83. *Interactions between Non-bonded Atoms, and the Structure of cis-Decalin.*

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An attempt has been made to calculate the energy differences between the staggered and the opposed form of ethane, between the boat and the chair form of *cyclo*hexane, and between *cis*- and *trans*-decalin. In each case the results are in qualitative agreement with experiment. The calculations support the formulation (III) for *cis*-decalin as compared with the Sachse–Mohr structure (II).

THE important part that the phenomena of steric hindrance play in chemistry is well appreciated, and any method that promises its evaluation in a quantitative or even semi-quantitative way is well worth attention. A semi-quantitative attempt at the calculation of such effects has been given by Dostrovsky, Hughes, and Ingold (*J.*, 1946, 173; compare A. G. Evans, *Trans. Faraday Soc.*, 1946, **42**, 719 : Westheimer and Mayer, *J. Chem. Physics*, 1946, **14**, 733) for the symmetrical S_N2 mechanism of alkyl halide substitution. The following treatment is based on a simple adaptation of their ideas.

For substances not containing dipoles the interaction energy, I.E., between non-bonded atoms may be expressed by equations of the types

$$\text{I.E.} = \Sigma\psi_{ij} = \Sigma\left(\frac{-a}{r_{ij}^6} + be^{-\mu r_{ij}}\right) \quad \cdots \quad \cdots \quad \text{(i)}$$

$$\text{I.E.} = \Sigma\psi_{ij} = \Sigma\left(\frac{-a}{r_{ij}^6} + \frac{b'}{r_{ij}^{12}}\right) \quad \cdots \quad \cdots \quad \text{(ii)}$$

in which ψ_{ij} is the interaction energy between a pair of non-bonded atoms, r_{ij} is the distance apart of the nuclei of the pair, and a, b, μ, and b' are constants. The first term, $-a/r_{ij}^6$, represents the dispersion energy, of which the constant a can be calculated from London's formula (*Trans. Faraday Soc.*, 1937, **33**, 8), whilst the second represents the repulsion energy resulting from the interpenetration of electronic sheaths. Unfortunately, there is considerable uncertainty as to the precise evaluation of this second term. If the repulsion expression of equation (i), the form of which is in agreement with quantum-mechanical considerations, be employed, then μ, for saturated hydrocarbons, may be set equal to 4·6, this being the same as the corresponding constant of the exponential repulsion term for helium atoms (Slater and Kirkwood, *Physical Rev.*, 1931, **37**, 682). If, however, the repulsion term, as in equation (ii), is assumed to vary as r_{ij}^{-12} as suggested by Hill (*J. Chem. Physics*, 1946, **14**, 465), then b' can be calculated by putting $d\psi_{ij}/dr_{ij} = 0$ when $r_{ij} = r_{0ij}$, the sum of the van der Waals radii of the pair of non-bonded atoms under consideration. The constant b of equation (i) can be obtained in the same way as b' once a value for μ has been assumed.

In order to test the validity of such equations, calculations with saturated hydrocarbons seem particularly attractive, and in some cases there are quantitative checks on the accuracy of the figures obtained. By summing the interaction energy between every possible pair of non-bonded atoms, some attempt at the evaluation of the energy differences, $\Delta\Sigma\psi_{ij}$, between the staggered and the opposed form of ethane, between the boat and the chair form of *cyclo*hexane, and between *cis*- and *trans*-decalin has been made. The results are set out in the table. In the case of *cis*- and *trans*-decalins it is necessary to consider the novel form of the *cis*-compound recently proposed by Bastiansen and Hassel (*Nature*, 1946, **157**, 765) on the basis of electron-diffraction measurements. *trans*-Decalin may be represented by the formulæ (I*a*)

(I*a*.)   (I*b*.)   (II.)   (III.)
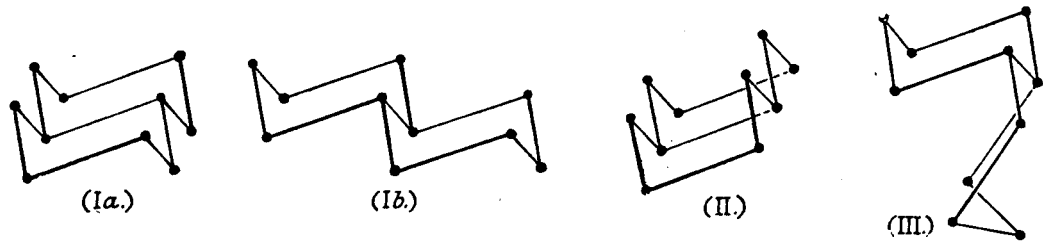
or (I*b*) which are identical, and *cis*-decalin by the Sachse–Mohr formula (II) or by the recently proposed formula (III).

A van der Waals radius of 1·6 A. has been used for carbon but, as there is some uncertainty about this radius for hydrogen, the calculations have been made with both the value 1·2 A., preferred by Pauling (" Nature of the Chemical Bond ", p. 187), and the value 1·3 A. suggested by Mack (*J. Amer. Chem. Soc.*, 1932, **54**, 2141). Certainly a larger van der Waals radius for hydrogen could not be justified. Application of the formula proposed by Dostrovsky, Hughes, and Ingold (*loc. cit.*) for the variation of van der Waals radii has not been made in detail, but such corrections would certainly not alter qualitatively the stability order; indeed, with ethane, the quantitative differences in $\Delta\Sigma\psi_{ij}$ produced thereby are small. In any case the reasons for using this formula are not compelling.

	Differences in non-bonded interaction energy. $\Delta\Sigma\psi_{ij}$ in kcals.				Stability order as shown by $\Delta\Sigma\psi_{ij}$.
	$be - 4\cdot6r_{ij}$ repulsion term.		$b'r_{ij}^{-12}$ repulsion term.		
Substance.	$r_{0HH} = 2\cdot4$ A.	$r_{0HH} = 2\cdot6$ A.	$r_{0HH} = 2\cdot4$ A.	$r_{0HH} = 2\cdot6$ A.	
Ethane	0·09	0·27	0·09	0·39	Staggered > opposed
*cyclo*Hexane	1·31	2·47	2·73	6·85	Chair > boat
trans- and *cis*-Decalin, (I) and (II)	3·39	4·55	5·29	15·51	*trans* > *cis*
trans- and *cis*-Decalin, (I) and (III)	0·52	3·06	3·48	8·23	*trans* > *cis*
cis-Decalin, (II) and (III) ...	2·87	1·49	1·81	7·28	(III) > (II)

A number of interesting points arise from the table of calculated energy differences. First, while the stability order for ethane is qualitatively in agreement with that now generally accepted, the energy differences are all far too small to correspond to the observed energy barrier of about 3 kcals. (compare Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 3191). Since the existence of this high energy barrier has been confirmed by so much evidence, including precision heat-of-combustion data (see, *e.g.*, Spitzer and Huffman, *ibid.*, 1947, **69**, 211; Pitzer, *Science*, 1945, **101**, 672), it must be admitted that the potential functions used here are inadequate for quantitative calculation, at least in the case of ethane. It is very difficult, nevertheless, to see how the repulsion terms of equations (i) and (ii) could be modified in any reasonable manner, whilst retaining a hydrogen van der Waals radius of 1·2—1·3 A., so as to give agreement with experiment. This was doubtless appreciated by Aston *et al.* (*J. Chem. Physics*, 1944, **12**, 336), who showed that the observed energy barriers in organic molecules could be accounted for by an empirical expression for the interaction energy, (iii), containing only a repulsion term. In this expression k is an arbitrarily assigned constant chosen to give agreement with experiment.

$$\text{I.E.} = \Sigma\psi_{ij} = \Sigma\frac{+\,k}{r_{ij}^{6}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

This is very different from any of the previously proposed functions, such as those given by (i) and (ii), which have some theoretical support.

Secondly, the stability order for *cyclo*hexane is in agreement with the view generally held, but the energy differences are much lower than those anticipated on the basis of Aston's equation (iii) (compare Kumler, *J. Amer. Chem. Soc.*, 1945, **67**, 1901) and the known energy barrier in ethane.

Thirdly, the calculations support the claim of Bastiansen and Hassel (*loc. cit.*) that *cis*-decalin is to be represented by (III) rather than (II). By using Aston's empirical function (iii), the greater stability of (III) over (II) would be much enhanced. A direct check with the *trans*- and *cis*-decalins is possible from the observed difference of about 5 kcals. in the heats of combustion, *trans*-decalin being the more stable isomer in agreement with calculation. It will be seen that the use of the $b'r_{ij}^{-12}$ repulsion term and of a van der Waals radius of 1·2 A. for hydrogen gives satisfactory agreement with experiment, though this is not of great significance in view of the interaction energy minimising factors discussed below. It is noteworthy that the interesting $3(\alpha) : 9(\alpha)$-epoxy-compounds, for example $3(\alpha) : 9(\alpha)$-epoxy-Δ^{11}-cholenic acid methyl ester (IV), prepared by Kendall and his collaborators (*J. Biol. Chem.*, 1946, **164**, 569), are most probably to be formulated as derived from a modified form of (III), shown with part of the rest of the steroid molecule in (V), by conversion of ring A of the cholane skeleton into the boat form of *cyclo*hexane. The very small amount of angle strain required for the formation of these epoxy-compounds on the basis of formula (V) is shown in the scale drawing (VI), which represents a plane cut through the steroid molecule to include C_3, C_9, C_{10}, and the oxygen bridge. Formulation of these

compounds from the Sachse–Mohr *cis*-decalin (II) would require an impossible extension of valency bonds or distortion of valency angles.   It is also possible to satisfy steric requirements

(VI.)

Angle strain :

$C_3\widehat{O}C_9 \sim 8°, \; O\widehat{C}_9C_{10} \sim 3°.$

(IV.)

(V.)
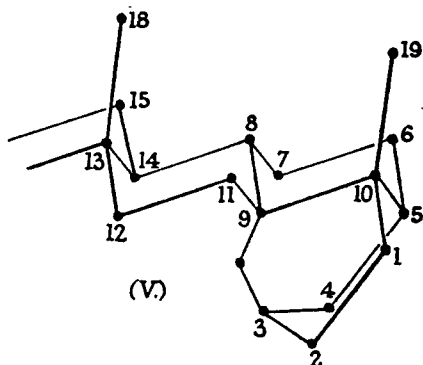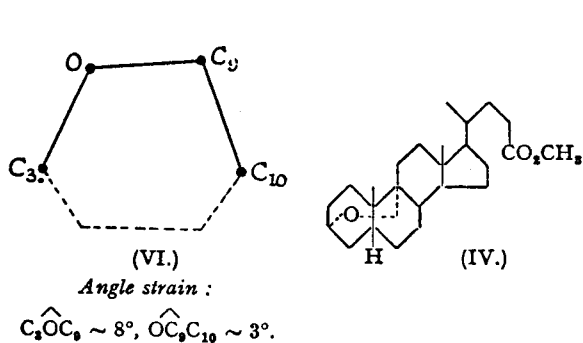
and at the same time to formulate these epoxy-compounds as derived from a two-boat *cis*-decalin not identical with (II) (see Shoppee, *Ann. Reports*, 1946, **43**, 200).   Although this formulation is equally probable geometrically, it is less probable from the energetic view point and so is not illustrated here.   This alternative structure preserves the special peculiarity of (III), namely that the configurations of the valencies about the C_9 and C_{10} atoms (decalin enumeration) are staggered, whereas in the conventional Sache–Mohr *cis*-decalin (II) they are opposed.

It is, of course, appreciated that while the form (III) of *cis*-decalin is more stable than (II) in solution or in the gas phase, this does not necessarily imply that it will be packed more conveniently into a crystal lattice, for in the lattice non-bonded interactions of atoms with those of the neighbouring molecules may play a dominant part.

The calculations on the basis of equations (i) and (ii) have assumed the constancy of covalent bond lengths and of the tetrahedral angle.   Strictly speaking, this is not justified because the extension of valency bonds and especially the flexing of valency angles will lead to a minimising of the calculated energy differences.   Although this would not alter qualitatively the calculated order of stabilities, it would lead to an appreciable quantitative diminution of the values of $\Delta\Sigma\psi_{ij}$.   This is specially so because the calculated energy differences are chiefly dependent on strong repulsive interaction between a few pairs of atoms, for example between the pair of upper hydrogen atoms attached to C_1 and C_4 in the case of the boat form of *cyclo*hexane.   In view, however, of the fact that these considerations cannot account for the failure of the potential functions of equations (i) and (ii) in explaining quantitatively the high energy barrier to rotation in ethane, it would be pointless to extend the calculations in this manner at present.   Indeed, until this energy barrier can be evaluated quantitatively, it would seem that calculations of the type made in this paper must be regarded as having only qualitative significance.

Added February 20th, 1948.   Since this paper was submitted for publication Westheimer (*J. Chem. Physics*, 1947, **15**, 252) has reported the calculation of the activation energy for the racemisation of 2 : 2′-dibromodiphenyl-4 : 4′-dicarboxylic acid, using, in part, a similar approach to the one adopted here.   For the constant μ of the exponential repulsion term in equation (i) above Westheimer selects a value of 6·06.   Both this value and the one, 4·6, employed here are considerably higher than that, 2·9, adopted by Dostrovsky, Hughes, and Ingold (*loc. cit.*).   Indeed, the non-bonded interaction energy equation of the latter authors cannot be applied in the general case because, in the absence of dipolar interaction, it gives attractive potentials at *all* values of *r*.