N.m.r. Studies of Rate Processes and Conformations. Conformational Rate Processes in Eight-membered Heterocycles*

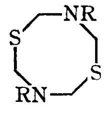
By J. M. LEHN and F. G. RIDDELL

(*Institut de Chimie, Esplanade, Strasbourg; Laboratoire associé au C.N.R.S.*)

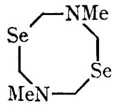
THE introduction of symmetrically placed heteroatoms into a ring system simplifies the proton resonance spectrum and often has the further advantage of raising the barriers to ring inversion easing low-temperature kinetic studies.[1]

We have examined the n.m.r. spectra of compounds (I) and (II) at varying temperatures. The sulphur-containing compounds were prepared according to the literature.[2] Compound (II) was obtained similarly using H_2Se. Satisfactory analytical data were obtained for (Ic) (m.p. 95°). Compound (II) (m.p. 136—138°, sealed tube) was identified by its mass and n.m.r. spectra.

At 30° the spectra of these compounds display a broad singlet for the methylene protons and the expected patterns for the nitrogen substituents. On raising the temperature the ring proton signal sharpens and on lowering the temperature it splits into an AB quartet (Figure 1),† the other signals remaining unchanged.



(Ia: R=Me)
(Ib: R=Et)
(Ic: R=Pr^i)
(Id: R=Ph)



(II)

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* Previous Paper in this series, see J. E. Anderson and J. M. Lehn, *Bull. Soc. chim. France*, 1966, 2402.

† The A and B parts of the AB spectra have equal areas. In (Ib), (Ic), and (Id), they have equal height. In the *N*-methyl compounds (Ia) and (II) the high-field doublet is broadened, presumably due to long range coupling of one of the methylene protons with the methyl group.

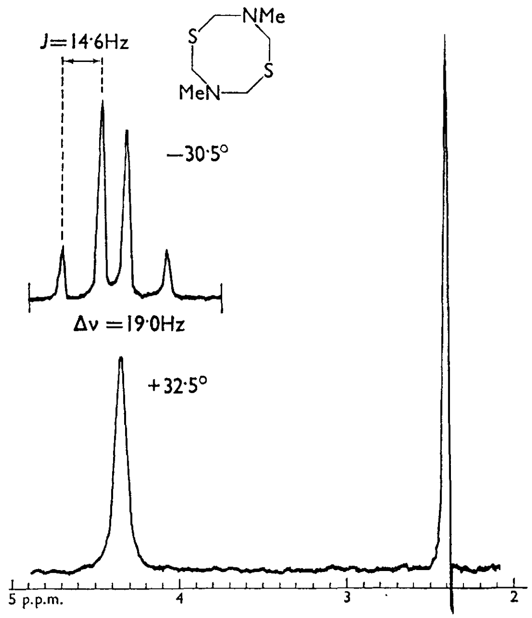
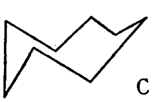


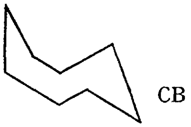
FIGURE 1

Ring methylene signal in the spectrum of compound (Ia) *at different temperatures* (internal reference: Me_4Si).

The coalescence temperature (T_C), the chemical shift difference (Δν), and the coupling constants (J) are listed in the Table. From these values the free energies of activation at the coalescence temperatures ΔG^*_C may be calculated using the Eyring rate equation and the exchange rate at the coalescence (k_C)[3,‡]. The ΔG^*_C values found for the present systems are much higher than the value found by Anet and Hartman[4] for deuterated cyclo-octane (8·1 kcal./mole).

The present results require the existence at low temperature of two magnetically distinct families of protons, each family containing one proton from every ring methylene group. This requirement may be interpreted in terms of those conformations calculated by Hendrickson[5] and by Wiberg[6] to be of lowest energy in the case of cyclo-octane: the crown C and the chair–boat forms CB. For the compounds (I) and (II) there are three possible chair–boat forms (two of C_s and one of C_1 symmetry) which by rapid interconversion (*via* pseudorotation)[7] lead to the required two families of protons. Interconversion of the chair–boat and the crown forms (which may stretch or pseudorotate) by wagging of a methylene group or a hetero-atom does not affect the magnetic integrity of each family. Rapid averaging by these processes at low temperatures would lead to two magnetically distinct families of protons; the slow process interconverting these families becoming the observed rate process [see also compound (III) in ref. 7]. Such a "mixture" of conformations has recently been suggested for cyclo-octane itself.[7]





Another, simpler explanation would be the existence of a large preponderance of only *one* of these low-energy forms at low temperatures, probably the crown form which stretches and pseudorotates rapidly. For compound (Ia) neither Δν nor J of the AB quartet alters (within experimental error) between −30 and −65°. This would be consistent with the existence of only one

TABLE

Spectral data for ring protons in compounds (I) *and* (II)**

Compound	Solvent	Chemical shift difference Δν (at T°) in Hz	Coupling constant J in H_z (at T°)	(T°)	Coalescence temperature T_C°	Activation energy ΔG^*_C kcal./mole at T_C
(Ia)	$CDCl_3$	19·0	14·6	−30	25	14·8 ± 0·2
(Ib)	$CDCl_3$	29·9	14·6	−21	24	14·6 ± 0·2
(Ic)	$CDCl_3$	45·6	14·6	−30	17	14·1 ± 0·2
(Id)	C_5D_5N	30·8	15·2	−30	0	13·4 ± 0·2
(II)	$CDCl_3$	14·5	12·4	−23	15	14·4 ± 0·2
Polydeuterocyclo-octane	C_2H_3Cl	18·8	—	−135	−111	8·1 (ref. 4)

** The spectra were measured on a Varian A-60 Spectrometer.

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‡ A transmission coefficient of one has been used since the shape of the potential curve is unknown.

stable conformation (*e.g.*, the crown form) and not with an equilibrating mixture (of the three chair–boat forms) unless all the components have nearly equal energies. Octasulphur S_8 and octaselenium Se_8 and $S_4(NH)_4$ exist in the crown form[8] suggesting a possible analogy.‡ Our studies are continuing.¶

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‡ A decision between the alternative explanations put forward may follow from the *X*-ray crystallographic analysis of compounds (Ia) being conducted by Professor R. Weiss of this Institute.

¶ We thank Professor Anet for stimulating discussions at the G.E.C.O. VII meeting (Pont-à-Mousson, September 1966).