Molecular Deformation in 3 : 4-5 : 6-*Dibenzophenanthrene.*

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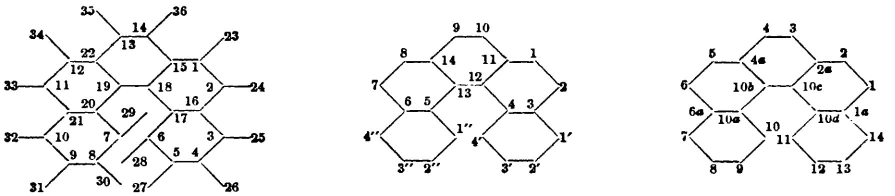
Steric limitations prevent the molecule 3 : 4-5 : 6-dibenzophenanthrene from being planar. On the basis of a plausible potential function for out-of-plane displacements of the various atoms, the molecular deformation is calculated. Excellent agreement with McIntosh, Robertson, and Vand's experimental values is obtained. The loss of resonance energy as a result of the deformation is estimated to be 18 kcal. mole^{-1}. The total strain energy may be about 28 kcal. mole^{-1}.

RECENTLY one of us (Senent, *Anales Real Soc. Esp. Fís. Quím.*, 1954, **50**, *B*, 337) calculated bond orders and resonance energy for 3 : 4-5 : 6-dibenzophenanthrene (I) by the method of molecular orbitals. As then stated a proper study of this molecule requires (*a*) the determination of its molecular diagram, on the hypothesis that it is planar, followed by (*b*) a study of its deformation. As shown, there is serious overcrowding between the hydrogen atoms numbered 28 and 29, and also between the carbon atoms numbered 6 and 7. It is generally found that non-bonded carbon atoms do not approach closer than 3·0 Å, and that the shortest hydrogen–hydrogen distances in aliphatic hydrocarbon crystals (see, *e.g.*, the accurate electron-diffraction values of B. K. Weinstein and Z. G. Pinsker, 3rd Internat. Congr. Crystall., Moscow, 1954, **10**, 154) are 2·49—2·50 Å. Now if the hexagons are approximately regular, the distance $C_{(6)}$–$C_{(7)}$ will be about 1·4 Å, so that all four atoms $C_{(6)}$, $C_{(7)}$, $H_{(28)}$, $H_{(29)}$ in this region are well within the forbidden distances, if the molecule is assumed to be planar. It is clear that since $C_{(6)}$ and $C_{(7)}$ are too close together, no bending of the bonds 6–28, 7–29 will remove the overcrowding. It is also clear that although this overcrowding could be relieved in principle by splaying-out the two " legs " of the molecule in such a way that the system remained coplanar, this would involve considerable changes in bond lengths and bond angles. Some similar calculations for diphenyl by Longuet-Higgins and Coulson (briefly reported by Coulson in " Quantum-Mechanical Methods in Valence Theory," Office of Naval Research, U.S.A., 1951, p. 42) suggest that this type of relief of steric strain requires a good deal more energy than if it is achieved by buckling the molecule out of a plane. A buckled shape has in fact recently been discovered experimentally by McIntosh, Robertson, and Vand (*Nature*, 1952, **169**, 322; *J.*, 1954, **1661**). It is reasonable, therefore, to suppose that the overcrowding in (I) is relieved by displacements of the various C and H atoms in a direction normal to the original undisturbed molecular plane. This is the model adopted in the present paper. It is supported by the three-dimensional diagram of the molecule shown in Fig. 5 of the paper by McIntosh *et al.* We shall show that by a simple application of the potential function for perpendicular displacements of the atoms of an aromatic hydrocarbon molecule, described in the preceding paper, it is possible to predict the details of the out-of-plane distortion with excellent fidelity. At the same time an estimate is obtained of the loss of resonance energy as a result of the deformation.



(I*a*) (I*b*) (I*c*)

(*a*) Numbering used in this paper. This numbering was chosen for convenience in description and mathematical analysis.
(*b, c*) Standard organic chemical numberings (cf. Table).

Let us take the plane of the undistorted molecule as the plane $z = 0$, and suppose that in the distortion the atom r is displaced a perpendicular distance z_r. The resulting changes in bond lengths and angles are of the second order of small quantities, and may therefore be neglected, unless the z_r fluctuate rapidly from atom to atom. We further suppose that these displacements are the only ones which take place. The potential energy of the deformed molecule will be a function $V(z_1, \dots . z_{36})$ of the co-ordinates z_r. Presumably the equilibrium values of the z_r will be such as minimise V subject to the van der Waals constraints in the region of atoms 6, 7, 28, and 29. In order to proceed further, therefore, we must discuss (*a*) the analytical form of V, and (*b*) the limiting values of z_6, z_7, z_{28}, and z_{29}.

It is shown in the paper which precedes this that a satisfactory potential function can be devised, which will account for the out-of-plane vibration frequencies in ethylene, benzene, and naphthalene with the use of only two distinct force constants. Now the C–C and C–H bonds in our present molecule must evidently resemble those of benzene and naphthalene quite closely. We may therefore adopt this potential function and use it to define V. Better agreement with experiment could no doubt be obtained if we chose a larger number of force constants, or even different values from those estimated from benzene; but we shall be able to show that by adopting these values we are led to an excellent agreement with the experimentally measured deformation. And our calculations have the advantage of making no appeal to any experimental results other than the fundamental frequencies of benzene, and the van der Waals radii of carbon and hydrogen. According to this theory $V(z_1 \dots . z_{36})$ may be regarded as the sum of two sets of terms. The first set measures the lack of planarity of the three bonds around every carbon atom in the skeleton of the molecule; the second set may be interpreted as measuring the torsion around each of the C–C bonds. The precise form of these terms depends on whether the atoms concerned are carbon or hydrogen. For a carbon such as $C_{(19)}$ surrounded by other carbon atoms the lack-of-planarity term in V amounts to

$$\tfrac{1}{2}k_1\left\{z_{18} + z_{20} + z_{22} - 3z_{19}\right\}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For a carbon atom such as $C_{(14)}$ which has one hydrogen as neighbour the corresponding term involves the C–C and the C–H distance (a and b respectively). It is

$$\tfrac{1}{2}k_1\left\{\frac{a}{b}z_{36} + z_{15} + z_{13} - \left(2 + \frac{a}{b}\right)z_{14}\right\}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For a bond such as $C_{(18)}$–$C_{(19)}$ entirely surrounded by other carbon atoms, the torsion term is

$$\tfrac{1}{2}k_2\left\{z_{15} - z_{17} + z_{20} - z_{22}\right\}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For a bond such as $C_{(1)}$–$C_{(15)}$ where there is one neighbouring hydrogen atom, the torsion term is

$$\tfrac{1}{2}k_2\left\{\frac{a}{b}z_{23} - z_2 + z_{18} - z_{14} + \left(1 - \frac{a}{b}\right)z_1\right\}^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Finally, for a bond such as $C_{(1)}$–$C_{(2)}$ surrounded by two hydrogen atoms, the torsion term is

$$\tfrac{1}{2}k_2\left\{\frac{a}{b}z_{24} - z_{16} + z_{15} - \frac{a}{b}z_{23} + \left(1 - \frac{a}{b}\right)(z_2 - z_1)\right\}^2 \quad . \quad . \quad . \quad . \quad (5)$$

The complete expression for V is the sum of terms (1)—(5) for each carbon atom and for each carbon–carbon bond. There are altogether 48 such squared terms. The appropriate numerical values of the parameters are:

$$a = 1{\cdot}40\ \text{Å},\ b = 1{\cdot}08\ \text{Å},\ k_1 = 0{\cdot}1474 \times 10^5\ \text{dynes cm.}^{-1},$$
$$k_2 = 0{\cdot}0551 \times 10^5\ \text{dynes cm.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We have still to discuss the displacements z_6, z_7, z_{28}, z_{29}. Viewed along the molecular plane in the direction of the axis of symmetry the overcrowded region must resemble Fig. 1, in which the horizontal line represents the undistorted molecule, and in which one half of the molecule has been deflected above the original plane, and the other half below it. The $C_{(6)}$–$C_{(7)}$ distance is found by McIntosh *et al.* to be 3·0 Å. This value is about the shortest carbon–carbon distance found in organic molecules, and is identical with the corresponding distance in 3 : 4-benzophenanthrene, recently studied by Herbstein and Schmidt (*J.*, 1954, 3302). It suggests that we may take the van der Waals radius of carbon in this somewhat compressed system as 1·5 Å. We should then expect the $C_{(7)}$–$H_{(28)}$ distance to be about $1{\cdot}5 + 1{\cdot}2 = 2{\cdot}7$ Å. Now the undistorted $C_{(6)}$–$C_{(7)}$ distance, represented by A–B in Fig. 1, will be about 1·4 Å, and the $C_{(6)}$–$H_{(28)}$ and $C_{(7)}$–$H_{(29)}$ bond lengths are 1·08 Å. Simple trigonometry shows that under these conditions $z_6 = -z_7 = 1{\cdot}32$ Å, $z_{28} = -z_{29} = 1{\cdot}36$ Å. These are the final values which we have adopted.

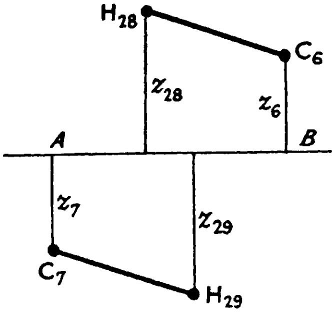


FIG. 1. *The overcrowded region.*

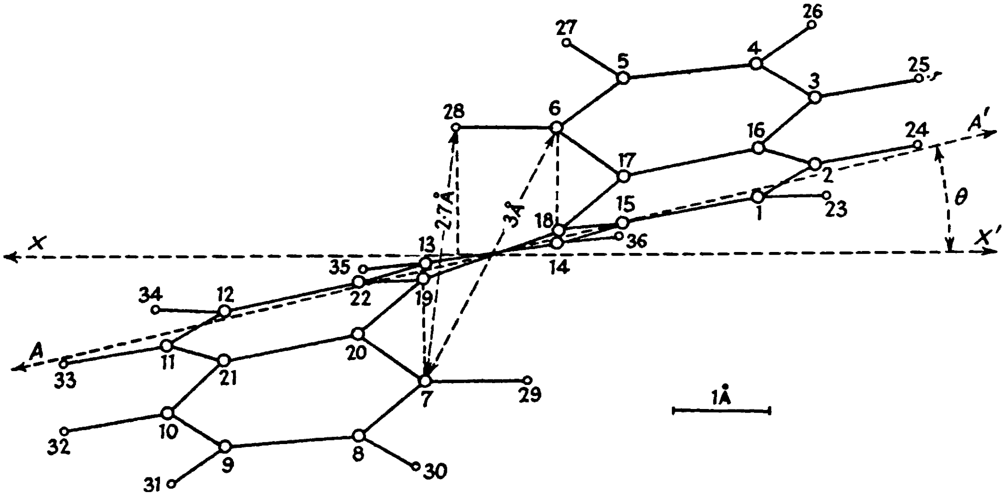
Our problem is now very simple : it is to find the minimum value of $V(z_1 \ldots\ldots z_{36})$ with the above values for z_6, z_7, z_{28}, and z_{29}. We must therefore put $\partial V/\partial z_r = 0$ for all the remaining z_r. This provides us with a set of 32 linear equations. But the set reduces to 16 on account of the molecular symmetry according to which the right half of (I) is displaced upwards and the left half symmetrically downwards. The values of z_r which satisfy these conditions are shown in the Table, all displacements being measured in Å. It will be noticed that some of these displacements are quite large, of the order of 2 Å. But since the displacements of different atoms vary smoothly from atom to atom, the apparently large displacements do not destroy the validity of our potential function.

Calculated and experimental displacements (*values in parentheses are assumed*).

Carbon atoms numbered according to							Hydrogen atoms numbered according to			
(I*a*)	(I*b*)	(I*c*)	z_r	$z_r - \theta\rho_r$	Expt.	Δr	(I*a*)	(I*b*)	(I*c*)	z_r
1	1	2	$0{\cdot}63_0$	−0·07	−0·15	−0·08	23	1	2	$0{\cdot}61_7$
2	2	1	$1{\cdot}95_2$	0·09	0	−0·09	24	2	1	$1{\cdot}16_9$
3	1′	14	$1{\cdot}62_9$	0·80	0·78	−0·02	25	1′	14	$1{\cdot}79_8$
4	2′	13	$1{\cdot}96_3$	1·31	1·45	0·14	26	2′	13	$2{\cdot}36_8$
5	3′	12	$1{\cdot}85_0$	1·53	1·71	0·18	27	3′	12	$2{\cdot}19_2$
6	4′	11	(1·32)	1·15	1·20	0·05	28	4′	11	(1·36)
14	10	3	$0{\cdot}11_8$	−0·06	−0·16	−0·10	36	10	3	$0{\cdot}20_0$
15	11	2*a*	$0{\cdot}33_2$	0·03	0·02	−0·01				
16	3	14*a*	$1{\cdot}12_5$	0·43	0·40	−0·03				
17	4	10*d*	$0{\cdot}85_2$	0·48	0·55	0·07				
18	12	10*c*	$0{\cdot}27_6$	0·09	0·20	0·11				

Fig. 2 shows the displaced molecule, according to our calculations, when viewed along the original molecular plane. Comparison of this with Fig. 5 in the paper by McIntosh, Robertson, and Vand shows that our description is qualitatively correct. However the accuracy is almost quantitative, as may be seen as follows. It is not possible, from the *X*-ray analysis, to tell which would have been the basic plane from which we have measured our z-displacements. But Professor Robertson has been kind enough to draw what he calls a medium plane through the molecule, and has measured the perpendicular displacements of the carbon atoms from this plane. (We cannot yet say anything about the hydrogen atoms, which are not experimentally resolved : our comparisons therefore are solely for the positions of the carbon atoms.) Trial-and-error suggests that the plane which Robertson has chosen for this purpose is defined by its trace A–A' in Fig. 2, the common line of this plane and the basic plane X–X' being the two-fold axis of symmetry of the molecule. We must therefore convert our z_r-values into corresponding displacements from A–A' instead of from X–X'. To the accuracy which is warranted by our whole analysis this may be achieved by replacing z_r by $(z_r - \theta\rho_r)$, where θ = angle between A–A' and X–X', and ρ_r is the axial distance of atom C_r from the axis of symmetry. These " reduced displacements " are also shown in the Table, where they are compared with the experimental values. The differences Δ_r shown are all satisfactorily small. When it is recalled that Robertson estimates his accuracy as of the order 0·1 to 0·2 Å, the agreement is all that could be desired ; for the maximum Δ_r is only 0·18 Å, and the mean Δ_r is only 0·08 Å. The numerical value of θ to give the best fit has been taken to be 0·24 radian (13° 45′).

FIG. 2. *The dibenzophenanthrene molecule when projected in a direction perpendicular to the axis of symmetry.*



The figures denote the numbers (r) of the atoms and the small circles show their calculated displacements (z_r). θ = 0·24 radian.

The agreement represented in the Table is almost too good ; for the molecular-orbital calculations of Senent (*loc. cit.*) show that the bond orders of the outer, or exposed, bonds $C_{(13)}$–$C_{(14)}$, $C_{(1)}$–$C_{(2)}$, $C_{(3)}$–$C_{(4)}$, $C_{(11)}$–$C_{(12)}$, and $C_{(9)}$–$C_{(10)}$ are all rather larger than the average benzene order (1·746, 1·764, 1·764, 1·710, 1·710, respectively, to be compared with benzene 1·667). This will lead to a shortening of these bonds, and therefore to a partial opening-out of the molecule, within its own molecular plane. As a result the distance A–B in Fig. 1 is likely to be rather greater than the value 1·40 Å which we assumed on the basis of five regular hexagons. This would tend to reduce the magnitudes of the displacements z_r which were needed to relieve the overcrowding. It seems likely that the chief effect of all this would be to diminish all calculated z_r in such a way that the angle θ was reduced without an equivalent decrease in the " reduced displacements." But in no case should we expect this effect to be large, and it is not possible to deal with it properly until the experimental values of the bond lengths have been determined with greater precision than at present.

We can use the z_r values of the Table to estimate the energy of deformation. This will consist of two parts : the van der Waals repulsive overlap energy due to the closeness of the four overcrowded atoms $C_{(6)}$, $C_{(7)}$, $H_{(28)}$, and $H_{(29)}$, together with the energy required to distort the molecular framework. The second of these energies is identical with the loss of π-electron resonance energy and the energy of bending the σ-electron bonds. It is measured by the value of $V(z_1 \ldots\ldots z_{36})$ when we substitute the equilibrium values of the z_r. Now since V is a homogeneous polynomial of degree 2, it follows that

$$\sum_1^{36} z_r \frac{\partial V}{\partial z_r} = 2V$$

In equilibrium all $\partial V/\partial z_r = 0$ except for the four overcrowded atoms. Thus the energy of distortion is given quite simply by

$$z_6 \frac{\partial V}{\partial z_6} + z_{28} \frac{\partial V}{\partial z_{28}}$$

This amounts to 0·77 ev = 17·9 kcal. mole^{-1}. The first of the strain-energy terms is less easy to estimate, for we know practically nothing about the magnitudes of these repulsive forces between non-bonded atoms. Since they are believed to come into operation very suddenly as the internuclear separation is reduced, and then to increase rapidly, it seems probable that they will contribute rather less than the deformation energy terms; for if the repulsive terms were larger than the deformation terms, we could reduce the total strain energy by increasing the atomic displacements. This is because the deformation energy varies only as the square of the z_r values, but the repulsive forces vary as some higher power such as the inverse twelfth power of the distance. We are inclined to think that a value of the order of 10 kcal. mole^{-1} is likely. Then the total strain energy would be about 28 kcal. mole^{-1} and the resonance energy for the molecule (calculated by Senent, *loc. cit.*, to have the value 162 kcal. mole^{-1}) would have to be reduced by this amount. In view of our ignorance of the magnitude of the repulsive forces, no great reliance should be placed on this value. But it is likely to be correct as regards order of magnitude. The fact that it is so small in relation to the deformations z_r shows how relatively easy it is to build up quite large displacements in aromatic molecules of this sort by a series of small distortions around each of the carbon atoms of the molecular framework.

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