

300. *Overcrowding Distortions in Aromatic Molecules and Crystals.*

By M. ASGAR ALI and C. A. COULSON.

Calculation of the loss of resonance energy (called deformation energy) due to steric deformation in the three overcrowded molecules, 3 : 4-5 : 6-dibenzophenanthrene, 5 : 6-7 : 8-dibenzoperylene, and 1 : 12-5 : 6-7 : 8-tribenzoperylene, shows that the large size and more rigid character of the polynuclear framework exerts hardly any influence on the strain energy. It is suggested, on the basis of similar calculations, that in tetrabenzoperopyrene, where there are two overcrowded regions, the molecule takes up a propeller-like shape. An estimate is made of the deformation energy per molecule in the molecular crystals of chrysene and 20-methylcholanthrene, where accurate X-ray analysis by Iball shows that the molecules are deformed out of a plane. The energies turn out to be very small. ~ 50 cal., *viz.*, per mole.

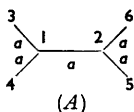
COULSON and SENENT¹ have developed a simple potential function for the out-of-plane displacements of ethylenic and aromatic molecules. This involves the use of only two force constants. It has been applied with success to account for the out-of-plane frequencies of ethylene and benzene, and of molecules as complex as naphthalene. A further application² of this potential function was to the calculation of out-of-plane displacements and energy of overcrowding in 3 : 4-5 : 6-dibenzophenanthrene (I) where

¹ Coulson and Senent, *J.*, 1955, 1813.

² *Idem*, *J.*, 1955, 1819.

both theory and experiment showed that the overcrowding was relieved almost wholly by displacements of the various carbon and hydrogen atoms in a direction normal to the mean plane of the molecule. In the present study we make use of the Coulson-Senent potential function (hereafter referred to as C.S.) in three ways. In the first we consider the displacements and overcrowding energy in a series of polynuclear hydrocarbons (I—III), of which the first is that already dealt with by Coulson and Senent. The purpose of these calculations is to discover the extent to which the molecular deformations depend on additional structure and rigidity in the carbon framework. Our second problem concerns the prediction of the configuration of the recently reported tetrabenzoperopyrene³ (IV) where there are two regions of overcrowding, and two main alternative ways exist whereby this can be relieved. Finally we make use of the C.S. potential function to discuss certain polynuclear hydrocarbons, notably chrysene and 20-methylcholanthrene, where recent accurate X-ray analysis has shown that the molecules are distorted in the solid phase, presumably as a result of intermolecular forces.

Force-field and Method of Calculation.—We assume, as in the pioneer work of Coulson and Senent, that in all these molecules the relief of overcrowding takes place by displacements of atoms perpendicular to the undistorted molecular plane. All other changes in the molecular shape, such as bond lengths and interbond angles, are supposed to be negligible. Then the potential energy V is a function only of the atomic displacements $z_1 \dots$ so that $V = V(z_1, \dots)$. We presume that the equilibrium values of the z_r are such as to minimise V . For the explicit expression of V , we use the C.S. function. This is the sum of a set of terms, one for every carbon atom around which the three bond directions are not coplanar ("lack-of-planarity" term), and one for each carbon-carbon bond around which there is any degree of torsion ("torsion" term). These terms may all be found from a generalisation of the formulæ given in ref. 1, and appropriate to a situation in which all five bond lengths (see *A*) are equal. There it was shown that the lack-of-planarity term at carbon $C_{(1)}$ is



Part of a condensed polynuclear hydrocarbon.

$$\frac{1}{2}k_1(z_2 + z_3 + z_4 - 3z_1)^2$$

and the torsion term around $C_{(1)}-C_{(2)}$ is

$$\frac{1}{2}k_2(z_3 - z_4 + z_5 - z_6)^2$$

If some or all of the four bond lengths such as $C_{(1)}-C_{(3)}$ are different from a , these formulae need modification. All such modifications are included in the following rule. If a bond such as $C_{(1)}-C_{(3)}$ has its length b then, in these two formulæ, z_3 must be replaced by

$$z_1 + \frac{a}{b}(z_3 - z_1)$$

If more than one such bond is altered, all the corresponding changes in the z_r must be made. When this has been done, $V(z_1 \dots)$ is merely the sum of the necessary total of planarity and torsion terms. In the cases of (I, II, III), for example, there are 22, 28, and 30 planarity terms, and 26, 34, and 37 torsion terms respectively. In our calculations the numerical values adopted are those chosen by Coulson and Senent¹ from a study of vibrational frequencies:

$$a = \text{C-C} = 1.40 \text{ \AA}; \quad b = \text{C-H} = 1.08 \text{ \AA}$$

$$k = 0.1474 \times 10^5 \text{ dynes cm.}^{-1}; \quad k_2 = 0.0553 \times 10^5 \text{ dynes cm.}^{-1}.$$

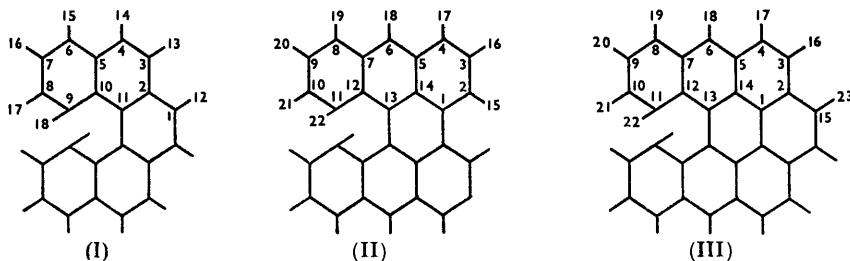
Of (I—III), experimental values of the z_r are available only for (I). We have therefore used the same values for the displacements of the four atoms (two hydrogen and two carbon) in the overcrowded region in both (II) and (III). As it will appear that the

³ Clar and Ironside, *Proc. Chem. Soc.*, 1958, 150.

deformation energy is almost the same in all three molecules, this serves *a posteriori* to justify our assumption of equal displacements in the overcrowded regions. This is all the more likely since the actual displacements in the overcrowded region are determined very largely by the repulsive overlap forces between the charge-clouds of the non-bonded atoms. In going from (I) to (II) to (III) we might have expected slightly smaller displacements than in (I). But the repulsive energy increases very rapidly as the atoms get closer together. Hence the balance between repulsive energy and overcrowding energy is expected to occur with almost the same displacements in the overcrowded region in all three cases. Thus we shall take:

$$z \text{ for overcrowded carbon} = 1.32 \text{ \AA}; \quad z \text{ for overcrowded hydrogen} = 1.36 \text{ \AA}$$

Our problem therefore reduces to finding the minimum value of the quadratic function $V(z_r)$ with the restriction that in the overcrowded region the z -values have the numerical



values shown above. Thus we have to solve the set of equations $\partial V / \partial z_r = 0$. When this is done, and the z_r have been calculated, the deformation energy is simply $\frac{1}{2} \sum_{\text{overcrowded atoms}} z_r (\partial V / \partial z_r)$.

The total strain energy, of course, is the sum of this deformation energy and the repulsive overlap energy between the atoms of the overcrowded region.

The latter will be a constant in all our calculations, though its precise value must remain unknown until we possess more information about the interatomic forces. Our calculations were made on a Ferranti Pegasus electronic computer. This machine could be programmed, not only to write down and solve the equations, but also to make the final calculations of the deformation energy.

Results for Molecules (I—III).—Tables 1 and 3 show both the actual predicted displacements (in Å) and the deformation energy. Column 3 of Table 1 is a recalculated version of the Coulson–Senent work in ref. 2, and, apart from one copying mistake (the C₍₂₎ atom in the phenanthrene region for which the true value is 0.95 Å, whereas the previously reported value was 1.95 Å) the two calculations agree excellently.

It will be seen that the displacements and the deformation energy in these molecules are very similar. The displacements far away from the overcrowded region, though somewhat different, appear to make very little contribution to the deformation energy. Thus the rigidity of the molecular framework has virtually no influence on the displacements in and near to the overcrowded region.

Application to Tetrabenzoperopyrene (IV).—There are two ways in which the overcrowding can be relieved. In the first, the atoms on one side of the axis (b) have positive displacements, and those on the other side have negative ones. This set of displacements is symmetrical about the axis (a). But in the other scheme, it is almost as if the top half of the molecule were rotated in one direction around the axis (a), and the bottom half were rotated in the opposite direction: the result is a kind of propeller-shape. Both possibilities must be considered. The more probable configuration will then be that which gives rise to the lower energy of deformation V . In both cases there are 42 planarity terms and 52 torsion terms, though the number of simultaneous linear equations to be

TABLE 1. *Calculations of z_r (in Å) for molecules (I—IV).*

Atom	(I) (Coulson and Senent)	(I) (Present calcn.)	(II)	(III)	(IV) (First config.)	(IV) (Second config.)
1	0.11	0.114	0.117	0.128	1.716	0
2	0.33	0.316	0.197	0.248	1.549	0.373
3	0.63	0.619	0.458	0.515	1.153	0.348
4	0.95	0.946	0.680	0.715	1.189	0.765
5	1.12	1.109	0.641	0.659	1.697	1.311
6	1.62	1.644	0.950	0.963	1.985	1.856
7	1.96	1.993	1.104	1.110	1.846	1.887
8	1.85	1.873	1.630	1.637	(1.32)	(1.32)
9	(1.32)	(1.32)	1.976	1.981	0.861	0.675
10	0.85	0.823	1.864	1.865	0.291	0.155
11	0.27	0.258	(1.32)	(1.32)	0.474	0
12	0.20	0.197	0.824	0.826	0.917	0
13	0.61	0.610	0.262	0.263	2.026	0
14	1.16	1.176	0.328	0.336	1.751	0.670
15	1.79	1.827	0.046	0.118	1.916	1.344
16	2.36	2.418	0.505	0.591	2.391	2.288
17	2.19	2.231	0.908	0.949	2.171	2.349
18	(1.36)	(1.36)	1.184	1.203	(1.36)	(1.36)
19			1.809	1.819		
20			2.394	2.400		
21			2.219	2.220		
22			(1.36)	(1.36)		
23				0.212		

TABLE 2. *Calculated and observed displacements (10^{-3} Å) for chrysene (V) and 20-methylcholanthrene (VI).**

Atom	(V) obs.	(V) calc. approx. <i>a</i>	(V) calc. approx. <i>b</i>	(VI) obs.	(VI) calc. approx. <i>a</i>	(VI) calc. approx. <i>b</i>
1	-4			+25		
2	+1			+20		
3	+5			-9		
4	+4			-28		
5	+2			-18		
6	-13			+5		
7	-3			+15		
8	+10			+10		
9	+9			-2		
10	+4			+2		
11	-1			+6		
12	-5			-11		
13	-4			+23		
14	-2			+10		
15	+13			+1		
16	+3			-17		
17	-10			-25		
18	-9			-5		
19		-1.0	+1		+50	+55
20		+6.0	+7		+35	+52
21		+1	+11		-35	-56
22		-24	-33		-24	-30
23		-7	-6		-1	+9
24		+15	+17		-26	-74
25		+1	-2		+2	-6
26		-6	-8		-32	-41
27		-1	-11		-12	-3
28		+24	+33	+18		
29		+7	+6	+4		
30		-15	-17	-25		

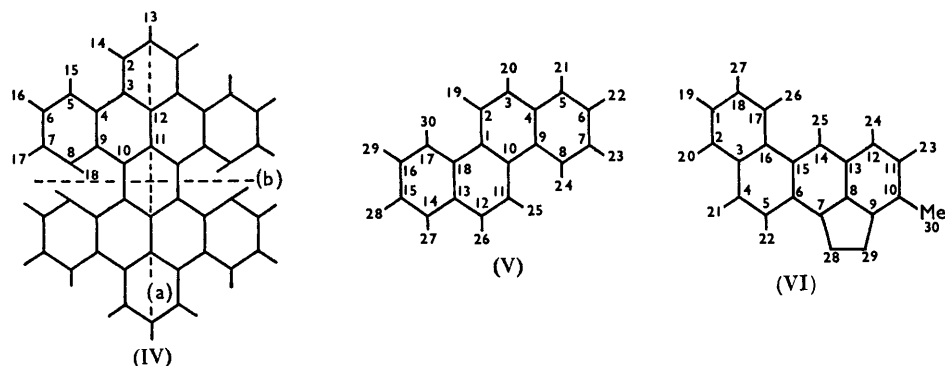
* + and - signs indicate displacements above and below the mean plane of the molecule.

TABLE 3. *Deformation energies (kcal./mole).*

(I)	17.9 *	17.98 †	(V)	(Approx. <i>a</i>)	0.025
(II)		18.54	(V)	(Approx. <i>b</i>)	0.040
(III)		18.60	(VI)	(Approx. <i>a</i>)	0.155
(IV)	(First Config.)	41.5	(VI)	(Approx. <i>b</i>)	0.260
(IV)	(Second Config.)	36.3			

* Ref. 1. † Present calcn.

solved is about one-quarter of the sum ($42 + 52 = 94$) on account of the two symmetry axes. The results are shown in Tables 1 and 3. Now despite the fact that the C.S. potential function neglects certain cross-terms, it seems entirely reasonable that the true sequence of deformation energies should be as in these calculations. We are therefore led to propose the second, *i.e.*, propeller, shape for this molecule. If the calculated energy difference between the two tautomeric forms is taken to be the true value, then less than 1 in 10^4 molecules would be found in the alternative shape at room temperature.



Molecular Crystals: Chrysene and 20-Methylcholanthrene.—Iball⁴ has found that, in their crystalline form, chrysene and 20-methylcholanthrene are slightly buckled. The observed displacements z_r of the various atoms are shown in Table 2 [see (V) and (VI) for system of numbering used] measured in units of 10^{-3} Å. These are, admittedly, small displacements but a statistical test, for which we are grateful to Dr. J. S. Rollett, shows that they are almost certainly significant. They must be the result of intermolecular forces, associated with the molecular packing. These may be partly attractive dispersion forces and partly repulsive overlap forces, with the former predominating. It is of some interest to estimate the energy involved in these deformations. This cannot be done by direct evaluation of the potential energy function $V(z_1 \dots)$ because only the positions of the carbon atoms are known. The experimental analysis was not sufficiently detailed to pick out the hydrogen atoms. But the value of $V(z_1 \dots)$ depends rather seriously upon the hydrogen displacements. We have therefore adopted two independent sets of assumptions, between which the truth is almost certain to lie. In (a) we suppose that the intermolecular forces act only on the hydrogen atoms. Then $\partial V / \partial z_r = 0$ for each carbon atom, but not for the hydrogens. This set of equations, coupled with the known carbon-atom displacements, can then be used to calculate the positions of the hydrogen atoms, and also the value of V . In (b) we suppose that the intermolecular forces act only on the carbon atoms, so that $\partial V / \partial z_r = 0$ for each hydrogen, but not for carbon. Again we calculate the positions of the hydrogen atoms, and the value of V . Since there are more carbon than hydrogen atoms, there are more equations than unknowns in method (a). In that situation a least-squares procedure was used to find the best z_r . Since the relative uncertainties in the measured carbon-atom displacements are quite large, this procedure seems entirely reasonable.

When writing down the C.S. potential for methylcholanthrene the following approximations were introduced. (1) We neglect strain in the 5-membered saturated ring, since this is not likely to distort the molecule in an out-of-plane direction. (2) To permit us to write down planarity terms associated with the carbon atoms where the 5-ring joins the aromatic framework, we replace the saturated part of the 5-ring by two hypothetical carbon atoms at a valency angle of 120° . The 20-methyl group is similarly replaced by a hydrogen atom at the appropriate distance.

⁴ Iball, personal communication.

The results of the two calculations (*a*) and (*b*) are shown in Tables 2 and 3. In all cases the deformation energy is very small, being of the order of one-hundredth part of the sublimation energy. Thus it is easy to see that out-of-plane displacements of this magnitude (or even rather larger) may arise in the process of packing the separate molecules into the crystal. Indeed it seems likely that such degrees of non-planarity may be more common than has hitherto been suspected. Highly accurate *X*-ray analysis may reveal more of these cases in the future. Some words of J. M. Robertson⁵ seem appropriate: "The molecule (anthracene) which we proved planar in 1932 and much more accurately planar in 1950, is now found to be non-planar. The carbon atom 9 in anthracene deviates most from the mean plane, by 0.012 Å. This is the carbon atom which is approached directly by a hydrogen atom from a neighbouring molecule."

Our sincere thanks are offered to Dr. Iball for providing us with the observed displacements in chrysene and methylcholanthrene in advance of publication; to Dr. J. S. Rollett for much helpful discussion and for the programme by which we determined the deformation and the energy on the Pegasus computer; and to Messrs. Ferranti for allowing us machine time for these calculations. One of us (M. A. A.) also acknowledges the West Bengal Lytton Moslem Scholarship from the Government of West Bengal.

MATHEMATICAL INSTITUTE, OXFORD.

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⁵ Robertson, *Rev. Mod. Phys.*, 1958, **30**, 158.
