

residue filtered off, washed with water yielding 32 % of light yellow crystals of 2-phenylamino-1,3,4-thiadiazole (2c), m.p. 171–172 °C.

2,4-Dihydro-4-phenyl-3*H*-1,2,4-triazole-3-thione (3c) was precipitated from the alkaline filtrate by acidification with glacial acetic acid. Yield 42 % of colourless crystals, m.p. 164–165 °C.

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Conformational Analysis. XVI. The Enthalpy and Entropy Difference Between Twist and Chair Forms of the 1,3-Dithian Ring

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Conformational equilibria of substituted six-membered heterocycles have been widely investigated and the conformational energies obtained have led to at least a qualitative understanding of the different forces and interactions in these compounds. 1,3-Dithians are especially suitable for studies of conformational equilibria since $-ΔG^{\circ}$ -values may be determined for a particular group at all three nonequivalent sites (2, 4/6 and 5) of the ring and moreover, acid-catalysed equilibration of epimeric derivatives normally occurs readily thus permitting the use of the reliable direct equilibrium method. For this purpose one must find models in which a given substituent biases one conformation for each isomer. In cyclohexanes the most commonly used models have a *t*-butyl group¹ ($-ΔG^{\circ} \sim 24 \text{ kJ mol}^{-1}$) located in position 4 with respect to the group studied. In 1,3-dithians, however, *cis*-2,5-dialkyl substituted derivatives are seldom biased^{1,2} and hence unsuitable as direct models of the twist-chair equilibrium. Consequently, it is preferable to employ, e.g., *r*-2-alkyl,*cis*-4,*cis*-6-dimethyl-(1) and *r*-2-alkyl,*trans*-4,*trans*-6-dimethyl-1,3-dithians (2) as model compounds¹⁻³ to determine the chair-twist enthalpy and entropy differences (Fig. 1). For this purpose epimeric 2-*t*-butyl-4,6-dimethyl-1,3-dithians were prepared in an acid-catalysed condensation reaction from *meso*-2,4-pentanedithiol and 2,2-dimethylpropanal.¹ Epimers were separated by preparative gas chromatography and then equilibrated at three temperatures using trifluoroacetic acid as catalyst. The samples were analysed by gas chromatography. The resulting equilibrium constants and thermodynamic parameters are shown in Table 1.

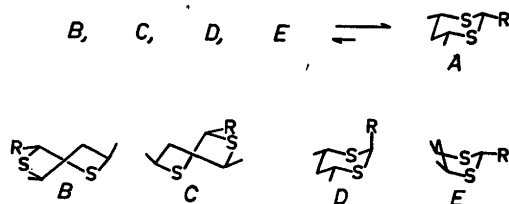


Fig. 1. The studied epimeric equilibria. 1 (A) is *r*-2-alkyl,*cis*-4,*cis*-6-dimethyl- and 2 (B–E) *r*-2-alkyl,*trans*-4,*trans*-6-dimethyl-1,3-dithian. *a*, R = *t*-Bu; *b*, R = *i*-Pr.

Table 1. The results from the equilibration experiments ($2a \rightleftharpoons 1a$). K is the equilibrium constant ($1a/2a$).

T/K	K	$-\Delta G^\circ/kJ\ mol^{-1}$
321.2	77.1 ± 3.4	11.60
341.2	53.3 ± 1.2	11.28
361.2	36.7 ± 0.6	10.82
$-\Delta H^\circ/kJ\ mol^{-1}$	17.9 ± 0.7	
$-\Delta S^\circ/J\ mol^{-1}\ K^{-1}$	19.5 ± 2.0	

It has been pointed out that *r*-2-*t*-butyl,*trans*-4,*trans*-6-dimethyl-1,3-dithian (*2a* in Fig. 1) has two twist forms (B and C) which are free from extra nonbonded interactions due to the substituents.² The other possible conformations (D and E) may be excluded due to the axial *t*-butyl group (D) and to the availability of the much more stable twist forms (cf. E to B and C).² Eliel and Hutchins reported $-\Delta G^\circ \sim 11.4$ kJ mol⁻¹ for the equilibrium $2a \rightleftharpoons 1a$ at 342 K.¹ Owing to the experimental difficulties they were not able to determine the equilibrium constant as a function of temperature and hence the enthalpy and entropy differences remained unknown. Pihlaja² pointed out, however, that the free energy difference fits best to an equilibrium between the 1,4- (B) or 3,6-twist (C) form and a chair form (A) of the 1,3-dithian ring. The results presented herein confirm the postulate² that *2a* exists almost exclusively in the twist conformations B and C. In addition to $-\Delta G^\circ = 11.2$ kJ mol⁻¹ at 342 K which is very close to the value reported by Eliel and Hutchins¹ our results allow the estimation of $\Delta H^\circ_{CT} = 17.9 \pm 0.7$ kJ mol⁻¹ and $\Delta S^\circ_{CT} = 19.5 \pm 2.0$ J mol⁻¹ K⁻¹ for the equilibrium between the 1,4- or 3,6-twist form and a chair form. This result is in close agreement with the averaged most probable values proposed earlier for the chair-twist equilibrium of the unsubstituted 1,3-dithian ring (ΔH°_{CT} 16.9 \pm 1.2 kJ mol⁻¹ and ΔS°_{CT} 19.0 \pm 2.0 J mol⁻¹ K⁻¹).³

To test the accuracy of the above result we may now evaluate the free energy difference for the equilibrium in Fig. 1 when R=i-Pr. The *r*-2-isopropyl,*trans*-4,*trans*-6-dimethyl derivative (*2b*) should include about 37 % of the twist forms and 63 % of the chair form (D) if the thermodynamic parameters for the chair-twist equilibrium are equal to those presented above and $-\Delta G^\circ$ (*2ax*-i-Pr) has the value 9.7 kJ mol⁻¹ derived in our previous report.² Hence $-\Delta H^\circ$ for the epimer equilibrium at 342 K will be 12.7 kJ mol⁻¹ and $-\Delta S^\circ = 0.37 \times 19.5 + \Delta S_{mix}$ ("B+C"+D) = 7.2 + 5.5 = 12.7 J mol⁻¹ K⁻¹. Thus $-\Delta G^\circ$ (342) for the epimer equilibrium should be 8.4 kJ mol⁻¹ in fair agreement with the value 8.2 kJ mol⁻¹ reported by Eliel and Hutchins.¹ It is worth emphasizing that

this treatment does not make any allowance for the possible differences in the rotational entropy of the isopropyl group in the various conformations (A, "B+C", D) but in the light of the above result these differences are likely to be small.

As a conclusion isomer *2a* exists predominantly and isomer *2b* appreciably in the twist form (B or C). Moreover, the values of the thermodynamic parameters from this and previous reports^{1,2,4,5} confirm that 1,3-dithians may attain twist conformations relatively easily. In a forthcoming paper we shall try to clarify the contribution of the twist forms to the conformational equilibria in *cis*-2,5-dialkyl-1,3-dithians in some detail.⁵

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Correction to "Studies on the Kolbe Electrolysis. XII. * Complete Racemization of Optically Active Radicals from (—)-2- Methyloctadecanoate in a Mixed Coupling Reaction"

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On p. 907, in the left-hand column, fifth paragraph from above (line 27), the sentence beginning with "This permits us to conclude..." a deplorable error has sneaked in. As follows from the optical rotation data given in the paper, the word "retention" in this sentence should be replaced by "racemization".

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