried out.

RESULTS AND DISCUSSION

The photoelectron spectra of 1,4-dithiacycloheptane (1,4-DTCH), 1,5-dithiacyclooctane (1,5-DTCO), 1,5-dithiacyclononane (1,5-DTCN), 1,4,7-trithiacyclononane (1,4,7-TTCN), and 1,6-dithiacyclodecane (1,6-DTCD) are shown in Fig. 1. The photoelectron spectrum of 1,4-dithiane

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†The term "mesocycle" has been defined previously[3] as medium-sized ring.

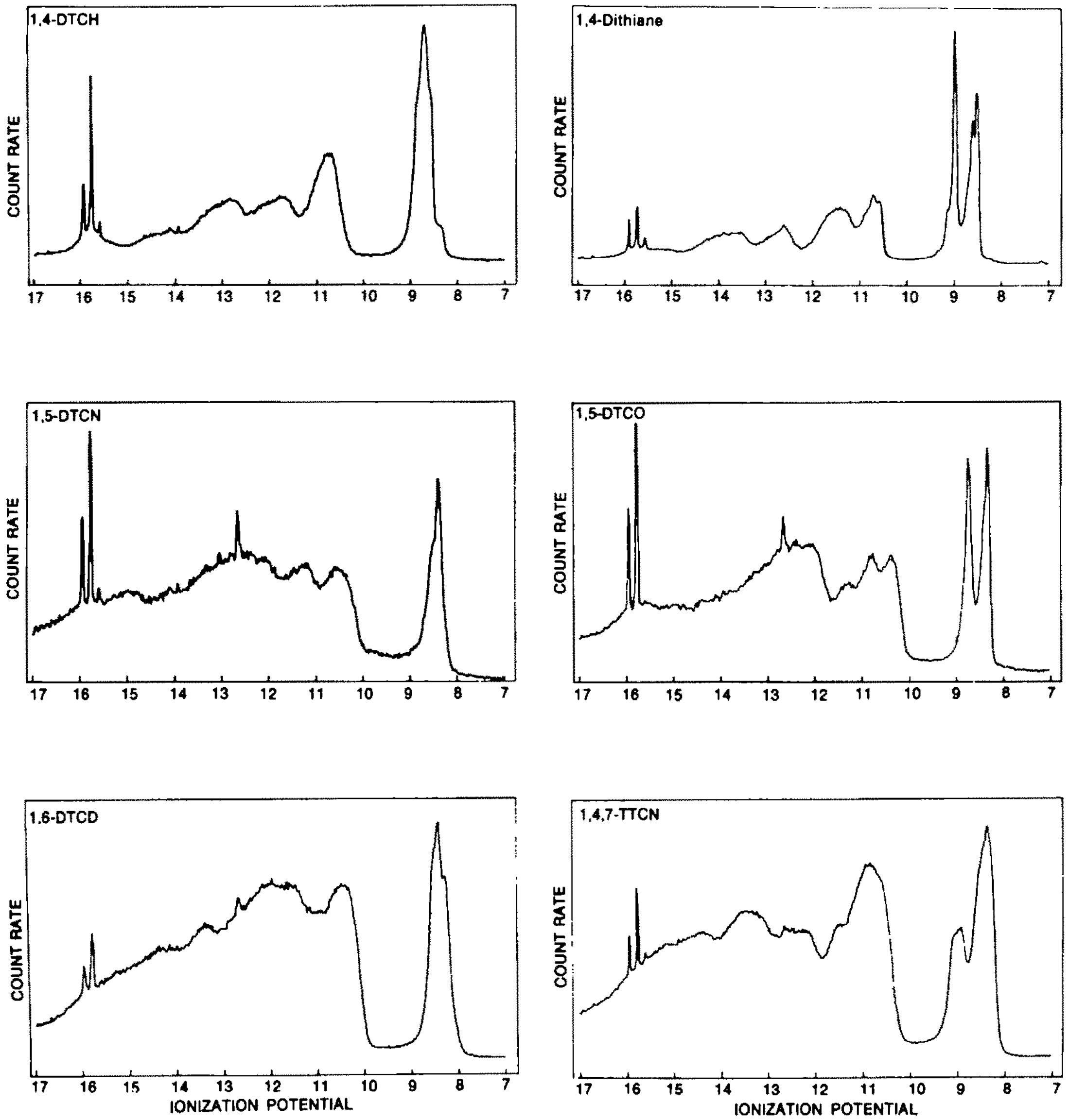

Fig. 1. Photoelectron spectra of the mesocyclic polythioethers.

has been included for comparison purposes. The lowest energy conformations ($E_{rel} \leq 3.0$ kcal/mole) for the mesocyclic polythioethers, based upon the molecular mechanics (MMI) calculations are shown in Figs. 2–6.

The molecular mechanics calculations indicate a symmetrical twist-chair conformation (C_2 symmetry) to be the most stable for 1,4-DTCH (Fig. 2). This conformation is adopted by 1,4-DTCH in the solid state as determined by X-ray diffraction.[10] The EH and CNDO/2 calculations predict a somewhat large splitting of the S–S lone pairs of 0.39 and 0.32 eV, respectively, for this conformation. An overly large splitting is also obtained using the MMI-EH and MMI-CNDO/2 procedure for the chair conformation of 1,4-dithiane (0.44 and 0.79 eV, respectively) which is known to exist in the chair conformation in the gas phase.[24] The MINDO/3 calculations with full geometry optimization predict a splitting of 0.007 eV for 1,4-DTCH in the C_2 twist-chair conformation, in excellent agreement with the observed photoelectron spectrum.

The photoelectron spectrum of 1,5-DTCO shows a large splitting of the S–S lone pairs of 0.43 eV, indicative of a relatively large degree of mixing. This suggests that the conformation adopted is one where the S atom lone pair orbitals point toward each other. The only low energy conformations with this geometrical relationship are the boat-chair (A) and the twist-chair-chair (Fig. 3). The MMI computations indicate the boat-chair conformation to be the most stable. However, the conclusion that this is the conformation adopted by 1,5-DTCO must be regarded as tentative because there are some problems, discussed below, in the geometries calculated by MMI for 1,5-DTCO.†

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†Unfortunately the X-ray crystal structure determination for 1,5-DTCO has not been done. The compound is a liquid at room temperature and initial attempts to grow suitable crystals at low temperatures were unsuccessful. The X-ray crystal structure of the iodine complex of 1,5-dithiacyclooctane (1,5-DTCO-2I$_2$) has been determined by Hope and Nichols.[25] Both the boat-chair as well as the twist-chair-chair conformations are present in the asymmetric unit.

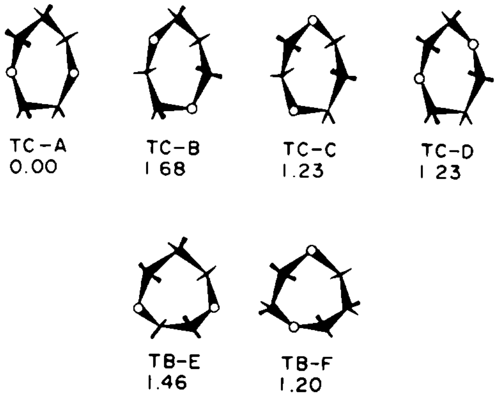

Fig. 2. Conformations of 1,4-DTCH with $E_{rel} \leq 3.0$ kcal/mole.

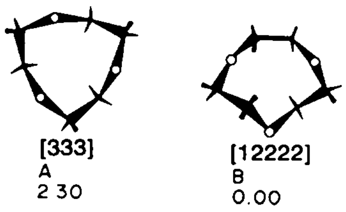

Fig. 5. Conformations of 1,4,7-TTCN with $E_{rel} \leq 3.0$ kcal/mole.

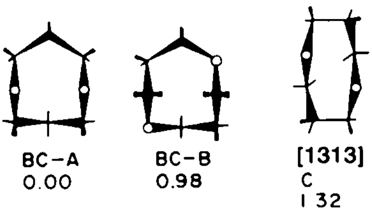

Fig. 3. Conformations of 1,5-DTCO with $E_{rel} \leq 3.0$ kcal/mole.

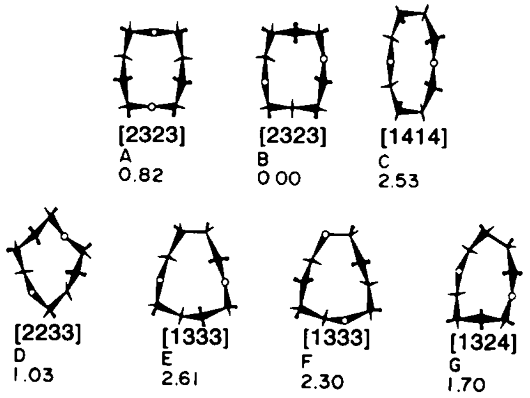

Fig. 6. Conformation of 1,6-DTCD with $E_{rel} \leq 3.0$ kcal/mole.

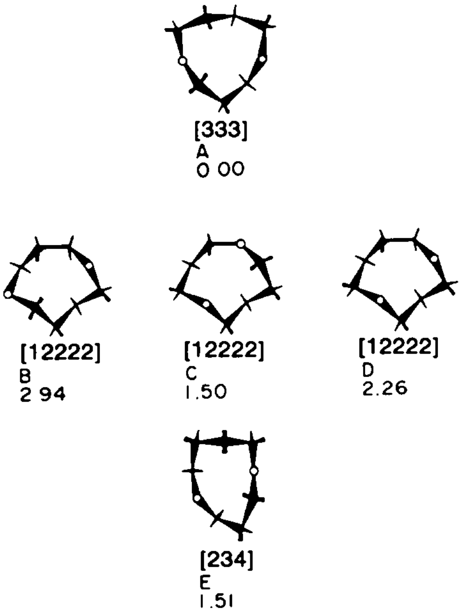

Fig. 4. Conformations of 1,5-DTCN with $E_{rel} \leq 3.0$ kcal/mole.

Using the MMI geometry for the boat-chair conformation, EH and CNDO/2 calculations predict a very large splitting of the sulfur-sulfur lone pair orbitals: 1.09 and 1.46 eV, respectively. The splittings calculated using MINDO/3 are similarly large: 1.10 eV. The twist-chair-chair conformation, however, gives slightly better agreement with the observed splitting. Calculations using EH or CNDO/2 with MMI calculated geometry for this conformation, and MINDO/3 give relative orbital energies of 0.81, 1.04 and 1.09 eV respectively. The unusually large splitting calculated for 1,5-DTCO can be attributed to both the MMI as well as MINDO/3 geometry optimizations. These geometries bring the transannular sulfur atoms extremely close: 3.25 and 3.32 Å for the boat-chair conformation using MMI and MINDO/3 respectively; 3.40 and 3.34 Å for the twist-chair-chair conformation using MMI and MINDO/3 respectively (*cf* the van der Waals contact distance of 3.70 Å).[26]

From the experimental data available it appears as if the cyclooctane ring system prefers the boat-chair conformation except when there is extensive replacement of ring C atoms or extensive substitution of the ring hydrogens.[27] Cyclooctane itself has been found by ^{13}C and ^{1}H NMR to exist predominantly in the boat-chair conformation[28] in agreement with theoretical calculations.[29] This conformation has also been observed in many crystalline derivatives of cyclooctane: *cis*- and *trans*-1,2-cyclooctane-dicarboxylic acid,[30] dimeric cyclooctanone peroxide,[31] 1-amino-cyclooctane-carboxylic acid hydrobromide,[32] *trans*-1,4-dichlorocyclooctane,[33] cyclooctane-1,5-diol,[34] and cyclooctane-1,5-dione.[34] Analysis of the NMR spectra of the oxocanes indicates that oxocane itself adopts predominantly a boat-chair conformation,[35] as does 1,3-dioxocane,[35,36] but 1,3,6-trioxocane and 1,3,5,7-tetroxocane exist as mixtures of boat-chair and chair-chair (crown-type) conformations.[35,36] However, 1,3,5,7-tetrathiocane has been found to prefer, both in the crystalline state as well as in solution, the boat-chair conformation.[37] Analysis of the ^{1}H and ^{13}C NMR spectra of 1-thiacyclooctane-5-one indicate that this compound also exists as an unsymmetrical boat-chair conformation.[38] On the other hand, cyclooctasulfur adopts a crown conformation in both the solid state, as determined by X-ray[39] and neutron diffraction[39e] and in the gas phase as determined by photoelectron spectroscopy.[40] Force field calculations also indicate the crown conformation to be the most stable.[41]

The X-ray crystal structure of 1,5-DTCN indicated a [333] or twist-boat-chair conformation of C_2 symmetry in the solid state. The molecular mechanics calculations also indicate this conformation to be the most stable (Fig. 4). The calculated S lone pair splittings for this conformation are in excellent agreement with a PES (0.10 and 0.05 eV respectively for EH and CNDO/2, compared to 0.1 eV observed). However, MINDO/3 calculations, with geometry optimization, give a somewhat large splitting of 0.35 eV. This large splitting seems to be due to a significantly smaller transannular S–S distance from MINDO/3 (3.63 Å) than from MMI (4.00 Å) or the X-ray crystal structure (4.11 Å).[10]

X-ray crystal structure analysis has shown 1,4,7-TTCN to adopt a symmetrical [333] conformation in the solid state.[11] Molecular mechanics calculations, however, indicate the [12222] conformation of C_2 symmetry (Fig. 5) to be more stable by 2.30 kcal/mole. The photoelectron spectrum of 1,4,7-TTCN shows the sulfur lone pair orbitals to be split into two bands of intensity ratio 2 : 1. This result is in qualitative agreement with what would be expected for the mixing of three equivalent orbitals (as in the [333] conformation). This is supported by MINDO/3 calculations on the [333] and [12222] conformations. The calculations for the [333] conformation of 1,4,7-TTCN indicate two degenerate orbitals and one orbital of lower energy for the sulfur lone pairs, with a splitting of 0.63 eV (compared to 0.6 eV, observed). Note that the transannular S–S distance calculated by MMI is 3.38 Å, and by MINDO/3 is 3.61, compared to 3.45 Å observed in the X-ray crystal structure. All of which are significantly shorter than the van der Waals contact distance of 3.70 Å.[26]

The conformation of 1,6-dithiacyclodecane obtained from an X-ray crystal structure analysis is a [2323] (boat-chair-boat) of C_{2h} symmetry. The molecular mechanics calculations, however, indicate another [2323] conformation to be slightly more stable (Fig. 6). These MMI results are supported by MINDO/3 calculations, which indicate the [2323] conformation (**B**) to be 1.63 kcal/mole more stable than (**A**). As in the case of 1,5-DTCO and 1,5-DTCN, the calculated splitting of the sulfur lone pairs is unusually large (0.77 eV, compared with *ca* 0.15 eV, observed). Again, this can be attributed to the extremely close arrangement of the sulfur atoms as calculated by MINDO/3 (3.38 Å).

However, it is clear that the boat-chair-boat conformation found in the solid state by X-ray diffraction techniques is not the conformer in the gas phase. Using the solid state geometry or MMI geometry optimization of this conformer gives a splitting of the sulfur-sulfur lone pair orbitals which is too small. Therefore, although 1,6-DTCD adopts a boat-chair-boat conformation in the gas phase it is of type **B** not type **A** which is found in the crystalline material. This conclusion is supported by the observation that the solid state IR spectrum of 1,6-DTCD markedly differs from the IR spectra of this compound dissolved in either carbon disulfide or chloroform. The solid state IR spectra for both 1,4-DTCH and 1,5-DTCN, on the other hand, are similar to the solution IR spectra.

CONCLUSIONS

Comparison of the orbital energy levels calculated by various semi-empirical MO methods with the gas phase photoelectron spectra of several mesocyclic polythioethers, together with molecular mechanics conformational analysis, has made it possible to assign the gas phase conformations of 1,4-DTCH, 1,5-DTCN, 1,4,7-TTCN, 1,6-DTCD, and tentatively 1,5-DTCO. The twist-chair conformation of C_2 symmetry adopted by 1,4-DTCH and the twist-boat-chair, [333], conformations adopted by 1,5-DTCN and 1,4,7-TTCN in the gas phase are the same conformations as found in the solid state. Although the conformation of 1,6-DTCD is a boat-chair-boat both in the gas phase and solid state, the S atoms occupy conformationally different sites in the two states.

The technique of using molecular mechanics or MINDO/3 calculations for geometry optimization and evaluation of the conformational energies of mesocyclic polythioethers, coupled with the use of semi-empirical MO methods for comparison with photoelectron spectra, provides a reasonably useful method for gas phase conformational analysis. However, for certain cases MMI (1,4-dithiane, 1,4-DTCH, and 1,5-DTCO) and MINDO/3 (1,5-DTCO, to some extent 1,5-DTCN, and 1,6-DTCD) predict extremely close transannular S–S distances which lead to erroneously large mixing of the S–S lone pair orbitals. It appears that further theoretical and experimental studies are needed to improve the understanding (or at least parameterization) of S–S lone pair interactions.†

Acknowledgments—The authors thank the National Institutes of Health (Grant No. HL 15104) for support of this work, Dr. Dennis L. Lichtenberger of the University of Arizona for many helpful discussions, and NRCC (Lawrence Berkeley Laboratory of the University of California) for a CDC version of the MMI program and an expanded CDC version of the MINDO/3 program. We also thank the University of Arizona Computer Center for a generous allotment of computer time.

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† It may be that better results would be obtained with MNDO calculations parameterized for sulfur[42] but a program suitable for such calculations in a CDC version was not available to us.

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