Racemization of two Hexaheterohelicenes

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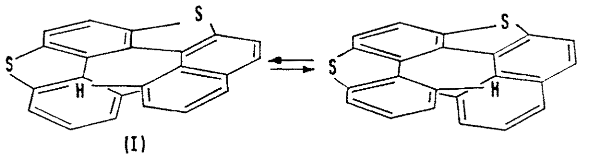
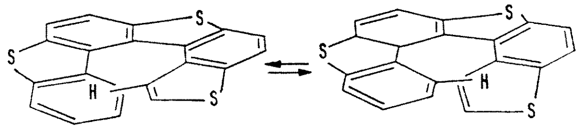
Summary Activation parameters for the racemisation of the hexaheterohelicenes (I) and (II) are reported.

WE described[1] the preparation and resolution of the hexaheterohelicene benzo[*d*]naphtho[1,2-*d*′]benzo[1,2-*b* : 4,3-*b*′]-dithiophen (I). In addition we have now synthesized a new helicene, thieno[3,2-*e*]benzo[1,2-*b* : 4,3-*b*′]bis[1]benzothiophen (II) in an analogous manner. Details of the synthesis will be publisned elsewhere. As in the case of (I), the compound (II) could be obtained as optically active crystals by slow crystallization from benzene. The largest rotation observed was $[\alpha]^{20}_{436} + 3640°$. Both helicenes racemized in solution at room temperature.[†] It seemed of interest to study the racemization in more detail. Single crystals of (I) or (II) were dissolved in 6 ml. chloroform. The optical rotation of the solution was followed in a thermostatted cell (10 cm. path length; Zeiss polarimeter). From the first-order plots the racemization rate constant (2 *k*), the reaction rate constant (*k*), and the half life ($t\frac{1}{2}$) were determined. The results are shown in Tables 1 and 2. From the usual Arrhenius plots the activation energies were derived; the other activation parameters, shown in Table 3, were calculated from the formulae:[2]



(I)



(II)

TABLE 1. *Racemization rates of* (I).

T (°K)	$t_{\frac{1}{2}}$ (min.)	$2k$ (min.$^{-1}$) $\times 10^4$	k (sec.$^{-1}$) $\times 10^6$
313·0	31·5	220	184
303·0	128	54·2	45·2
298·5	241	28·6	24·0
289·2	930	7·5	6·2

TABLE 2. *Racemization rates of* (II)

T (°K)	$t_{\frac{1}{2}}$ (min.)	$2k$ (min.$^{-1}$) $\times 10^4$	k (sec.$^{-1}$) $\times 01^6$
298·4	13·0	533	444
293·1	25·0	277	231
288·0	51·6	134	112
283·3	95	72	60

$$\Delta H^{\ddagger} = E_a - \boldsymbol{R}T$$

$$\Delta S^{\ddagger} = (E_a/T) + 4{\cdot}58 \log (k/T) - 49{\cdot}20$$

$$\Delta G^{\ddagger} = 47{\cdot}22\, T - 4{\cdot}58\, T \log k/T.$$

TABLE 3. *Activation parameters of the racemization of* (I) *and* (II)

	E_a (kcal./mole)	$\Delta H^{\ddagger}$ (kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}$ (kcal./mole)
(I)	26·0 (±0·6)	25·4 (±0·6)	5·5 (±2)	23·7 (±0·1)
(II)	22·6 (±0·6)	22·0 (±0·6)	0 (±2)	22·0 (±0·1)

The compound (II) racemizes approximately 18 times faster than (I), equivalent to a difference of only 1·7 kcal./mole in $\Delta G^{\ddagger}$. Dreiding models or careful line drawings reveal that in the imaginary planar and undistorted molecules the distance between the nearest carbon atoms in the terminal rings would have to be 1·12 Å for compound (I),[3] 1·23 Å for compound(II), whereas it would be 1·40 Å for pentahelicene (dibenzo[*c,g*]phenanthrene). As derivatives of the latter compound have too low an optical stability for resolution,[4] it seems possible to predict with this simple model the order of optical stability of helicenes.

Kinetic data of comparable compounds are scarce, the racemization proceeding either too slowly or too quickly.[5] The racemization of some overcrowded hydrocarbons is mentioned without details,[5-7] an exception being 1-fluoro-12-methylbenzo[*c*]phenanthrene,[8] for which Newman[8] reported $E_a = 31{\cdot}3$ kcal./mole and $\Delta S^{\ddagger} = -2{\cdot}8$ e.u.

[†] It can easily be deduced from bond length and bond angle data that in the helicene series the optical stability decreases as the number of thiophen rings relative to benzene rings increases. A benzene ring bends the molecule over 60°, a thiophen ring over 45°. Eight thiophen rings condensed in the right way would give exactly one turn of a helix.

Biphenyl-type compounds[9] and some bithienyls have been studied.[10] As a rule, the entropy of activation for the racemization of these compounds has a rather large negative value, making an important contribution to the optical stability. We do not, however, believe that the small or positive entropy effects found by us necessarily implies that a different mechanism of racemization is operative. It seems more likely that the *ortho*-substituents present in the optically active biphenyls are severely restricted in rotational and vibrational motions in the transition state, resulting in a negative entropy of activation. Such an effect can hardly be expected in our case, where only hydrogen atoms are involved.

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[3] This distance is actually 2·9 Å as is shown by *X*-ray investigation. G. Stulen and G. J. Visser, following communication.
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[5] M. S. Newman and R. M. Wise, *J. Amer. Chem. Soc.*, 1956, **78**, 450.
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[8] M. S. Newman, R. G. Mentzer, and G. Slomp, *J. Amer. Chem. Soc.*, 1963, **85**, 4018.
[9] See, *e.g.*, D. M. Hall and M. M. Harris, *J. Chem. Soc.*, 1960, 490.
[10] S. Gronowitz and J. E. Skramstad, *Arkiv Kemi*, 1968, **28**, 115.