

THE CONFORMATIONAL BEHAVIOR IN
THIA AND DITHIAMETACYCLOPHANES

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Thia- and dithiametacyclophanes have been shown to undergo several types of interesting conformational behavior. The coalescence temperature method has been widely used to estimate the various conformational energy barriers. Dithia[n]metacyclophanes exhibit a unique flipping process, the barrier of which largely depends on the substituent at the [n+6]-position. An inversion process is common among thia- and dithia[m.n]metacyclophanes ($m = n$ or $m \neq n$). However, substituent(s) at the 9- and/or 18-position(s) of dithia[3.3]metacyclophanes results in variability of the conformer preferred. Most medium-sized dithiametacyclophanes seem to be conformationally very mobile but three dithia[3.1.3.1]metacyclophanes are known to demonstrate a novel "twist-inversion" fluxional behavior.

In the past 25 years, a substantial literature has accumulated concerning the syntheses and properties of metacyclophanes¹⁻¹⁰. In particular, [2.2]metacyclophanes have been widely used as models for the investigation of intramolecular and transannular steric and electronic interactions^{11,12}. The stereochemistry¹¹ of [2.2]metacyclophanes is also well-known. An equally substantial number of thia- and dithiametacyclophanes have also been reported during recent years. They were prepared largely as precursors for the corresponding metacyclophanes and/or metacyclophanedienes^{3-10,13}. However, the stereochemical aspect of these thia- and dithiametacyclophanes has also been well-studied and demonstrates some interesting conformational processes. The longer C-S bond and the lower bending energy of a C-S-C bridge provide more conformational flexibility in the thia- and dithiametacyclophanes than in their metacyclophane counterparts, thus resulting in lower conformational energy barriers.

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THE COALESCENCE TEMPERATURE METHOD

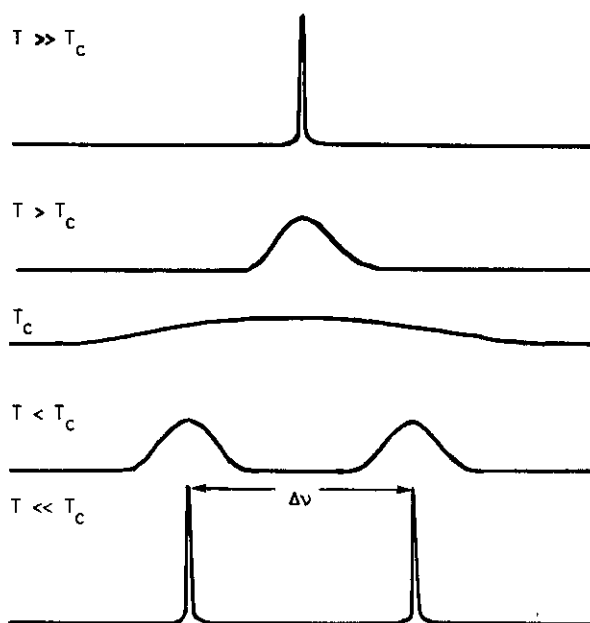


FIGURE 1 Temperature-dependent ^1H -NMR spectra of a simple conformational interconversion.

Variable temperature ^1H -NMR spectroscopic studies have widely been used to obtain information on dynamic molecular movements, in particular the determination of the energy barriers to conformational interconversion^{14,15} and for rotation about sterically hindered carbon-carbon single bonds¹⁶⁻²¹. However, since the practically measurable temperature range in ^1H -NMR studies is from -180°C to $+200^\circ\text{C}$, the range in energy barriers that can be studied is thus restricted from 20 to 110 kJ/mole.

For a relatively simple conformational interconversion process, for example where the low-temperature spectrum consists of two peaks and these collapse and reappear as a single peak at the average position at high temperatures (Figure 1), the coalescence temperature (T_c) method to estimate $\Delta G_c^\ddagger$ (the transition state free energy at coalescence) is most often used^{14,15} as a measure of the energy barrier for such a process. This method simply involves the measurement of the coalescence temperature (T_c) and the frequency separation ($\Delta\nu$) of the peaks concerned at the low temperature limit (Figure 1). The rate constant (k_c) and free energy of activation ($\Delta G_c^\ddagger$) for the exchange at T_c can then be calculated from equations [1] and [2]

$$k_c = \frac{\pi \Delta\nu}{\sqrt{2}} \quad [1]$$

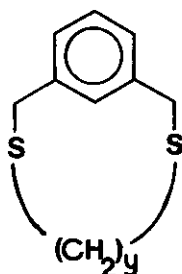
$$\Delta G_c^\ddagger = 2.303RT_c (10.319 + \log T_c - \log k_c) \quad [2]$$

$$\Delta G_c^\ddagger (\text{kJ/mole}) = 0.019 T_c (9.972 + \log \frac{T_c}{\Delta\nu}) \quad [3]$$

respectively¹⁴. Equation [2] is transformed to equation [3] for the purpose of direct calculation.

The simple method discussed above is, however, not without limitations. For example, the linewidth of the signals must be small in comparison to the $\Delta\nu$ value. Secondly, the $\Delta G_c^\ddagger$ values so obtained should only be compared within similar examples such that $\Delta S_c^\ddagger$ is approximately constant.

DITHIA[n]METACYCLOPHANES



	<u>y</u>	<u>Reference</u>
1	2	22
2	3	22, 23, 24
3	4	25, 26
4	5	22
5	6	22

As far as the parent dithia[n]metacyclophanes are concerned, the members **1-5** have been reported. They have all been shown to exhibit a conformational flipping process $A \rightleftharpoons B$ (Figure 2; $X = H$). The presence of the two sulfur atoms greatly simplifies the $^1\text{H-NMR}$ signals for the benzylic protons, which could be easily monitored to indicate the flipping process. For example, the benzylic protons of dithia[6]metacyclophane **1** appear as a singlet ($\delta 3.66$)²² at $+120^\circ\text{C}$, indicating a fast conformational equilibrium $A \rightleftharpoons B$ (Figure 2; $X = H$). At -50°C , however, the process is frozen and the benzylic protons now appear as a clear AB system ($\delta_A = 4.26$, $\delta_B = 3.69$, $J_{AB} = 10 \text{ Hz}$)²².

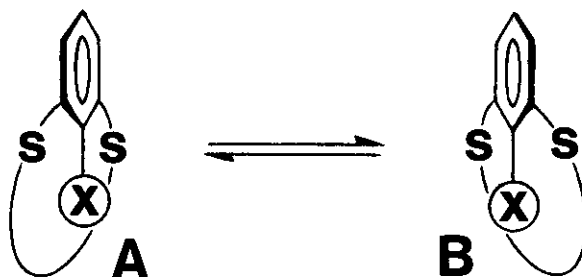
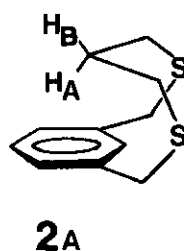
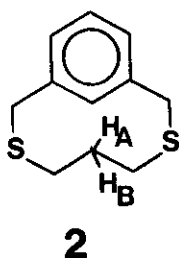
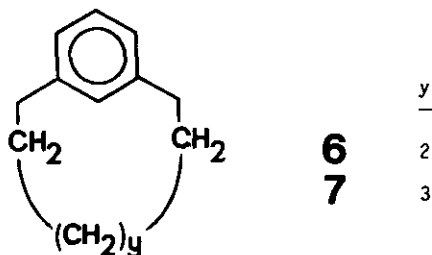


FIGURE 2 Conformational flipping in dithia[n]-metacyclophanes.

The central methylene protons could sometimes be monitored to demonstrate the flipping process as illustrated by dithia[7]metacyclophane^{23,24}. In its ¹H-NMR spectrum at ambient temperature, the protons H_A and H_B appear as a quintuplet at δ 0.45 indicating the fast equilibrium $A \rightleftharpoons B$ (Figure 1; X = H). As the temperature is lowered, the signal for protons H_A and H_B collapse ($T_c = -50^\circ\text{C}$) and subsequently reappear (-95°C) as two broad peaks at δ -0.21 (H_A) and δ 1.71 (H_B) respectively. The high-field signal for H_A is consistent with a frozen conformation as shown in **2A** in which H_A is located directly above the cavity of the π -electron cloud and thus experiencing a shielding effect.



Using the coalescence temperature method¹⁴, the respective energy barriers of the conformational flipping in **1** and **2** are estimated to be 51.9²² and 42.7^{23,24} kJ/mole. These values are respectively smaller than those obtained for a similar flipping process in [6]-metacyclophane **6** (72.8 kJ/mole)³ and [7]metacyclophane **7** (48.1 kJ/mole)³, consistent with



the fact that the longer and more flexible C-S-C bond results in lower energy barrier.

The larger members of the dithia[n]metacyclophane family are conformationally very mobile giving temperature-independent ^1H -NMR spectra within the respective temperature range studied (Table 1). The flipping process in these larger rings is thus not easily frozen due to small energy barriers (Table 1).

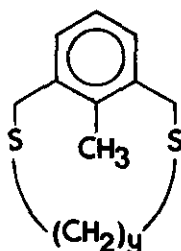
TABLE 1 Comparison of energy barrier for conformational flipping in dithia[n]metacyclophanes and [n]metacyclophanes.

[n]Cyclophane	T_c ($^{\circ}\text{C}$)	$\Delta G_c^\ddagger$ (kJ/mole)	Reference
[6]-1	-20 ^a	51.9	22
[6]-6	-76.5 ^b	72.8	3
[7]-2	-50 ^b	42.7	23, 24
[7]-7	-28 ^b	48.1	3
[8]-3	<-80 ^a	<38.1	25, 26
[9]-4	<-60 ^a	<43.1	22
[10]-5	<-70 ^a	<41.0	22

^aCoalescence temperature of the benzylic protons.

^bCoalescence temperature of the central methylene protons.

Introduction of an intraannular substituent such as $-\text{CH}_3$ at the [n+6]-position of a dithia[n]metacyclophane is expected to greatly increase the barrier to conformational flipping. Thus the dithia[n]metacyclophanes **8-15** have been prepared²⁷ but compounds **8-12** show no evidence for conformational flipping $A \rightleftharpoons B$ (Figure 1; $X = \text{CH}_3$) as a result of the steric hindrance of the methyl substituent ($T_c > 180^{\circ}\text{C}$, $\Delta G_c^\ddagger > 95.0$ kJ/mole). The lack of flipping process in these cyclophanes is indicated by their ^1H -NMR spectra showing clear AB systems for

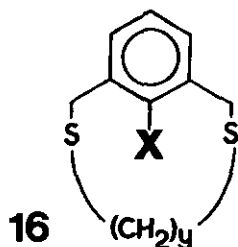


	y		y
8	3	12	7
9	4	13	8
10	5	14	9
11	6	15	10

the benzylic protons at all temperatures studied²⁷. Where the chain is sufficiently long, flipping $A \rightleftharpoons B$ (Figure 1; $X = CH_3$) for example in **13** - **15**, becomes possible. The AB systems for the benzylic protons in **13** and **14** collapse at 60°C and -30°C respectively before reappearing as singlets, corresponding to energy barriers of 69.4 and 50.2 kJ/mole respectively²⁷.

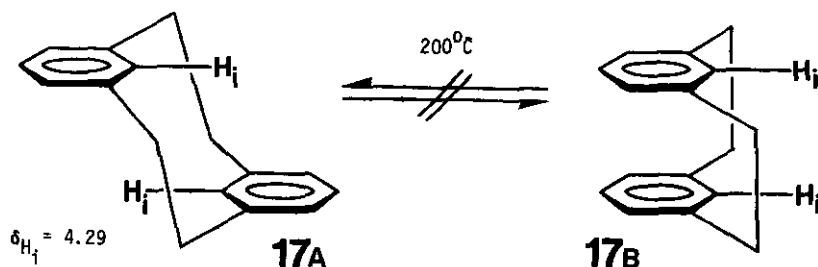
TABLE 2 Comparison of energy barrier for conformational flipping in dithia[n]metacyclophanes **16** with different substituents X.

X	n	$\Delta G_C^\ddagger$ (kJ/mole)	Reference
H	7	42.7	23, 24
F	10	44.0	22
OH	10	68.3	28
NH ₂	10	100.5	28
NO ₂	12	63.7	28
Cl	12	64.5	28
CH ₃	12	69.5	27
Br	12	94.2	28
CN	12	98.8	28
CN	13	60.7	28
Br	13	64.5	28
OCH ₃	13	75.0	27
OCH ₃	14	44.0	27
I	14	61.2	28
SCH ₃	14	72.9	28
COOCH ₃	14	98.8	28
SOOCH ₃	16	70.8	28

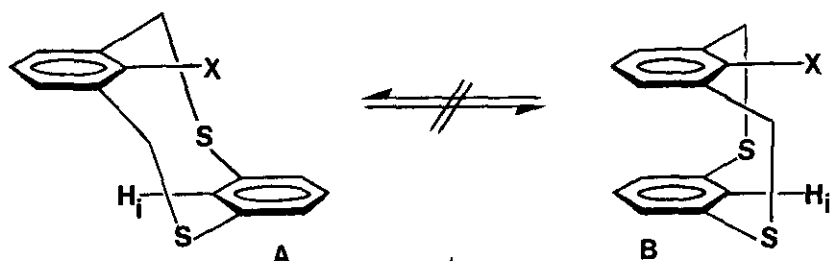


Dithia[n]metacyclophanes **16** with other substituents at the [n+6]-position (Table 2) have also been reported and they show the same flipping process $A \rightleftharpoons B$ (Figure 1) when it is allowed^{22,27,28}. With a given n-value, all members studied exhibit only one identical fluxional process (flipping) and differ only in the substituent X. Thus the relative $\Delta G_C^\ddagger$ values so obtained for the energy barriers could be directly used to reflect the "size" (or steric hindrance) of the substituent X — the higher the energy barrier ($\Delta G_C^\ddagger$), the larger the "size" of X (Table 2). Due to the synthetic variability which results in the syntheses^{22,27,28} of a large number of dithia[n]metacyclophanes **16**, a reasonably complete list could be obtained by the above method to provide information concerning the relative spatial requirement ("size")²⁹ of these common substituents (Table 2).

THIA AND DITHIA [m.n]METACYCLOPHANES (m = n or m ≠ n)



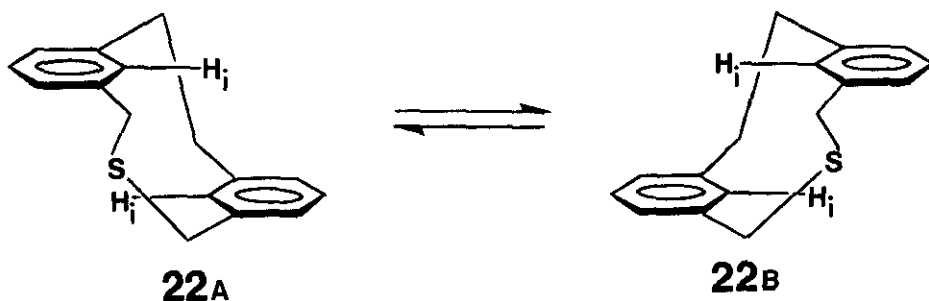
The parent [2.2]metacyclophane **17**, which was first prepared by Pellegrin in 1899³⁰, has been shown from ¹H-NMR³¹ and X-ray crystallographic³² studies to exist in the *anti*-, stepped conformation **17A** in both solution and solid state. Variable temperature ¹H-NMR studies³³ reveal that there is no conversion between **17A** and **17B** up to 200°C. Replacement of two bridging methylene units with sulfur links, as in dithia[2.2]metacyclophanes **18 - 21**, still



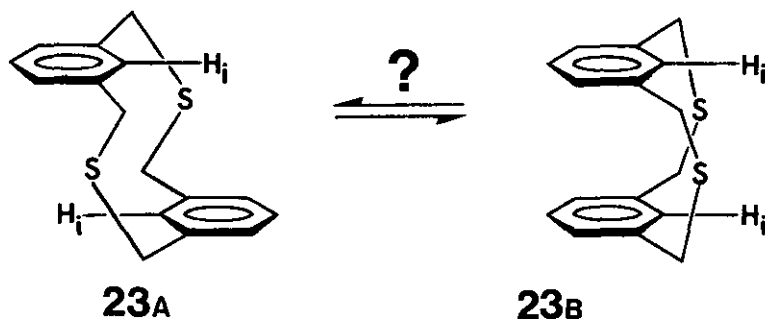
	X	δ_{H_i}
18	—	—
19	H	4.41
20	F	5.62
21	Cl	5.21
	Br	5.07

does not allow free anti-syn conversion. The preferred conformation of these dithia[2.2]-metacyclophanes is again the anti-, stepped **A** as indicated by the shielded proton signals for H_i which lies above the opposite benzene ring. The lack of any conformational process is evident by the fact that the AB systems in **18 - 21** remain unchanged up to 180°C ($\Delta G_C^\ddagger > 96.6$ kJ/mole).

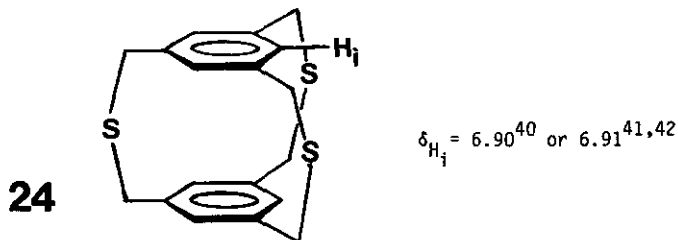
The increase of one sulfur atom in one of the chains of [2.2]metacyclophane, however, makes an inversion process in thia[3.2]metacyclophane **22** comparatively easier^{35,36}. At 55°C, the $-\text{SCH}_2-$ and $-\text{CH}_2\text{CH}_2-$ protons appear as two separate singlets indicating a fast equilibrium process. At -54°C, however, clear AB ($\delta_A = 3.45$, $\delta_B = 3.84$) and apparent A_2B_2 ($\delta_A = 2.22$, $\delta_B = 3.08$) systems were observed for the respective $-\text{SCH}_2-$ and $-\text{CH}_2\text{CH}_2-$



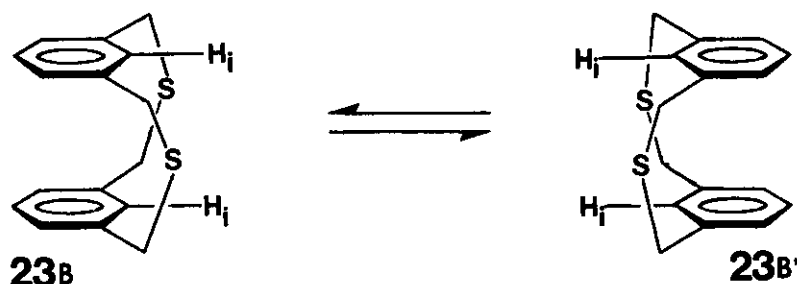
protons. The H_i protons appear at $\delta 5.43$ suggesting that the frozen anti-conformer **22A** or **22B**. The fact that only one conformation is frozen could indicate that the equilibrium at higher temperature involves the fast inversion **22A** $\rightleftharpoons$ **22B**. Using the coalescence temperature of the $-\text{CH}_2-\text{CH}_2-$ protons ($T_c = 0.5^\circ\text{C}$), the barrier to inversion in **22** was estimated at 34.8 kJ/mole, a value much smaller than those obtained for a series of [3.2]metacyclophanes ($\Delta G_c^\ddagger = 66.1 - 79.9$ kJ/mole)³⁷, again showing the higher conformational flexibility due to the longer C-S-C bridge.



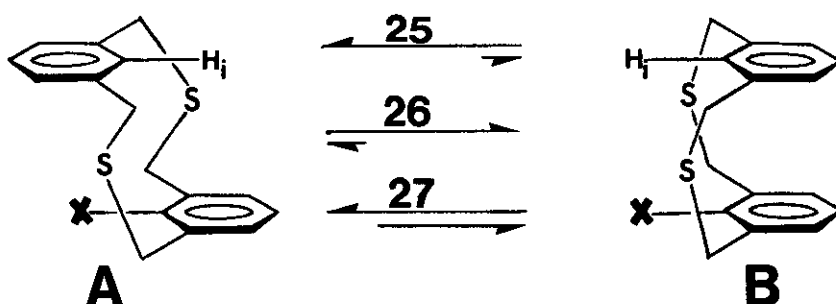
The most striking result is perhaps obtained from the parent dithia[3.3]metacyclophane **23**. After its preparation^{35,36,38} was reported, initial $^1\text{H-NMR}$ studies suggested a rapid equilibrium at room temperature between the anti- and syn-conformers (**23A** $\rightleftharpoons$ **23B**) and assumed the signal at $\delta 6.6$ to be the averaged chemical shift for the internal protons (H_i)^{35,36,38}. However, a more detailed study was reported recently which gives conclusive indication that **23** exists as the syn-conformer **23B** both in the solid state (X-ray crystallography)³⁹ and in solution ($^1\text{H-NMR}$ studies)³⁹. The $^1\text{H-NMR}$ signal³⁹ for H_i at $\delta 6.82$ (CDCl_3 , 10°C) and other aromatic protons at



$\delta 6.91$ are in fact comparable to that of the model compound **24**⁴⁰⁻⁴². With carbon disulfide as a solvent, the H_i protons appear at $\delta 6.62$ and remain invariant with temperatures between -80°C and $+80^\circ\text{C}$. This could then suggest an easy and fast inversion process between **23B** and **23B'** (syn $\rightleftharpoons$ syn) with no appreciable concentration of the anti-conformer **23A** $\rightleftharpoons$ a result entirely opposite to that found in thia[3.2]metacyclophane **22** (anti $\rightleftharpoons$ anti).



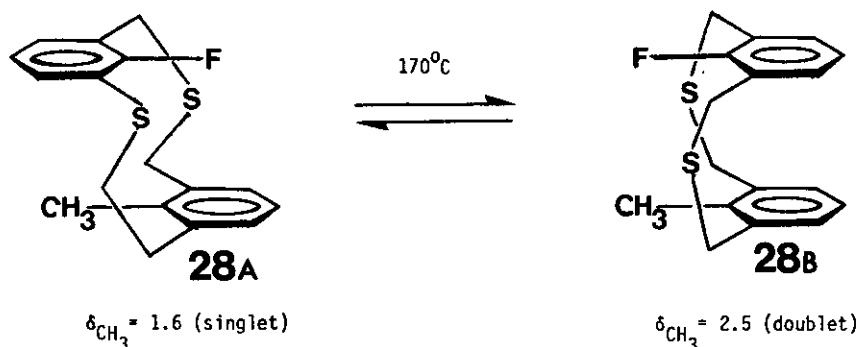
Interestingly, replacement of one of the H_i protons in dithia[3.3]metacyclophane with a substituent leads to variability in conformational preference at room temperature. However, the preference, which could easily be determined by the signal of the H_i proton, is apparently independent of the steric hindrance of the substituent X. For example, the amino-substituent in **25**



	X	δ_{H_i}
25	NH ₂	4.9
26	NO ₂	7.3
27	CH ₃	5.6

effectively freezes the process in favor of the anti-conformer **25A** shielding the H_i signal to $\delta 4.9$ ⁴³. The nitro-substituent in **26**, however, results in a very strong preference for the syn-conformer **26B**⁴³ having the H_i proton signal appear at $\delta 7.3$. Surprisingly, with a methyl-substituent, a fast equilibrium exists between **27A** and **27B** (with perhaps a slightly stronger preference for **27A**) giving an averaged H_i signal at $\delta 5.6$ ²⁷. From the studies of [n+6]substituted dithia[n]metacyclophanes as discussed earlier, the relative "size" (spatial requirement) of the three substituents is in the order NH₂ > NO₂ > CH₃. Thus the conformational preference in these 9-substituted dithia[3.3]metacyclophanes is clearly not controlled by the steric effect

of the substituent alone. The true effect is not fully understood.

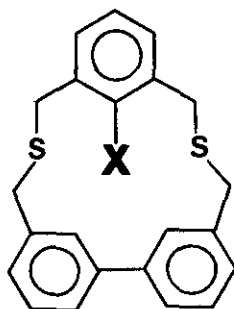


The anti-syn inversion process in dithia[3.3]metacyclophanes is, however, best demonstrated by **28**²⁷. At room temperature, the process is frozen and both **28A** and **28B** exist as rigid and stable conformers. The methyl group of **28A** appear as a shielded singlet at $\delta 1.6$ and that of **28B**, due to the coupling with the neighboring fluorine atom, show up as a doublet at $\delta 2.5$. These signals collapse at about 105°C and reappear at 170°C as a singlet at $\delta 2.0$ indicating the fast equilibrium between **28A** and **28B**. With two "large" substituents at the 9- and 18-positions of the dithia[3.3]metacyclophane system, stable syn- and anti-conformers such as **29** and **30** have been isolated^{44,45}. However, they are no longer thermally interconvertible due to large energy barriers induced by the steric hindrance of the two methyl groups.

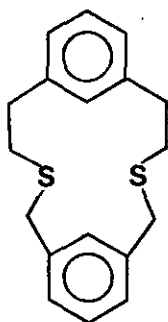


MEDIUM-SIZED DITHIAMETACYCLOPHANES

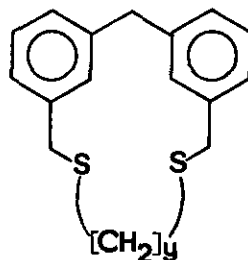
Medium-sized dithiametacyclophanes such as dithia[3.0.3]metacyclophanes **31**⁴⁶ and **32**²⁷, dithia[4.4]metacyclophane **33**^{47,48} and dithia[n.1]metacyclophanes **34-36**^{43,49} have been reported. However, though their respective $^1\text{H-NMR}$ spectra at room temperature indicate free conformational movements in these molecules, no variable temperature studies have been made in an attempt to investigate any possible frozen conformers at lower temperatures.



31 X = H
32 X = CH₃

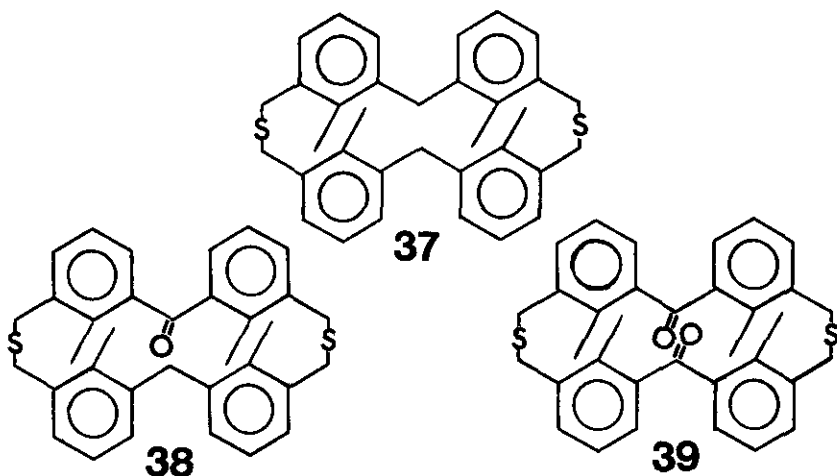


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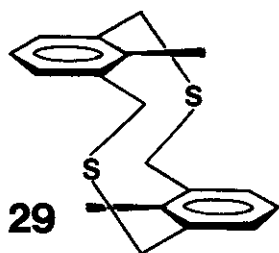
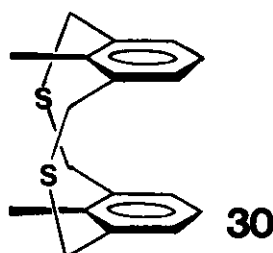
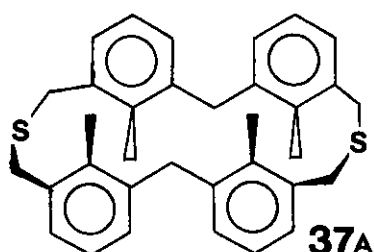
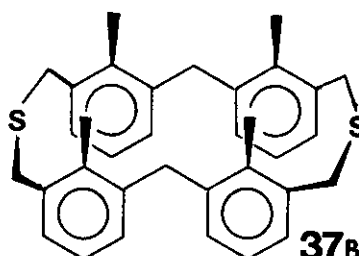


34 y = 1
35 y = 2
36 y = 3

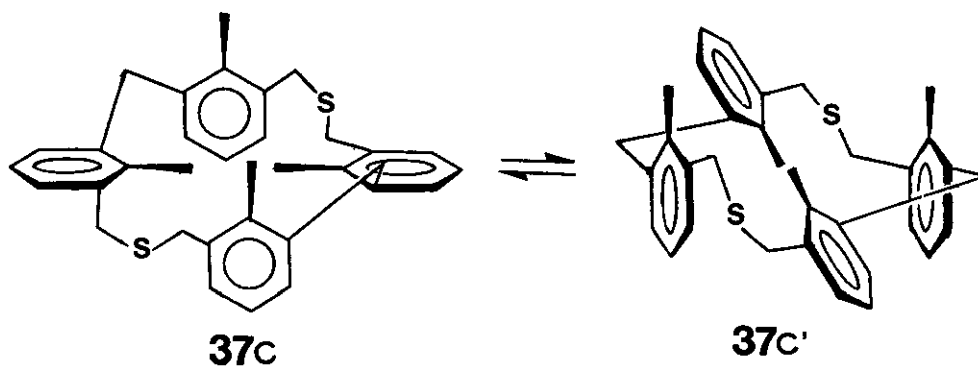
In the studies of annelated annulenes and cyclophanes^{50,51}, dithia[3.1.3.1]metacyclophanes **37** - **39** were prepared as potential precursors. The ¹H-NMR spectrum of dithia[3.1.3.1]metacyclophane **37** at 0°C is relatively simple (Table 3), showing a multiplet at δ7.2 - δ6.7 for the aromatic protons and three separate singlets at δ3.84, δ3.63 and δ1.78 for the central -CH₂-, bridging -CH₂S- and methyl protons respectively. It was initially thought that **37** is conformationally very mobile due to its large 20-membered ring. However, a single conformation of **37**



is observed at -100°C. In the ¹H-NMR spectrum (-100°C), there are two types of methyl protons — a highly shielded singlet at δ1.18 typical of an *anti*-methyl group (compared with **29**)⁴⁴ and a normal *syn*-methyl group (compared with **30**)⁴⁴ at δ2.38. These data indicate that the frozen conformer cannot be the *anti,anti*-conformer **37A** or the *syn,syn*-conformer **37B** in both

**29**
anti-isomer; $\delta_{\text{CH}_3} = 1.30$ **30**
syn-isomer; $\delta_{\text{CH}_3} = 2.54$ anti,anti-isomer :**37A**syn,syn-isomer :**37B**

of which the four methyl groups are identical. Examination of molecular models suggests another possibility for the fixed conformation of **37**, namely conformer **37C**, which possesses a pair each of anti- and syn-methyl groups. The anti-methyl protons in **37C** are located in the shielding cones of two benzene rings, which would then be expected to produce a larger combined shielding effect than that experienced by the methyl protons in dithia[3.3]metacyclophane **29**. This is indeed observed ($\delta_{\text{CH}_3} = 1.16$ for **37C** compared to $\delta_{\text{CH}_3} = 1.30$ for **29**). In the high temperature

**37C****37C'**

spectrum (0°C), the methyl signal occurs at the average (± 0.01 ppm) position of the corresponding peaks in the low temperature spectrum (-100°C) (Table 3), thus indicating a true fluxional process consistent with $37\text{C} \rightleftharpoons 37\text{C}'$ (in fact $37\text{C} \equiv 37\text{C}'$), rather than one conformer transferring to a different conformer.

TABLE 3 $^1\text{H-NMR}$ data⁵¹ of dithia[3.1.3.1]metacyclophanes **37-39**

Phane	T ($^{\circ}\text{C}$)	Ar-H	Ar-CH ₂ -	-SCH ₂ -	Ar-CH ₃
37	0	$\delta 7.2-6.7$ (m)	$\delta 3.84$ (s)	$\delta 3.63$ (s)	$\delta 1.78$ (s)
	-100	$\delta 7.3-6.2$ (m)	--- $\delta 4.4-2.9$ (m) ---	---	$\delta 2.42$ (s), $\delta 1.16$ (s)
38	-20	$\delta 7.4-6.8$ (m)	$\delta 3.97$ (s)	$\delta 3.76$ (s)	$\delta 2.00$ (s), $\delta 1.88$ (s)
	-100	$\delta 7.7-6.3$ (m)	--- $\delta 4.3-3.1$ (m) ---	---	$\delta 2.75$ (s), $\delta 1.34$ (s) $\delta 2.48$ (s), $\delta 1.20$ (s)
39^a	+35	$\delta 7.4-7.2$ (m)	---	$\delta 3.67$ (s)	$\delta 1.88$ (s)

^aToo insoluble for low-temperature studies

The comparison of the $^1\text{H-NMR}$ spectra of dithia[3.1.3.1]metacyclophanes **37-39** (**39** is too insoluble in most organic solvents to allow low-temperature studies) reveals close similarities among them. By analogy, it is thus believed that all three members exhibit the same fluxional process as indicated by $37\text{C} \rightleftharpoons 37\text{C}'$ independent of a change at the central bridge(s) ($>\text{CH}_2$ or $>\text{C}=\text{O}$).

Using the coalescence temperature method, the energy barriers of **37** and **38** are estimated to be 39.4 and 38.7 kJ/mole respectively⁵¹ (Table 4). Apparently, the fluxional barrier in the dithia[3.1.3.1]metacyclophane system is not affected significantly by changing the central sp^3 -methylene bridge to a sp^2 -carbonyl function. This is probably due to the flexible C-S-C bridges which compensate for the induced geometrical strain, if any, imposed by the carbonyl center in **38**.

The fact that **37-39**, with 20-membered macro-rings, still exhibit a novel conformational behavior should prompt the reinvestigation of the possible conformational processes in dithia-metacyclophanes **31-36** (12- to 14-membered rings). It will also be interesting to compare these results with other medium-sized dithiametacyclophanes as they become available.

TABLE 4 Thermodynamic data⁵¹ for the barrier of the fluxional process in dithia[3.1.3.1]metacyclophanes **37** and **38**.

Cyclophane	$\Delta\nu$ (Hz)	$T_{\Delta\nu}$ (°C) ^a	T_c (°C) ^b	$\Delta G_c^\ddagger$ (kJ/mole)
37	113.4	-100	-70	39.4
38	121.1	-100	-73	38.7

^aTemperature at which $\Delta\nu$ is measured.

^bThe coalescence temperature.

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