Conformational Isomerization of 4,6,10,11,15,17,21,22,23,24,25,26,27,28-Tetradecamethylpentacyclo-$[16,2,2,1^{3,7},2^{9,12},1^{14,18}]$octacosa-3,5,7,9,11,14,16,18,20,22,23,26-dodecaene

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THE recent determinations[1] of the thermodynamic parameters connected with ring inversions has been partially prompted, *inter alia*, by the possibility of testing the reliability of existing intramolecular potential functions.[2,3] The difference in torsional strain energy between the transition state (half-chair) and the minimum-energy state (chair) accounts for the largest part of the energy barrier in most of the ring inversions studied so far.[2,3]

Here we report the n.m.r. variable-temperature study of the title compound, also known as cyclobis(mesityldimethylenedurene) (DUREM), a ring whose conformational isomerization is largely dominated by interactions between pairs of nonbonded atoms.

The compound was prepared as described in ref. 4. The ^1H n.m.r. spectra of saturated solutions in $CDCl_3$ and in C_2HCl_5 were recorded on a Varian HA-100 spectrometer equipped with a variable temperature accessory.

The low-temperature spectra are composed of six sharp lines; at $-37°$ the chemical shifts, in p.p.m., referred to $MeSi_4$, are: $\delta_A = 0{\cdot}790$; $\delta_B = 1{\cdot}454, 2{\cdot}367$; $\delta_C = 2{\cdot}430$; $\delta_D = 4{\cdot}005$; $\delta_E = 6{\cdot}790$. The line-shape of peaks B is temperature dependent and can be used to extract the chemical exchange rates.

The rates were determined by means of a complete line-shape analysis method,[5,1d] treating the eight duryl methyls as an AB system without coupling. The activation parameters, derived from the Arrhenius plot of the measured rates, are reported in the Table.

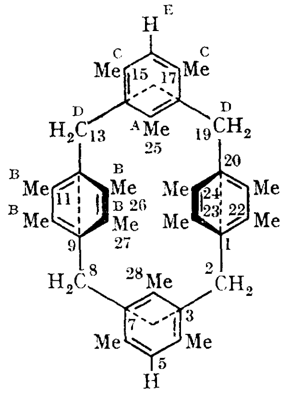
On the basis of the spectrum at low temperature it is possible to select two different symmetrical conformations for the minimum-energy state, a "chair-like" and a "boat-like" form. These terms refer to the idealized hexagon which is outlined by a dotted line in (I). Both forms account, at least qualitatively, for the chemical-shift difference between the two different kinds of methyl group)

Activation parameters[a] *determined from the temperature dependence of the conformational isomerization rate of* DUREM

Solvent	T_c (°K)	A (sec.$^{-1}$)	E_a (kcal./mole)	H‡ (kcal./mole)	G‡ (kcal./mole)	S‡ (e.u.)
$CDCl_3$	301	$1{\cdot}7 \times 10^{11}$	$12{\cdot}3 \pm 0{\cdot}2$	$11{\cdot}7 \pm 0{\cdot}2$	$14{\cdot}6 \pm 0{\cdot}2$	-9
C_2HCl_5 [b]	320	$3{\cdot}0 \times 10^{11}$	$13{\cdot}3 \pm 0{\cdot}2$	$12{\cdot}7 \pm 0{\cdot}2$	$15{\cdot}3 \pm 0{\cdot}2$	-8

[a] The quantity T_c is the temperature at which the B methyl proton resonance coalesces to a single line; A and E_a are the Arrhenius frequency factor and activation energy.

[b] Pentachloroethane.



(I)

B existing at low temperature. In fact in both models four duryl methyls are under the influence of diamagnetic shielding arising from the mesityl rings while the other four are under the influence of the paramagnetic shielding of the same rings.

A preliminary calculation of the internal conformational energy† indicates that the boat-like form is much more stable than the chair-like form.

A more detailed account of the determination of the activation parameters in $CDCl_3$ and in C_2HCl_5, together with a more refined conformational analysis will be reported later.

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† The criteria on which this calculation was based are very similar to those described in ref. 2 and 3.

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