399. *The Structure of Overcrowded Aromatic Compounds. Part VII.*[1] *Out-of-plane Deformation in Benzo*[c]*phenanthrene and* 1,12-*Dimethylbenzo*[c]*phenanthrene.*

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The molecular deformations of the two compounds whose crystal structures are described in the preceding paper have been used to test a theoretical potential function for out-of-plane deformation essentially due to Coulson and Senent. Good agreement is found, almost within experimental error, and possible improvements in the form of the function are indicated. The influence of the deformations on chemical behaviour and ultraviolet spectra is qualitatively explained, but quantitative predictions are not possible.

THE crystal-structure analyses reported in Part VI[1] of this series were undertaken in order to provide accurate data on the out-of-plane deformations of aromatic molecules subject to severe overcrowding. It is now pertinent to enquire, first, how well the observed deformations can be explained by theoretical models of molecular deformability and, further, what effect these deformations may have on the physical and chemical properties of the compounds under study.

Deformation Parameters.—With a molecule as severely distorted from planarity as are the two considered here, the usual practice of indicating atomic displacements from some mean reference plane is somewhat inadequate for describing the nature of the deformation. A more useful description requires the specification of the deviations from coplanarity of sets of adjacent atoms in a manner that is independent of any arbitrary choice of reference system. Further, linear measures of atomic displacements provide less convenient parameters for definition of molecular deformation than do the angles made by the several bonds to the same or to adjacent atoms, since the latter can be more directly related to expressions for the strain energy of the deformed molecule. Following Coulson and Senent,[2] we direct our attention exclusively to two kinds of out-of-plane deformation: (*a*) the non-coplanarity of the three bonds to an aromatic carbon atom; and (*b*) the angle of torsion, about an aromatic bond, between the planes of the adjacent bonds at its two ends.

For the first kind of deformation we define a bending parameter ε as follows. Let the three bonds radiating from the aromatic carbon atom $C_{(r)}$ be denoted by the vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$. Then we define

$$\varepsilon_r = [\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3]/r_1r_2r_3$$

This quantity vanishes when the three bonds are coplanar and has, in general, a magnitude

$$|\varepsilon_r| = \sin\psi_1 \sin\chi_1 = \sin\psi_2 \sin\chi_2 = \sin\psi_3 \sin\chi_3$$

where ψ_1 is the angle between $\mathbf{r}_2$ and $\mathbf{r}_3$, etc., and χ_1 is the angle between $\mathbf{r}_1$ and the plane of $\mathbf{r}_2$ and $\mathbf{r}_3$, etc. The sign of ε_r depends on the order of numbering of the three vectors; it is positive if the vectors are numbered in a counter-clockwise sense as seen from a point inside the smaller solid angle defined by the three vectors.

The second kind of deformation is measured by a torsion parameter τ defined as follows. Let the aromatic carbon atoms $C_{(r)}$ and $C_{(s)}$, bonded to each other, form the further bonds $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{s}_1$, $\mathbf{s}_2$, respectively, so that $\mathbf{r}_1$ is *cis* to $\mathbf{s}_1$ and $\mathbf{r}_2$ is *cis* to $\mathbf{s}_2$ (see Fig. 1). Let these four bonds be projected on to a plane normal to the bond $C_{(r)}$–$C_{(s)}$ to yield the vectors $\mathbf{r}_1'$, $\mathbf{r}_2'$, $\mathbf{s}_1'$, and $\mathbf{s}_2'$ in this plane. Let ϕ_i $(i = 1, 2)$ be the angle between $\mathbf{r}_i'$ and $\mathbf{s}_i'$, measured

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[1] Part VI, preceding paper.

[2] Coulson and Senent, *J.*, 1955, 1813.

counter-clockwise from $\boldsymbol{r}_i'$ to $\boldsymbol{s}_i'$ as seen along the line from $C_{(s)}$ to $C_{(r)}$. We then define the angle of torsion

$$\tau_{rs} = \tfrac{1}{2}\,(\phi_1 + \phi_2)$$

It is positive if the bond $C_{(r)}$–$C_{(s)}$ is twisted in the sense of a right-handed screw.

It is easy now to express the potential energy of out-of-plane deformation, according to the approximation of Coulson and Senent, in terms of the parameters ε and τ. For a carbon atom $C_{(r)}$ bonded to atoms $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$, Coulson and Senent have assumed a potential-energy contribution arising from the non-coplanarity of these four atoms having the form, when all bond lengths are equal and all bond angles 120°,

$$V_r = \tfrac{1}{2}k_1(z_1 + z_2 + z_3 - 3z_r)^2 = \tfrac{1}{2}k_1 p_r^2$$

where z_i (i $= r$, 1, 2, 3) is the distance of atom $C_{(i)}$ from a common reference plane. This expression is most likely to be valid when all z_i are small. In such a case our bending parameter ε_r is given, to a good approximation, by

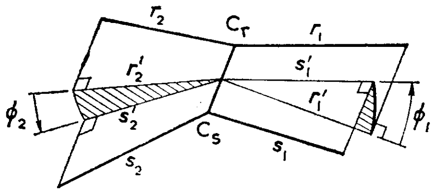

FIG. 1. Definition of torsion parameter $\tau_{rs} = \frac{1}{2}(\phi_1 + \phi_2)$ for bond $C_{(r)}$–$C_{(s)}$.

$$\varepsilon_r = p_r\, 3^{1/2}/2a,$$

where a is the common bond length. Thus we can rewrite V_r as

$$V_r = \tfrac{1}{2}k\ \varepsilon_r^2,$$

where $k_\epsilon = 4a^2k_1/3$.

For benzene, with $a = 1{\cdot}40$ Å, Coulson and Senent deduce from the infrared frequencies a value of $k_1 = 0{\cdot}1474 \times 10^5$ dynes/cm. This corresponds to a value of $k_\epsilon = 3{\cdot}852 \times 10^{-12}$ erg.

In a similar fashion we can write the energy of torsion of a bond $C_{(r)}$–$C_{(s)}$ as $V_{rs} = \frac{1}{2}k_\tau\tau_{rs}^2$, where τ_{rs} is the bond torsion in radians and k_τ is related to the corresponding force constant k_2 of Coulson and Senent by $k_\tau = 3a^2k_2 = 3{\cdot}240 \times 10^{-12}$ erg/rad² for benzene.

If we assume the benzene force constants to be applicable to any aromatic molecule we can write the out-of-plane deformation energy of such a molecule as

$$V_d = \tfrac{1}{2}\,(3{\cdot}852\textstyle\sum\varepsilon_r^2 + 3{\cdot}240\sum\tau_{rs}^2) \times 10^{-12}\ \text{erg}. \qquad (1)$$

This expression is equivalent to that given by Coulson and Senent when the molecule is nearly planar but has the advantage that it is independent of any arbitrary choice of reference plane and may therefore be applied with greater confidence to a molecule that is severely non-planar.

On the other hand it suffers from the serious drawback that it cannot readily be used for the prediction of molecular deformations since, for a cyclic system, the several parameters ε_r and τ_{rs} are not mutually independent. In fact, for a fully aromatic hydrocarbon the number of parameters exceeds the number of internal degrees of freedom for out-of-plane deformation by three times the number of aromatic rings. For example, benzo[*c*]phenanthrene contains four aromatic rings and 30 atoms. Letting any 3 atoms determine a reference plane, we can define the out-of-plane molecular deformation by means of the distances from this plane of the remaining 27 atoms. But the number of parameters appearing in equation (1) is $18 + 21 = 39$ since the molecule contains 18 aromatic carbon atoms linked by 21 aromatic bonds. Thus these parameters are related by twelve equations, whose form is exceedingly complicated. To predict the molecular configuration one would have to minimise V_d with respect to the 39 parameters ε_r and τ_{rs}, subject to these twelve conditioning equations, with whatever further restrictions might be imposed to allow for the steric requirements of the overcrowded atoms.

Calculation of Deformation Forces.—We have circumvented this difficulty by reversing the calculation. Rather than derive from the theoretical potential function a predicted molecular configuration for comparison with experiment, we have applied the potential function to the observed configurations of the two molecules, described in Part VI,[1] calculating the net out-of-plane deformation force F_d on each atom. These calculated forces should, ideally, vanish at all positions except where steric repulsion balances the net deformation force. If they do not, a change in the theoretical potential function may be indicated.

A practical obstacle to this programme was the inaccuracy of the experimental hydrogen positions. If these positions had been used in the calculation of the molecular deformation the results would have been grossly inaccurate. Instead, we proceeded in two stages as follows: (*a*) we calculated the equilibrium positions of the hydrogen atoms in accordance with the observed carbon positions, using the theoretical potential function; and (*b*) we calculated the deformation force F_d on each carbon atom based on the observed carbon positions and the calculated hydrogen positions.

In stage (*a*) it was assumed that each exocyclic C–H bond made equal angles with the two adjacent C–C bonds. The bending parameters ε_r of the secondary carbon atoms and the torsion parameters τ_{rs} of the bonds between them were expressed as functions of the angles made by the several C–H bonds with the planes of the respectively adjacent C–C bonds. The equilibrium values of these angles were then determined by the condition that the net out-of-plane force on each of the hydrogen atoms should vanish. Intermolecular forces were neglected.

In stage (*b*) it was necessary to differentiate equation (1) with respect to the out-of-plane co-ordinate of each carbon atom in turn. Specification of the out-of-plane direction at each atom was somewhat arbitrary; for 1,12-dimethylbenzo[*c*]phenanthrene the following choice was made.

At each of the secondary carbon atoms $C_{(1)}$ to $C_{(6)}$: normal to the plane of the two adjacent aromatic C–C bonds; at each of the tertiary carbon atoms $C_{(7)}$ and $C_{(8)}$: normal to the plane of the three ligand carbon atoms; at the methyl atom $C_{(11)}$: perpendicular to the exocyclic bond $C_{(1)}$–$C_{(11)}$ in the plane containing this bond and the normal to the plane of $C_{(2)}$–$C_{(1)}$–$C_{(7)}$. This is the direction of the force on $C_{(11)}$ arising from the bending ε_1 of atom $C_{(1)}$.

It was found, however, that scarcely any significant error would have resulted if the individual forces on each atom, due to the several deformations ε_r and τ_{rs} in its environment, had simply been added algebraically without regard to their slight non-parallelism. This simpler procedure was accordingly adopted for benzo[*c*]phenanthrene, where the error entailed should be even smaller because of the nearer approach to planarity.

The calculations for 1,12-dimethylbenzo[*c*]phenanthrene proceeded exactly as indicated. The positions of the five hydrogen atoms in the asymmetric unit were determined from one set of three [for $H_{(2)}$, $H_{(3)}$, and $H_{(4)}$] and one set of two [for $H_{(5)}$ and $H_{(6)}$] simultaneous equations. These equations, though not quite linear, were readily solved by two successive linear approximations. The deformation parameters so derived, together with those referring to $C_{(1)}$ and the tertiary carbon atoms, which were determined explicitly by the experimental carbon co-ordinates, led to a direct evaluation of the deformation forces F_d on all carbon atoms. These results are indicated in Fig. 2(B).

For benzo[*c*]phenanthrene the above procedure had to be modified because the steric repulsions acting on the overcrowded hydrogen atoms, being of unknown magnitude, precluded a direct calculation of the positions of these atoms. Accordingly, the repulsive forces on these atoms, assumed equal and opposite by symmetry, were introduced as an adjustable parameter T. The deviations, from the respective C–C–C planes, of eight of the exocyclic C–H bonds, and thus the deformation parameters involving the corresponding secondary carbon atoms, were determined in terms of this parameter from two sets of four simultaneous nearly linear equations. The other four hydrogen positions

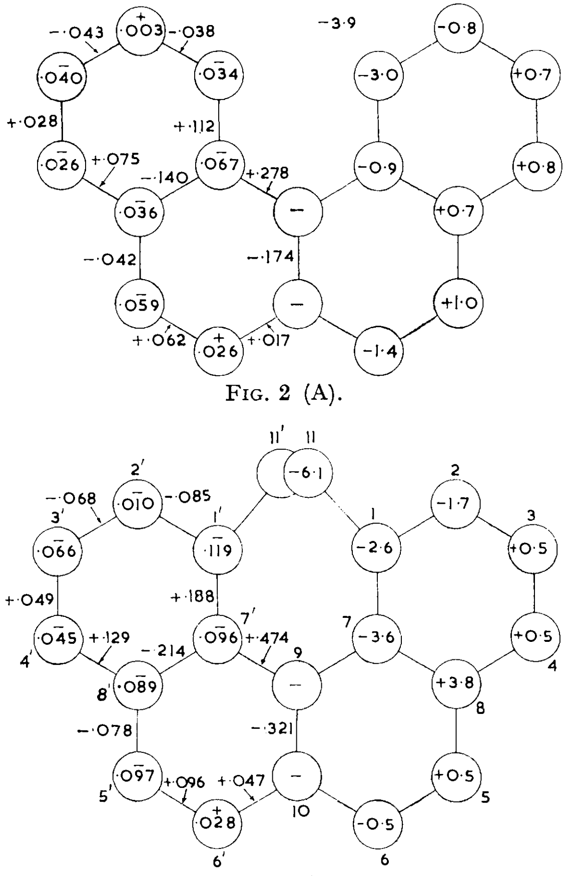

FIG. 2 (A).

FIG. 2 (B).

FIG. 2. Out-of-plane molecular deformation in (A) benzo[*c*]phenanthrene (average of two halves of molecule) and (B) its 1,12-dimethyl derivative. Left-hand side of each figure shows bending parameters ε_r, inside circles, and torsion parameters τ_{rs}, in radians, alongside bonds. At right are net calculated out-of-plane deformation forces F_d (opposite in sign to those at left), in units of 10^{-5} dyne. ε_r positive for solid angle concave towards observer, τ_{rs} positive for torsion having sense of right-handed screw, F_d positive towards observer; reversal of all three sign conventions leads to enantiomorphic molecule.

were derived from two pairs of simultaneous equations that did not involve the parameter T. The value of T was then adjusted so as to minimise the sum of squares of the calculated out-of-plane forces F_d on all carbon atoms except the two in the overcrowded positions. The resulting deformations and forces are indicated in Fig. 2(A).

The experimental hydrogen positions may be compared with the calculated positions to provide an approximate test of the validity of the calculation. This comparison, expressed in terms of the angles of out-of-plane bending of the exocyclic C–H bonds, is indicated in Table 1. For benzo[*c*]phenanthrene the Table gives the average values for symmetry-related bonds. The agreement is poor for the parent compound, but it is much better for the dimethyl-derivative. The uncertainty in the hydrogen positions is, however, too large for the test to have more than qualitative significance.

The accuracy of the calculated forces is, of course, limited by the experimental errors in the atomic co-ordinates. The force on each atom is particularly sensitive to the position of that atom and rather less sensitive to the positions of neighbouring atoms. Taking the standard deviations of the out-of-plane co-ordinates of the carbon atoms in both structures as $\sim 0{\cdot}005$ Å, and assuming the positional errors of different atoms to be statistically independent, we can estimate the standard deviation of the calculated force F_d on a tertiary carbon atom at about $1{\cdot}3 \times 10^{-5}$ dyne and of that on a secondary carbon atom at about $0{\cdot}8 \times 10^{-5}$ dyne. At the methyl-carbon atoms (11) the standard deviation is $<0{\cdot}3 \times 10^{-5}$ dyne.

TABLE 1.

Calculated and observed angles of bending of exocyclic C–H bonds relative to planes of adjacent C–C bonds, in radians, for (A) benzo[*c*]phenanthrene and (B) its 1,12-dimethyl derivative. Figures for the former compound are averages for two halves of molecule.

	Parent (A)		Me_2 deriv. (B)	
Atom	Calc.	Obs.	Calc.	Obs.
H-1	0·04	$\bar{0}{\cdot}\bar{0}\bar{3}$	—	—
H-2	0·00	0·13	0·01	0·09
H-3	0·05	0·06	0·08	0·11
H-4	0·03	0·15	0·05	0·07
H-5	0·07	0·26	0·11	0·05
H-6	$\bar{0}{\cdot}\bar{0}\bar{3}$	$\bar{0}{\cdot}\bar{0}\bar{4}$	$\bar{0}{\cdot}\bar{0}\bar{3}$	$\bar{0}{\cdot}\bar{0}\bar{5}$

The differences between the calculated forces on symmetry-related atoms in benzo[*c*]phenanthrene were generally within the estimated experimental uncertainty despite the slight asymmetry of the observed molecular configuration. Since it is likely that the major effect of intermolecular forces is to increase the deformation of one half of the molecule while reducing that of the other half, we assume that the average observed configuration is very close to that of the isolated molecule. The average values, both for the deformations and for the resulting forces, are accordingly given in Fig. 2(A).

Comparison of Figs. 2(A) and 2(B) reveals a close correspondence between the two molecules. The deformations are generally similar, apart from a uniform difference in scale. This difference is reflected in the calculated deformation energies V_d of the two molecules, obtained by summation of the separate bending and torsion contributions according to equation (1). The values found for V_d are: for benzo[*c*]phenanthrene, $0{\cdot}510 \times 10^{-12}$ erg $= 7{\cdot}33$ kcal./mole; for the dimethyl derivative $1{\cdot}500 \times 10^{-12}$ erg $=$ $21{\cdot}59$ kcal./mole. The ratio of the calculated energies corresponds to an average ratio of $(21{\cdot}59/7{\cdot}33)^{1/2} = 1{\cdot}72$ between corresponding deformations; the individual values depart but little from this average ratio.

The total strain energy due to the intramolecular overcrowding comprises the deformation energy, estimated above, plus the energy of compression of the overcrowded atoms. The latter is likely to contribute a relatively small portion of the total overcrowding energy because of the very steep dependence of the compression forces on the interatomic distances.[3] On the other hand, there is reason to expect that the calculated deformation energies may be somewhat overestimated because the calculations have combined a theoretical potential function with the observed molecular deformations. Since the potential function used is only an approximation and the observed configuration suffers from experimental error, this configuration must differ somewhat from that which would

[3] Coulson and Senent, *J.*, 1955, 1819.

minimise the theoretical deformation energy. This difference is, indeed, implied by the non-vanishing calculated forces F_d shown in Fig. 2. Hence, we must regard as quite satisfactory the agreement of the calculated energy of deformation for benzo[*c*]phenanthrene with the estimate of 6—7 kcal./mole deduced [4] for the total overcrowding energy from the experimental resonance energy.[5]

For the most part the calculated forces indicated in Fig. 2 do not, except at the overcrowded positions, depart significantly from zero. We may conclude that to the present degree of experimental precision the Coulson–Senent potential function is in good agreement with the observed deformations of these two molecules. In view of the extreme simplicity of this function, which contains only two force constants, having everywhere the same values despite wide differences in chemical environment, this agreement must be regarded as excellent.

Nevertheless, some of the calculated values of F_d, particularly at atoms $C_{(7)}$ and $C_{(8)}$ in 1,12-dimethylbenzo[*c*]phenanthrene, appear rather too large to be due entirely to co-ordinate errors. (A small portion, only, of the calculated force at $C_{(7)}$ may be offset by repulsion between that atom and $H_{(\alpha')}$, as indicated in Fig. 5 and Table 10 of Part VI.) The complete agreement in sign between corresponding values of F_d for the two molecules further suggests that these figures have a non-random origin.

Part of the difficulty may be associated with the artificial attempt to separate out-of-plane from in-plane deformations; because of the molecular non-planarity there will be at each atom, in whatever direction we may designate " out-of-plane," some contribution from the in-plane deformations of bond stretching or compression and valency-angle strain. From the observed bond angles, however, one can estimate that the " in-plane " forces are almost certainly too small to yield " out-of-plane " components of any significant magnitude.

On the other hand, there are two ways in which the potential function described above might be modified, with marked improvement in the experimental agreement. Instead of a single value of k_τ for all aromatic bonds, the torsion force constant might more reasonably be taken proportional to the mobile bond order. Some such refinement was, in fact, suggested by Coulson and Senent [2] when they proposed their simpler function. Secondly, some allowance should be made for anharmonicity in the torsional potential. A natural way to do this would be to replace τ^2 in equation (1) by $\sin^2 \tau$, thus making the torsion energy a maximum for $\tau = \pi/2$. These two modifications would lower, by nearly one-third, the calculated restoring forces associated with the torsion of the 7,9-bond in 1,12-dimethylbenzo[*c*]phenanthrene. This bond has the lowest calculated bond order [6] and is, correspondingly, the longest aromatic bond in both molecules, and it is also the most severely twisted. Such a decrease would, in itself, reduce the calculated deformation forces at $C_{(7)}$ and $C_{(8)}$, as well as at $C_{(1)}$, by about 2×10^{-5} dynes, thus disposing of the only appreciable discrepancies between theory and experiment.

It is evident that quantitative test of such refinements of the potential function would unduly strain the accuracy of the present crystallographic data. However, data such as these can be useful as a guide to the kind of improvements, suggested by theoretical considerations, that are likely to prove important.

The calculated forces on the overcrowded atoms in both molecules provide a rough indication of the repulsive forces between these atoms. Unfortunately, the force between the overcrowded hydrogen atoms in benzo[*c*]phenanthrene and the positions of these atoms have both been derived by very indirect reasoning and cannot, therefore, be considered very reliable. For the dimethyl derivative, it appears from the observed interatomic distances (Part VI, Table 10) that the largest repulsive forces must be those (*a*) between the two methyl groups, (*b*) between the 11-methyl group and $C_{(1')}$, and (*c*) between the

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[4] Herbstein and Schmidt, *J.*, 1954, 3302.

[5] Magnus and Becker, *Erdöl u. Kohle*, 1951, **4**, 115.

[6] Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906.

11′-methyl group and $C_{(1)}$, symmetrical to (*b*). With the forces acting on the methyl groups themselves compounded of carbon–carbon, carbon–hydrogen, and hydrogen–hydrogen interactions, it is not possible to resolve the calculated forces F_d into individual interatomic repulsions. Moreover, it is clear that the largest repulsions are between pairs of atoms whose separations fall on the steeply rising portion of the curve relating interatomic repulsion to distance. Where at least one atom of such a pair is hydrogen, as is apparently the case for nearly all the strong repulsions, the uncertainty in the hydrogen position would invalidate any quantitative comparison with theoretical repulsive-potential functions even if the repulsive force itself could be deduced unambiguously. This means that by slight adjustments of the hydrogen co-ordinates, within their estimated errors, agreement could be achieved between the present data and almost any reasonable repulsive-potential function.

Chemical Implications of Deformation.—Of particular interest from a chemical viewpoint is the observation that in both molecules the calculated non-planarity is greater at atom $C_{(5)}$ than at any other exposed carbon atom (Table 1). This is the position, in benzo[*c*]phenanthrene, that Newman and Kosak[7] found most reactive toward bromine, nitric acid, and the Friedel–Crafts reagent. Since the calculated free valence[6] and the self polarisability[8] are also greatest at this position, though by a very slight margin, its reactivity cannot be unequivocally ascribed to the out-of-plane deformation. Nevertheless, one expects that the deformation of a secondary carbon atom should promote substitution at this position by lowering the corresponding localisation energy.[9] It is not easy, however, to estimate the magnitude of this effect. Very crudely, we may imagine that in the transition state, with the carbon atom under attack hybridised tetrahedrally and thus effectively removed from the aromatic system,[10] the torsion force constants associated with the two π-bonds formed by this atom must vanish. This will leave the exocyclic C–H bond free to assume the preferred tetrahedral orientation. Thus, the formation of the Wheland intermediate results, at least, in the release of that part of the deformation energy associated with the bending of the carbon atom at the point of attack and with the torsion of its two aromatic bonds. For a secondary carbon atom $C_{(r)}$, bonded to $C_{(s)}$ and to $C_{(t)}$, this energy is

$$W_r = \tfrac{1}{2}k_\epsilon \epsilon_r^2 + \tfrac{1}{2}k_\tau(\tau_{rs}^2 + \tau_{rt}^2).$$

The net localisation energy must, then, be smaller by this amount than that to be expected for a planar molecule. Of course, we must suppose that the opening of two twisted π-bonds will permit extensive relaxation of the deformation of the rest of the molecule. Thus the total reduction in localisation energy, due to the deformation, must exceed the quantity W_r which we have deduced by imagining the rest of the molecule to be rigidly fixed in its initial configuration. Yet we may hope that at least for comparison among different positions in the same molecule, or in closely similar molecules, the actual steric reduction in localisation energy will be approximately proportional to the calculated values of W_r.

Except that it is concerned with out-of-plane rather than in-plane deformation, the situation considered here is closely analogous to the phenomenon known as *I*-strain,[11] which applies principally to the distortion of valency angles in small rings. There is the further distinction, however, that whereas the effect of the *I*-strain on activation energies depends on the difference in strain energy associated with a carbon atom in two states of hybridisation, the out-of-plane deformation energy associated with a particular carbon atom is here assumed to vanish entirely in the tetrahedral state because of the freedom of rotation about the pure σ bonds.

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[7] Newman and Kosak, *J. Org. Chem.*, 1949, **14**, 375.

[8] Badger and Walker, *J.*, 1954, 3238.

[9] Szwarc and Leavitt, *J. Amer. Chem. Soc.*, 1956, **78**, 3590.

[10] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

[11] Brown and Gerstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2926.

Using the values of k_ϵ and k_τ derived above and the calculated deformation parameters shown in Fig. 2, we find the values of W_r listed in Table 2. Except for the overcrowded position 1, the maximum value of W is seen to occur, in both molecules, at position 5. At all positions the values calculated for the dimethyl compound exceed those for its parent by a factor close to three. These results appear to offer a satisfactory explanation for the high yields of 5-substituted products obtained from benzo[*c*]phenanthrene. They indicate, further, that the 1,12-dimethyl derivative should be appreciably more reactive and should display even greater orientational specificity.

The only quantitative data available on the influence of deformation on the reactivity of the benzophenanthrene system come from the measurements of Levy, Newman, and Szwarc[12] on the methyl affinities of benzo[*c*]phenanthrene and of several of its methyl derivatives, including the 1,12-derivative. For the parent hydrocarbon and for all its monomethyl derivatives except that substituted in the 1-position, they report methyl affinities, at 85°, of 64 ± 10, to be compared with values of 108 for 1-methyl- and 183 for 1,12-dimethyl-benzophenanthrene. Coulson[13] has demonstrated a close linear relation between the logarithms of the methyl affinities r per atom of several alternant hydrocarbons and the smallest calculated localisation energies E_a of these molecules. According to this empirical relation,

TABLE 2.

Calculated steric reduction W_r of localisation energies for various positions, in cal./mole, in (A) benzo[*c*]phenanthrene and (B) its 1,12-dimethyl derivative.

Position	1	2	3	4	5	6
W_r: compound A	(358)	77	106	168	227	115
,, B	(1384)	280	283	498	617	285

$$\log_{10} r = 16{\cdot}66 - 6{\cdot}57E_a, \qquad (2)$$

where E_a is in units of β, the average resonance integral for an aromatic C–C bond, and r is $6/n$ times the observed methyl affinity, n being the number of equivalent positions competing for methyl addition as indicated by equal values of their localisation energies. If we assume that only the 5- and the 5′-position are active, then $6/n$ takes the value 3. Substituting in equation (2) the observed methyl affinities cited above, we find apparent localisation energies of 2·19β, 2·15β, and 2·12β, respectively, for benzo[*c*]phenanthrene and its 1-methyl and 1,12-dimethyl derivative. The difference of 0·07β between the parent and the dimethyl derivative is evidently to be attributed to the greater deformation of the latter molecule. If we substitute a value of $\beta = 19$ kcal./mole, deduced[4] from a comparison of the experimental and theoretical resonance energies of several planar polycyclic hydrocarbons, this difference is found to be 1·3 kcal./mole. This is somewhat over three times the difference between the calculated values of W_5 for the two molecules. The qualitative agreement is probably all that could be expected, and the discrepancy is in the direction foreseen.

It might seem that this agreement could be improved simply by the use of a smaller value for β. And, in fact, it has been shown[14] that the correlation of relative reaction rates with calculated localisation energies generally requires a value of β much smaller than that appropriate to the calculation of resonance energies. Indeed, if we rewrite equation (2) in the form

$$r = 4{\cdot}6 \times 10^{16} \exp\left(-15{\cdot}13\ E_a/\beta\right)$$

and seek to identify the localisation energy E_a with the heat of activation ΔU in

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[12] Levy, Newman, and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 4225.

[13] Coulson, *J.*, 1955, 1435.

[14] Bavin and Dewar, *J.*, 1956, 164; Dewar, Mole, and Warford, *ibid.*, p. 3581.

the Arrhenius expression exp $(-\Delta U/kT)$ or, at least, with that part of ΔU that varies for different compounds, then for $T = 358°$ we must have $\beta = 10{\cdot}8$ kcal./mole.

However, it appears[14] that the reason for the small apparent value of β is that, especially in highly exothermic reactions, the transition state for aromatic substitution is not the Wheland intermediate but a species more nearly resembling, in configuration and energy content, the initial separate reactants.[15] The activation energy ΔU thus includes only a small fraction of the calculated E_a. By the same token, if in the transition state the carbon atom under attack is not fully tetrahedral, the relaxation of the deformation energy cannot be complete. What we have assumed in the comparison above is simply that ΔU varies linearly with E_a, calculated for the Wheland intermediate, in all the compounds considered. If this assumption, which is apparently valid for those compounds to which equation (2) applies, remains valid for our compounds, then we are justified in deriving from equation (2) apparent values of E_a for them. These values are, then, appropriate to the Wheland intermediate, to which our calculations of W_r also apply. We have chosen to base our correlation of these two quantities on a value of β derived from resonance-energy calculations simply because this method gives consistent values for a large number of aromatic molecules.[16]

We conclude that overcrowding and chemical reactivity can be, at least semi-quantitatively, correlated. To verify this conclusion and to give it greater precision will require further study, both structural and chemical, of additional overcrowded compounds. The structural information, preferably obtained by a method, such as neutron diffraction, permitting accurate location of hydrogen atoms, is needed for the precise determination of the potential-energy function for out-of-plane deformation. Information on chemical reactivity, especially for groups of related compounds differing in degree of overcrowding, is essential for understanding the relation between overcrowding and the activation energies for various types of reaction. This kind of relation can then be of use in the formulation of reaction mechanisms. Progress in this area is thus expected to accompany parallel progress in the broader field of chemical reactivity.

Ultraviolet Spectra.—The influence of overcrowding on ultraviolet spectra and on ionisation potentials should be even more directly traceable. Cromartie and Murrell[17] have shown, for a series of overcrowded alternant hydrocarbons, how frequency shifts in the *p*-absorption bands resulting from substitution in the overcrowded positions may be related to the contribution of the highest normally occupied molecular orbitals to the mobile bond orders of the C–C bonds that are most twisted on substitution. Most of the examples discussed by these authors concerned the effect of substitution in position 4 or 5 of phenanthrene or in corresponding positions of larger molecules containing a phenanthrene nucleus. In each of these molecules it was plausibly assumed that the bond corresponding to 4a,4b in phenanthrene was the most severely twisted. If the highest occupied orbital had a node through this bond, substitution usually produced a hypsochromic shift; if not, a bathochromic shift was observed.

From Fig. 2 it is evident that the most twisted bonds in benzo[*c*]phenanthrene and its 1,12-dimethyl derivative are, in descending order, 7,9, 9,10, and 7,8. Pullman and Pullman[16] give the calculated energies of the several molecular orbitals in benzo[*c*]-phenanthrene. With these data it is easy to substitute in the appropriate molecular-orbital equations and so recompute the coefficients c_{rj} of the several atomic orbitals ϕ_r in any molecular orbital ψ_j. The products of these coefficients, for the highest occupied molecular orbital, corresponding to the several C–C bonds are listed in Table 3. We see that the values of this product are quite small for bonds 7,9 and 7,8 but large and positive for bond 9,10. A bathochromic shift is accordingly expected to accompany substitution in the overcrowded positions of this molecule. Badger and Walker[8] found indeed

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[15] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[16] Pullman and Pullman, "Les Théories Electroniques de la Chimie Organique," Masson, Paris, 1952.

[17] Cromartie and Murrell, *J.*, 1961, 2063.

anomalous bathochromic shifts of all the prominent ultraviolet bands in the spectrum of benzo[*c*]phenanthrene on methyl substitution at position 1 and much smaller shifts associated with substitution at any other position.

TABLE 3.

Products of coefficients c_rc_s for highest occupied molecular orbital.

Bond	c_rc_s	Bond	c_rc_s	Bond	c_rc_s	Bond	c_rc_s	Bond	c_1c_s	Bond	c_rc_s
1—7	0·006	2—3	$\bar{0}\cdot\bar{0}\bar{3}\bar{9}$	4—8	$\bar{0}\cdot\bar{0}\bar{1}\bar{8}$	5—8	0·020	6—10	$\bar{0}\cdot\bar{0}\bar{3}\bar{0}$	7—9	$\bar{0}\cdot\bar{0}\bar{0}\bar{7}$
1—2	0·055	3—4	0·069	7—8	0·001	5—6	0·038	9—10	0·095		

The observed shifts were, however, too small, and the identification of the first π–π^* transition too uncertain, to warrant an attempt at quantitative calculation of the effect. But it can readily be shown that if we assume that the effect of bond torsion is to reduce the corresponding resonance integral β_{rs} according to the accepted equation[18]

$$\beta_{rs} = \beta_0 \cos \tau_{rs} \tag{3}$$

and try to calculate the spectral shift by a perturbation treatment along the lines indicated by Cromartie and Murrell,[17] we shall obtain an underestimate of the actual shift. Moreover, this discrepancy is not linked to any chosen value for the parameter β_0 but appears even if we merely try to estimate, according to equation (3), the relative shift of the lowest π–π^* excitation energy between benzo[*c*]phenanthrene and its 1-methyl derivative on the resonable assumption that the latter molecule is intermediate in out-of-plane deformation between the parent and the 1,12-dimethyl derivative. The calculated relative shift, which does not depend on the value assigned to β_0, is barely half that found experimentally, even after allowance for the conjugative effect exhibited by all methyl substituents.

It may be noted that a similar first-order perturbation treatment based on equation (3) leads to a calculated value of the torsion force constant k_τ of benzene that is almost 50% smaller than the empirical value derived above. We may, accordingly, suspect that this equation underestimates the effect of overcrowding on the π-electron energy of the molecule. Further effort is evidently required before molecular-orbital theory can be expected to provide, in this area as in many others, quantitative rather than merely qualitative predictions of molecular properties.

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REHOVOTH, ISRAEL.
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[18] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3345; Coulson, in " Steric Effects in Conjugated Systems," ed. Gray, Academic Press, New York, 1958, p. 8.