CONFORMATIONAL EFFECTS OBSERVED IN AN N.M.R. STUDY

OF $\angle 7\angle$(2.6)DITHIAMETACYCLOPHANE[1]

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The recent report by Vogtle[2] on the synthesis and a temperature-dependent n.m.r. study of $\angle 8\angle$(2.7)dithiametacyclophane prompts us to report our results on the analogous, smaller-ring compound, $\angle 7\angle$(2.6)-dithiametacyclophane (I).

Originally, I was obtained, quite unexpectedly, in 18% yield by adding m-xylylene dibromide to a solution of the bis-dithiane III[3] and n-butyl-lithium in tetrahydrofuran. Although the mechanism for the formation of I in this reaction is not clear, its structure was confirmed by independent syn-thesis through the reaction of m-xylylene dibromide with the dianion of propane-1,3-dithiol. The latter reaction gave I in 43% yield, together with the expected dimer II, formed in 10% yield. Aside from its independent synthesis, the structure of the metacyclophane I[a] (m.p. 105-106°) was indi-cated by its n.m.r. spectrum (in CD_2Cl_2 at room temperature): a 1H singlet
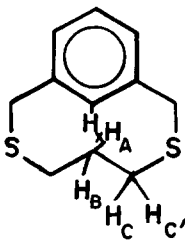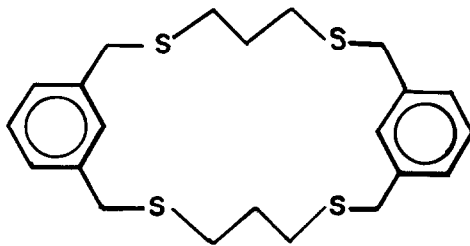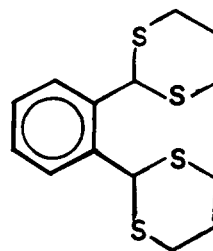
I   II   III

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[a] All new compounds showed satisfactory elemental analyses.

at τ 2.34 (H_X), a 3H multiplet at τ 2.6-3.0 (aromatic protons), a 4H singlet at τ 6.17 (benzylic protons), a 4H triplet at τ 6.41 (J=7.5Hz; $H_{C,C'}$, and a 2H quintuplet at τ 9.55 (J=7.5Hz; $H_{A,B}$), as well as by the presence of a strong parent ion (m/e=210) in the mass spectrum of I.
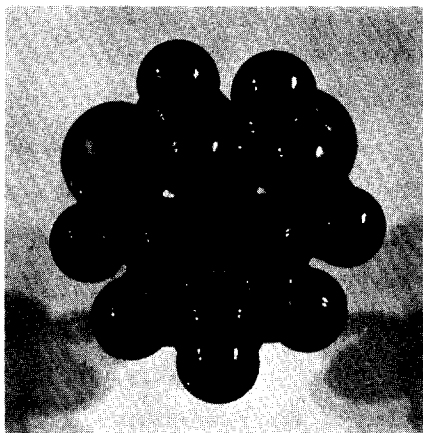

Fig. 1. - A Fisher-Hirschfelder-Taylor model of one possible conformation for $\underline{/7\_/}$(2.6)dithiametacyclophane (I).

On examination of a model of I (Figure 1) it can be seen that in one extreme conformation, the proton H_A is pushed directly into the cavity of the π-cloud of the benzene ring. The n.m.r. spectrum of I (Figure 2) indicates that at room temperature the bridging atoms invert back and forth and give an "average" position for all of the protons. As the sample is cooled, the quintuplet for the protons H_A and H_B at first collapses and then reappears as two peaks at τ 8.29 and τ 10.21, which would be consistent with some such "frozen" conformation as shown in Figure 1. From the difference in chemical shift of H_A and H_B at -95°C ($\Delta\upsilon_{AB}$=196Hz) and the temperature of collapse T_c= -50°C), the energy of the barrier to change this conformation is calculated[5] as $\Delta G^{\pm}$=10.2 kcal/mole. Further cooling appears to lead to yet a
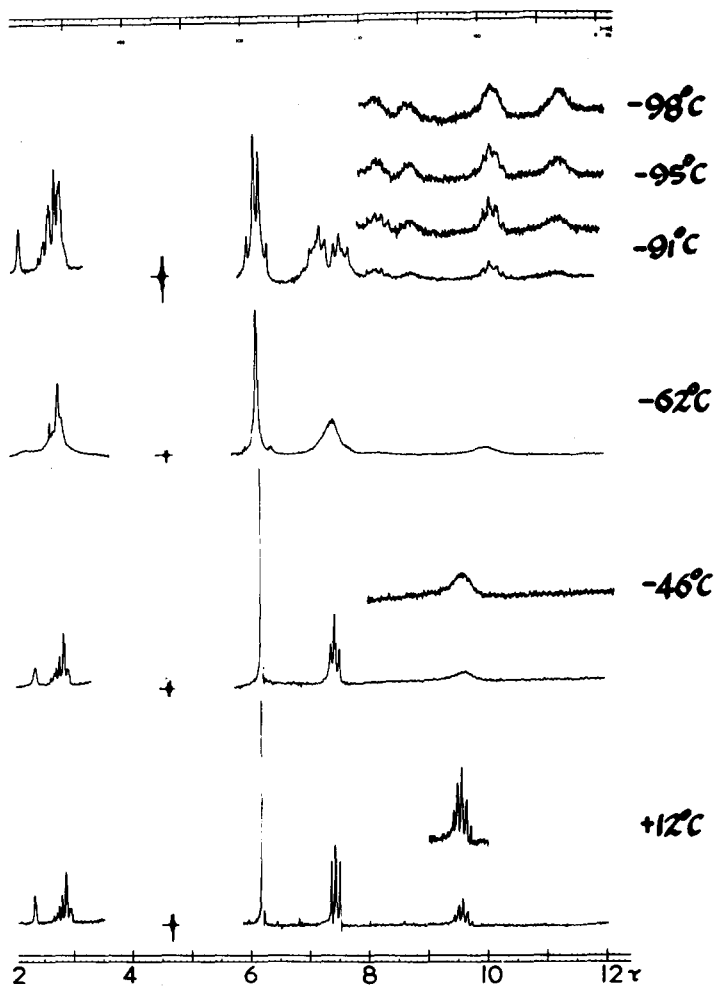
Fig. 2. - N.M.R. spectra of ∠7_7(2.6)dithiametacyclophane (I) in methylene chloride, showing particularly the temperature dependence of the signals for the H_A and H_B protons. Spectra were measured using a Varian HA-100 MHz spectrometer.

different conformation for which the barrier to inversion is $\Delta G^{\pm}$=8.7 kcal/mole (Δv_{AB}=254Hz; T_c= -80°C). The higher field signal of H_A at τ 11.36 in this conformation would suggest that this proton is pushed further into the cavity of the π-clouds than in the previous case. The situation is further complicated by the fact that the ring proton H_X, the benzylic protons and the methylene protons $H_{C,C'}$ all go through similar processes, and hence the preferred conformation at low temperature cannot easily be specified. When the proton H_X is replaced by a bulkier F atom, the molecule does then appear to exist in a single conformation until 180°.[2]

The larger ring compound II[a] (m.p. 123-124°; m/e=420) in contrast shows a normal n.m.r. spectrum (an 8H singlet at τ 2.81 (aromatic protons), an 8H singlet at τ 6.37 (benzylic protons), an 8H triplet at τ 7.65 (J=7Hz; $-S-CH_2-$) and a 4H quintuplet at τ 8.40 (J=7Hz; $-CH_2-$)). The difference in chemical shift between the corresponding methylene protons of II and H_A in I is (at -95°C) 3.0 p.p.m. This represents the largest chemical shift obtained in a metacyclophane in which protons experience a shielding effect due to the proximity of a nearby benzene ring,[4,6] and reflects the abnormal properties shown by a molecule containing a constrained 10-membered ring.[7]

REFERENCES

1. We express our thanks to the National Science Foundation for their support of this investigation.

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