Racemisation Parameters for 8′-Methyl-1,1′-binaphthyl-8-carboxylic Acid. Negligible Steric Retardation by the Carboxylic Acid Group

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THE Arrhenius parameters and transition-state theory functions for racemisation in *NN*-dimethylformamide solution of optically active 1,1′-binaphthyl, 1,1′-binaphthyl-8-carboxylic acid, and 1,1′-binaphthyl-8,8′-dicarboxylic acid are remarkably alike.[1]

The racemisation of optically active 8-methyl-1,1′-binaphthyl has recently been studied.[2] We have now resolved 8′-methyl-1,1′-binaphthyl-8-carboxylic acid[3] through its brucine salt and observed its racemisation in *NN*-dimethylformamide solution at eight temperatures between 70° and 105°. The racemisation parameters calculated from the velocity constants are almost identical with those for the 8-methyl-1,1′-binaphthyl:—

	E_{rac} (k.cal. mole^{-1})	$\log_{10}A$	$\Delta F^{\ddagger}$ (k.cal. mole^{-1})	$\Delta H^{\ddagger}$ (k.cal. mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
1,1′-Binaphthyl[1]	22·5	12·1	23·5	21·9	−5·2
1,1′-Binaphthyl-8-carboxylic acid[1]	22·4	12·0	23·5	21·8	−5·5
1,1′-Binaphthyl-8,8′-dicarboxylic acid[1]	22·1	11·3	24·4	21·5	−9·1
8-Methyl-1,1′-binaphthyl[2]	25·3	11·7	27·2	24·6	−7·3
8′-Methyl-1,1′-binaphthyl-8-carboxylic acid	25·3	11·6	27·4	24·6	−7·7

The 8-carboxylic acid group appears to make no significant measurable steric contribution to the energy barrier to racemisation. One possible explanation is that it is equally effective in its steric influence on the energy of the ground state and of the transition state; this is not the case for the methyl group.[2]

Proof of the situation of the methyl group and the carboxylic acid group in the 8- and 8′-positions rests on (a) the synthesis from 1,1′-binaphthyl-8,8′-dicarboxylic acid, (b) ready decarboxylation to 8-methyl-1,1′-binaphthyl, and (c) formation of a mixed anhydride (with acetic anhydride) accompanied by ring closure to form 13-methyl-7-oxodibenz[*a*,*kl*]anthracene on long boiling.

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[1] A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 1963, 2365.
[2] A. S. Cooke and M. M. Harris, submitted for publication.
[3] The (±)-acid was prepared in 1965 by A. S. Cooke and M. M. Harris (unpublished).