

The ^1H and ^{13}C nmr Spectra of the "Onium" Salts of Dithiacyclophanes

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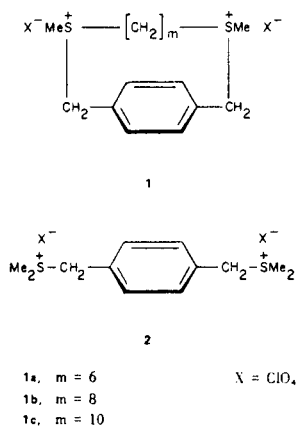
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The ^1H and ^{13}C nmr spectra of three cyclic sulphonium salts of dithiacyclophanes have been recorded and compared with those of the open-chain analogue. The ^1H spectra indicate that methylation of the dithiacyclophanes gives a mixture of conformational isomers with slightly different chemical shifts for the benzylic protons. The ^{13}C spectra indicate that the smaller rings adopt an unsymmetrical conformation with respect to the aromatic ring but that in the larger ring studied, the aromatic carbon atoms are magnetically equivalent. The relevance of these results to the reactivity of the aromatic ring is discussed.

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In the course of our work on the reactivity of bridged aromatic systems deactivated by positive poles (2), we have recently synthesized several cyclic salts derived from dithiacyclophanes having different ring sizes (3). The present study reports certain aspects of the ^1H and ^{13}C nmr spectra of some of these salts with special reference to the flexibility of the methylene chain and its relationship to the reactivity of the aromatic ring.



The ^1H nmr spectra (60 MHz) of the bridged ions **1a-c** produced by methylation of the corresponding dithiacyclophanes and of the open chain analogue **2** are shown in Fig. 1. The results for the bridged ions **1b** and **1c** are as expected: in particular the diastereotopic benzylic protons give the expected A - B type quartet ($J = 12$ Hz). However, the spectrum of the bridged ion **1a** gives a double quartet for these protons and there is a partial splitting of the peak for the methyl groups at 3.15 δ . Moreover, the two quartets and the two components of the methyl peaks are of unequal intensity.

Our interpretation of this is that methylation of the corresponding dithiacyclophane, gives a mixture of two conformational isomers of the ion **1a**, with methyl groups and methylenic chains in different environments. According to the statement that cyclic sulphonium salts possess a great threshold pyramidal stability of the inversion centers (4), in the most strained rings inversion at sulphur would be expected to be slow (5) at room temperature. The partial separation of the two isomers for **1a** has been in fact achieved by fractional crystallisation with acetone (see experimental) from the original mixture.

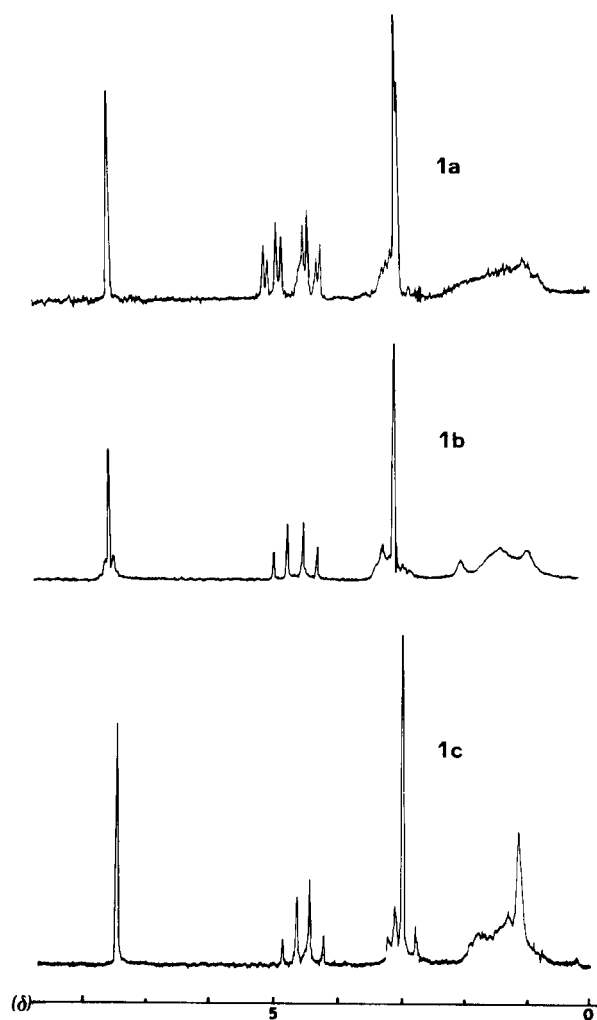


Figure 1. 60 MHz ^1H nmr spectra of **1a**, -**c** compounds in trifluoroacetic acid solution. TMS was used as the internal standard.

In principle methylation on the corresponding dithia-cyclophanes to give the cyclic salts **1b** and **1c** should also yield a mixture of conformational isomers for each salt. The absence of any evidence for such a mixture in the nmr spectra at 60 MHz could arise either because the reaction yields a preponderance of one isomer or because the two isomers have very similar nmr spectra (6). From the spectra of **1a** and **1b** it appears that the differences between the ^1H nmr spectra of the isomers decrease with an increase in the length of the methylene bridge probably because of the corresponding increase in the flexibility of the system. It is reasonable, therefore, that the two isomers of the ion **1c** should have very similar spectra.

More direct evidence on the effect of the flexibility of the methylene bridge is provided by the ^{13}C nmr spectra and these are shown in Fig. 2. The signals for the methyl

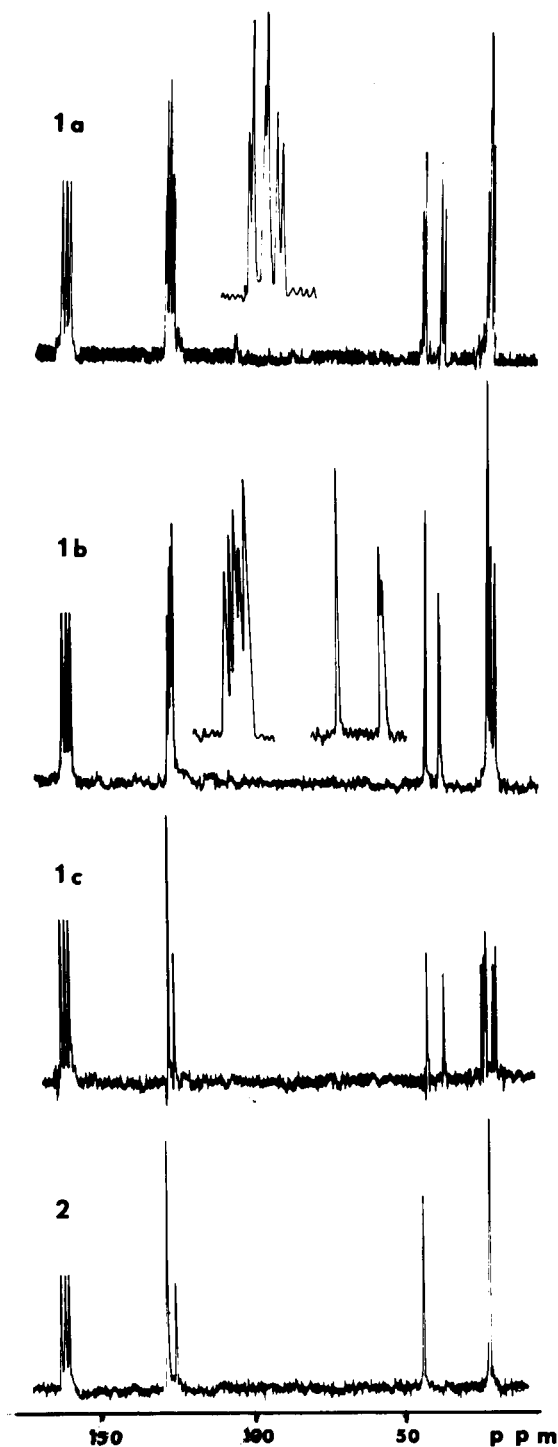
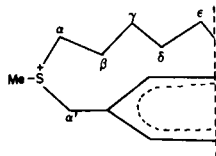


Figure 2. 25.15 MHz ^{13}C nmr spectra of **1a**, -**c** and **2** compounds in d_2 -formic acid solution. Low-field triplets are due to deuteroformic acid.

groups and for the aromatic carbon atoms are assignable from undecoupled spectra; inner methylenes are easily

Table

^{13}C Carbon Nmr Chemical Shifts (ppm to TMS) for Sulphonium Perchlorates **1a-c** and **2** in d_2 -Formic Acid at Probe Temperature



Compound	$\delta_{\text{C}_{\text{Ar}_x}}$ (a)	$\delta_{\text{C}_{\text{Ar}}}$	$\delta_{\text{C}_{\alpha'}}$	$\delta_{\text{C}_{\alpha}}$	$\delta_{\text{C}_{\beta}}$	$\delta_{\text{C}_{\gamma}}$	$\delta_{\text{C}_{\delta}}$	$\delta_{\text{C}_{\epsilon}}$	$\delta_{\text{C}_{\text{S-Me}}}$
2	129.9	132.7	47.2						24.7
1c	130.6	132.6	46.3	40.6	27.7	(26.3	26.3	23.0) (b)	23.9
		133.3							
1b	131.2	132.8	47.7	42.9	26.5	25.6	24.1		25.3
		132.2		42.6					
		132.0							
		133.9							
1a	131.9	133.6	48.5	42.2	26.6	24.5			25.6
		132.5							
	131.5		47.7	41.4	25.8	25.5			25.5
		132.4							

(a) Substituted aromatic carbon. (b) These assignments may be interchanged.

recognisable from their relative intensities and chemical shifts but in **1c** the assignment of the signals of the central methylene groups cannot be made with certainty. The ^{13}C chemical shifts are collected in the Table.

As before, the simplest spectrum of the bridged ions is given by that with the largest ring **1c** and the chemical shifts in this spectrum are very similar to the corresponding shifts in the spectrum of open-chain ion **2**. Both spectra have one line for the substituted aromatic atoms and for the unsubstituted aromatic carbon atoms. In contrast, the spectrum of the ion **1b** shows four lines for the unsubstituted aromatic carbon atoms. This result suggests, therefore, that the methylene chain adopts an unsymmetrical conformation with reference to the aromatic carbon atoms and that this is sufficient to make them magnetically non-equivalent. From the symmetry of the system, there must be four equivalent unsymmetrical conformations of any given type such that equilibrium between them would cause the unsubstituted aromatic carbon atoms to become magnetically equivalent on a time-averaged basis. Since this equivalence is not observed the results also imply that the conversion of one unsymmetrical conformation to another equivalent unsymmetrical conformation is slow on the nmr time-scale and the same appears to be true for the ion **1a**.

On this interpretation, the single line for the unsubstituted aromatic carbon atoms in the ion with the largest ring **1c** arises because of rapid equilibration between the unsymmetrical conformations.

One implication of the above work on the ^1H nmr spectra is that the kinetic studies of nitration for **1a** were carried out (2) on mixtures of conformational isomers although this was not recognized at that time. Fortunately, there is no reason to believe that these isomers should differ significantly in their reactivity to nitronium ions and so the observed rate coefficient should apply to both. Another implication, deriving from the ^{13}C nmr spectra is that the largest ring being also the most flexible, should adapt itself most easily to the conformation giving the most solvated and hence most stable transition state. This may be responsible in part for the greater reactivity of this system. Finally, with $m = 10$, the similarity of the ^{13}C nmr spectra of the bridged ion **1c** to that of the open-chain ion **2**, suggest that no significant strain is introduced by the bridge, likewise in smaller rings **1a** and **1b** where the negligible variations of the ^{13}C resonances (Table) and the literature data for cyclophanes (7) lead to the same conclusion. The strain is not, therefore, the cause of the lower reactivity of the bridged relative to the open chain ions in accord with the

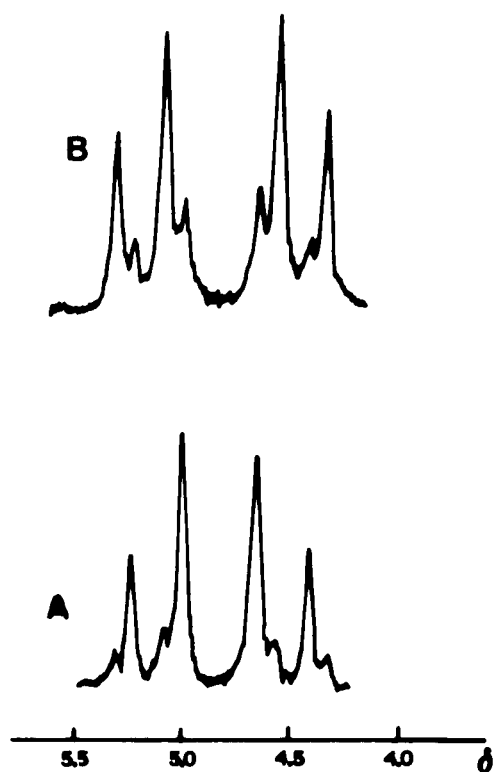


Figure 3. Benzylic protons 60 MHz ^1H nmr spectra of isomers A and B in trifluoroacetic acid solution; ppm to TMS as internal standard.

conclusions reached on the basis of the kinetic results.

EXPERIMENTAL

^1H nmr spectra were recorded with a Jeol C-60 HL spectrometer operating at 60 MHz. ^{13}C nmr spectra were obtained at natural abundance with a Jeol PS/PFT 100-JE C 6 spectrometer at 25.15 MHz, operating in the pulse Fourier mode. No more than 256 transients were found necessary for a suitable S/N ratio

despite the poor solubility of the components. Pulse was in order of 7 μ seconds, ($\theta = 35^\circ$) with a repetition time of ca. 2 seconds for avoiding the effects due to long relaxation times. Spectra were determined in d_2 -formic acid for preventing overlapping of the compounds resonances with those of the solvent. Probe temperature was ca. 30° .

Compounds **1a-c** and **2** were obtained as described previously (3). The separation of the two isomers was achieved by fractional crystallisation from acetone: the isomer mixture of **1a** (1.0 g., 2.08 mmoles), was dissolved in ca. 600 ml. of AnalaR grade acetone and warmed at 40° under stirring for 30 minutes. The clear solution was left at room temperature and when the original volume was concentrated to ca. 50 ml. by spontaneous evaporation, a crystalline product (0.35 g., 0.73 mmole) was recovered whose ^1H nmr spectrum (A in Fig. 3) appeared consistent with an 85% pure isomeric species. Evaporation of the residual solvent afforded (0.55 g., 1.14 mmoles) of a solid material which from the ^1H nmr spectrum (B in Fig. 3) was identified as a mixture enriched in the second conformational isomer. The elemental analyses of both A and B isomers were perfectly consistent with that of **1a**.

REFERENCES AND NOTES

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- (5) In d_6 -dimethylsulphoxide as solvent, the ^1H nmr spectrum of **1a** gives evidence of an approach to conformational equilibrium when the temperature is raised to 90° . However, the incipient cleavage of the salt after a few minutes prevents a detailed study of the temperature effects in this molecule.
- (6) At 270 MHz, the ^1H nmr spectrum of **1b**, again shows a small amount (less than 10%) of a second isomer but the corresponding spectrum for the ion **1c** is consistent with the presence of only one species.
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