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CONFORMATIONAL ANALYSIS OF MESOCYCLIC POLYTHIOETHERS

CRYSTAL AND MOLECULAR STRUCTURES OF 1,4-DITHIACYCLOHEPTANE, 1,5-DITHIACYCLONONANE AND 1,6-DITHIACYCLODECANE

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Abstract—The crystal and molecular structures of 1,4-dithiacycloheptane (1,4-DTCH), 1,5-dithiacyclononane (1,5-DTCN), and 1,6-dithiacyclodecane (1,6-DTCD) have been determined by single crystal X-ray studies. These compounds crystallize in the space groups $P2_12_12_1$ (No. 19), $P2_1/c$ (No. 14), and $P2_1/n$, respectively with $a = 5.409(1)$, $b = 10.883(2)$, $c = 11.390(2)$ Å, $Z = 4$; $a = 9.600(4)$, $b = 12.378(8)$, $c = 7.904(3)$ Å, $\beta = 113.31(3)°$, $Z = 4$; and $a = 5.290(1)$, $b = 12.853(3)$, $c = 6.850(2)$ Å, $\beta = 93.39(2)°$, $Z = 2$, respectively. The nonhydrogen atoms were located using direct methods and the hydrogen atoms were found by Fourier difference maps. Full-matrix least-squares refinement led to conventional R factors of 0.0459, 0.0558 and 0.0314, respectively. The conformations adopted by 1,4-DTCH, 1,5-DTCN and 1,6-DTCD, in the crystalline state, are twist chair (C_2 symmetry), twist boat chair (C_2 symmetry), and boat chair boat (C_{2h} symmetry), respectively. The transannular S–S distances are 3.583, 4.108 and 4.864 Å, respectively.

This paper and the following one present results on the conformations of some medium-sized ring polysulfides. The results are of relevance to conformational analysis of both saturated heterocycles and medium-sized rings.

There is considerable interest in conformational analysis of saturated heterocyclic rings.[1] Studies on ring systems with one or more S atoms have been made particularly with 5- and 6-membered rings.[1,2] The effects of changes in bond length, bond angle, torsion angle, bending force constants and van der Waals radius as well as dipole and lone pair interactions when a S atom is substituted for a C atom have been investigated.[1,2] For 6-membered rings, the most stable conformation is invariably a chair[1,2] except when substituents attached to the ring preclude this[1d] and for certain 3,3,6,6-substituted-*s*-tetrathianes,[3] e.g. duplodithioacetone, whose lowest energy conformer is a twist form. Nevertheless, sulfur substitution has important effects on the precise geometry of the ring and on their dynamic properties.[1,2]

The conformations adopted by medium-sized rings has elicited considerable interest. The conformations of such cycloalkanes have been investigated both experimentally[4] and theoretically.[5] Conformational analysis of medium-sized rings whose ring consists solely of S atoms has also been undertaken. Crystal and molecular structures of cycloheptasulfur,[6] cyclooctasulfur,[7] cyclodecasulfur,[8] and some of their derivatives,[9] determined by X-ray crystallographic techniques have been reported. The relative energies of different conformers of sulfur rings have been calculated using the molecular mechanics (force field) method.[10] Owing to our interest in the oxidation of organosulfides[11] including mesocyclic† polythioethers[13] and possible relevance of such oxidations to biological processes such as oxidative phosphorylation,[14] we have initiated conformational studies on medium-sized rings containing both C and S atoms. As part of this program the crystal and molecular structures of 1,4-dithiacycloheptane (1,4-DTCH), 1,5-dithiacyclononane (1,5-DTCN), 1,6-dithiacyclodecane (1,6-DTCD), and 1,4,7-trithiacyclononane[15] were determined by single crystal X-ray crystallographic techniques. This paper presents the results for the three mesocyclic dithioethers. In an accompanying paper, our studies on the conformations of mesocyclic polythioethers in the gas phase are presented.

RESULTS AND DISCUSSION

The crystal data for 1,4-DTCH, 1,5-DTCN and 1,6-DTCD are listed in Table 1. The final atomic parameters are compiled in Tables 2, 3 and 4 respectively. Stereoscopic views of the molecules and atomic numbering schemes are shown in Figs. 1–3 respectively. The bond lengths, S–S interatomic distances, bond angles, and selected torsion angles for these compounds are listed in Table 5.

A comparison of the average bond lengths and bond angles of the three mesocyclic dithioethers of this study and three other cyclic polythioethers is presented in Table 6. Perusal of this table reveals the listed compounds to have comparable S–C bond lengths, close to the normal S–C bond length of 1.81 Å.[16] The average C–C bond lengths for 1,4-DTCH, 1,5-DTCN and 1,6-DTCD are slightly longer than those for the other compounds listed in the table but the same as the C–C bond length in ethane or cyclohexane (1.53 Å)[16] or diamond (1.54 Å).[16] The C–S–C and S–C–C bond angles are greater for the medium-sized ring polythioethers (1,4-DTCH, 1,5-DTCN, 1,6-DTCD and 1,4,7-TTCN) than for the 6-membered ring heterocycle. These angles are the same for the medium-sized polythioethers and the 14-membered ring heterocycle but the C–C–C bond angle is greater in 1,4-DTCH, 1,5-DTCN and 1,6-DTCD than in the 14-membered ring heterocycle. The C–S–C bond angles in all of the compounds listed in Table 6 except 1,4-dithiacyclohexane are significantly larger than that of dimethyl sulfide which is 98.87(17)°.[17]

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†The term "mesocycle" has been defined previously[12] as medium-sized ring.

Table 1. Crystal data for the mesocyclic dithioethers[a]

Compound	1,4-Dithiacycloheptane	1,5-Dithiacyclononane	1,6-Dithiacyclodecane
Molecular formula	$C_5H_{10}S_2$	$C_7H_{14}S_2$	$C_8H_{16}S_2$
Molecular weight	134.25	162.30	176.33
Space Group	$P2_12_12_1$ (No. 19)[b]	$P2_1/c$ (No. 14)[c]	$P2_1/n$[d]
Cell Dimensions[e]			
a, Å	5.409(1)	9.600(4)	5.290(1)
b, Å	10.883(2)	12.378(8)	12.853(3)
c, Å	11.390(2)	7.904(3)	6.850(2)
β, deg		113.31(3)	93.39(2)
V, Å^3	670.1(2)	862.6(7)	465.0
Z	4	4	2
d_{obsd}, g cm^{-3} [f]	1.310(10)	1.253(10)	1.246(10)
d_{calcd}, g cm^{-3}	1.318	1.250	1.259
Crystal shape	Plate (cut to cube)	Rectangular needle	Rectangular parallelepiped
Size, mm	0.3 x 0.3 x 0.3	0.2 x 0.2 x 0.3	0.3 x 0.3 x 0.5
Radiation, Å	λ(MoKα) 0.71069	λ(MoKα) 0.71069	λ(MoKα) 0.71069
Monochromator	Graphite crystal	Graphite crystal	Graphite crystal
Supplied power	50 kV, 30 mA	50 kV, 20 mA	50 kV, 30 mA
Data collected method	θ-2θ scan	θ-2θ scan	θ-2θ scan
Scan speed, deg min^{-1}	Variable (2.0 - 29.3) determined as a function of peak intensity	Variable (2.0 - 29.3)	Variable (2.0 - 29.3)
Scan range (2θ), deg	MoKα - 1.0 to MoKα + 1.0	MoKα - 1.0 to MoKα + 1.0	MoKα - 1.0 to MoKα + 1.0
Ratio of total background time to peak scan time	0.5	0.5	0.5
Standard reflections	(0,0,4), (0,6,0), (4,0,0) after every 97 readings	(0,0,2), (0,4,0), (4,0,0) after every 22 readings	(0,0,4), (0,4,0), (4,0,0,) after every 97 readings
Max. derivation of standards, %	3.4	3.1	1.5
2θ limit deg	4.0 - 50.0	4.0 - 50.0	4.0 - 50.0
No. of unique data	719	1632	887
No. of data used in the calc.	683	1119	730
Absorption coeff. (μ_λ), cm^{-1}	6.38	5.21	4.79

[a] The standard deviation of the least significant figure is given in parentheses in this table and in the following tables.

[b] The space group was unambiguously determined by the systematic absences: $h00$: $h = 2n+1$; $0k0$: $k = 2n+1$; 00ℓ: $\ell = 2n+1$.

[c] The space group was unambiguously determined by the systematic absences: $\bar{h}0\ell$: $\bar{\ell} = 2\bar{n}+1$; $0\bar{k}0$: $\bar{k} = 2\bar{n}+1$.

[d] The space group was unambiguously determined by the systematic absences: $\bar{h}0\ell$: $\bar{h} + \ell$; $2n+1$; $h00$: $h = 2n+1$; $0k0$: $k = 2n+1$; 00ℓ: $\ell = 2n+1$. The space group $P2_1/n$ is an alternative setting of $P2_1/c$ (No. 14).

[e] The cell dimensions were obtained, in each case, from a least squares refinement of setting angles of 25 reflections.

[d] The densities, in each case, were determined by the flotation method using an aqueous sodium iodide solution.

Table 2. Fractional atomic coordinates and thermal parameters for 1,4-dithiacycloheptane

Atom	x	y	z	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.5768(2)[b]	0.6343(1)	0.9668(1)	0.0313(5)	0.0058(1)	0.0053(1)	-0.0025(2)	0.0008(2)	0.0007(1)
S(2)	0.3683(2)	0.3604(1)	1.1106(1)	0.0262(4)	0.0056(1)	0.0065(1)	-0.0015(2)	0.0009(2)	0.0009(1)
C(1)	0.3154(10)	0.5388(4)	0.9314(4)	0.0288(19)	0.0061(4)	0.0058(4)	-0.0012(7)	-0.0030(7)	0.0004(3)
C(2)	0.3413(10)	0.4016(4)	0.9571(5)	0.0299(19)	0.0066(4)	0.0056(4)	-0.0010(8)	-0.0003(8)	0.0000(3)
C(3)	0.6810(9)	0.4106(5)	1.1442(5)	0.0244(17)	0.0069(4)	0.0067(4)	0.0010(8)	-0.0018(8)	0.0008(4)
C(4)	0.7065(10)	0.5419(5)	1.1904(4)	0.0274(19)	0.0083(5)	0.0054(4)	-0.0017(8)	-0.0022(7)	0.0000(4)
C(5)	0.5554(10)	0.6395(4)	1.1258(4)	0.0348(19)	0.0055(4)	0.0057(4)	-0.0011(9)	0.0008(7)	-0.0015(3)
H(1)	0.2838[c]	0.5463	0.8432	4.01[d]					
H(2)	0.1680	0.5683	0.9740	4.01					
H(3)	0.4901	0.3723	0.9134	3.87					
H(4)	0.1898	0.3606	0.9230	3.87					
H(5)	0.7837	0.4031	1.0721	4.01					
H(6)	0.7488	0.3566	1.2074	4.01					
H(7)	0.8869	0.5648	1.1776	4.40					
H(8)	0.6643	0.5427	1.2722	4.40					
H(9)	0.6126	0.7195	1.1544	4.21					
H(10)	0.3799	0.6241	1.1490	4.21					

[a] Anisotropic thermal parameters are in the form: $\exp[-(\underline{h}^2\beta_{11} + \underline{k}^2\beta_{22} + \underline{l}^2\beta_{33} + 2\underline{hk}\beta_{12} + 2\underline{hl}\beta_{13} + 2\underline{kl}\beta_{23})]$.

[b] Estimated standard deviations in parentheses.

[c] Hydrogen atom parameters were not refined.

[d] Temperature factors for the hydrogen atoms were set according to $\underline{B}_H = \underline{B}_N + 1$, where N is the atom to which H is bonded.

Table 3. Fractional atomic coordinates and thermal parameters for 1,5-dithiacyclononane

Atom	x	y	z	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.1456(1)[b]	0.3495(1)	0.9133(2)	0.0124(2)	0.0055(1)	0.0251(3)	-0.0016(1)	0.0034(2)	-0.0018(1)
S(2)	0.3856(1)	0.6170(1)	1.1803(2)	0.0156(2)	0.0078(1)	0.0213(3)	-0.0048(1)	0.0081(2)	-0.0046(1)
C(1)	0.3366(5)	0.3591(3)	1.0875(7)	0.0117(6)	0.0055(3)	0.0262(13)	0.0009(4)	0.0019(7)	0.0026(6)
C(2)	0.3413(5)	0.4055(4)	1.2677(6)	0.0161(8)	0.0102(5)	0.0148(11)	-0.0023(5)	0.0013(7)	0.0050(6)
C(3)	0.2780(5)	0.5222(4)	1.2586(5)	0.0142(7)	0.0081(4)	0.0091(8)	-0.0037(4)	0.0056(6)	-0.0012(4)
C(4)	0.2392(6)	0.6825(3)	0.9856(7)	0.0213(9)	0.0043(3)	0.0304(14)	0.0002(4)	0.0143(10)	-0.0005(5)
C(5)	0.1374(5)	0.6081(3)	0.8344(6)	0.0154(7)	0.0061(3)	0.0199(11)	0.0030(4)	0.0074(7)	0.0031(5)
C(6)	0.2255(4)	0.5335(3)	0.7517(5)	0.0130(6)	0.0056(3)	0.0100(8)	0.0021(3)	0.0057(6)	0.0013(4)
C(7)	0.1606(5)	0.4174(4)	0.7193(6)	0.0162(7)	0.0087(4)	0.0159(10)	0.0008(5)	0.0033(7)	-0.0037(5)
H(1)	0.3985[c]	0.4079	1.0413	5.45[d]					
H(2)	0.3844	0.2856	1.1105	5.45					
H(3)	0.4498	0.4053	1.3600	5.53					
H(4)	0.2813	0.3554	1.3142	5.53					
H(5)	0.2840	0.5458	1.3839	4.23					
H(6)	0.1675	0.5245	1.1707	4.23					
H(7)	0.2904	0.7334	0.9276	5.78					
H(8)	0.1746	0.7271	1.0330	5.78					
H(9)	0.0614	0.6525	0.7346	4.82					
H(10)	0.0803	0.5606	0.8905	4.82					
H(11)	0.3354	0.5306	0.8391	3.71					
H(12)	0.2198	0.5658	0.6318	3.71					
H(13)	0.2241	0.3721	0.6726	5.42					
H(14)	0.0543	0.4220	0.6178	5.42					

[a] Anisotropic thermal parameters are in the form: $\exp[-(\underline{h}^2\beta_{11} + \underline{k}^2\beta_{22} + \underline{l}^2\beta_{33} + 2\underline{hk}\beta_{12} + 2\underline{hl}\beta_{13} + 2\underline{kl}\beta_{23})]$.

[b] Estimated standard deviations in parentheses.

[c] Parameters for hydrogen atoms were not refined.

[d] Temperature factors for the hydrogen atoms were set according to $\underline{B}_H = \underline{B}_N + 1$, where N is the atom to which H is bonded.

Table 4. Fractional atomic coordinates and thermal parameters for 1,6-dithiacyclodecane

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	β_{11}^{a} or $\underline{B}$, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	0.00330(10)^b	0.86825(4)	0.25490(7)	0.0378(3)	0.0056(4)	0.0178(2)	0.0002(1)	0.0036(1)	0.0018(1)
C(1)	0.2558(4)	0.9619(2)	0.2982(3)	0.0324(8)	0.0071(2)	0.0174(5)	0.0009(3)	-0.0033(5)	0.0004(2)
C(2)	0.2473(4)	1.0612(2)	0.1739(3)	0.0283(7)	0.0055(1)	0.0199(5)	-0.0006(3)	-0.0011(5)	-0.0009(2)
C(3)	-0.0071(4)	1.1173(2)	0.1611(3)	0.0365(8)	0.0055(1)	0.0161(5)	0.0016(3)	0.0010(5)	-0.0018(2)
C(4)	-0.0506(4)	1.1880(2)	-0.0172(4)	0.0488(10)	0.0047(1)	0.0219(5)	0.0024(3)	0.0011(6)	-0.0010(2)
H(1)	0.4189^c	0.9248	0.2800	4.62^d					
H(2)	0.2523	0.9840	0.4399	4.62					
H(3)	0.2909	1.0415	0.0362	4.36					
H(4)	0.3791	1.1110	0.2279	4.36					
H(5)	-0.0219	1.1589	0.2813	4.69					
H(6)	-0.1445	1.0621	0.1534	4.69					
H(7)	0.0680	1.2489	-0.0004	5.24					
H(8)	-0.2298	1.2148	-0.0207	5.24					

[a] Anisotropic thermal parameters are in the form: $\exp[-(\underline{h}^2\beta_{11} + \underline{k}^2\beta_{22} + \underline{l}^2\beta_{33} + \underline{2hk}\beta_{12} + \underline{2hl}\beta_{13} + \underline{2kl}\beta_{23})]$.

[b] Estimated standard deviations in parentheses.

[c] The hydrogen atom parameters were not refined.

[d] Temperature factors for the hydrogen atoms were set according to $\underline{B}_H = \underline{B}_N + 1$, where N is the atom to which H is bonded.

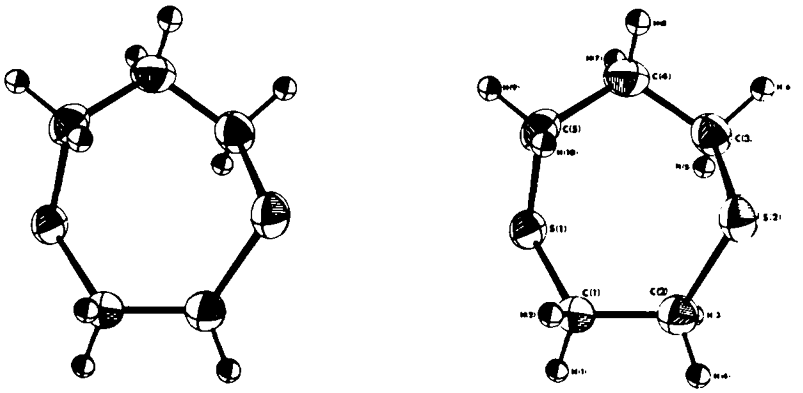

Fig. 1. ORTEP[33] steoreoscopic view and numbering of 1,4-dithiacycloheptane. The H atoms have been assigned arbitrary thermal parameters. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

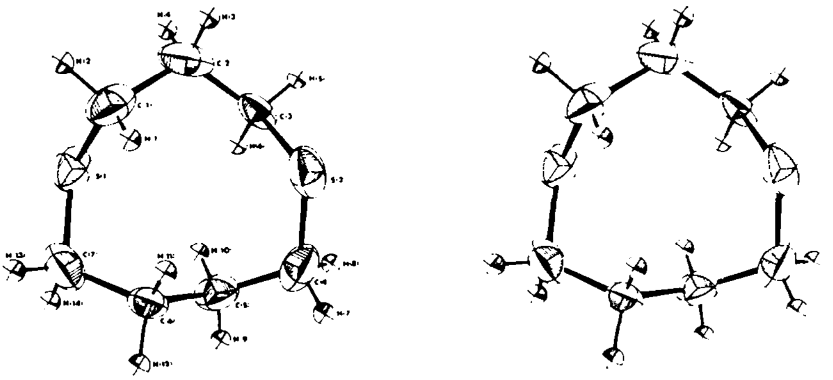

Fig. 2. ORTEP[33] stereoscopic view and numbering of 1,5-dithiacyclononane. The H atoms have been assigned arbitrary thermal parameters. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

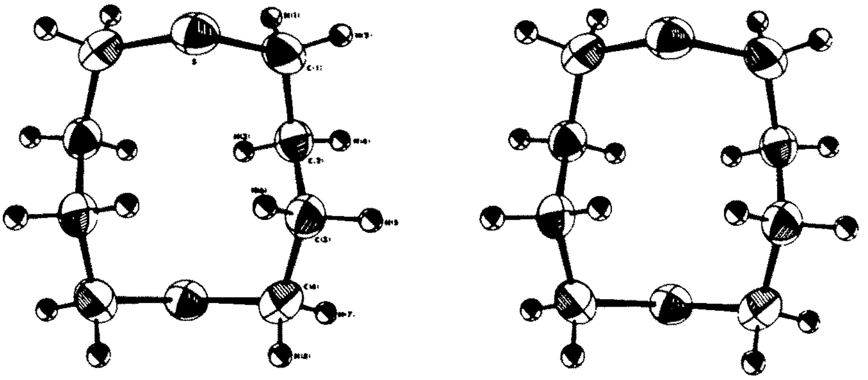

Fig. 3. ORTEP[33] stereoscopic view and numbering of 1,6-dithiacyclodecane. The H atoms have been assigned arbitrary thermal parameters. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

Table 5. Interatomic distances (Å), angles (deg), and torsion angles (deg)[a] in the mesocyclic dithioethers

Compound	Atoms	Distance	Atoms	Angle	Atoms	Torsion Angle
1,4-DTCH	S(1)-C(1)	1.801(5)	S(1)-C(1)-C(2)	116.7(4)	C(5)-S(1)-C(1)-C(2)	-74.1
	S(1)-C(5)	1.815(5)	C(1)-S(1)-C(5)	101.0(3)	C(1)-S(1)-C(5)-C(4)	92.9
	S(2)-C(2)	1.811(5)	S(1)-C(5)-C(4)	115.1(4)	C(3)-S(2)-C(2)-C(1)	-73.1
	S(2)-C(3)	1.818(5)	S(2)-C(2)-C(1)	115.7(4)	C(2)-S(2)-C(3)-C(4)	91.2
	C(1)-C(2)	1.529(6)	C(2)-S(2)-C(3)	101.8(3)	S(1)-C(1)-C(2)-S(2)	65.7
	C(3)-C(4)	1.530(7)	S(2)-C(3)-C(4)	115.9(4)	S(2)-C(3)-C(4)-C(5)	-44.2
	C(4)-C(5)	1.529(7)	C(3)-C(4)-C(5)	115.8(4)	C(3)-C(4)-C(5)-S(1)	-47.4
	S(1)···S(2)	3.583(2)				
1,5-DTCN	S(1)-C(1)	1.810(4)	S(1)-C(1)-C(2)	112.5(4)	C(7)-S(1)-C(1)-C(2)	127.9
	S(1)-C(7)	1.804(6)	C(1)-S(1)-C(7)	102.6(3)	C(1)-S(1)-C(7)-C(6)	-54.3
	S(2)-C(3)	1.825(5)	S(1)-C(7)-C(6)	117.1(4)	C(4)-S(2)-C(3)-C(2)	125.7
	S(2)-C(4)	1.814(5)	S(2)-C(3)-C(2)	110.4(4)	C(3)-S(2)-C(4)-C(5)	-55.6
	C(1)-C(2)	1.520(8)	C(3)-S(2)-C(4)	102.9(3)	S(1)-C(1)-C(2)-C(3)	-60.9
	C(2)-C(3)	1.558(7)	S(2)-C(4)-C(5)	115.9(4)	C(1)-C(2)-C(3)-S(2)	-60.2
	C(4)-C(5)	1.519(6)	C(1)-C(2)-C(3)	116.2(4)	S(2)-C(4)-C(5)-C(6)	-56.7
	C(5)-C(6)	1.560(7)	C(4)-C(5)-C(6)	113.7(4)	C(4)-C(5)-C(6)-C(7)	138.4
	C(6)-C(7)	1.546(6)	C(5)-C(6)-C(7)	111.7(4)	C(5)-C(6)-C(7)-S(1)	-53.9
	S(1)···S(2)	4.108(3)				
1,6-DTCD	S-C(1)	1.810(2)	S-C(1)-C(2)	117.7(2)	S-C(1)-C(2)-C(3)	48.5
	C(1)-C(2)	1.534(3)	C(1)-C(2)-C(3)	115.0(2)	C(1)-C(2)-C(3)-C(4)	-157.3
	C(2)-C(3)	1.524(3)	C(2)-C(3)-C(4)	114.7(2)	C(2)-C(3)-C(4)-S'	52.0
	C(3)-C(4)	1.529(3)	C(3)-C(4)-S'	117.3(2)	C(3)-C(4)-S' -C(1)'	68.4
	C(4)-S'[b]	1.812(3)	C(4)-S' -C(1)'	105.8(2)	C(4)-S' -C(1)'-C(2)'	-69.9
	S···S'	4.864(1)				

[a] Torsion angles for A-B-C-D are defined as positive for clockwise rotation of C-D toward A-B, while looking down the B-C bond.

[b] The primed atoms represent symmetry related atoms.

Table 6. Comparison of structural features of cyclic polythioethers

Compound	S-C(ave) Å	C-C(ave) Å	S···S(ave) Å	C-S-C(ave) deg	S-C-C(ave) deg	C-C-C(ave) deg	Ref.
1,4-dithiacyclohexane[a] (p-dithiane)	1.811	1.490	3.452	99.0	112.7	--	34
1,4-dithiacycloheptane	1.811	1.529	3.583	101.4	115.9	115.8	this work
1,5-dithiacyclononane	1.813	1.541	4.108	102.8	114.0	113.9	this work
1,4,7-trithiacyclononane	1.822	1.510	3.450	102.8	115.0	--	14
1,6-dithiacyclodecane	1.811	1.529	4.864	105.8	117.5	114.9	this work
1,4,8,11-tetrathiacyclotetradecane (α form)	1.808	1.509		102.9	114.2	111.6	35

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[a] No hydrogen atoms.

The conformation of 1,4-dithiacycloheptane in the crystalline state is a twist-chair with approximate C_2 symmetry as seen in Fig. 1.† The twist-chair conformation has been found to be the lowest energy conformation, by vibrational spectral analysis, for cycloheptane, oxepane and 1,3-dioxepane.[18] This is in agreement with several strain-energy calculations on the conformations of cycloheptane.[5a,b,d] A conformational analysis from temperature dependent CD measurements also indicates a twist-chair to be the most stable conformation for cycloheptanone.[19] Empirical force field calculations[10] for cycloheptasulfur predict the twist chair to be the most stable conformation, in apparent conflict with X-ray crystal structure analysis[6] as well as vibrational spectral analysis,[20] which indicate a chair conformation. However, the twist-chair conformation for S_7 is calculated by Kao and Allinger[10] to be only 0.3 kcal/mole more stable than the chair.

The conformation of 1,5-DTCN, in the crystalline state, is the [333] or twist-boat-chair (TBC) conformation as shown in Fig. 2.‡ Solution NMR spectroscopy[21] as well as strain energy calculations[5a–c,e] indicate the most stable conformation of cyclononane to be the [333] conformation. The 9-membered ring of 1-hydroxycyclononanyl dimethyl phosphate has this conformation as determined by X-ray crystallographic analysis.[22] This conformation is also adopted by trimeric acetone peroxide,[23] 1,4,7-trithiacyclononane,[15] as well as 1,1,4,4-tetramethylcyclononane and related derivatives.[24] In contrast, 1,4,7-trioxacyclononane has been found by ^{13}C NMR and IR spectroscopy,[25] to exist both in solution and in the solid in an unsymmetrical [234] conformation (C_1 symmetry). Force field calculations indicate the most stable conformation of cyclononasulfur,[10] also, to be the [234] conformation. Some derivatives of cyclononane: cyclononylamine hydrobromide,[26] and cyclononanone-mercuric chloride,[27] on the other hand, crystallize in the [12222] (C_2 symmetry) conformation.

The conformation of 1,6-DTCD, as revealed by this study, is a [2323] or boat-chair-boat (BCB) conformation (C_{2h} symmetry) as seen in Fig. 3. Strain-energy conformational analysis of cyclodecane predicts the [2323] conformation to be the most stable.[5a–c] This prediction is in agreement with X-ray crystal structure analyses of various cyclodecane derivatives: *cis*-1,6-diaminocyclodecane dihydrochloride,[28] *trans*-1,6-diaminocyclodecane dihydrochloride,[29] *trans*-1,6-dibromocyclodecane,[30] and cyclodecylamine hydrochloride,[31] which all crystallize in [2323] conformations. Cyclodecasulfur, however, is calculated to adopt a "crown" conformation (D_{5d} symmetry)[10] but crystallizes in a conformation having D_2 symmetry.[8]

The conformation adopted by the mesocyclic polythioethers, 1,4-DTCH, 1,5-DTCN, 1,4,7-TTCN and 1,6-DTCD, is that corresponding to the parent cycloalkane and not that of the corresponding all S compound. The effect of substituting a S atom for a CH_2 group in these ring systems is to increase the degree of puckering owing to the smaller C–S–C bond angle than the corresponding C–C–C bond angle. However, the effect is not uniformly distributed around the ring. Comparison of the torsion angles found for 1,4-DTCH, 1,5-DTCN and 1,6-DTCD, with the corresponding torsion angles calculated by Hendrickson[5b] is revealing. As shown in Table 7, all of the torsion angles are increased, albeit unequally, in 1,4-DTCH relative to the corresponding angles in the twist-chair conformer of cycloheptane. In 1,5-DTCN, the average of the first set of six torsion angles is greater than that of the corresponding angles in the twist-boat-chair conformer of cyclononane. However, some of those torsion angles are perhaps slightly smaller than the corresponding hydrocarbon angles. For the next set of three torsion angles the magnitudes are greater in 1,5-DTCN and the increase in the C(4)–C(5)–C(6)–C(7) dihedral angle is particularly striking. For 1,6-DTCD the torsion angles are increased in the first set but decreased significantly in the second set. The C(1)–C(2)–C(3)–C(4) dihedral angle is substantially increased. Thus the C atoms attached to C(5) and C(6) in 1,5-DTCN and those attached to C(2) and C(3) in 1,6-DTCD are closer to being *anti* than the corresponding C atoms in the parent cycloalkane.

An alternative view of the effect on geometry of introducing S atoms into these medium-sized rings is illustrated in the schematic drawing for 1,4-DTCH, 1,5-DTCN and 1,6-DTCD, shown in Fig. 4. This perspective in which an average ring plane is defined is similar to that of Wiberg.[32] In addition, it focuses attention on the position of the C–S–C flaps relative to the rest of the ring and to each other which is particularly appropriate for our studies on S–S interactions. The dihedral angle (ϕ, ϕ') between the C–S–C planes and the average plane of the ring C atoms in these compounds is greater than that between the corresponding C–C–C planes, i.e. $X = CH_2$, and the average plane of the ring C atoms excluding X in the all carbon analogues. That is, the C–S–C flaps are moved toward the center of the ring relative to the corresponding C–C–C flaps in the parent cycloalkane.

In addition, for 1,4-DTCH, 1,5-DTCN and 1,6-DTCD, the S atoms occupy positions which allow the S lone pairs to point inward, toward the ring, avoiding transannular H–H steric interactions, but pointing away from each other, avoiding lone pair-lone pair interactions (Fig. 5). The consequences of these dispositions of the S atoms with regard to the vertical ionization potentials for these compounds are discussed in detail in the accompanying paper. The S–S transannular distance and angle between the S orbitals bearing the unshared electron pairs are key factors determining the extent of lone pair-lone pair interaction.

EXPERIMENTAL

Preparation of crystals. The three compounds were prepared by a modification of the procedure published by Musker *et al.*[36] In all cases, clear colorless crystals, suitable for X-ray diffraction were obtained by slow evaporation of sat sols of each compound in pentane.

Collection and reduction of the X-ray intensity data. In each study, a well-formed crystal, sealed in a quartz capillary, was mounted on a Syntex $P2_1$ auto diffractometer equipped with a scintillation counter and MoKα radiation with graphite monochromator. The automatic centering, indexing, and least squares routines were carried out to obtain the cell dimensions which are given in Table 1.

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†1,4-Dithiacycloheptane adopts a conformation such that the molecule is chiral. The non centrosymmetric space group $P2_12_12_1$ requires only one enantiomer in the unit cell. Thus spontaneous resolution has occured.

‡1,5-Dithiacyclononane adopts a conformation such that the molecule is chiral, but the space group $P2_1/c$ requires both enantiomers in the unit cell.

Table 7. Comparison of the absolute magnitude of the torsion angles (deg) for mesocyclic dithioethers and those of the corresponding cycloalkane conformer

Mesocyclic Dithioether[a]	Atoms	Angle (deg)	Cycloalkane (Conformer)[b]	Label	Angle (deg)
1,4-DTCH	C(3)-C(4)-C(5)-S(1)	47.4	Cycloheptane (TC)	ω_7	39.1
	S(2)-C(3)-C(4)-C(5)	44.2		ω_1	
	C(1)-S(1)-C(5)-C(4)	92.9		ω_6	88.1
	C(2)-S(2)-C(3)-C(4)	91.2		ω_2	
	C(5)-S(1)-C(1)-C(2)	74.1		ω_5	72.3
	C(3)-S(2)-C(2)-C(1)	73.1		ω_3	
	S(1)-C(1)-C(2)-S(2)	65.7		ω_4	54.3
1,5-DTCN	S(1)-C(1)-C(2)-C(3)	60.9	Cyclononane (TBC)	ω_9	56.0
	C(1)-C(2)-C(3)-S(2)	60.2		ω_1	
	C(1)-S(1)-C(7)-C(6)	54.3		ω_7	
	C(5)-C(6)-C(7)-S(1)	53.9		ω_6	
	S(2)-C(4)-C(5)-C(6)	56.7		ω_4	
	C(3)-S(2)-C(4)-C(5)	55.6		ω_3	
	C(7)-S(1)-C(1)-C(2)	127.9		ω_8	124.8
	C(4)-S(2)-C(3)-C(2)	125.7		ω_2	
	C(4)-C(5)-C(6)-C(7)	138.4		ω_5	
1,6-DTCD	C(3)-C(4)-S'-C(1)'	68.4	Cyclodecane (BCB)	ω_1,ω_5	66.0
	C(4)-S'-C(1)'-C(2)'	69.9		ω_{10},ω_6	
	C(2)-C(3)-C(4)-S'	52.0		ω_2,ω_9	54.9
	S-C(1)-C(2)-C(3)	48.5		ω_4,ω_7	
	C(1)-C(2)-C(3)-C(4)	157.3		ω_3,ω_8	152.0

[a] This work.

[b] Data taken from Ref. 5b.

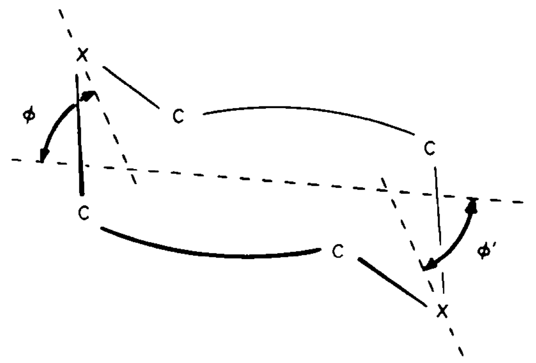

Fig. 4. Schematic drawing of the C–X–C flaps and average plane of the ring C atoms for 1,4-DTCH, 1,5-DTCN, 1,6-DTCD and the corresponding cycloalkanes.

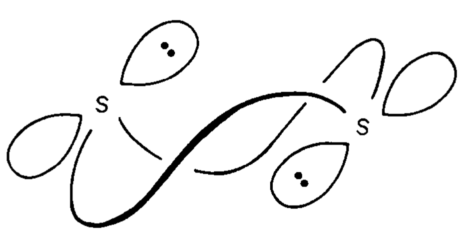

Fig. 5. Schematic drawing of the orientation of the S atoms in mesocyclic dithioethers.

The data were reduced to F_o and $\sigma(F_o^2)$ by the following procedures. The integrated intensities were calculated from the relationship

$$I = [c - (\mathrm{LB} + \mathrm{RB})/\mathrm{rt}]S$$

where c is the peak count, LB the left background count, RB the right background count, rt the ratio of the total background time to the peak scan time, and S the scan rate. The polarization correction for the parallel–parallel mode of the diffractometer was chosen assuming the monochromator to be 50% perfect and 50% mosaic. Initial standard deviations were calculated by:

$$\sigma(\mathrm{I}) = [c + (\mathrm{LB} + \mathrm{RB})/(\mathrm{rt})^2]^{1/2}S.$$

Lorentz and polarization corrections were applied to all reflections.

Solution and refinement of the structures

(a) 1,4-*Dithiacycloheptane* (1,4-*DTCH*). The structure was solved by the direct methods program MULTAN.[37] The positions of all nonhydrogen atoms were obtained from an "E-map" based on the solution with the highest combined figure-of-merit value (2.44) and the lowest residual index (16.2%). The structure was refined by full-matrix least-squares techniques.[38] Refinement was initiated using neutral atom scattering factors for all species.[39] Several cycles of isotropic refinement converged at

$$R = \sum \left| |F_o| - |F_c| \right| \Big/ \sum |F_o| = 0.0874$$

and

$$R_w = \left[\sum w(|F_o| - |F_c|)^2 \Big/ \sum wF_o^2 \right]^{1/2} = 0.1207.$$

The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting factor

$$w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$$

where *p*, the factor to prevent overweighting of strong reflections was set equal to 0.03.

The "goodness of fit" is defined by

$$\mathrm{GOF} = \left[\sum w(|F_o| - |F_c|)^2/(n-m)\right]^{1/2}$$

where *n* is the number of reflections used in the refinement and *m* is the number of variable parameters. Anisotropic refinement reduced R to 0.0642 and R_w to 0.0917. A difference electron density map revealed all of the ten H atoms. The ten H atoms were added to the model in geometrically ideal positions. Temp factors for the H atoms were set according to $B_H = B_N + 1$, where N is the atom to which H is bonded. H atom parameters were not refined. Several cycles of anisotropic refinement led to convergence with $R = 0.0459$, $R_w = 0.0649$ and GOF = 3.440. The final atomic parameters for 1,4-DTCH with their standard deviations are given in Table 2.

(b) 1,5-*Dithiacyclononane* (1,5-*DTCN*)

The structure was solved by the direct methods program MULTAN.[37] The positions of all nonhydrogen atoms were obtained from an "E-map" based on the soln with the highest combined figure-of-merit (3.00) and the lowest residual index (32.8%). Isotropic full-matrix least-squares[38] refinement led to $R = 0.1493$ and $R_w = 0.1840$. Anisotropic refinement led to $R = 0.0788$ and $R_w = 0.1034$. All of the H atoms were located from a difference electron density map and added to the model in geometrically ideal positions. Final refinement led to convergence with $R = 0.0558$, $R_w = 0.0673$ and GOF = 2.633. The final atomic parameters for 1,5-DTCN with their standard deviations are given in Table 3.

(c) 1,6-*Dithiacyclodecane* (1,6-*DTCD*)

The structure was solved by the direct methods program MULTAN.[37] The positions of all nonhydrogen atoms were obtained from an "E-map" based on the solution with the highest combined figure-of-merit (2.87) and the lowest residual index (18.8%). Full-matrix least-squares refinement[38] led to isotropic convergence at $R = 0.0942$ and $R_w = 0.1432$. Anisotropic refinement gave $R = 0.0687$ and $R_w = 0.1080$. All of the hydrogen atoms were located from a difference electron density map and added to the model in geometrically ideal positions. Final refinement led to convergence with $R = 0.0314$, $R_w = 0.0480$ and GOF = 2.301. The final atomic parameters for 1,6-DTCD with their standard deviations are given in Table 4.

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