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Proton and Carbon-13 Nuclear Magnetic Resonance Study of the Atropisomeric Forms of 4,4,9,17-Tetramethyl-2,6-dithia[7.1]paracyclophane and Its Tetraoxide

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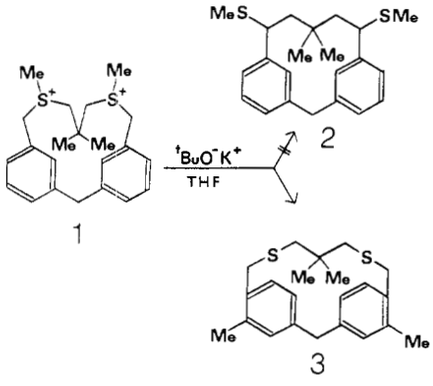
We were intrigued by the recent report of Finch, Gemenden, and Korzun[1] that the attempted Stevens rearrangement of the bissulfonium salt of 4,4-dimethyl-2,6-dithia[7.1]metacyclophane, **1,** did not provide a route to the [5.1]metacyclophane, **2,** but instead yielded the double Sommelet rearrangement product, viz., 4,4,9,17-tetramethyl-2,6-dithia[7.1]paracyclophane, **3.**



Furthermore, the time-dependent ^1H NMR spectra of **3** have been interpreted in terms of an initial anti atropisomer, **3a,** with the *gem*-dimethyl group "inside" the molecular framework, and consequently experiencing some shielding owing to the proximity of the aromatic rings. The formation of the syn atropisomer, **3b,** was deduced from the appearance of two new methyl singlets, one resonating at higher field than Me_4Si, while the intensity of the original *gem*-dimethyl singlet concomitantly decreased.

This fascinating result poses several problems, e.g., why is the Sommelet rearrangement leading to a sterically rigid molecule preferred to the Stevens which would have given a relatively less strained molecule? Does this system allow the investigation of anomalous ^{13}C NMR chemical shifts brought about by ring currents and/or related effects?

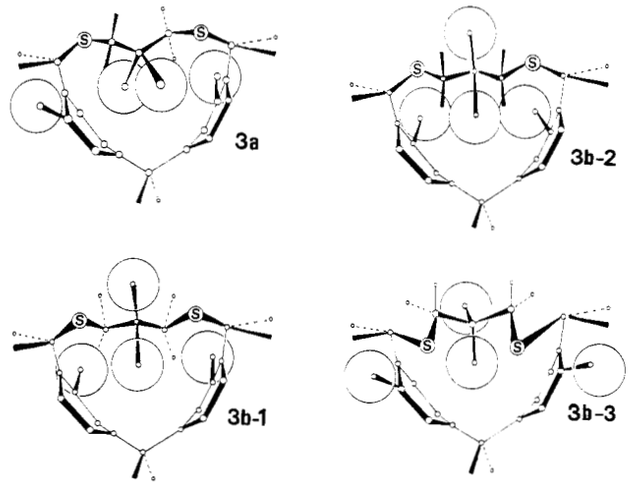


Figure 1. Possible molecular conformations of the atropisomeric forms of **3.**

Our investigation has confirmed the original ^1H NMR observations of Finch et al.,[1] but we have serendipitously obtained evidence for a third atropisomer of **3** not previously reported.

Results and Discussion

The ^1H NMR spectrum of the initial atropisomer, **3a,** is consistent with a molecule of C_2 symmetry such as that depicted in Figure 1. Such a structure accounts not only for the *gem*-dimethyl singlet but also the AB quartets exhibited by the methylene groups at $C_{1,7}$ and $C_{3,5}$. It is noteworthy that the *gem*-dimethyl protons and also the methylene protons at $C_{3,5}$ are considerably upfield of the positions one would normally have anticipated; these upfield shifts for protons positioned above aromatic rings have traditionally been rationalized solely in terms of a ring current model.[2,3] However, recent work[4,5] has elucidated the major contributions made by local anisotropic effects.

Now, the formation of the syn atropisomer, **3b,** must proceed via the rotation of one of the benzene rings with appropriate adjustment of the seven-membered bridging moiety to produce eventually a molecule of C_s symmetry, as required by the ^1H NMR spectrum. It is possible to construct a number of conformations for the syn atropisomer and some of these are shown in Figure 1. **3b-1** shows the most obvious product whereby rotation of an aromatic ring (with the aromatic methyl of necessity remaining on the "outside" of the molecule) pushes the *gem*-dimethyl group such as to place one C_4-methyl group directly above both aromatic rings (and thus receive an extraordinarily high shielding) while the other C_4-methyl moves "outside". However, examination of molecular models shows that a conformation such as **3b-1** provides little hindrance to the continued rotation of the *gem*-dimethyl moiety leading eventually to the third atropisomer, **3c,** in which both *gem*-dimethyl groups are "outside". This would imply that the activation energy barrier between **3b** and **3c** should be small and thus readily overcome at room temperature. However, the transition from the intermediate to the final product requires heat or an extended time interval and hence steric restraints in the intermediate atropisomer appear to be present. One should mention here that molecular models clearly demonstrate that the benzene rings show considerable deviation from planarity, but such effects are not uncommon in cyclophanes.[6,7]

Another possibility, **3b-2,** to be considered is that the aromatic methyls and the *gem*-dimethyl group are on the same

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Table I. ^{1}H NMR Chemical Shift[a] Data

compd	1,7-H	3,5-H	C_4-CH_3	Ar-CH_3	14-H	Ar-H
3a	3.73, 3.48 (J = 12.7)[b]	1.46, 1.25 (J = 12.4)	0.25	2.24	3.69	6.91–7.01
3b	3.85, 3.50 (J = 12.2)	1.92, 1.00 (J = 12.6)	0.51, −0.23	2.31	3.68	6.74–7.00
3c	3.62	2.51	0.96	2.31	3.76	6.93–7.08
4a	4.36, 4.01 (J = 14.3)	2.13	1.31	2.34	3.85	6.97–7.16
4b	4.32, 4.00 (J = 14.2)	2.34, 1.98 (J = 14.2)	1.33, 1.30	2.29	3.85	7.07

[a] Chemical shifts are quoted in ppm relative to internal Me_4Si and are considered to be within ±0.03 ppm. [b] Coupling constants (J) are quoted in Hz and are considered to be within ±0.2 Hz.

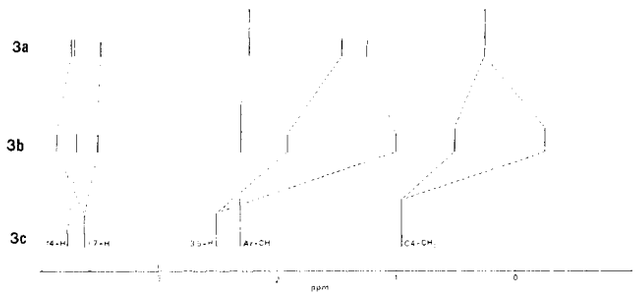


Figure 2. Proton chemical shift correlation diagram.

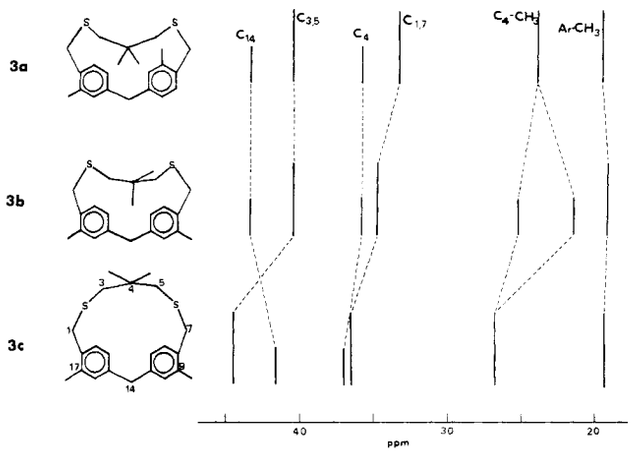


Figure 3. Carbon-13 chemical shift correlation diagram.

side of the molecule and thus the "inside" C_4-methyl is locked in position and cannot rotate past the syn aromatic methyls without considerable effort. A third possibility for the intermediate atropisomer, which still maintains the required mirror plane, is depicted in **3b-3** in which the sulfur atoms are disposed in a similar arrangement to the 1,5 interaction found in S_8. However, this conformation is considered less likely than **3b-1** or **3b-2** since the AB quartet attributable to the methylene protons at $C_{3,5}$ shows an even greater chemical shift difference (see Figure 2 and Table I) than in the initial anti atropisomer, **3a.** This suggests that one of these $C_{3,5}$ methylene protons is in the proximity of the aromatic rings while its partner points away from the rings, a situation which does not occur in **3b-3.**

Perhaps the simplest explanation is that the molecule essentially adopts conformation **3b-1** but, due to the interaction of the syn methyls, the two aromatic rings are not parallel. This could conceivably push the aromatic hydrogens at C_{12}, C_{13}, C_{19}, and C_{20} into the path of the "inside" C_4-methyl group and hinder its rotation outwards. Efforts to measure NOE's between the methyl groups and the aromatic ring protons were inconclusive.

Now, when the sample was heated at 50 °C for 50 h in an attempt to hasten the formation of **3b** from **3a,** a deceptively simple ^{1}H NMR spectrum was obtained in which the methyls and methylene protons appeared as singlets resonating at "normal" frequencies (see Figure 2). We initially suspected that a skeletal rearrangement had occurred, but the mass spectra of the initial and final products were identical and matched that previously obtained by Finch.[1] Apparently the molecule was now sufficiently flexible to allow rapid interconversion of the syn and anti forms and the *gem*-dimethyl moiety was now completely "outside" the cyclic framework of the molecule. This interconversion process is still rapid at −70 °C as the spectrum is scarcely changed at this temperature.

anti-**4a** and *syn*-**4b,** 4,4,9,17-tetramethyl-2,6-dithia[7.1]-paracyclophane 2,2,6,6-tetroxides, have been separated by Finch[1] and their ^{1}H NMR spectra (see Table I) indicate that in both cases the *gem*-dimethyl group is disposed similarly to the situation in **3c,** i.e., on the "outside" of the molecular framework. Conceivably, oxidation of **3** at low temperature might yield the sulfones with the *gem*-dimethyl moiety "inside" the molecular cavity.

The ^{13}C NMR spectra of the atropisomeric forms of **3** are of particular interest since they allow a study of the chemical shifts of ^{13}C nuclei in differing positions relative to the aromatic rings. Previous investigations[8,9] have suggested that contributions to ^{13}C NMR chemical shifts from ring currents and related phenomena should normally be small. However, we have here an extreme situation, in some ways analogous to the bridged annulenes discussed by Boekelheide,[10] whereby a ^{13}C nucleus is locked in close proximity to two aromatic rings. Now, taking as our standard the final product, **3c,** in which the C_4-methyl groups are reasonably distant from the rings, we see that placing the C_4-methyls "inside" the molecular cavity, as in **3a,** leads to an upfield shift of 2.8 ppm (see Figure 3). In the intermediate case, **3b,** where the proton spectrum suggests that one methyl is positioned almost centrally above both rings, the *gem*-dimethyl ^{13}C nuclei are separated by no less than 3.7 ppm; furthermore, the high-field ^{13}C nucleus is the one to which the very high field protons are bonded.

It is tempting to attribute some of this shielding to a combination of ring current and aromatic carbon local anisotropic effects; however, the presence of the sulfur atoms cannot be neglected as anti-γ and γ-gauche effects on ^{13}C shifts are well documented.[11,12] Thus, the data here support the assertion[10] that the behavior of ^{13}C nuclei above aromatic systems parallels the well-established upfield shifts of protons.

This is further evidenced by the ^{13}C chemical shifts of the sulfones, in particular the syn isomer, **4b.** In this case, symmetry considerations predict different shielding effects on the methyl groups at C_4, and indeed their chemical shifts differ

Table II. ^{13}C NMR Chemical Shift[a] Data

compd	Ar-CH_3	C_4-CH_3	$C_{1,7}$	C_4	$C_{3,5}$	C_{14}	$C_{12,20}$[b]	$C_{10,16}$[b]	$C_{13,19}$[b]	$C_{11,15}$[b]	$C_{9,17}$[b]	$C_{8,18}$[b]
3a	19.4	23.9	33.2	35.7	40.4	43.2	(125.6)	(129.7)	(132.2)	(132.9)	(138.2)	(144.7)
3b	19.1	21.4, 25.1	34.7	35.7	40.4	43.2	(124.6)	(130.7)	(132.4)	(132.6)	(138.2)	(144.9)
3c	19.4	26.7	36.5	36.9	44.5	41.6	(126.6)	(130.2)	(131.4)	(134.7)	(137.3)	(140.8)
4a	20.1	26.3	62.6	35.6	60.1	42.2	(126.9)	(130.6)	(131.7)	(125.8)	(138.8)	(146.7)
4b	20.0	27.3, 25.6	62.1	35.6	60.3	43.4	(126.3)	(131.2)	(131.2)	(125.9)	(138.9)	(146.8)

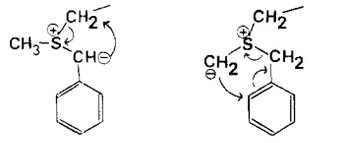
[a] Chemical shifts are quoted in ppm downfield from Me_4Si and are considered to be within ±0.1 ppm. [b] Assignments of aromatic ring carbons are tentative.

by 1.7 ppm. In the case of **3b**, the chemical shift difference of 3.7 ppm indicates the presence of a strong shielding effect on the ^{13}C nucleus above the aromatic rings.

The chemical shifts for most of the other ^{13}C nuclei in **3a** and **3b** are very similar (see Table II), but a number of changes are observed in the spectrum of **3c**. These changes may very well be the result of the relief of steric strain and similar effects have previously been noted in thia derivatives of [2.2]metacyclophane.[13]

One of the more curious facets of this problem is the facile formation of the 2,6-dithia[7.1]paracyclophane, a very rigid molecule which takes considerable time before it eventually gains some degrees of freedom, rather than the relatively strain-free [5.1]metacyclophane. Finch[1] has suggested that the proposed radical pair mechanism for the Stevens rearrangement[14] would disfavor the [5.1]metacyclophane route.

An alternative way of viewing this reaction is via Baldwin's rules for ring closure.[15] The Stevens rearrangement to yield the [5.1]metacyclophane can be classified as the disfavored 3-endo-tetrahedral process, see below, while the Sommelet rearrangement can be viewed as a 5-endo-trigonal process



which, while normally not a favored process, is facilitated by the presence of a second row element such as sulfur.[16]

Experimental Section

The samples for this investigation were kindly provided by Dr. Neville Finch of the Pharmaceuticals Division, CIBA-GEIGY Corp., Summit, N.J. ^1H and ^{13}C NMR spectra were obtained on a Bruker WH90 spectrometer operating in the FT mode at 90 MHz (+25 °C) and 22.62 MHz (+30 °C), respectively. Concentrations of 0.2 to 0.3 M in methylene chloride were used throughout and Me_4Si was used as the internal standard.

Carbon-13 chemical shift assignments, except for aromatic ring carbons, were essentially straightforward (see Table II) and any ambiguities were resolved by selective proton decoupling. Unequivocal assignment of the aromatic ring carbons was not attempted in this study; however, proton-bearing carbons ($C_{10,16}$, $C_{12,20}$, $C_{13,19}$) were readily distinguished from non-proton-bearing carbons; proposed ring carbon chemical shift assignments were based on substituent effects.

As noted by Finch,[1] the equilibration of the anti and syn forms of **3** occurred over a several-hour period at room temperature. The appearance of peaks attributable to **3c** was observed only after 2 days at 50 °C or after several weeks at room temperature.

Conclusions

^1H and ^{13}C NMR studies show that 4,4,9,17-tetramethyl-2,6-dithia[7.1]paracyclophane, which is initially produced as the anti atropisomer, **3a**, rearranges via the syn atropisomer, **3b**, in which one C_4-methyl group is held in close proximity to both of the aromatic rings. Eventually, the relatively unstrained conformation **3c** is obtained in which the C_4-dimethyl group is no longer confined within the central molecular cavity. The ^{13}C nuclei positioned directly above the arene rings exhibit modest upfield chemical shifts.

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Registry No.—**3**, 66514-08-7; **4**, 66514-09-8.

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Diphenylamino Isocyanate Dimers

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The thermolysis of N,N-disubstituted carbamoyl azides has been extensively investigated by Stolle and his co-workers.[1,2] These authors had shown that *N,N*-diaryl and *N*-alkyl-*N*-aryl carbamoyl azides yield 1-substituted 3-hydroxy-1*H*-indazoles as major products as evidenced by independent synthesis. Occasionally small amounts of by-products

