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CONFORMATIONAL EFFECTS IN 1,2-DITHIETANE, 1,2-DITHIETE, 1,3-DITHIOLE, 2,3-DIHYDRO-1,4-DITHIIN AND 1,4-DITHIIN RADICAL CATIONS[1]

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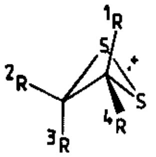
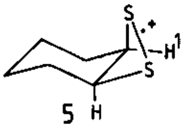
Abstract - 1,2-Dithietane radical cations exist in a nonplanar conformation. With trans-3,4-dimethyl substituents, the barrier to ring flip is >5 kcal/mol. Cyclohexene derivatives **7-10** possess a measurable barrier to ring flip. However, the radical cations **11-16** have a much lower barrier and only conformationally time-averaged ESR spectra are observed at -90 °C. The 2,3-dihydro-1,4-dithiin ring of **11** or **19** is conformationally mobile but is locked in a half-chair conformation in **12** and **13**.

We have prepared, and where possible studied the effect of temperature, on a series of 1,2-dithietane radical cations (**1-6**) and a series of radical cations which are cyclohexene-1,2-dithiol derivatives (**7-16**). These derivatives are representatives of the dithiete (**17**), 1,3-dithiole (**18**), 2,3-dihydro-1,4-dithiin (**19**) and 1,4-dithiin (**20**) series of radical cations which have been previously described in H_2SO_4 solution.[2-4]





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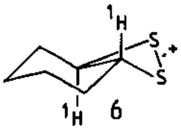

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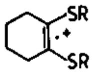
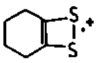


7, R=n-Bu
8, R=i-Pr

1, $^1R-^4R = H$
2, $^1R = CH_3$: $^2R-^4R = H$
3, $^1R,^2R = CH_3$: $^3R,^4R = H$
4, $^1R,^3R = CH_3$ $^2R,^4R = H$



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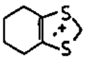

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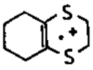

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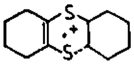

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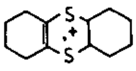

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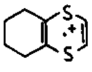

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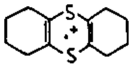

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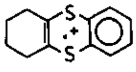

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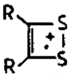
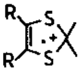
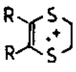
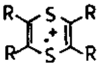
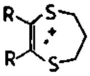
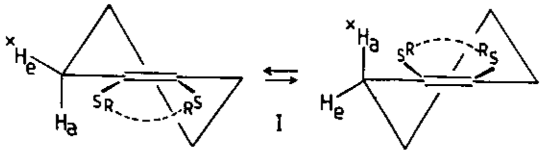






		17[2]	18[2,3]	19[4]	20[2,5]	21
g-value ($R = CH_3$)		2.0155	2.0095	2.0080	2.0089	2.0093
a_R^H (G)	R = H	2.8	---	3.4	2.8	---
	$R = CH_3$	2.2	6.2	5.7	2.1	5.3

Addition of $HSCH_2CH_2SH$ to H_2SO_4 at room temperature has previously been reported[4,6] to yield a weak signal of **1** (a^H = 3.7 (4H) G, g = 2.0193). Mono or 1,2-disubstituted derivatives of $HSCH_2CH_2SH$ undergo further oxidation upon treatment with H_2SO_4 to form dithiete radical cations (e.g., **9**, **17** (R = Me)) as the first persistent radical species detectable by ESR spectroscopy. However, reaction of mono or 1,2-disubstituted derivatives of $HSCH_2CH_2SH$ with Al_2Cl_6 in CH_2Cl_2 at 25 °C for 10-30 min leads to persistent ESR signals which we ascribed to the 1,2-dithietane radical cations **2-6** with g = 2.0187 ± 0.0003. Stereochemistry is maintained with meso-$HSCH(CH_3)CH(CH_3)SH$ forming **3**, dl-$HSCH(CH_3)CH(CH_3)SH$ forming **4**, cis-c-$C_6H_{10}(SH)_2$ forming **5** and trans-c-$C_6H_{10}(SH)_2$ forming **6**. The ESR hyperfine splittings confirm our previous assumption that **1** exists in a puckered conformation which undergoes a rapid ring flip at room temperature ($\tau < 10^{-8}$s). Derivatives **2-5** from -95 to 25 °C give no evidence of ring inversion, and the results are interpreted in terms of the population of only a single conformation. A consistent interpretation of the hfsc is that in **1** the quasi-axial hydrogens (^1H and ^3H) have a large hyperfine splitting (~7-8 G) and that the quasi-equatorial hydrogens (^2H, ^4H) have a small (<0.5 G) coupling. The magnitude of this interaction reflects the dihedral angle between the C-H bond and the sulfur orbital containing unpaired electron density with an added complication from a 1,3-interaction for the quasi-equatorial hydrogen atoms. Since the SOMO of $-S\overset{\cdot +}{-}S-$ is antisymmetric, this homohyperconjugation interaction will in effect cancel some part of the 1,2-hyperconjugative interaction for the quasi-equatorial hydrogen atoms.[4] For the cis-dimethyl analogue **3**, the ESR spectrum is a doublet with a^H = 7.6 G for the quasi-axial hydrogen (^3H) and <0.5 G for the quasi-equatorial hydrogen atom. The methyl group in the quasi-axial position shows a hfs with a^H = 1.1 G. Alkyl substituents prefer the quasi-axial position since the trans-dimethyl derivative **4** gives no hfs ($\Delta H_{1/2}$ = 2.5 G, presumably from unresolved Me hfs), and the monomethyl derivative **2** has a resolved hfs for a single hydrogen only (a^H = 8.5 G). Dithietane radical cation **5** has a single quasi-axial hydrogen (relative to the dithietane ring), and the hfsc for ^1H is assigned as 7.6 G. On the other hand, the dithietane radical cation **6** derived from the trans dithiol exists in a conformation with two quasi-axial hydrogen atoms (the only possible conformation with a chair cyclohexane ring) with a^H = 6.30 (2H) G.[7] The radical cation **6** is also detected by ESR in the reaction of cyclohexene with sulfur or S_2Cl_2 in the Al_2Cl_6/CH_2Cl_2 system (Reaction 1).

$$c\text{-}C_6H_{10} + S_2Cl_2 \text{ or } S_8 \xrightarrow[25\ ^\circ C]{Al_2Cl_6/CH_2Cl_2} \mathbf{6} \qquad (1)$$

Radical cations **7-15** possessing the cyclohexene ring were expected to display temperature dependent ESR spectra from the conformation equilibria involving the half-chair cyclohexene conformers.[8] Indeed 7 (g = 2.0082, prepared by oxidation with Al_2Cl_6/CH_2Cl_2) gave a time-averaged spectrum at -10°C with a^H = 10.5 (4H), 5.8 (4H) G with a coalescence temperature of -70 °C and a frozen conformation at -95 °C with a^H = 14.2 (2H), 6.8 (2H), 5.8 (4H) G; $\Delta H^{\ddagger}$ = 5.6 kcal/mol, $\Delta S^{\ddagger}$ = 3.5 eu. Radical cation 8 (R = i-Pr, g = 2.0080) had a much lower barrier with selective line broadening below -20 °C which yielded $\Delta H^{\ddagger}$ = 2.8 kcal/mol, $\Delta S^{\ddagger}$ = -8.8 eu.[9] The 1,3-dithiole radical cation **10** (g = 2.0101) prepared by Al_2Cl_6/CH_2Cl_2 at -30 °C displayed the expected line broadening effect with a^H (axial) = 11.0 (2H), a^H (equatorial) = 5.5 (2H), a^H (methylene) = 26.6 (2H) G at -90 °C coalescing to a triplet of pentets at -80 °C with a^H = 8.20 (4H), 26.6 (2H) G and with $\Delta H^{\ddagger}$ = 6.2 kcal/mol, $\Delta S^{\ddagger}$ = 5.6 eu.[4] At room temperature, **10** decomposed to 9 (g = 2.0155, a^H = 3.04 (4H) G) which upon cooling below -50 °C gave the line broadening expected for a ring flip with $\Delta H^{\ddagger}$ = 6.0 kcal/mol, $\Delta S^{\ddagger}$ = 3.8 eu.[9] Surprisingly, the dihydrodithiin and dithiin derivatives **11-16** gave no evidence of cyclohexene ring inversion at -95 °C in CH_2Cl_2 and four equivalent α-hydrogen atoms were observed for the cyclohexene ring (Table 1).



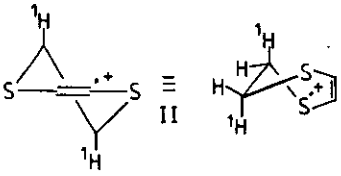
I

Table 1. Hyperfine Splitting Constants for **11-16**, -95 °C in CH_2Cl_2

Structure	g-Value	Cyclohexene a^H (4H)	Other a^H (in Gauss)
11	2.0080	7.34	6.85 (2H), 2.26 (2H), 0.73 (2H)
12	2.0082	7.9	6.1 (2H)
13	2.0082	7.6	7.6 (1H), 1.6 (2H)
14	2.0088	3.2	2.6 (2H)
15	2.0092	2.88 (8H)	
16	2.0082	4.1	0.95 (2H)

The barrier to cyclohexene ring flip (**I**) seems to be a function of the C=C-S angle with larger angles giving rise to a lower barrier. Nonbonded interactions between the R group in 7 and 8 and the cyclohexene α-methylene hydrogen atoms also leads to a lower barrier, presumably by destabilizing the ground state more than the transition state for ring flip.

The radical cation of 2,3-dihydro-1,4-dithiin (**19**) is a cyclohexene derivative and exists in a half-chair structure with $\Delta H^{\ddagger}$ = 2.3 kcal/mol, $\Delta S^{\ddagger}$ = -20 eu (coalescence temperature ~ 70 °C).[4] Similarly, **11** displayed selective line broadening above -10 °C with $\Delta H^{\ddagger}$ = 2.3 kcal/mol, $\Delta S^{\ddagger}$ = -20 eu for the heterocyclic ring only. The half-chair structure for the dihydro-1,4-dithiin ring (**II**) with a large hfs by the quasi-axial hydrogen atom (^1H) is firmly established by the observation that **12** has a large hfsc for two cyclohexane hydrogen atoms (**III**), but **13** has a large α-coupling to only one cyclohexane hydrogen atom in the quasi-axial position relative to the heterocyclic ring (**IV**).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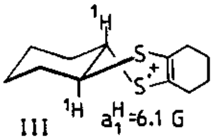
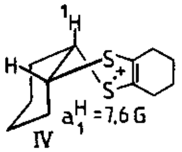
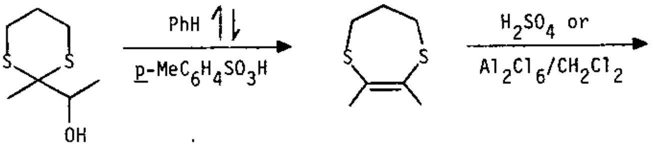


III



IV

The 2,3-dimethyl-1,4-dithiepin derivative **21** has also been synthesized (Reaction 2). The α-methylene hydrogens have a^H = 5.3 (2H) and 1.85 (2H) G, coalescing at ~ 60 °C with $\Delta H^{\ddagger}$ = 5.8 kcal/mol, $\Delta S^{\ddagger}$ = -9.5 eu.



21 (2)

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9. Based upon the assumption that a^H (axial) = 2 a^H (equatorial).[8]

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