

### 453. Conformations of the Cyclohexa-1,4-diene Ring System.

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The relative stabilities of various conformations of cyclohexa-1,4-diene, 9,10-dihydroanthracene, and 9,10-dihydro-1,2:5,6-dibenzanthracene (I) have been calculated, account being taken of angle strain and interactions between non-bonded hydrogen atoms. In agreement with experiment, calculations indicated the dihydroanthracene as folded (dihedral angle \*  $\sim 150^\circ$ ), and the dihydrodibenzanthracene as planar. The calculations for cyclohexa-1,4-diene indicate a folded molecule, in approximate agreement with dipole-moment measurements but not with deductions from infrared and Raman spectroscopy.

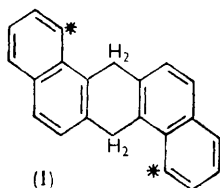
INFORMATION regarding the conformation of the cyclohexa-1,4-diene ring is contradictory. Simple considerations <sup>1</sup> based on minimisation of angle strain within the ring suggest that

\* In this paper "dihedral angle" is used to specify the angle between the planes containing carbon atoms in positions (a) 6,1,2,3 and (b) 6,5,4,3 of the cyclohexa-1,4-diene ring.

<sup>1</sup> Beckett and Mulley, *Chem. and Ind.*, 1955, 146.

the molecule should be folded, with symmetry  $C_{2v}$  and a dihedral angle of about  $141^\circ$ . Measurements<sup>2</sup> have shown that 1,4-dichlorocyclohexa-1,4-diene has a dipole moment of 0.3 D, from which it has been concluded that the ring is folded but flatter than expected for tetrahedral angles at the methylene groups. On the other hand, Raman and infrared spectra of cyclohexa-1,4-diene itself have been interpreted<sup>3</sup> in terms of a structure deviating only slightly from the rigorous  $D_{2h}$  (planar) conformation.

More conclusive evidence should be obtained from crystal-structure analyses, where results are available for two molecules containing the cyclohexa-1,4-diene ring. The structure of 9,10-dihydroanthracene was determined<sup>4</sup> from two-dimensional projections down [010] and [100]. It was folded about the axis through the methylene-carbon atoms, with a dihedral angle of  $145^\circ$ . The measured dipole moment of 0.4 D shows that the molecule is also folded in solution.<sup>5</sup> On the other hand crystallographic data<sup>6,7</sup> show that 9,10-dihydro-1,2:5,6-dibenzanthracene (I)



(space group  $P2_1/a$ ; 2 molecules per unit cell) is centrosymmetric, which eliminates a folded structure. From a chemical point of view the only structure compatible with a molecular centre of symmetry is planar or "essentially planar," and this has been confirmed by Iball and Young<sup>7</sup> using projections down the three principal crystallographic axes. There is thus a well-established experimental difference between the conformations of 9,10-dihydroanthracene and 9,10-dihydro-1,2:5,6-dibenzanthracene.

The present problem is to calculate the conformation of cyclohexa-1,4-diene, and to use similar theoretical considerations to explain the difference between the conformations of the other two compounds.

#### CALCULATION OF MOLECULAR STRAIN ENERGIES

Fischer-Hirschfelder models show that there are two balancing factors: the cyclohexa-1,4-diene ring is strainless only in the folded conformation, and flattening it introduces angle strain; however, flattening the ring changes the distances between non-bonded hydrogen atoms and in particular increases the short distances between the hydrogen atoms marked \* in formula (I) and the *lin*\* hydrogen atoms of the methylene groups. Thus there are qualitative indications that the stable conformations of the cyclohexadiene and dihydroanthracene will be folded, while that of the dihydrodibenzanthracene be approximately planar. Detailed calculations substantiate these.

The interaction energy between non-bonded hydrogen atoms was calculated as follows. The distances between non-bonded hydrogen atoms were calculated for dihedral angles of the central cyclohexa-1,4-diene ring of  $140^\circ$ ,  $150^\circ \dots 180^\circ$ , bond lengths being assumed to be C-C 1.54, C=C 1.34, C-C (aromatic) 1.40, C-H 1.08 Å. All bond angles were assumed to be  $120^\circ$  in the flat conformation, except that the angles between the hydrogen atoms of the methylene groups were taken as  $109^\circ 28'$ . Symmetrical folding of the molecules about the axis through the methylene groups changed only the C-C-C angles at these groups. The approximation of maintaining the HCH angle constant for C-C-C angles varying between  $109^\circ 28'$  and  $120^\circ$  is justified by quantum-mechanical calculations.<sup>8</sup> In the present work only those distances that changed with dihedral angle were calculated, as only energy differences between conformations were required; also only nearest neighbours were considered.

Three alternative functions have been suggested for interaction between non-bonded hydrogen atoms. The first is the function, labelled  $V(\sum^3)$  in Fig. 1, which was calculated by Hirschfelder

\* Nomenclature of ref. 1.

<sup>2</sup> Miyagawa, Morino, and Riemschneider, *Bull. Chem. Soc. Japan*, 1954, **27**, 177.

<sup>3</sup> Gerding and Haak, *Rec. Trav. chim.*, 1949, **68**, 293.

<sup>4</sup> Ferrier and Iball, *Chem. and Ind.*, 1954, 1296.

<sup>5</sup> Campbell, Le Fèvre, Le Fèvre, and Turner, *J.*, 1938, 404.

<sup>6</sup> Iball, *J.*, 1938, 1074.

<sup>7</sup> Iball and Young, *Acta Cryst.*, 1958, **11**, 476.

<sup>8</sup> Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1.

and Linnett<sup>8</sup> for interaction between two hydrogen atoms in the triplet state (*i.e.*, with parallel electron spins); its use has been advocated by Howlett.<sup>10</sup> An alternative function, labelled  $E_{H,H}$  in Fig. 1, is based on the approximation of perfect pairing and the assumption that the electron spins in the approaching hydrogen atoms have a random relative orientation; this function was first proposed by Eyring<sup>11</sup> (for a simplified discussion see Coulson<sup>12</sup>) and has been used recently by Adrian.<sup>13</sup> A third alternative which is rather similar to  $E_{H,H}$  has been used by Pritchard and Sumner,<sup>14</sup> namely,  $nV(^3\Sigma)$  where  $n = 0.5$ . The present calculations are by the first two functions. Although the absolute magnitudes of the strain energies obtained differ considerably for the two [they are always larger for  $V(^3\Sigma)$ ], the energy differences between the various conformations are similar. As a random relative orientation of electron spins appears more probable than a parallel orientation, the  $E_{H,H}$  function appears the more suited to the present calculations.

The calculation of steric interaction energies is further complicated by the allowance for the variation of the van der Waals function with angle between the covalent-bond vector and the

FIG. 1. Interaction energies between non-bonded hydrogen atoms.  $V(^3\Sigma)$  is from the quantum-mechanical calculations<sup>9</sup> of the interaction between two hydrogen atoms in the triplet state.  $E_{H,H}$  is from Eyring's formula.<sup>11</sup>

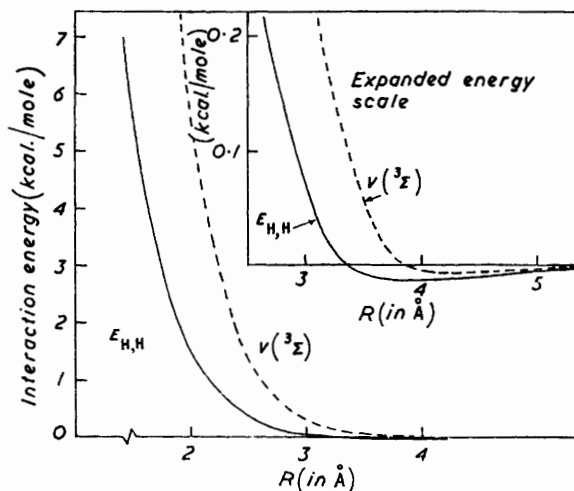
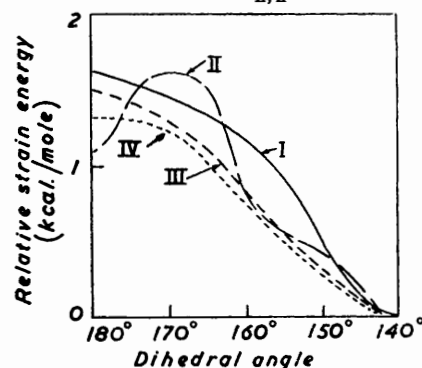


FIG. 2. Curves of relative strain energy in cyclohexa-1,4-diene as a function of dihedral angle. Curves (i) and (ii) were calculated by using  $V(^3\Sigma)$ , without and with allowance for variation of van der Waals interaction with angle; (iii) and (iv) are analogous curves calculated with  $E_{H,H}$ .



vector between the centres of the non-bonded atoms. For this Howlett's method was used.<sup>10</sup> These calculations have been carried out only for cyclohexa-1,4-diene, as the effects expected for the other two compounds are very small. Even for cyclohexa-1,4-diene the angular factor has little influence on the interaction energies (see Fig. 2).

Angle strain is absent from the ring only when the angles at the methylene-carbon atoms are  $109^{\circ} 28'$ ; this occurs for a dihedral angle of about  $141^{\circ}$ . For other values of the dihedral angle, the strain in the ring will be least when the angle distortions are shared over the whole ring rather than concentrated at the methylene groups. On the simplifying assumption that the bending force constant is the same for all the angles of the ring, the angle-strain energy will be least when all the angle distortions are equal. In these circumstances the angle-strain energy will be close to one-third of what it would be had the angle strains been concentrated at the methylene groups. Sharing of the angle strain over the ring has been found experimentally in the dihydrodibenzanthracene, where the planar central ring has angles of  $123^{\circ} 24'$ ,  $115^{\circ} 40'$  (at the methylene group), and  $122^{\circ} 28'$ . With these assumptions and when the bending force constant for tetrahedral C-C-C bond angles is taken as the average value ( $k_s = 0.8 \times 10^{11}$

<sup>9</sup> Hirschfelder and Linnett, *J. Chem. Phys.*, 1950, **18**, 130.

<sup>10</sup> Howlett, *J.*, 1958, 4353.

<sup>11</sup> Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 3191.

<sup>12</sup> Coulson, "Valence," Oxford Univ. Press, 1952, p. 166.

<sup>13</sup> Adrian, *J. Chem. Phys.*, 1958, **28**, 608.

<sup>14</sup> Pritchard and Sumner, *J.*, 1955, 1041.

erg/radian<sup>2</sup>), the angle-strain energy is given<sup>16</sup> by  $E(\Delta\theta) = 6 \times 17.5(\Delta\theta)^2$  cal./mole, where  $\Delta\theta$  is the change in degrees from the nominal value of the angle ( $120^\circ$  or  $109^\circ 28'$ ). The changes in the bond angles produce small changes in the interatomic distances and hence in the steric-interaction energies, but no correction has been made for this.

FIG. 3. Relative strain energy as a function of dihedral angle for 9,10-dihydroanthracene.

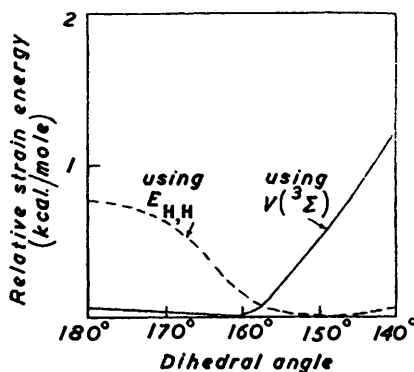
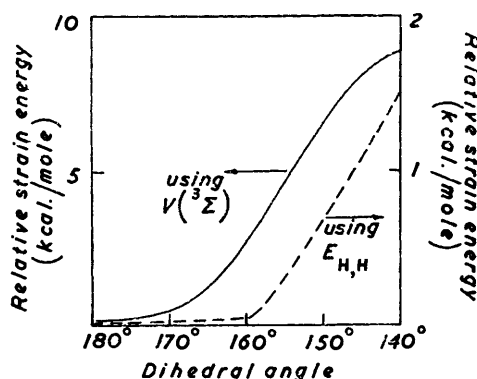


FIG. 4. Relative strain energy as function of dihedral angle for 9,10-dihydro-1,2:5,6-dibenzanthracene.



The total strain energy is given by the algebraic sum of steric-interaction energy and angle-strain energy, and the potential barrier between two conformations is obtained by taking the minimum value of the strain energy as zero. The results of the calculations are summarised in Figs. 2, 3, and 4, where the potential barriers are plotted as a function of dihedral angle for our three substances.

#### DISCUSSION

The results for cyclohexa-1,4-diene show that the stable conformation has a dihedral angle of about  $140^\circ$ . The potential barrier to transformation from the "folded" to the "reverse folded" conformation is about 1.5 kcal./mole. The differences among the energy curves calculated for the various interaction functions considered are not large.

For 9,10-dihydroanthracene use of the  $E_{H,H}$  function indicates a dihedral angle of about  $150^\circ$ , with a potential barrier of about 0.8 kcal./mole between the "folded" and the "reverse folded" conformations. The results for the  $^3\Sigma$  interaction function are not as satisfactory; although there is a minimum at about  $162^\circ$ , it is very shallow, while the experimental dihedral angle of  $145^\circ$  gives a positive strain energy of 0.9 kcal./mole.

Both strain-energy curves obtained for the dihydrodibenzanthracene (I) indicate the planar conformation as the more stable; however, for this molecule the differences between the two curves are rather marked.

The stable conformations predicted by the calculations are in good agreement with experiment for 9,10-dihydroanthracene and 9,10-dihydro-1,2:5,6-dibenzanthracene, while that calculated for cyclohexa-1,4-diene favours the folded conformation. However, the calculated dihedral angle (about  $140^\circ$ ) is not in very good agreement with that deduced from the dipole-moment measurements (about  $160^\circ$ ).

For the two simpler molecules the potential barrier between the two stable conformations is small and thus there is no possibility of isolating a particular conformation of substituted derivatives. If anything, the heights of the potential barriers have been somewhat over-estimated by the present calculations, for the possibility of outward bending of C-H bonds has been neglected.

The method used in these calculations has two major defects. First, the molecules have been taken as rigid, whereas some relief of repulsion between non-bonded atoms will

<sup>16</sup> Westheimer in "Steric Effects in Organic Chemistry," ed. Newman, John Wiley and Sons, New York, 1956, p. 533.

be obtained by bending of C-C-H bond angles. Secondly, it has been assumed that the molecular vibrations will not change with conformation. Although both these simplifications will affect the heights and detailed shapes of the potential barriers, their effects do not appear to be large enough to alter the qualitative conclusions drawn from the calculations.

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