# Conformational Analysis of *trans*-2,6-Dithiabicyclo[5.4.0]undecane-4-spiro-1′-cyclobutane, -cyclopentane, and -cyclohexane by $^1$H and $^{13}$C Nuclear Molecular Resonance Spectroscopy

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The high-field $^1$H and $^{13}$C d.n.m.r. spectra of the title compounds are presented. The coalescence effects in the spectra of spirocyclohexane derivatives are discussed and assigned to the conformational process, namely restricted pseudorotation of the dithiepane ring.

We have recently published the results of $^{13}$C d.n.m.r. investigation of *cis*-2,6-dithiabicyclo[5.4.0]undecane-4-spiro-1′-cyclobutane, -cyclopentane, and -cyclohexane.[1] In the temperature-dependent n.m.r. spectra two coalescence processes have been found. The first one interconverts the molecule into its mirror image and occurs by an inversion of the *cis*-fused bicyclic system. The second one is connected with the restricted pseudorotation of the dithiepane ring.

In this paper we report the results of a high-field $^1$H and $^{13}$C d.n.m.r. investigation of the spiro-cyclobutane (**1a**), -cyclopentane (**1b**), and -cyclohexane (**1c**) derivatives of *trans*-2,6-dithiabicyclo[5.4.0]undecane.

The conformational mobility of this *trans*-bicyclic system is different from the previously investigated *cis*-isomer[1] as a *trans* fusion prevents the molecule from undergoing an inversion such as is seen in the *trans*-decalin molecule.[2] However, interconversion and pseudorotation of the seven-membered ring is still possible.

## Results

Variable-temperature $^1$H and $^{13}$C n.m.r. studies of compounds (**1a**—**c**) revealed spectral variations only for compound (**1c**). Table 1 summarises the $^1$H n.m.r. data obtained at high and low temperature for all three compounds while Table 2 summarises the corresponding $^{13}$C chemical shifts. The observed characteristic spectral changes are described next. The partial 400.13 MHz $^1$H n.m.r. spectrum of (**1c**) shown in Figure 1 reveals an AB pattern for the methylene protons at positions 3 and 5. This signal undergoes asymmetrical broadening at low temperatures. The high-field half of the AB signal broadens first and attains maximum broadening near 243 K, then at 203 K gives two doublets at 2.19 and 2.96 p.p.m. The low-field half of the high-temperature AB pattern reaches maximum broadening between 233 and 223 K and at 203 K two doublets at δ 2.56 and 2.85 are observed. These four signals in the lowest-temperature spectrum are of equal intensity.

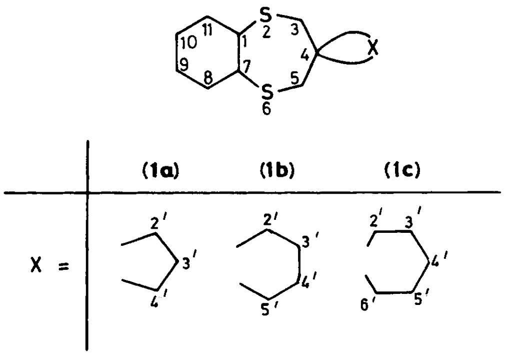

**Table 1.** $^1$H N.m.r. parameters for compounds (**1a**—**c**)

| Comp. | $T$(K) | δ/p.p.m. A | B | $CH_2S\nu_{AB}$/Hz | $J_{AB}$/Hz |
|---|---|---|---|---|---|
| (**1a**) | 283 | 3.15 | 2.95 | 68 | 15.8 |
| | 233 | 3.13 | 2.97 | 60 | 15.8 |
| (**1b**) | 283 | 3.08 | 2.60 | 190 | 15.8 |
| | 233 | 3.07 | 2.61 | 185 | 15.8 |
| (**1c**) | 283 | 2.84 | 2.68 | 67 | 15.8 |
| | 203 | 2.96 | 2.19 | 310 | 15.0 |
| | | 2.85 | 2.56 | 115 | 14.3 |

Similarly, in the 100.6 MHz $^{13}$C n.m.r. spectra of the compounds investigated the conformational-motion effects are observed only for (**1c**). Here coalescence processes involving signals of the seven- and the spiro-annulated six-membered ring and of C-8/C-11 leading to 1:1 splittings in the lowest-temperature spectrum, were found. On the other hand, the signals due to the spiro atom C-4 and atoms C-4′ and C-9/C-10 are unaffected.

The free energy of activation ($\Delta G_c^\ddagger = 11.3 \pm 0.2$ kcal mol$^{-1}$) was calculated for four AX spin systems (C-7/C-1, C-3/C-5, C-3′/C-5′ and C-2′/C-6′) using approximation equations for the reaction rates at the coalescence temperature.[3]

## Discussion

During the coalescence process, the $^{13}$C n.m.r. signals of C-2′, C-3′, C-5′, and C-6′ split into two and the distance between C-2′ and C-6′ in the lowest-temperature spectrum was approximately 4 p.p.m. This cannot be explained by a slowing down of the spirocyclohexane-ring inversion since that process interconverts the molecule into itself. The observed process therefore seems to be an interconversion of two different conformations of the seven-membered ring. These conformations are equally populated as is shown by the integration of the 3-H/5-H region of $^1$H n.m.r. spectrum recorded at 203 K.

The conformational behaviour of seven-membered saturated rings is well established. Experimental results[4,5] and molecular-mechanics calculations[6] show that 1,4-dithiacycloheptane prefers a twist-chair (TC) rather than twist-boat (TB) conformation. These forms can undergo two different types of conformational process.[7] One is TC $\rightleftharpoons$ TB interconversion

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† This research was carried out at Ruhr-Universität Bochum.

**Table 2.** $^{13}$C N.m.r. chemical shifts for compounds (**1a**—**c**) at high and low temperatures[a,b]

| | *T*/K | C-1/C-7 | C-3/C-5 | C-4 | C-8/C-11 | C-9/C-10 | C-2′ | C-3′ | C-4′ | C-5′ | C-6′ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (**1a**) | 283 | 57.51 | 44.30 | 45.08 | 34.14 | 27.12 | 33.36 | 15.24 | 33.36 | — | — |
| | 233 | 57.28 | 44.03 | 44.88 | 33.91 | 26.99 | 33.17 | 15.27 | 33.17 | — | — |
| (**1b**) | 283 | 57.55 | 44.44 | 50.16 | 33.98 | 27.15 | 39.11 | 25.81 | 25.81 | 39.11 | — |
| | 233 | 57.27 | 44.21 | 49.90 | 33.77 | 27.03 | 38.93 | 25.83 | 25.83 | 38.93 | — |
| (**1c**) | 283 | 57.16 | 42.98[c] | 39.67 | 33.99 | 27.25 | 36.41[c] | 22.85 | 27.15 | 22.85 | 36.41[c] |
| | | 56.55 | 47.28 | | 33.55 | | 37.77[d] | 22.93 | | 22.93 | 37.77[d] |
| | 203 | | | 39.17 | | 27.02 | or | or | 26.97 | or | or |
| | | 56.34 | 37.77[d] | | 33.48 | | 33.92 | 22.25 | | 22.25 | 33.92 |

[a] For signal assignment see ref. (1). [b] Signals show small up-field shifts with decreasing temperature. [c] Signals are broadened due to coalescence effects. [d] Signals of C-3(C-5) and C-2′(C-6′) in the lowest-temperature spectrum are overlapped.

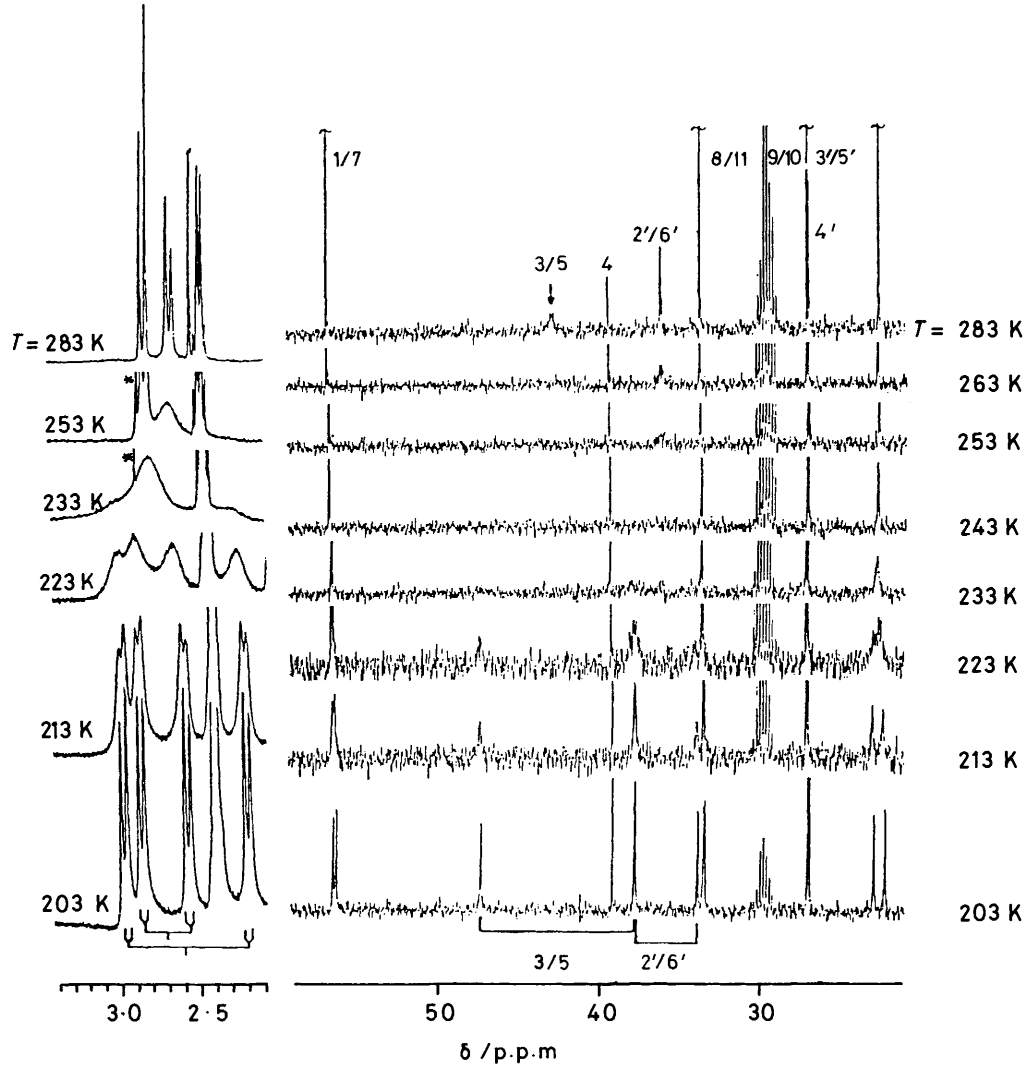

**Figure 1.** Partial 400.13 MHz $^{1}$H n.m.r. (left) and 100.6 MHz $^{13}$C n.m.r. spectra (right) of (**1c**) in [$^{2}$H$_6$]acetone–carbon disulphide (1:1) at several temperatures (* denotes signal of water)

and the second is a TC or TB pseudorotation. The energy barriers for these processes in 6,6-dimethyl-1,4-dithiacycloheptane are less than 8 kcal mol$^{-1}$.[8]

An inspection of molecular models shows that the pseudorotation of the dithiepane ring in the molecules investigated is restricted due to the annelation. In Figure 2 conceivable TC conformations are depicted. Structure A is a flexible TC with C-2′ and C-6′ being in isoclinal positions. Structure B is a rigid TC with C-2′ and C-6′ in very different stereochemical environments since both sulphur atoms are in *gauche* orientation with respect to C-2′ but antiperiplanar to C-6′.

The A $\rightleftharpoons$ B interconversion is a pseudorotation with a barrier of *ca.* 11 kcal mol$^{-1}$. This value is much higher than that for monocyclic dithiepanes[8] but is in the same range as for *cis* analogues of (**1c**).[1] In the transition state C, which has to be passed during A $\rightleftharpoons$ B pseudorotation, the C-2′ methylene

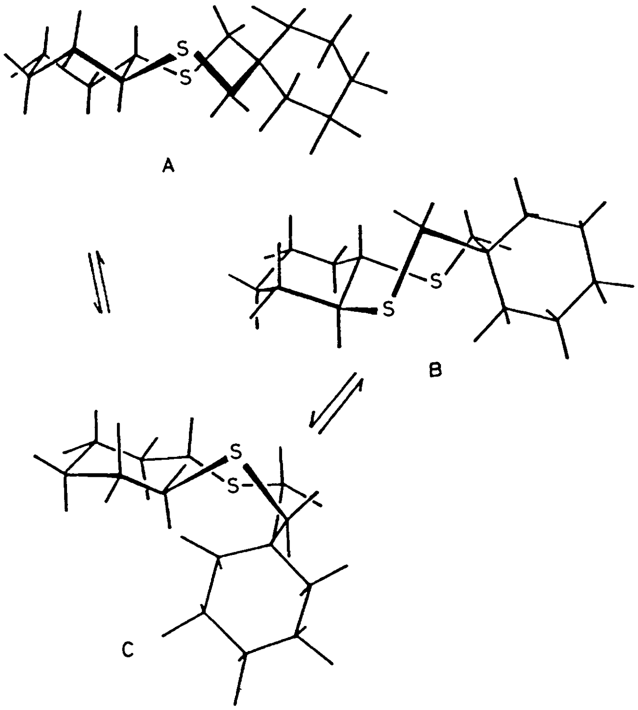

**Figure 2.** Possible TC conformations of (**1c**)

group is very close to the axial hydrogen atom at position 2. This steric compression may be the reason for such a high barrier for the process outlined, as well as the low barriers for (**1a**) and (**1b**). In the last two cases this steric interference is somewhat relieved owing to the smaller bond angles C(2′)–C(4)–(4′) in (**1a**) and C(2′)–C(4)–C(5′) in (**1b**).

## Experimental

The synthesis of the compounds (**1a**—**c**) has been reported earlier.[9] The temperature-dependent $^1H$ and $^{13}C$ n.m.r. spectra were recorded at 400.13 and 100.6 MHz, respectively, on a Bruker AM-400 spectrometer. The measurements were carried out with *ca.* 1 mol $l^{-1}$ solutions in $[^2H_6]$acetone–carbon disulphide (1 : 1). All chemical shifts are referenced to internal $SiMe_4$.

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## References

1 B. Rys and H. Duddeck, *Tetrahedron*, 1985, **41**, 889.
2 E. D. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Wiley–Interscience, New York, 1965; J. Dale, 'Stereochemie und Konformationsanalyse,' Verlag Chemie, Weinheim, 1978.
3 J. Sandström, *Endeavour*, 1974, **33**, 111; J. Sandstrom, 'Dynamic N.M.R. Spectroscopy,' Academic Press, London, 1982.
4 M. J. Cook, G. Ghaem-Maghami, F. Kaberia, and K. Bergensen, *Org. Magn. Reson.*, 1983, **21**, 339.
5 W. N. Setzer, G. S. Wilson, and R. S. Glass, *Tetrahedron*, 1981, **37**, 2735.
6 W. N. Setzer, B. R. Coleman, G. S. Wilson, and R. S. Glass, *Tetrahedron*, 1981, **37**, 2743.
7 G. Favini, *J. Mol. Struct. THEOCHEM.*, 1983, **93**, 139.
8 W. Tochterman, *Top. Curr. Chem.*, 1970, **15**, 378.
9 S. Smoliński and B. Rys, *Monatsh. Chem.*, 1979, **110**, 279.

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