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THEORETICAL CALCULATION OF STERIC EFFECTS IN CONJUGATED SYSTEMS—I

PHENANTHRENE, TRIPHENYLENE AND CHRYSENE

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Abstract—An improved method of calculating deformations in overcrowded molecules is given; this is applicable to conjugated systems with one set of equivalent non-bonded interactions. A theorem is proved concerning the relation of in-plane and out-of-plane deformation in such systems. Three applications are given and others discussed. The deformations in phenanthrene etc. are predicted to be small, and the molecules planar.

INTRODUCTION

A MOLECULE is said to be overcrowded[1,2] if, when we assign to bond-lengths and bond-angles their standard values, at least one pair of non-bonded atoms are closer to each other than the sum of their accepted van der Waals radii. The uncertainties, both in the van der Waals radii and the standard molecular geometry, do not greatly reduce the usefulness of this definition. If the atoms were to remain very close to each other, and the rest of the molecule were unaltered, there would be a considerable van der Waals repulsion energy. If on the other hand the molecule were deformed so that the overcrowded atoms were separated to the sum of their van der Waals radii, there would be a considerable strain energy. In practice obviously a compromise is reached, so that the task of anyone wishing to calculate the actual geometry of such a molecule is to set up functions for both the van der Waals energy and the strain energy, and to minimize their sum with respect to all the independent parameters.

Numerous authors have done this for particular groups of molecules. Westheimer *et al.*[3] and also Hill[4] investigated especially the (untwisted) transition-state for the racemization of substituted diphenyls, considering only in-plane distortion.[5,6] Coulson *et al.*[7–11] have investigated overcrowded condensed aromatic hydrocarbons; they used

[1] F. Bell and D. H. Waring, *J. Chem. Soc.* 2689 (1949); E. Harnik, F. H. Herbstein, G. M. J. Schmidt and F. L. Hirschfeld, *Ibid.* 3288 (1954).
[2] M. S. Newman in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) p. 476. Wiley, New York (1956).
[3] F. H. Westheimer and J. E. Mayer, *J. Chem. Phys.* **14,** 733 (1946); F. H. Westheimer, *Ibid.* **15,** 252 (1947); M. Rieger and F. H. Westheimer, *J. Amer. Chem. Soc.* **72,** 19 (1950).
[4] T. L. Hill, *J. Chem. Phys.* **14,** 465 (1946); **16,** 399, 938 (1948).
[5] This work is reviewed by F. H. Westheimer in Ref. 2, p. 542.
[6] See also K. E. Howlett, *J. Chem. Soc.* 4353 (1957); 1055 (1960).
[7] C. A. Coulson and S. Senent, *J. Chem. Soc.* 1813, 1819 (1955).
[8] C. A. Coulson in *Theoretical Organic Chemistry, Kekulé Symposium*, p. 56, Butterworths, London (1959).
[9] M. Asgar Ali and C. A. Coulson, *J. Chem. Soc.* 1558 (1959).
[10] C. A. Coulson and A. Golebiewski, *Tetrahedron* **11,** 125 (1960).
[11] C. A. Coulson and A. Golebiewski, *J. Chem. Soc.* 4948 (1960).

the hard sphere approximation (i.e. a fixed non-bonded distance, not a van der Waals potential curve), and considered only out-of-plane distortion. A number of related calculations have also been reported,[12–16] of which Hendrickson's[16] work on cycloalkanes most nearly parallels the present work.

We have so far confined our attention to those compounds of trigonally-hybridized carbon where one may legitimately distinguish deformation in and out of the mean plane of the carbon atoms. Although the former predominates for the problems of Ref. 5, and the latter for those of Refs. 7–11, there will undoubtedly be cases where both should be included, and this we have done. The use of a van der Waals potential curve is clearly an improvement over the hard sphere approximation (although it need not necessarily alter the main conclusions of Refs. 7 and 9); furthermore, using a general rather than a specific form for this potential (until numerical results are required) renders the algebra less inelegant, and this aim is further achieved by adopting matrix notation. Bond-stretchings due to overcrowding have been quite rightly neglected in almost all previous work; they are however relevant to the comparison of theoretical and experimental bond-lengths in certain conjugated compounds, and we have included them. In Section 2, we give a general analysis incorporating these refinements. Then, in Section 3, we discuss the choice of potential functions and numerical parameters, and, in Section 4, apply the method to specific cases. A subsequent paper[17] will give results in the study of the cyclopolyenes C_nH_n (annulenes).[18]

GENERAL ANALYSIS

The energy due to steric effects in an overcrowded molecule (of the type we are discussing)which has one set of t equivalent non-bonded interactions may be written as

$$V = t \cdot U(R) + V_x + V_z \tag{1}$$

where $U(R)$ is the van der Waals potential between atoms separated by a distance R, and V_x, V_z are respectively the in- and out-of-plane deformation or strain energies. Also

$$V_x = \tfrac{1}{2}\mathbf{x}'\mathbf{K}\mathbf{x} \tag{2}$$

and

$$V_z = \tfrac{1}{2}\mathbf{z}'\mathbf{A}\mathbf{z} \tag{3}$$

where $\mathbf{x}$ is a vector, of order m, of in-plane deformation parameters, usually taken as increases in bond-lengths above standard values and increases in bond-angles above $2\pi/3$; $\mathbf{z}$ is a vector, of order n, of perpendicular displacements out of the plane; and $\mathbf{K}$ and $\mathbf{A}$ are symmetrical square matrices of force-constants (The prime, here and throughout, signifies transposition). The effect of the deformation on the separation of the overcrowded atoms is given by

$$R = R_0 + R_x + R_z + R_{xz} \tag{4}$$

[12] C. A. Coulson and D. Stocker, *Mol. Phys.* **2**, 397 (1959); D. Stocker, quoted in Ref. 8.
[13] A. I. Kitaigorodskii, *Tetrahedron* **9**, 183 (1960).
[14] I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 175 (1946); P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. Mackie, *Ibid.* 3200 (1955).
[15] R. Pauncz and D. Ginsburg, *Tetrahedron* **9**, 52 (1960).
[16] J. B. Hendrickson, *J. Amer. Chem. Soc.* **83**, 4537 (1961).
[17] C. W. Haigh, to be published.
[18] F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.* **84**, 260 (1962).

where R_0 is its value when no deformation is allowed, and R_x, R_z are the increases due respectively to in- and out-of-plane deformation occurring separately; and R_{xz} is the additional separation when both occur together. It is found in practice that $\mathbf{x}$ is so small that a first-order linear approximation is legitimate for R_x. R_z is by symmetry an even function of the z_j's, and we retain only the terms of order z_j^2 (in line with the harmonic approximation of (3)), and thus omit R_{xz}. This restricts our treatment to cases where out-of-plane distortion is not too severe.[18a] Equation (4) may now be written as

$$H(R, \mathbf{x}, \mathbf{z}) \equiv \boldsymbol{\alpha}'\mathbf{x} + \tfrac{1}{2}\mathbf{z}'\mathbf{B}\mathbf{z} - (R - R_0) = 0 \tag{5}$$

where $\mathbf{B}$ is a symmetrical square matrix. The usual redundancy conditions (angle-sums and projections), of which we will assume there are l, may be written as[19]

$$\left.\begin{aligned} g_k(\mathbf{x}) \equiv \mathbf{c}'_k\mathbf{x} + d_k = 0, \qquad k = 1, 2 \ldots l, \\ \text{or, in an obvious notation} \\ \mathbf{g}(\mathbf{x}) \equiv \mathbf{C}\mathbf{x} + \mathbf{d} = 0 \end{aligned}\right\} \tag{6}$$

where $\mathbf{C}$ is a rectangular $l \times m$ matrix. Now, introducing Lagrangian multipliers ρ; $\sigma_1, \sigma_2 \ldots \sigma_l$, with $\boldsymbol{\sigma}$ the vector of σ's, we have to minimize

$$W \equiv V(R, \mathbf{x}, \mathbf{z}) + \rho H(R, \mathbf{x}, \mathbf{z}) + \boldsymbol{\sigma}'\mathbf{g}(\mathbf{x})$$

with respect to $\mathbf{x}$, $\mathbf{z}$ and R.
Now

$$W = tU(R) + \tfrac{1}{2}\mathbf{x}'\mathbf{K}\mathbf{x} + \tfrac{1}{2}\mathbf{z}'\mathbf{A}\mathbf{z} + \rho\boldsymbol{\alpha}'\mathbf{x} + \tfrac{1}{2}\rho\,\mathbf{z}'\mathbf{B}\mathbf{z} - \rho(R - R_0) + \boldsymbol{\sigma}'\mathbf{C}\mathbf{x} + \boldsymbol{\sigma}'\mathbf{d}$$

Differentiating w.r.t. R: $$t\,.\,dU/dR = \rho \tag{7}$$

Differentiating w.r.t. all z_j $$(\mathbf{A} + \rho\mathbf{B})\mathbf{z} = 0 \tag{8}$$

Differentiating w.r.t. all x_i $$\mathbf{K}\mathbf{x} + \rho\boldsymbol{\alpha} + \mathbf{C}'\boldsymbol{\sigma} = 0 \tag{9}$$

Eliminating $\mathbf{x}$ from (9) and (6), we solve for $\boldsymbol{\sigma}$, obtaining

$$\boldsymbol{\sigma} = \mathbf{E}^{-1}\mathbf{d} - \rho\mathbf{E}^{-1}\mathbf{C}\mathbf{K}^{-1}\boldsymbol{\alpha} \tag{10}$$

where $\mathbf{E} \equiv \mathbf{C}\,\mathbf{K}^{-1}\,\mathbf{C}'$, a symmetrical $l \times l$ matrix.

Substituting back in (9) we obtain

$$\mathbf{x} = -\rho(\mathbf{1} - \mathbf{K}^{-1}\mathbf{C}'\mathbf{E}^{-1}\mathbf{C})\mathbf{K}^{-1}\boldsymbol{\alpha} + \mathbf{x}_0 \tag{11}$$

where $$\mathbf{x}_0 \equiv -\mathbf{K}^{-1}\mathbf{C}'\mathbf{E}^{-1}\mathbf{d} \tag{12}$$

From (8) $$\mathbf{A}^{-1}\mathbf{B}\mathbf{z} = \lambda\mathbf{z} \tag{13}$$

where $$\lambda \equiv -1/\rho \tag{14}$$

[18a] If we were to expand $U(R)$ as a power series about $R = R_0$, and then substitute (4) into this expression, we clearly ought to retain in U terms of $O(z^4)$ to permit a minimum value of V to occur when $\mathbf{z} \neq 0$. But it would then seem consistent to include such terms also in (3) and (4). Their neglect in (3) can be justified on the same grounds as footnote 19 and Ref. 7. As to (4), an actual computation, in one case, of the neglected terms of order xz^2, x^2 and z^4 showed that they altered $R - R_0$ by 0·1%.

[19] It may seem inconsistent to include a quadratic term in z_j in (5) but not in (6), for (5) is actually a redundancy equation for a ring completed by one non-bonded distance. The justification is that for moderate out-of-plane deformation, the bonds will make small angles with the mean plane, but the line joining the overcrowded atoms will not; the assumptions must be checked *a posteriori*.

Now (13) can be fulfilled in two ways:

Case a: $\mathbf{z} = 0$. This is not trivial: it implies *no out-of-plane deformation* and $V_z = 0$. Eliminating $\mathbf{x}$ and ρ from (5), (7) and (11) we find

$$R - R'_0 + (t/f)\, D(R) = 0 \tag{15}$$

where

$$R'_0 \equiv R_0 + \boldsymbol{\alpha}'\mathbf{x}_0, \tag{16}$$

$$1/f \equiv \boldsymbol{\alpha}'(\mathbf{1} - \mathbf{K}^{-1}\mathbf{C}'\mathbf{E}^{-1}\mathbf{C})\mathbf{K}^{-1}\boldsymbol{\alpha}, \tag{17}$$

and

$$D(R) \equiv dU/dR. \tag{18}$$

Equation (15) is a transcendental equation in the one variable R, which is solved numerically, obtaining a value R_a, hence, from (7) and (11), ρ_a and $\mathbf{x}_a$. After some manipulation we find that

$$V_x = \rho^2/2f + V_0 \tag{19}$$

which is true not only in case a. Here

$$V_0 \equiv \tfrac{1}{2}\mathbf{d}'\mathbf{E}^{-1}\mathbf{d} \tag{20}$$

and, using (7) and (15), we find (in case a only)that

$$V_x = \tfrac{1}{2}f(R_a - R'_0)^2 + V_0 \tag{21}$$

We may note that $\mathbf{x}_0$ and V_0 are a measure of the small deformations arising from the non-equality of the skeletal bond-lengths, and R'_0 is the value of R adjusted for this, before steric effects are considered.

Case b: $\mathbf{z} \neq 0$. Equation (13) is now an eigenvalue problem. For reasons to be justified below, we select the highest eigenvalue λ_1, hence obtaining ρ_b, and the corresponding eigenvector $\boldsymbol{\zeta}$. We can immediately obtain $\mathbf{x}_b$ from (11); hence, using (17)

$$\boldsymbol{\alpha}'\mathbf{x}_b = -\rho_b/f + \boldsymbol{\alpha}'\mathbf{x}_0 \tag{22}$$

If, by analogy with (16), we define

$$R_1' \equiv R_0 + \boldsymbol{\alpha}'\mathbf{x}_b = R_0' - \rho_b/f, \tag{23}$$

then from (19)

$$V_x = \rho_b^2/2f + V_0 = \tfrac{1}{2}f(R_1' - R_0')^2 + V_0 \tag{24}$$

Note that $\mathbf{x}_b$ and V_x are now independent of the curve $U(R)$. Equation (7) may now be solved numerically, obtaining $R = R_b$.

Now let

$$\mathbf{z} = \gamma\boldsymbol{\zeta}, \tag{25}$$

where γ is to be determined.

Substituting in (5):

$$\boldsymbol{\alpha}'\mathbf{x}_b + \tfrac{1}{2}\gamma^2\boldsymbol{\zeta}'\mathbf{B}\boldsymbol{\zeta} - (R_b - R_0) = 0 \tag{26}$$

Thus, eliminating γ from (25) and (26):

$$\mathbf{z} = \pm\sqrt{\left[\frac{R_b - R_1'}{\tfrac{1}{2}\boldsymbol{\zeta}'\mathbf{B}\boldsymbol{\zeta}}\right]}\cdot\boldsymbol{\zeta} \tag{27}$$

Also, from (3) and (8)

$$V_z = -\tfrac{1}{2}\rho_b\,\mathbf{z}'\mathbf{B}\mathbf{z}$$

And, from (5) and (23), using (7),

$$V_z = -\rho_b(R_b - R_1') = -t(R_b - R_1')\,.\,D(R_b) \tag{28}$$

Thus we have determined two complete stationary energy states. We must now consider the conditions under which these solutions are true minima, and are also real. We must first eliminate l independent variables from (2) (5) and (6); this can be done by partitioning the matrix **K**, and as a result (2) becomes

$$V_x = \tfrac{1}{2}\boldsymbol{\chi}'\mathbf{F}\boldsymbol{\chi} + \boldsymbol{\mu}'\boldsymbol{\chi} + v$$

and (5) becomes

$$\boldsymbol{\beta}'\boldsymbol{\chi} + \tfrac{1}{2}\mathbf{z}'\mathbf{B}\mathbf{z} - (R - R_0) = 0 \tag{28a}$$

Here $\boldsymbol{\chi}$ is a vector of $m - l$ *independent* in-plane variables; and **F** is a symmetrical square matrix; $\boldsymbol{\mu}$, $\boldsymbol{\beta}$ are vectors; and v is a positive quantity, the formulae for none of which shall we require. Now if our solution is a true minimum, the symmetrical square matrix **Q** whose elements are $(\partial^2 V/\partial\chi_r\partial\chi_s)$ will be positive definite. But by differentiating twice, we find that

$$\mathbf{Q} = t\,.\,d^2U/dR^2\,.\,\boldsymbol{\beta}\boldsymbol{\beta}' + \mathbf{F} \tag{28b}$$

The first member is positive definite from its form; and the second because it is a matrix of force-constants; thus **Q** is positive definite. Accordingly, all stationary solutions are true minima in respect of the in-plane deformation co-ordinates.

It is now convenient to make a transformation of **z**. As **A** is symmetric and positive definite, and **B** is symmetric, there exists a real non-singular square matrix **T** such that

$$\mathbf{T}'\mathbf{A}\mathbf{T} = \mathbf{1}$$

and

$$\mathbf{T}'\mathbf{B}\mathbf{T} = \boldsymbol{\Lambda}$$

where $\boldsymbol{\Lambda}$ is a diagonal matrix whose elements, which we find convenient to arrange in descending order, are $\lambda_1, \lambda_2 \ldots \lambda_n$. **T** is actually the matrix of eigenvectors of $\mathbf{A}^{-1}\mathbf{B}$, and λ_j are the eigenvalues of $\mathbf{A}^{-1}\mathbf{B}$. Putting

$$\mathbf{y} = \mathbf{T}^{-1}\mathbf{z}$$

(3) becomes

$$V_z = \tfrac{1}{2}\Sigma_j y_j^2$$

and (5) becomes

$$R = R_0 + \boldsymbol{\alpha}'\mathbf{x} + \tfrac{1}{2}\Sigma_j\lambda_j y_j^2$$

Hence

$$\partial^2 V/\partial y_j^2 = 1 + t\lambda_j\,.\,dU/dR + t\lambda_j^2(d^2U/dR^2)\,y_j^2 \tag{29}$$

Case a: $\mathbf{z} = 0$, therefore $\mathbf{y} = 0$, and $\partial^2 V/\partial y_j^2 = 1 + t\lambda_j\,.\,(dU/dR)_{R_a}$. This is positive if

$$t\,.\,D(R_a) > -1/\lambda_j \text{ (see (18)).}$$

And $\partial^2 V/\partial y_j^2 > 0$ *for all* j *if*

$$t\,.\,D(R_a) > -1/\lambda_1 \tag{30}$$

Also

$$\partial^2 V/\partial y_j\,\partial y_{j'} = 0, \qquad j' \neq j.$$

Case b: From (7), (14) and (18)

$$t\,.\,D(R_b) = \rho_b = -1/\lambda_1 \tag{31}$$

From (29),

$$\partial^2 V/\partial y_j^2 = 1 - \lambda_j/\lambda_1 + t\lambda_j^2(d^2U/dR^2)_{R_b}\,.\,y_j^2 \tag{32}$$

For $j \neq 1$, $\lambda_j < \lambda_1$; and also as **y** is an eigenvector of a diagonal matrix, $y_j = 0$. For

$j = 1$, the first two terms on the R.H.S. of (32) cancel, and the third is positive. Thus for all j,

$$\partial^2 V/\partial y_j^2 > 0$$

If we had chosen, say, λ_2 instead of λ_1 as our eigenvalue, and obtained a complete alternative solution with $R = R_b^{(2)}$, then

$$(\partial^2 V/\partial y_1^2)_{R=R_b^{(2)}} = 1 - \lambda_1/\lambda_2 + 0 < 0$$

which justifies our choice of λ_1 to obtain a true minimum. Thus we see that case b, when we do choose the highest eigenvalue, always gives a true minimum.[20] But from (27), *the solution will only be real if*

$$R_b > R_1' \tag{33}$$

Now in case a, we solve numerically equation (15), and in case b equation (31); if $D(R)$ is plotted against R, these are straight lines; and, making use of (23), we find that they meet where $R = R_1'$. Now if the inequality (30) holds, then *a fortiori*

$$tD(R_1') > -1/\lambda_1,$$

for $D(R)$ is monotonically increasing in this region; and furthermore, inequality (33) cannot hold, because of (31). Conversely, if (33) holds, (30) does not, so that the two cases are mutually exclusive—see Fig. 1. $R = R_1'$ is clearly the dividing line between the two cases.

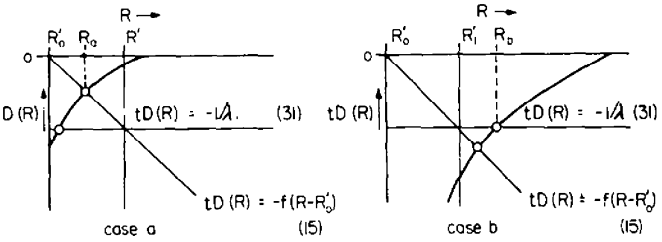

FIG. 1. The determination of R from equation (15) or (31)

To summarize:

a. *if* $D(R_1') > -1/\lambda_1$, *then there will be no out-of-plane distortion.*

b. *if* $D(R_1') < -1/\lambda_1$, *then there will be out-of-plane distortion; and the distortion* $\mathbf{x}$, *and hence* V_x, *is independent of the curve* $U(R)$ *provided it is "hard" enough to fulfil the stated inequality.* Other (equivalent) inequalities could be used to separate the two cases; but this one has the advantage that it can be applied before (15) or (31) is solved, so that only the appropriate one of these two equations need actually be solved.

It is interesting to note that in case a, from (11) and (7), $\mathbf{x}_a$ is (apart from the usually small term $\mathbf{x}_0$ which is independent of van der Waals effects) a constant vector multiplied by a numerical coefficient proportional to $D(R_a)$. Also, in case b, from (27), $\mathbf{z}$ is a

[20] For completeness, one should add that if $\mathbf{q}$ is a vector of order $m - l + n$ whose first $m - l$ elements are χ_i, and last n are y_i, then the matrix $\mathbf{S}$ whose elements are $\partial^2 V/\partial q_r\, \partial q_s$ can be partitioned (in case b) into the $(m - l + 1) \times (m - l + 1)$ matrix

$$\mathbf{Q}^+ = t(d^2U/dR^2)\boldsymbol{\beta}^+\boldsymbol{\beta}^{+\prime} + \mathbf{F}^+$$

(see (28a) and (28b)) and the $(n - 1) \times (n - 1)$ diagonal matrix $\mathbf{P}^-$ whose elements are $\partial^2 V/\partial y_j^2$, $j = 2,3 \ldots n$. Here $\boldsymbol{\beta}^+$ is of order $m - l + 1$, consisting of $\boldsymbol{\beta}$ and the extra element $\lambda_1 y_1$; and $\mathbf{F}^+$ is $\mathbf{F}$ with an extra row and column of noughts. Thus $\mathbf{S}$ is positive definite. For case a, $\partial^2 V/\partial \chi_i \partial y_j = 0$ for all i and j, so no further question arises.

constant vector multiplied by a numerical term depending on $D(R_b)$. Thus, within each of the two cases, the general shape of the molecule is independent of $U(R)$; variations in the "hardness" of this potential only affect the distortions by a multiplying factor. Finally, for actual computation, none of the analysis after equation (28) is required, except the inequality

$$D(R_1') \gtrless -1/\lambda_1.$$

If we now generalise this analysis to a case where there are *p non-equivalent* van der Waals interactions, it is easy to see the lines along which our equations are to be modified. In particular, (5) and hence (8) are replaced by *sets* of equations, whose solution would be less straightforward. We have carried out the analysis, and our results are more concise than those of Hill[4] for effectively the same problem. However, in almost all cases, the extent of the distortion will be such that the approximations outlined at the beginning of this Section will be of doubtful validity. Accordingly, an entirely different approach is indicated, and has been initiated; the calculation, in the field of mechanics, of large deformations of elastic shells may provide a helpful analogy.

POTENTIAL FUNCTIONS AND PARAMETERS

Beside choosing numerical values for the various parameters introduced in the preceding analysis, we also have to choose a functional form for $U(R)$. Initially we have confined our attention to molecules in which the only close approach is between pairs of hydrogen atoms each linked to separate carbon atoms:[21] the interaction of dipoles can reasonably be neglected; and the considerable number of published potential functions should at least bracket the truth.

There are good theoretical[22] and common-sense reasons for not simply adding formulae for the London-type attractive dispersion forces, calculated on the assumption of large separations, to formulae for exchange repulsion forces calculated or obtained experimentally at very small separations. Also, calculations for hydrogen molecules[23] cannot fairly be applied to hydrogen atoms linked to carbon.[24,4] But if this simple approach is doubtful, so unfortunately are most other methods of estimating our kind of van der Waals potential.[25,5] Most authors use a modified Buckingham or "6-exp" potential, which we may write

$$U = -AR^{-6} + B\exp(-CR) \tag{34}$$

A is obtained by using the formulae for dispersion forces.[26] C is estimated from parallel

[21] It may be objected that even in the simplest overcrowding exemplified by phenanthrene the non-bonded CC and CH interactions should be considered. This however cannot be done within the simple computational framework of Section 2; and when the calculations adumbrated at the end of that section are performed, we shall be able to assess the significance of our omission. In the meantime, preliminary calculations[17] on [18]-annulene using recent Urey-Bradley force constants suggest that the calculated bond-stretchings and compressions may be little altered, but that the angle-bendings may be noticeably increased when account is taken of these additional interactions.

[22] H. Margenau, *Phys. Rev.* **56**, 1000 (1939).

[23] J. de Boer, *Physica* **9**, 363 (1942); A. A. Evett and H. Margenau, *Phys. Rev.* **90**, 1021 (1953); *J. Chem. Phys.* **21**, 958 (1953), correcting earlier work.

[24] H. A. Stuart, *Molekülstruktur* pp. 32, 36, 44, Springer, Berlin (1934).

[25] For a fairly recent review see T. L. Cottrell, *Disc. Far. Soc.* **22**, 10 and discussion p. 75 *et seq.* (1956).

[26] For recent discussions see K. S. Pitzer, *Adv. Chem. Phys.* **2**, 59 (1959); L. Salem, *Mol. Phys.* **3**, 441 (1960).

situations; and B is generally determined by stipulating the value of R at which occurs the minimum in U. In Table 1 are given, in order of increasing "hardness", U and dU/dR at $R = 3{\cdot}5$ a.u. for several curves, and also the coefficients A, B and C for those which are of the form (34). We find it convenient to work in atomic units (1 a.u. = 627·71 kcal/mole; 1 a.u. = 0·52917 Å). All the curves were obtained by the type of method just described, except the following.

TABLE 1. H—H VAN DER WAALS POTENTIAL CURVES

No.	Name	A[a] (a.u.)	B[a] (a.u.)	C[a] (a.u.)	$U(3{\cdot}5)$[b] (kcal/mole)	$U(3{\cdot}5)$[b] (10^{-3} a.u.)	$-D(3{\cdot}5)$[c] (10^{-3} a.u.)
1	Barton (2.4)[27]	3·397	13·207	2·434	0·495	0.788	3·249
2	Hill[4]	1·312	55·46	2·996	0·524	0·835	3·417
3a[d]	—	5·886	10·892	2·257	0·526	0·838	3·630
3b[d]	—	8·529	10·685	2·158	0·606	0·965	4·141
4	Winstein[28]	3·573	29·14	2·636	0·581	0·926	4·232
5	Hendrickson[16]	3·573	15·93	2·434	0·776	1·237	4·410
6	Hendrickson-Bartell[16]	3·573	21·66	2·497	0·958	1·526	5·332
7	Barton (2·6)[27]	3·397	18·926	2·434	1·211	1·930	6·028
8	Bartell[29]	3·573	10·51	2·160	2·216	3·531	8·494
9a	Pauncz-Ginsberg[15]				4·628	7·373	10·866
9b[d]	—	3·247	2·960	1·625	5·186	8·262	13·272
10	Müller[30]	4·496	100·9	2·645	4·457	7·101	21·062
11a[d]	—				9·255	14·745	21·732
11b	Mason-Kreevoy[31]	6·495	5·921	1·625	10·371	16·523	26·544

[a] Coefficients in equation (34)
[b] Potential energy when $R = 3{\cdot}5$ a.u.
[c] $-dU/dR$ when $R = 3{\cdot}5$ a.u.
[d] See text.

Curves 3 were derived from Eyring's formula[32]

$$U = \tfrac{1}{4}E_1 + \tfrac{3}{4}E_3 \tag{35}$$

where E_1, E_3 are respectively the energies of the lowest singlet and triplet states of the hydrogen molecule. Details are given in an appendix.

Curves 9 are $U = \frac{1}{2}E_3$, and curves 11 are $U = E_3$. For 9a and 11a one uses

$$E_3 = R^{-1}(1 + 1{\cdot}167R + 0{\cdot}039R^2 + 0{\cdot}518R^3 + 0{\cdot}864R^4)\exp(-2{\cdot}3R) \tag{36}$$

This is a fit obtained by Buckingham[33] to the theoretical curve of Hirschfelder and Linnett.[34] For 9b and 11b, E_3 is a less accurate fit by Mason and Kreevoy[31] to the same theoretical curve. The only justification for these forms is that if one uses a valence-bond function and neglects the Coulomb integral, then (35) is the same as $U = \frac{1}{2}E_3$; this is actually equivalent to the term $-\frac{1}{2}\Sigma J_{ij}$ (summed over non-paired

[27] D. H. R. Barton, *J. Chem. Soc.* 340 (1948).
[28] D. Kivelson, S. Winstein, P. Bruck and R. L. Hansen, *J. Amer. Chem. Soc.* **83,** 2938 (1961).
[29] L. S. Bartell, *J. Chem. Phys.* **32,** 831 (1960).
[30a] A. Müller, *Proc. Roy. Soc.* **A154,** 624 (1936); [b] *Ibid.* **178,** 227 (1941).
[31] E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.* **77,** 5808 (1955).
[32] H. Eyring, *J. Amer. Chem. Soc.* **54,** 3191 (1932).
[33] R. A. Buckingham, *Trans. Far. Soc.* **54,** 453 (1958).
[34] J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.* **18,** 130 (1950).

orbitals) in the Approximation of Perfect Pairing.[35] As this approach neglects bond–bond repulsion, Mason and Kreevoy deliberately over-corrected by using 11b. Howlett[6] also used a simple exponential fit to the curve of Ref. 34. We may note that curves of the type described in this paragraph are without minima in the relevant range.

As steric effects do not seem to be important in the ethane rotational barrier problem,[36,4] we have not taken into account potentials based on this approach. Nor have we included potentials based on spectroscopic Urey-Bradley force-fields, which are probably not comparable, as they usually involve the interaction of hydrogen atoms bound to the same carbon atom.[37]

One method of limiting the range of possible potential functions which at least holds promise for the future is the analysis of I.R. crystal spectra, in which the lines are split by the intermolecular force-field. As Müller pointed out long ago,[30b] such tests involving the second derivative of the potential function are very sensitive; and, although present calculations are distinctly tentative, the splittings from paraffins,[38] methyl chloride[39] and ethylene[40] seem to agree better with predictions from curves 8 and 10 than with 1–7, which have smaller, and 9 and 11, which have larger curvatures.

As to the other parameters required by the method of Section 2, the out-of-plane force-constants forming **A** are determined by the method of Coulson and Senent,[7] with the most recent numerical values.[11] The in-plane force-constant matrix **K** is taken to be diagonal, the values being transferred from benzene: the values used were: C—C stretch 6·40, C—H stretch 5·08, CCC bend 0·740, CCH bend 0·849, all in millidyne $Å^{-1}$; these are based on the work of Cyvin.[41] We also propose to investigate the use of other force-constants.[17]

The other parameters depend on the geometry of the undeformed molecule. The bond-orders were obtained from a self-consistent molecular orbital treatment where available.[42] The bond-length–bond-order curve used in Ref. 42 was used for consistency, namely the unmodified Coulson relation:[43] the use of a more modern curve[44] however would have a negligible second-order effect on the calculated deformations. Undeformed C—H bonds were assigned the length 1·08 Å.

APPLICATIONS

The analysis of Section 2 was converted into a programme for the Oxford University Ferranti Mercury computer, and the functions and parameters of Section 3 were fed in, with the following results.

a. *Phenanthrene.* The numbering which we find convenient to use because of symmetry is shown in Fig. 2. The molecule has symmetry C_{2v} with no out-of-plane deformation, and C_2 when this does occur. (It is clear, in this and other cases where a pair of overcrowded atoms are related by a mirror plane and a diad in the undistorted

[35] See e.g. C. A. Coulson, *Valence*, (2nd Edition) pp. 175, 178. Oxford University Press, London (1961).

[36] E. Bright Wilson, *Adv. Chem. Phys.* **2**, 367 (1959).

[37] See e. g. J. Overend and J. R. Scherer, *J. Opt. Soc. Am.* **50**, 1207 (1962), giving earlier Refs.

[38] R. S. Stein, *J. Chem. Phys.* **23**, 734 (1955); R. G. Snyder, *J. Mol. Spectroscopy* **7**, 116 (1961).

[39] D. A. Dows, *J. Chem. Phys.* **35**, 282 (1961).

[40] *Idem*, *J. Chem. Phys.* **36**, 2836 (1962). But see also R. M. Hexter, *ibid.* **37**, 1347 (1962).

[41] S. Cyvin, *Acta Chem. Scand.* **11**, 1499 (1957).

[42] H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.* **A226**, 138 (1954).

[43] C. A. Coulson, *Proc. Roy. Soc.* **A169**, 413 (1939).

[44] C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc.* **A78**, 1315 (1961).

form, that overcrowding will be more efficiently relieved by displacements anti-symmetrical to the molecular plane i.e. the diad rather than the σ_v plane is retained in the distorted molecule). We neglected bond-stretching except for those bonds forming a ring with the single non-bonded interaction, and similarly in all other molecules.

Fig. 2 shows the unknown **x** to be determined, all angles here and subsequently being read as $(120° + \phi_1)$ etc., and the lengths being in Å, derived from the self-consistent calculations of Ref. 42. Rotation about the diad is prevented by fixing C_1

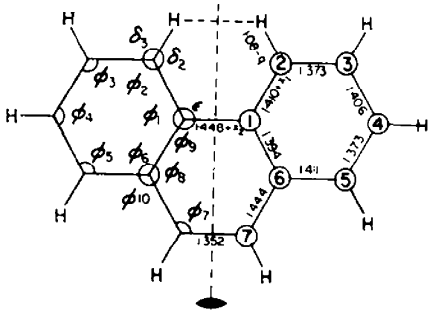

FIG. 2. Deformations in phenathrene.

in the mean molecular plane ($z_1 = 0$), so that **z** is of order 11. There are eight redundancy relations between the sixteen x_i. **K** is a diagonal matrix of order 16. **A** is the sum of seven non-planarity terms and nine torsion terms.[7] Five elements in α are non-zero; only a 2×2 sub-matrix of **B** is non-zero. R_0 comes to 1·778 Å.

The results are as follows. $V_0 = 0{\cdot}35$ kcal/mole, $R_0' = 1{\cdot}825$, $R_1' = 2{\cdot}134$ Å. For *all* curves, $\mathbf{z} = 0$, $V_z = 0$ i.e. case a applies. In Table 2, we give $\mathbf{x}_0$ and **x** using curves 1 and 11a. In Table 3, we give the results for all curves used; those x_i not given can be calculated using (11) which can be written

$$\mathbf{x} - \mathbf{x}_0 = \rho \mathbf{e} \tag{37}$$

where **e** is fixed independently of $U(R)$.

The calculations were repeated using the simple Hückel bond-orders[42] instead of the self-consistent ones. Although R_0 was slightly reduced to 1·752 Å, the final results are so little different as not to warrant their being recorded here.

No accurate crystallographic results are at present available for comparison, but a refinement is in progress.[45]

TABLE 2. DEFORMATIONS IN PHENANTHRENE[a]

x:	x_1	x_2	q	δ_2	δ_3	ε	ϕ_1	ϕ_2
$\mathbf{x}_0$:	−1·1	−3·2	0	0·06	−0·54	0·65	−0·61	0·47
Curve 1:	2·0	2·1	2·1	0·56	−1·21	1·16	−1·00	0·65
Curve 11a:	11·8	19·0	9·0	2·16	−3·38	2·80	−2·25	1·22

x:	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}
$\mathbf{x}_0$:	−0·02	0·36	0·03	−0·24	0·94	−0·89	−0·05	1·12
Curve 1:	0·04	0·21	0·11	−0·01	0·94	−0·78	−0·17	0·78
Curve 11a:	0·21	−0·26	0·37	0·72	0·96	−0·42	−0·54	−0·30

[a] lengths in milli Å; angles in degrees.

[45] R. Mason, *Mol. Phys.* **4**, 413 (1961), giving earlier Refs.

TABLE 3. DEFORMATIONS IN PHENANTHRENE

Curve:	1	2	3a	3b	4	5
x_2 (mÅ)	2·1	2·1	2·6	3·3	3·1	3·4
ε (deg)	1·16	1·17	1·21	1·28	1·26	1·29
R (Å)	1·890	1·891	1·897	1·905	1·902	1·907
U^a	0·36	0·39	0·36	0·38	0·36	0·53
$V_x{}^a$	0·10	0·10	0·12	0·15	0·14	0·16
V^a	0·46	0·49	0·48	0·53	0·51	0·69

Curve:	6	7	8	9a	10	11a
x_2 (mÅ)	4·3	5·1	7·6	11·3	13·4	19·0
ε (deg)	1·38	1·45	1·70	2·05	2·25	2·80
R (Å)	1·918	1·927	1·959	2·004	2·030	2·099
U^a	0·61	0·77	1·35	2·90	1·60	4·36
$V_x{}^a$	0·21	0·25	0·43	0·77	1·00	1·80
V^a	0·81	1·02	1·78	3·66	2·61	6·16

[a] energies in kcal/mole

b. *Triphenylene.* The planar molecule has symmetry D_{3h}; when out-of-plane distortion occurs, D_3 symmetry is assumed. The data are presented in Fig. 3 and Tables 4 and 5 in the same form as for phenanthrene. The jth carbon atom and the jth hydrogen atom have perpendicular displacements from the mean plane of z_j, h_j respectively. Hückel bond-orders have been used.[46] $R_0 = 1{\cdot}756$, $R_0' = 1{\cdot}780$, $R_1' = 1{\cdot}936$ Å. $V_0 = 0{\cdot}08$ kcal/mole. All curves tried fall under case a, except 11a, for which $z_1 = 0{\cdot}016$, $z_2 = 0{\cdot}139$, $z_3 = 0{\cdot}092$, $h_2 = 0{\cdot}341$, $h_3 = 0{\cdot}180$ Å. No accurate X-ray results are available.[47]

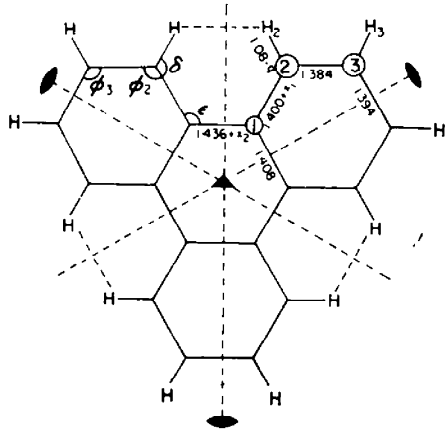

FIG. 3. Deformations in triphenylene.

[46] G. Berthier, C. A. Coulson, H. H. Greenwood and Mme. A. Pullman, *C. R. Acad. Sci., Paris* **226**, 1906 (1948).

[47] A. Klug, *Acta Cryst.* **3**, 165 (1950); V. Vand and R. Pepinsky, *Ibid.* **7**, 595 (1954); P. R. Pinnock, C. A. Taylor and H. Lipson, *Ibid.* **9**, 173 (1956).

TABLE 4. DEFORMATIONS IN TRIPHENYLENE[a]

x:	x_1	x_2	q	δ	ε	ϕ_2	ϕ_3
x_0:	−0·9	0	0	0·03	0·32	−0·05	0·37
Curve 1:	3·3	4·7	3·0	0·68	0·53	0·27	0·26
Curve 11a:	12·5	15·0	9·5	2·11	0·99	0·97	0·02

[a] lengths in mÅ; angles in deg.

TABLE 5. DEFORMATIONS IN TRIPHENYLENE

Curve	x_2 (mÅ)	δ (deg)	R (Å)	U^a	$V_x{}^a$	$V_z{}^a$	V^a
1	4·7	0·68	1·829	0·59	0·32	0	2·09
3a	5·1	0·74	1·833	0·61	0·38	0	2·22
7	7·5	1·07	1·858	1·17	0·82	0	4·32
9a	12·1	1·71	1·906	3·86	2·12	0	13·69
11a	15·0	2·11	2·081	4·60	3·24	6·02	23·07

[a] energies in kcal/mole.

c. *Chrysene.* The planar molecule has symmetry C_{2h}. The hydrogen atoms in each overcrowded pair are not however related by symmetry; if they are displaced in opposite directions out of the mean plane, we can still retain either a diad or a centre of symmetry, resulting respectively in C_2 or S_2 symmetry. Fig. 4 indicates the numbering and bond-lengths (from self-consistent calculations[42]). To locate the mean molecular plane, we choose $z_9 = 0$ for C_2 symmetry, $z_1 = z_9 = 0$ for S_2 symmetry. The results are given in Tables 6–8. Case b arises only for curve 11a, and the different symmetries are only relevant in this case. $R_0 = 1{\cdot}789$, $R_0' = 1{\cdot}811$ Å. $V_0 = 0{\cdot}48$ kcal/mole. $R_1' = 2{\cdot}005$ Å (C_2 symmetry); 2·003 Å (S_2).

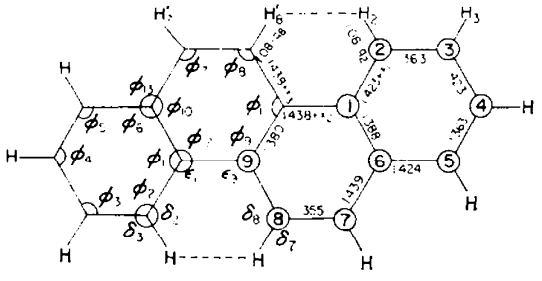

FIG. 4. Deformations in chrysene.

The results for C_2 and S_2 symmetries are extraordinarily similar, the latter being apparently more stable by the minute quantity 0·03 kcal/mole. Though the out-of-plane deformation appears dissimilar at first sight, the pattern in the overcrowded region is actually very similar when we allow for the change in reference plane; indeed $(h_2–h_8)$ is identical. Now this result is academic in the case of the hydrocarbon chrysene itself, whose planarity has been proved; and curve 11a is anyhow unreasonably steep. But it does raise the intriguing possibility that (say) tetrabromochrysene, substituted

TABLE 6. IN-PLANE DEFORMATIONS IN CHRYSENE[a]

x:	x_1	x_2	x_3	q_3	q_8	δ_2	δ_3	δ_7
x_0:	−0·9	−1·7	1·4	0	0	0·04	−0·43	0·20
Curve 1:	2·5	4·4	3·8	2·4	2·4	0·60	−1·19	−0·56
Curve 11a (C_2):	10·6	18·6	9·7	8·2	8·0	1·93	−2·98	−2·34

x:	δ_8	ε_1	ε_9	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5
x_0:	−0·17	0·50	0·19	−0·56	0·39	0·01	0·41	−0·05
Curve 1:	0·41	1·09	0·32	−1·04	0·59	0·10	0·24	−0·01
Curve 11a (C_2):	1·77	2·51	0·64	−2·19	1·06	0·29	−0·15	0·10

x:	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}
x_0:	−0·20	−0·40	−0·03	−1·76	0·56	1·57	0·06	−0·36
Curve 1:	0·12	−0·37	−0·15	−1·66	0·59	1·34	−0·05	−0·72
Curve 11a (C_2):	0·90	−0·29	0·57	−1·42	0·67	0·78	−0·32	−1·57

[a] lengths in mÅ; angles in deg.

TABLE 7. DEFORMATIONS IN CHRYSENE

Curve	x_1 (mÅ)	x_2 (mÅ)	$-\delta_3$[a]	ε_1[a]	ε_9[a]	R (Å)	U[b]	V_x[b]	V_z[b]	V[b]
1	2·5	4·4	1·19	1·09	0·32	1·869	0·43	0·20	0	1·07
3a	2·8	4·9	1·26	1·15	0·33	1·874	0·44	0·24	0	1·12
7	4·5	7·8	1·63	1·44	0·40	1·902	0·90	0·51	0	2·30
9a	8·3	14·6	2·47	2·11	0·55	1·966	3·24	1·48	0	7·95
11a (C_2)	10·6	18·6	2·98	2·51	0·64	2·135	3·91	2·30	3·09	13·21
11a (S_2)	10·5	18·5	2·96	2·49	0·63	2·138	3·88	2·27	3·16	13·18

[a] angles in degrees; [b] energies in kcal/mole.

TABLE 8. OUT-OF-PLANE DEFORMATIONS IN CHRYSENE (curve 11a)[a]

	z_1	z_2	z_3	z_4	z_5	z_6	z_7	z_8
C_2:	0·063	0·254	0·296	0·159	0·019	−0·012	−0·127	−0·105
S_2:	0	0·162	0·156	−0·002	−0·116	−0·096	−0·201	−0·145

	h_2	h_3	h_4	h_5	h_7	h_8
C_2:	0·439	0·448	0·193	−0·057	−0·216	−0·237
S_2:	0·366	0·287	−0·007	−0·212	−0·321	−0·309

[a] heights in Å.

in the four overcrowded positions, might exist (in the fluid phases) as an equilibrium mixture of dextro- and laevo-forms with a diad, and a centro-symmetric internally-compensated 'meso' form, in comparable proportions. In the solid state, packing considerations would determine the more stable form, but both types could perhaps be obtained.

A very accurate recent X-ray analysis of chrysene is available,[48] and it was hoped that this would provide a valuable test of our calculations. Most unfortunately, this hope could not be realised, for two distinct reasons. In Table 9 we have a measure of

TABLE 9. RMS DEVIATIONS BETWEEN THEORETICAL AND EXPERIMENTAL BOND-LENGTHS IN CHRYSENE[a]

Theory:	(1)	(1a)	(2)	(3)
Including bond 1–9′	15	16	18	15
Excluding bond 1–9′	11	11	17	13

(1) is simple Hückel theory;[42,48] (1a) is the same with a more modern bond-length–bond-order relation;[44] (2) is the self-consistent theory we used as basis;[43,45] (3) is a Pauling superposition valence-bond method.[48]

[a] in mÅ.

the accuracy of the theoretical calculations. As the average standard deviations of the experimental bond-lengths is 4 mÅ, it is clear that none of these theories is accurate enough[49] to form a basis for the discussion of changes as small as we predict: the largest x_2 is of the same order as the R.M.S. discrepancies, and x_1 and x_3 are about half as large. We can only confirm the general reasonableness of the suggestion[48,50] that the large discrepancy between theory and experiment in bond 1–9′ (42, 37, 30 and 34 mÅ for the four theories respectively) is due to the steric effect under discussion. On the other hand it must also be remembered that it is for such low-order bonds that the bond-length–bond-order curve is most uncertain.[51] For the same reason, comparison between experimental and predicted skeletal angles is not really meaningful: we can only note that theory and experiment do agree that ε_1 is comparatively large (Experimental 2·9°) but ε_9 (which is similarly situated with respect to the overcrowding) is considerably smaller (Experimental 0·5°). In fact, the large value of ε_1 determined experimentally seems to be the only unambiguous evidence of deformation due to overcrowding in this structure. It is possible that the method of Ref. 44 might provide a better theoretical base for calculations than those listed in Table 9. We observe finally, in connection with the carbon skeleton, that it is planar within experimental error, as predicted by all but curve 11a (except that atoms 3, 4, and 5 are slightly but

[48] D. M. Burns and J. Iball, *Proc. Roy. Soc.* **A257**, 491 (1960), superseding the preliminary results quoted in Ref. 9.

[49] For a recent discussion see A. Streitweiser, *Molecular Orbital Theory for Organic Chemists* p. 171 Wiley, New York (1961).

[50] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* **A258**, 278 (1960); D. W. J. Cruickshank, *Tetrahedron* **17**, 159 (1962).

[51] T. H. Goodwin, *J. Chem. Soc.* 4851 (1960) and earlier papers; C. A. Coulson and P. N. Skancke, *Ibid.* 2775 (1962).

significantly displaced—and this of course cannot be the result of intramolecular overcrowding).

Secondly, we may consider the positions of the hydrogen atoms. These have been determined with unusual precision for X-ray work, and here the inadequate π-electron theory is much less important. Further, Burns and Iball comment[48] that the distances H_2H_8', H_2H_3 are nearly equal, which—as is shown by a glance at Fig. 4—seems a promising indication of deformation due to overcrowding. Unfortunately this conclusion is less clear-cut than might appear. Firstly, the mean experimental C—H bond-length (distance between centres of electron density) is 1·00 Å. Now there can be little doubt that aromatic C—H bond-lengths (internuclear) are about 1·08 Å as illustrated by: benzene[52] 1·084; pyridine[53,54] $1{\cdot}084_3$, $1{\cdot}080_5$, $1{\cdot}077_3$; furan[54,55] 1·075, thiophen[56] 1·078, 1·081 Å. The effect of allowing for this is seen in Table 10.

TABLE 10. NON-BONDED HYDROGEN–HYDROGEN DISTANCES IN CHRYSENE[a]

	(A1)	(A2)	(B1)	(B2)
$H'_7H'_8$	2·307	2·314	2·346	2·390
$H_1H'_8$	2·089	2·022	2·006	1·939
H_2H_3	2·268	2·330	2·342	2·387

(A)—calculated from table 8 of Ref. 48: (1) Fourier (2) Least Squares.

(B)—as (A) but assuming constant internuclear CH bond-length of 1·084 Å.

[a] in Å.

The R.M.S. deviation between the six non-bonded hydrogen–hydrogen distances calculated according to the methods of columns (B1) and (B2) of Table 10 is 0·067 Å, and this can be taken as some measure of the accuracy, in the absence of published standard deviations. We may also note that H_2, H_3 are two of the least well resolved peaks in Fig. 4 of Ref. 48. Now for all the curves $U(R)$ that have minima in the right range, $U(2{\cdot}34$ Å) is negligible; in fact it is actually negative for all except Müller's curve 10. Thus the "buttressing" effects of H_3 and H_7' are practically identical and very small indeed, as has been tacitly assumed in all our calculations. Selected angles involving hydrogen are given in Table 11. The R.M.S. deviation of the twelve pairs of

TABLE 11. EXPERIMENTAL CCH ANGLES IN CHRYSENE[a]

	$120° + \delta_2 = H_2C_2C_1$	$120° + \delta_8 = H_8C_8C_9$	$H_3C_3C_2$	$H_7C_7C_8$	$H_5C_5C_6$
(1) Fourier	124·7	120·4	118·0	115·0	115·9
(2) Least Squares	120·6	120·3	116·9	117·5	115·4

[a] in degrees; calculated from table 8 of Ref. 48.

[52] A. Langseth and B. P. Stoicheff, *Canad. J. Phys.* **34**, 350 (1956); A. Almenningen, O. Bastiansen and L. Fernholt, *Kgl. Norske Vid. Selsk. Skr.* No. 3 (1958).

[53] B. Bak, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectroscopy* **2**, 361 (1958).

[54] A. Almenningen, O. Bastiansen and L. Hansen, *Acta Chem. Scand.* **9**, 1306 (1955).

[55] B. Bak, L. Hansen and J. Rastrup-Andersen, *Disc. Faraday Soc.* **19**, 30 (1955).

[56] B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectroscopy* **7**, 58 (1961).

entries in rows (1) and (2) of this complete Table is 2·6° which again can be taken as a measure of accuracy. Doubt is cast on the accuracy of the Fourier values by the unreasonable 4·3° difference between δ_2 and δ_8 for similarly situated overcrowded atoms, and by the improbably low value of angle $H_7C_7C_8$ where the only (very small) steric effect would tend to increase it. If for this reason we prefer the Least Squares results, we find that the bending in the overcrowded region is not significant; and in fact the only significant deviation of the C—H bonds from being external bisectors of the skeletal angles, that at H_5, can perhaps be accounted for by the *inter*molecular contact between H_5 and H_4' of an adjacent molecule (the contact distance is re-calculated to be 2·30 Å assuming the C—H bond length of 1·084 Å). We have also calculated the perpendicular distances of the hydrogen atoms from Burns and Iball's mean plane I: the largest value is 0·074 Å, but the R.M.S. difference between the heights calculated from the Fourier and Least Squares positions is 0·057 Å, so this cannot be considered significant. Thus, sadly, we conclude that, within the accuracy of experimental data on the hydrogen positions, no deductions can yet be made as to the effect of overcrowding on the geometry of the molecule.

In fine, the X-ray results are broadly compatible with our predictions based on all the curves except the "hardest", but, as we have shown, no detailed quantitative comparisons are meaningful.

DISCUSSION

The following conclusions may be derived from these results.

a. There is very little likelihood of non-planarity because of hydrogen–hydrogen repulsion in the type of system we have investigated. For reasons discussed in Section 3, curve 11 is improbably "hard", and only for this curve did case b (of Section 2) arise. This renders unlikely the very tentative suggestion that the similarly situated overcrowded hydrogen atoms in benzbisanthrene,[57] 1,2-7,8 dibenzocoronene[58] and hexabenzocoronene[59] are displaced out of the molecular plane.

b. Small changes spread over the molecule will significantly relieve overcrowding at very little "cost" in energy.

c. The total deformation energy V is predicted to be quite small. An interesting confirmation of this is the tentative estimate of 1½ kcal/mole per overcrowded hydrogen pair, derived from anomalies in the correlation of both the hydrogen-deuterium exchange constants and the basicities of the hydrocarbons' (tetrahedrally hybridized) conjugate bases against self-consistent field localization energies.[60]

d. The overcrowded atoms can be much closer than the sum of their so-called van der Waals radii, again at very little "cost" in energy i.e. the atoms are "softer" than has often been supposed. Alongside the figure of 1·97 Å for the internuclear distance in chrysene (averaged from columns B1 and B2 of Table 10) we may place, by way of confirmation, values of about 1·8, $1{\cdot}8_3$ and 2·0 in medium-size saturated rings,[61]

[57] J. Trotter, *Acta Cryst.* **11,** 423 (1958).
[58] J. M. Robertson and J. Trotter, *J. Chem. Soc.* 1115 (1961).
[59] J. M. Robertson and J. Trotter, *J. Chem. Soc.* 1280 (1961).
[60] G. Dallinga, P. J. Smit and E. L. Mackor in *Steric Effects in Conjugated Systems* (Hull Symposium) (Edited by G. W. Gray) p. 150. Butterworths, London (1958); and Refs. cited therein.
[61] R. F. Bryan and J. D. Dunitz, *Helv. Chim. Acta* **43,** 3 (1960); J. D. Dunitz and H. M. M. Shearer, *Ibid.* 18; E. Huber-Buser and J. D. Dunitz, *Ibid.* **43,** 760 (1960); **44,** 2027 (1961); **45,** 1036 (1962).

1·97 in crystalline diphenyl,[62] 2·04 in 3,4 benzophenanthrene[63] and 2·02 in its 1,12 dimethyl derivative, [63] and 2·24 in 1,8 diphenyl 1,3,5,7 octatetraene[64] (all in Å). This suggests that even where there is no overcrowding, packing considerations might allow hydrogen–hydrogen non-bonded distances to vary to an unusually large degree:[65] in fact we do find distances of 2·21 Å in bis *p*-chlorophenyl sulphone,[66] and 2·25 Å in 1,12 dimethyl 3,4 benzophenanthrene.[63] A "normal" value[67] may be taken as the two closest approaches of 2·49 and 2·52 Å found in n-triacontane.[68]

From the detailed discussion of chrysene, we deduce that the distortions predicted for single hydrogen–hydrogen interactions are so small that meaningful experimental checks are unlikely at present (although anomalous N.M.R. spectra may be of assistance[69]); the only clear exception is the special case of [18]-annulene.[17,18] Within the framework of the analysis of Section 2, more satisfactory comparisons should be available with bulkier substituents such as the halogens,[70] in spite of the uncertainties in non-bonded potentials,[12,25,71] directional effects and certain force-constants.[5] The displacements of heavier atoms can be determined much more accurately; also not only could substituted phenanthrenes etc. be considered, but also e.g. 1,8 X_2 naphthalene and *ortho* X_2 benzene.[12] The method presented in this paper will allow both the in-plane and out-of-plane deformations in such systems to be calculated with considerably greater ease and rapidity than hitherto.[72]

[62] Calculated from the X-ray data of G. B. Robertson, *Nature Lond.* **191,** 593 (1961); **192,** 1026 (1961). With a CH bond-length of 1·084 Å instead of 0·979 Å this would be 1·87 Å. See also A. Hargreaves, S. Hasan Rizvi and J. Trotter, *Proc. Chem. Soc.* 120 (1961); J. Trotter, *Acta Cryst.* **14,** 1135 (1961); and A. Hargreaves and S. Hasan Rizvi, *Ibid.* **15,** 365 (1962).

[63] F. L. Hirshfeld, Mrs. S. Sandler and G. M. J. Schmidt, *J. Chem. Soc.* in press. For earlier results see E. Harnik, F. H. Herbstein and G. M. J. Schmidt, *Nature Lond.* **168,** 158 (1951); F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.* 3302 (1954); F. L. Hirshfeld and G. M. J. Schmidt, *Acta Cryst.* **9,** 235 (1956); **13,** 1047 (1960).

[64] Calculated from the X-ray data of W. Drenth and E. H. Wiebenga, *Acta Cryst.* **8,** 755 (1955).

[65] E. Mack, *J. Amer. Chem. Soc.* **54,** 2141 (1932); J. M. Robertson, *Organic Crystals and Molecules* pp. 226–7, Cornell University Press, New York (1953).

[66] Calculated from the neutron-diffraction data of G. E. Bacon and N. A. Curry, *Acta Cryst.* **13,** 10 (1960).

[67] Kitaigorodskii, in his exhaustive treatment of molecular packing, uses (as a zero-order approximation) a fixed value of 2·34 Å; but his own extensive computations show many experimental separations of about 2·5 Å, and he specifically treats the paraffins as a special case using 2·7 and later 2·6 Å. Thus his work really seems to confirm our ideas, and in a later paper he actually quotes the range 2·10–2·70 Å. See A. Kitaigorodskii, *Organic Chemical Crystallography, passim.* (English translation of 1955 Russian edition) Consultants Bureau, New York (1961); *Kristallografiya* **2,** 456 (1958).

[68] Calculated from the solid-phase electron diffraction data of B. K. Vainshtein, A. N. Lobachev and M. M. Stasova, *Kristallografiya* **3,** 452 (1958). But note that the calculations of J. A. Ibers (*Acta Cryst.* **14,** 853 (1961)) imply that the internuclear distance will be slightly greater.

[69] B. P. Dailey, N. Jonathan and S. Gordon, *Spectrochim. Acta* **17,** 1133 (1961); *J. Chem. Phys.* **36,** 2443 (1962).

[70] Newman's classical work was concerned with methyl derivatives. See Ref. 2 and M. S. Newman, *J. Amer. Chem. Soc.* **62,** 2298 (1940).

[71] C. A. Coulson, *Tetrahedron* **17,** 260 (1962).

[72] And only a minor modification is required to include, in the calculations on the racemization of diphenyls, the out-of-benzene-plane distortions which were omitted by Westheimer *et al.*, but whose importance has recently been indicated. See Margaret M. Harris and Ann S. Mellor, *Chem. & Ind.* 557 (1961); Margaret M. Harris and Cheung King Ling, *Ibid.* 1378 (1962).

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Appendix

Derivation of curve 3. This is a purely theoretical curve based on equation (35). For E_1, values derived[73] by the Rydberg-Klein-Rees method from spectroscopic data were used for R up to 3·73 a.u.; for larger R, calculated values were available from the work of Hirschfelder and Linnett,[34] and of Dalgarno and Lynn.[74] The last two references also provide values for E_3. If one applies (35) to the figures of Ref. 34, as was done by Adrian,[75] one obtains a curve whose minimum occurs at far too large R, as Kitaigorodskii pointed out.[13] But (35) applied to the figures of Ref. 74 gives a minimum at 3·8 a.u. (2·0 Å), which is too small. Now the very smooth fit between the curves of Refs. 73 and 74 (see also Ref. 76) show that Dalgarno and Lynn's E_1 is undoubtedly preferable to Hirschfelder and Linnett's. For E_3, the situation is less clear: Hirschfelder and Linnett's variational results must lie above the true value, but Dalgarno and Lynn's perturbation theory results could be below it, and in fact their corresponding figure for H_2^+ *is* below the exact value. Further, Dalgarno and Lynn fixed one parameter by using a value of E_3 at 2·0 a.u. derived from the work of James *et al.*;[77] unfortunately they did not make use of the more extensive work of James and Coolidge[78] which extend out to 2·9 a.u. Taking these factors into account, we feel that an average of the results of Refs. 34 and 74 represents the best value of E_3 currently available: when (35) is now used, the minimum does occur at 4·7 a.u. (2·5 Å). As the abscissae are unevenly spaced in these various publications, we have taken the five published figures from Ref. 34 in the range 3–5 a.u., and interpolated E_1 and Dalgarno and Lynn's E_3 using the following fits, kindly supplied by Dr. F. J. Smith:[79]

$$R < 4 \text{ a.u.} \quad E_1 = -10^{-3}[169{\cdot}4 - 2{\cdot}595R + 0{\cdot}16638R^2 + 0{\cdot}46838R^3] + 0{\cdot}22346\{1 - \exp[0{\cdot}86(1{\cdot}5 - R)]\}^2 \quad (38)$$

$$R > 4 \text{ a.u.} \quad E_1 = -6{\cdot}5R^{-6} - 214R^{-8} - 32{\cdot}614\exp(-1{\cdot}78R) + 7{\cdot}82R^{-6}\exp(-3{\cdot}65R) \quad (39)$$

$$R < 4 \text{ a.u.} \quad E_3 = 2{\cdot}8861R^2\exp(-2{\cdot}35R) + 90{\cdot}5R^3\exp(-6{\cdot}034R) \quad (40)$$

$$R > 4 \text{ a.u.} \quad E_3 = -6{\cdot}5R^{-6} - 214R^{-8} + 10{\cdot}267\exp(-1{\cdot}77R) \quad (41)$$

energies and distances being in a.u. (As they have more parameters, these fits are naturally better than those of Fallon, Mason and Vanderslice[80] or of Buckingham[33]). Finally two iterations of a least squares programme gave the coefficients in Table 1 for curve 3a.

Since an improved "experimental" curve was published[76] during the course of our work, it was thought worthwhile to improve curve 3a as follows. E_1 was taken entirely from Ref. 76. A variational E_3 was obtained for 2·7 and 2·9 a.u. from Ref. 78, and from Ref. 34 for the same values as before. In each case, five-point Lagrangian interpolation was used to obtain values for $R = 3{\cdot}0(0{\cdot}1)4{\cdot}0$ a.u. Dalgarno and Lynn's E_3 was calculated from (40). The mean E_3 was then used as before, (35) was applied, and two further iterations of a least squares programme gave the improved coefficients listed as curve 3b.

It is clear that these two curves will be "softer" than the correct one because of bond–bond repulsion, and because the polarization of the hydrogen electron-clouds will be towards the carbons and not towards each other.[81]

[73] J.T. Vanderslice, E. A. Mason, W. G. Maisch and E. R. Lippincott, *J. Mol. Spectroscopy* **3**, 17 (1959).
[74] A. Dalgarno and N. Lynn, *Proc. Phys. Soc.* A**69**, 821 (1956).
[75] F. J. Adrian, *J. Chem. Phys.* **28**, 608 (1958).
[76] I. Tobias and J. T. Vanderslice, *J. Chem. Phys.* **35**, 1852 (1961).
[77] H. M. James, A. S. Coolidge and R. D. Present, *J. Chem. Phys.* **4**, 187 (1936).
[78] H. M. James and A. S. Coolidge, *J. Chem. Phys.* **6**, 732 (1938). Interestingly enough, these are better than the results of W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 219 (1960).
[79] F. J. Smith, private communication.
[80] R. J. Fallon, E. A. Mason and J. T. Vanderslice, *Astrophys. J.* **131**, 13 (1960).
[81] M. Asgar Ali, D. Phil. thesis, Oxford University (1960).