Conformation of 1,2,6-Cyclononatriene

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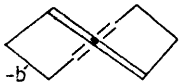
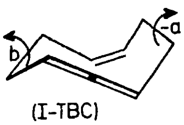
Summary 1,2,6-Cyclononatriene is shown by ^{13}C n.m.r. to exist in an unsymmetrical twist-boat-chair conformation that can undergo a hindered pseudorotation (barrier height of 12·9 kcal mol^{-1}) to achieve a C_2 time-averaged symmetry.

Cyclic medium-ring allenes are strained compounds whose detailed structures are largely unknown, despite some recent spectroscopic studies.[1] We now report that the ^{13}C n.m.r. spectrum of the title compound (I)[2] exhibits a dynamic n.m.r. effect near room temperature, as outlined in the Table. The presence of nine chemical shifts at −30 °C and below is best explained by a single unsymmetrical conformation for (I). Molecular models indicate that (I) can exist in a twist-boat-chair[3] (I-TBC) that is fairly rigid. A change in the sign of the torsional angle −a (from −a to a′) gives an axial-symmetrical conformation (I-TCC) (twist chair-chair[3]). On the other hand, a change of the torsional angle b to −b′ gives a different axial-symmetrical conformation, (I-TCB) (twist-chair-boat[3]). These three conformations appear to be the only low-energy minima available to (I). Since the n.m.r. data exclude the symmetrical conformations, (I) must exist virtually exclusively in the twist-boat-chair conformation, (I-TBC).



(I-TCB)



(I-TBC)

(I -TCC)

The pseudorotation that is responsible for the dynamic n.m.r. effect in (I) is a highly hindered process with a free energy barrier of about 13 kcal mol^{-1}. An examination of molecular models reveals that considerably more internal angle strain is involved in the change from (I-TBC) to (I-TCB) compared with the change from (I-TBC) to (I-TCC). We thus favour (I-TCC) as an intermediate in the lowest-energy pseudorotation process that gives rise to a C_2 time-averaged symmetry. We intend to carry our strain-energy calculations on (I) and related compounds in order to verify the qualitative deductions made above.

Table ^{13}C chemical shifts in 1,2,6-cyclononatriene

Temp/°C	C-1,3	C-2	C-4,9 C-5,8	C-6,7
+50	90·3	205·2	27·1, 28·9	130·4
−30	87·3, 93·4[b]	205·2	24·7, 29·1; 26·7, 30·9	129·5, 131·2

[a] Measured at 63·1 MHz in $CDCl_3$ solution with respect to Me_4Si. [b] Coalescence temperature is 15 ± 3 °C; $\Delta G^{\ddagger} = 12{\cdot}9 \pm 0{\cdot}2$ kcal mol^{-1}.

The present data strongly indicate that (I) is conformationally homogeneous near room temperature. This feature makes an electron diffraction study of the structure of (I), which is a volatile liquid, quite attractive and we hope that such a study will be undertaken.

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[1] C. Charrier, D. E. Dorman, and J. D. Roberts, *J. Org. Chem.*, 1973, **38**, 2644; G. C. Joshi, G. Nagendrappa, and D. Devaprabhakara, *Indian J. Chem.*, 1969, **7**, 296.

[2] L. Skatteböl, *Tetrahedron Letters*, 1961, 167.

[3] The names used are derived from the conformational nomenclature of cyclononane, see J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1967, **89**, 7047.