Theoret. chim. Acta (Berl.) 20, 263—272 (1971)

Theoretical Treatment of Overcrowding in Phenanthrene

ALEC GRIMISON

Puerto Rico Nuclear Center* and Department of Chemistry, University of Puerto Rico

Received June 22, 1970

A theoretical study has been made of the deformations in the phenanthrene molecule resulting from the hydrogen-hydrogen overcrowding. The applicability of the Coulson-Haigh approach to such steric effects has been shown to have considerable potential, although the quantitative application requires further attention. The calculations suggest that the slight aplanarity observed in experimental work is possibly caused by crystal forces, rather than being due to intramolecular repulsion.

Die Deformationen des Phenanthren-Moleküls, die von der gegenseitigen Störung der H-Atome herrührt, wurde theoretisch untersucht. Es wird gezeigt, daß die Coulson-Haigh-Methode auf derartige sterische Effekte erfolgreich anwendbar ist, obwohl die quantitative Auswertung noch weiter ausgearbeitet werden sollte. Die Berechnungen zeigen, daß die geringe experimentell beobachtete Nicht-Planarität möglicherweise durch Kristallkräfte, und nicht durch intramolekulare Kräfte verursacht wird.

Etude théorique des déformations dans la molécule de phénanthrène résultant de l'encombrement muel des hydrogènes. L'approche de Coulson-Haigh pour de tels effets stériques offre de grandes possibilités moyennant un examen plus poussé des applications quantitatives. Les calculs montrent que le faible défaut de planéité observé expérimentalement est peut-être dû aux forces cristallines plutôt qu'à la répulsion intramoléculaire.

Introduction

Phenanthrene (Fig. 1) is a molecule which exhibits the simplest type of overcrowding. Thus if standard bond lengths and bond angles are assumed, the distance between H(4) and H(5) is only 1.716 Å. This is well below the sum of the Van der Waals radii, 2.4 Å, so that in this "ideal" configuration there would be a considerable hydrogen-hydrogen repulsion energy. It is of fundamental interest to study the manner in which this repulsion energy can be diminished by deformations from the "ideal" geometry.

The most important theoretical calculation of the steric effects in phenanthrene was that of Coulson and Haigh [1]. It is necessary to study the compromise between Van der Waals repulsion energy and the strain energy due to deformations which separate the overcrowded atoms. The Coulson-Haigh treatment minimizes the sum of these energy terms as a function of all the independent parameters. There are a number of very useful features of this treatment. A Van der Waals potential $U(R)$ between the atoms separated by a distance R is assumed. If the treatment is limited to cases where the out-of-plane deformation is not too severe, the in-plane and out-of-plane deformations can be treated independently. It is then possible to establish inequalities on $\mathrm{d}U/\mathrm{d}R$ which separate two possible situations, depending on the "hardness" of the

---

* The Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the Atomic Energy Commission under Contract AT(40-1)-1833.

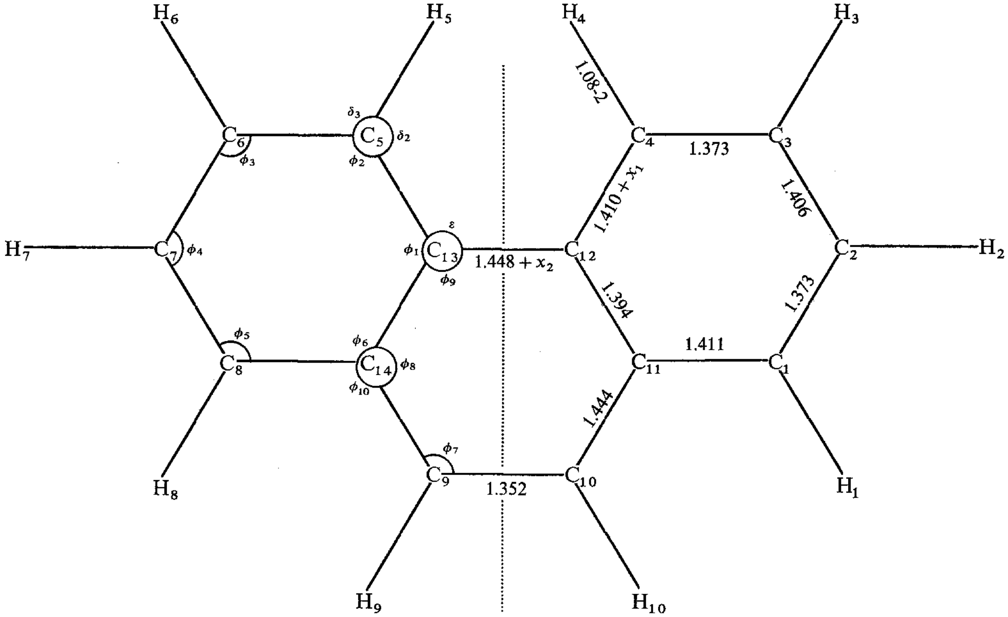

Fig. 1. Coulson-Haigh Model for phenanthrene geometry

potential $U(R)$. These situations are (i) no out-of-plane distortion will occur (ii) there will be out-of-plane distortion, but then the in-plane distortion will be independent of $U(R)$ provided it is "hard" enough to satisfy the appropriate inequality. These separations can be made before the appropriate equations are solved, so that only one set of equations needs to be solved. The out-of-plane deformation calculation requires a matrix of out-of-plane force-constants [2], and the in-plane calculation an array of in-plane force-constants. For a particular choice of $U(R)$, the results are then obtained as $\boldsymbol{z}$, a vector of out-of-plane distortion parameters, and $\boldsymbol{x}$, a vector of in-plane distortion parameters. For example, in phenanthrene [1] the components of $\boldsymbol{x}$ are $(x_1, x_2, q, \delta_2, \delta_3, \varepsilon, \phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6, \phi_7, \phi_8, \phi_9, \phi_{10})$ as shown in Fig. 1, where x_1, x_2, q are bond extensions due to steric effects and $\delta_2, \delta_3, \varepsilon$, etc. are angle openings above 120°. Actually these sixteen components only comprise eight independent variables.

A basic deformation vector $\boldsymbol{x}_0$ can be defined which allows for the deformations from "ideal" geometry due to variations in the skeletal bond lengths, but without including steric repulsion effects. A very valuable result of the Coulson-Haigh formalism is then that

$$\boldsymbol{x} - \boldsymbol{x}_0 = (\mathrm{d}U/\mathrm{d}R)\,\boldsymbol{e},$$

where $\boldsymbol{e}$ is a constant vector independent of $U(R)$. Thus the relative variation in the components of $\boldsymbol{x}$ is constant, and a function only of the "hardness" of the potential assumed. With a reliability which is essentially determined by the appropriateness of the force-constant values, the eight independent variables

Table 1. *Phenanthrene deformation vectors*[a]

$\mathrm{d}U/\mathrm{d}R(10^{-3}$ a.u.) at $R = 3.5$ a.u.	x_1	x_2	q	δ_2	δ_3	ε	ϕ_1	ϕ_2
0.000(x_0)	−1.1	−3.2	0	0.06	−0.54	0.65	−0.61	0.47
3.249	2.0	2.1	2.1	0.56	−1.21	1.16	−1.00	0.65
10.866	7.3	11.3	5.9	1.43	−2.39	2.05	−1.68	0.96
21.732	11.8	19.0	9.0	2.16	−3.38	2.80	−2.25	1.22
Exptl[b]	2.0	16.0	0	1.60	−1.50	2.75	−1.50	−0.10

$\mathrm{d}U/\mathrm{d}R$	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}
0.000(x_0)	−0.02	0.36	0.03	−0.24	0.94	−0.89	−0.05	1.12
3.249	0.04	0.21	0.11	−0.01	0.94	−0.78	−0.17	0.88
10.866	0.13	−0.05	0.25	0.39	0.95	−0.58	−0.37	0.19
21.732	0.21	−0.26	0.37	0.72	0.96	−0.42	−0.54	−0.30
Exptl[b]	1.35	0.25	−0.05	0.10	0.80	0.45	−1.25	−0.55

[a] Lengths in milli Å, angles in degrees.

[b] See later.

have now been expressed as a function of *one* independent variable, proportional to $\mathrm{d}U/\mathrm{d}R$. This is illustrated for three different H–H Van der Waals potential curves in Table 1 (values derived from Ref. [1]).

The hardest potential curve investigated by Coulson and Haigh was that corresponding to the last entry in Table 1 ($\mathrm{d}U/\mathrm{d}R = 21.732$). They found that for even this hardest potential, the treatment predicts no out-of-plane distortion, so that there appears to be very little likehood of non-planarity because of hydrogen-hydrogen repulsion. However, the neglect of non-bonded interactions indicates that a "harder" curve than that usually assumed may be appropriate.

At that time, no accurate crystallographic analysis of phenanthrene was available, and the geometry of the underformed molecule was obtained via bond orders from a self-consistent π-electron molecular orbital treatment. Shortly after, Trotter [3, 4] reported the crystal structure of phenanthrene based on X-ray diffraction studies. This study suggested a structure in general accordance with bond-order calculations, but with a small deviation from planarity, the two outer rings being displaced in opposite directions from the plane of the central ring by about 0.04 Å. Further experimental work on electrical conductivity and polarization, heat capacity, thermal expansion, and X-ray powder data indicate a phase transition at about 70° C, and suggested [5, 6] a dipole moment of $2-3 \times 10^{-3}$ D. The heat capacity anomaly in phenanthrene involves an energy absorption of ~ 380 cal/mole at 72° C.

In order to confirm the role of the crowded hydrogen atoms in causing out-of-plane distortion of phenanthrene, and to try to provide data for the interpretation of the phase transition, a more precise X-ray and neutron diffraction study was completed by Kay, Okaya, and Cox [10]. This work confirmed that the distance between H(4) and H(5) is only 2.04 Å, well below the Van der Waals distance of 2.4 Å, and that this close approach forces a distortion from planarity. The overall nature of the distortion is that the top

Table 2. *Bond lengths in phenanthrene*

Atom pair	Experimental			Theoretical	
	X-Ray [3, 4]	X-Ray [10]	Neutron	Trotter [3, 4]	Coulson-Haigh [1]
C(1)–C(2)	1.381	1.374 ± 0.017	1.398 ± 0.018	1.390	1.373
C(2)–C(3)	1.398	1.386 ± 0.014	1.401 ± 0.016	1.405	1.406
C(3)–C(4)	1.383	1.399 ± 0.015	1.402 ± 0.010	1.391	1.373
[a]C(4)–C(12)	1.405	1.412 ± 0.008	1.406 ± 0.021	1.411	1.410
C(12)–C(11)	1.404	1.416 ± 0.008	1.423 ± 0.008	1.419	1.394
C(11)–C(1)	1.457	1.428 ± 0.005	1.417 ± 0.021	1.413	1.411
[a]C(11)–C(10)	1.390	1.450	1.455 ± 0.020	1.426	1.444
C(9)–C(10)	1.372	1.341	1.358	1.378	1.352
[a]C(12)–C(13)	1.448	1.464	1.465	1.434	1.448

[a] Subject to further distortions in lengths when d$U(R) \neq 0$, in Coulson-Haigh treatment.

ring is titled down and the other ring is tilted up, about the C(2)–C(7) axis. The deviations from planarity within each six-membered ring appear to be small, especially for the carbon atoms.

One further suggestion which appears consistently in all sets of data [3, 4, 10] is that in the crystal the two ends of the phenanthrene molecule are probably not equivalent, i.e. not only the C_{2v} but also the C_2 symmetry is lost as a result of the crystal forces. The angle C(12)–C(4)–H(4) is found to increase to only 121.6°, whereas Kay *et al.* point out [10] that in other overcrowded molecules, angles up to 126° can occur in order to relieve the overcrowded area.

With this accurate crystal structure available, we can proceed to evaluate the Coulson-Haigh approach. The starting point involves the values used for the basic, undistorted geometry. Coulson and Haigh's values were based on a bond distance calculation by Pritchard and Summer [11]. The appropriate experimental and theoretical values for the bond distances are compared in Table 2. The experimental results are averaged to preserve C_2 symmetry for comparison with the theoretical values, which refer to an isolated molecule calculation. The distances marked in the table are subject to further distortions in the Coulson-Haigh model when $\frac{\mathrm{d}U(R)}{\mathrm{d}R} \neq 0$. All sets of data are substantially in agreement although the later C(11)–C(10) distances are in much closer accord with theoretical estimates than the previous results. The new C(12)–C(13) distances are appreciably greater than the theoretical values, but this is a bond length to which a (positive) distortion correction must be added in the Coulson-Haigh treatment. The major discrepancy between the Coulson-Haigh results and the experimental data is the non-planarity of the phenanthrene molecule in the crystal. The fact that there is out-of-plane distortion seems to imply that either the H–H potential is much harder than considered by Coulson and Haigh, for the reasons mentioned, or that crystal forces are responsible for the aplanarity.

In Table 2 are listed the experimental values [10] for the components of the distortion vector $\boldsymbol{x}$. A careful comparison of the experimental values with the range of the theoretical values shows a very good agreement for the distortion parameters localized near the overcrowded site. Thus the values of x_1, x_2, δ_2, δ_3, ε, and ϕ_1, are within the range predicted between the softest ($\mathrm{d}U/\mathrm{d}R = 3.249$) and hardest ($\mathrm{d}U/\mathrm{d}R = 21.732$) potentials considered. A severe discrepancy occurs for q, no detectable shortening of the C(4)–H(4) bond having been observed. The value of ϕ_2 is obviously outside of the range. However, this value is not independent, but is fixed by the algebraic sum of δ_2 and δ_3. The general agreement for the parameters localized at greater distances from the overcrowded site is very poor. Particularly striking is the value for ϕ_3, which is at least six times the theoretical value. These comparisons give no firm indication of the hardness of the appropriate H–H potential. If attention is limited to the "local" distortions x_1, x_2, δ_2, δ_3, ε, and ϕ_1 which are reasonably described by the Coulson-Haigh approach, the experimental results are fairly evenly scattered around the second potential in the table ($\mathrm{d}U/\mathrm{d}R = 10.866$). However, the occurrence of out-of-plane deformation must be borne in mind.

As a result of the previous considerations, we have completed all-valence electron molecular orbital calculations on phenanthrene in a wide range of conformations. Two basic questions were studied in these calculations (1) the extent to which the experimental details of the phenanthrene geometry can be explained theoretically, including the origin of the out-of-plane deformation (2) the possible value of using the Coulson-Haigh approach to simplify the general problem of finding the configuration of lowest energy for a large molecule, where a complete minimization with respect to all independent variables is usually completely impractical.

Details of the Calculations

Calculations on phenanthrene were done using the Complete Neglect of Differential Overlap method [12] (CNDO 2), which includes all valence orbitals on all atoms in the molecule in a self-consistent field approach. Input to the computer program consisted of a variety of parameters, the values used being listed in Table 3, and the coordinates of the nuclei. It is important to note here that the large number of phenanthrene calculations were computationally feasible only because of the availability of Bailey's very highly efficient CNDO program [13]. As a measure of the power of this program a 10 iteration calculation on phenanthrene (66 orbitals) was completed in 60 seconds on an Atlas computer, or 6 seconds on an IBM 360/91.

Table 3. *Parameters used in* CNDO *calculations*

Atom	Orbital exponent	$-\beta^0$ (eV)	$IA_s = 1/2(I_s + A_s)$	IA_p
H	1.2	9	7.176	
C	1.625	21	14.501	5.572
N	1.95	25	19.316	7.275
O	2.275	31	25.390	9.111

The initial phenanthrene geometries calculated were (1) the ideal, planar geometry with all C–C bond lengths 1.400 Å, all C–H bond lengths 1.085 Å, and all bond angles 120°, and (2) the corrected non-planar X-ray diffraction coordinates [10]. Preliminary calculations showed that no significant changes arose from taking all C–H bond lengths as 1.085 Å rather than using the actual neutron diffraction values, so that the more precise X-ray carbon atom coordinates were used with the above C–H bond length.

A small computer program was then written to calculate and punch the atomic coordinates as a function of the particular distortion assumed. The normal input to the program consisted of the basic deformation vector $\boldsymbol{x}_0$ to be used, the undistorted bond lengths such as C(9)–C(10), and a parameter indicating the hardness of the H–H potential in the Coulson-Haigh model. However, options permitted the use of actual experimental $\boldsymbol{x}$ vectors, and the introduction and scaling of out-of-plane distortions (see below). The check on the accuracy of these coordinates was provided by calculation and print-out of the full distance matrix.

The first aspect to be studied was the slight non-planarity of phenanthrene. Since the out-of-plane distortion is very small ($\sim 1°$ in each direction), there is a negligible change in the x- and y-coordinates from the actual X-ray data if they are projected down onto the plane of the central phenanthrene ring. That is, for small distortions, the x- and y-coordinates remain constant. The basic z-coordinates were taken from the out-of-plane perpendicular distances of the various atoms, given by the X-ray data after averaging to maintain C_2 symmetry. These basic z-coordinates were then scaled proportionately by a factor ϱ_z with values from 0.0 to 5.0, where $\varrho_z = 1.0$ reproduces the (averaged) out-of-plane X-ray geometry, and $\varrho_z = 0.0$ is the (averaged) plane-projected X-ray geometry. Separate CNDO calculations were made for each set of coordinates. A similar out-of-plane scaling over the same range was also applied to the ideal geometry, using the X-ray z-coordinates.

For the in-plane distortions, a variety of energy minimizations were tested. First, it is possible to test the qualitative validity of the Coulson-Haigh approach in the present context. We have an experimental vector $\boldsymbol{x}$ from X-ray data (plane-projected) and a basic deformation vector $\boldsymbol{x}_0$. The undistorted bond lengths can also be taken from the averaged X-ray data, rather than from MO calculations. Varying $\boldsymbol{x}$ by scaling the one-parameter difference $\boldsymbol{x} - \boldsymbol{x}_0$ should now give a minimum energy near a scale factor of 1.0, corresponding to the experimental results. These calculations were carried out for a scale factor s of 0.1, 0.3, 0.8, 1.0, 1.2, 1.7 and 2.0.

Further deformations tested involved the direct use of the Coulson-Haigh method, with the energy being studied as a function of the hardness of the potential, and thus as a function of the scaling of the distortion. Any component of $\boldsymbol{x}$ can be chosen as a guide to this scaling, and since x_2 varied from 2.1 to 19.0 in the range of potential studied, we have used the relation $\boldsymbol{x} - \boldsymbol{x}_0 = \varrho \boldsymbol{e}$ with $\varrho = x_2/2$, so that $\varrho \propto \mathrm{d}U/\mathrm{d}R$. The energy was studied over a range of ϱ values, (1) with the bond-shortening q included, and with undistorted bond lengths from Coulson and Haigh, (2) with the bond-shortening q omitted, and with undistorted bond lengths from Coulson and Haigh, (3) with the bond-shortening omitted, and with undistorted bond lengths from the X-ray data.

Finally, the question of the opening up of the C(12)–C(4)–H(4) bond angle $(120 + \delta_2)$ was studied. Using the plane-projected X-ray geometry, the angle was varied from 118° to 126° ($\delta_2 = -2.0°$ to $+6.0°$) other coordinates remaining unchanged, and the total energy was recalculated for each geometry.

Results and Discussion

The results for the ideal, X-ray non-planar (experimental) and for scaling the X-ray out-of-plane distortion are shown in Table 4. There is a very slight discrepancy between the X-ray non-planar, and the X-ray scaled value for $\varrho_z = 1.0$, since the results are not identical. This difference is caused by the averaging across the pseudo-two fold axis to preserve C_2 symmetry, in the later values.

These results suggest quite clearly that the minimum energy configuration for the isolated molecule is probably the planar configuration, since the energy increases monotically with ϱ_z. If this is the case, then the small out-of-plane distortion observed is due to crystal forces. Kay *et al.* [10] have suggested an alternative explanation. They note that the out-of-plane distortion is so slight that there is very little accompanying increase in the H–H distance. If this distortion is present in the isolated molecule, it implies either that the H–H potential is very steep in this region, or the H–H potential is strongly anisotropic. Either or these effects, if present, should have appeared intrinsically in the present calculation. However, the possibility of anisotropic H–H repulsion cannot be ruled out, since the averaging of integrals necessary to preserve rotational invariance in the CNDO method might obliterate such an effect. This is rather serious defect of the CNDO method, particularly for such nearly planar systems where there is almost no arbitrariness in the choice of appropriate coordinate axes, so that preservation of rotational invariance is a somewhat academic concern.

Table 4. *Effect of scaling out-of-plane distortions*

Geometry	H–H Distance (Å)	Electronic energy (eV)	Nuclear energy (eV)	Total energy (eV)
Ideal	1.716	-13301.969	10388.849	-2913.121
X-Ray exptl.	2.040	-13184.251	10270.684	-2913.566
X-Ray vector, bond lengths, $\varrho_z = 0.0$	2.052	-13190.794	10277.259	-2913.535
0.5	2.053	-13190.571	10277.036	-2913.534
1.0	2.056	-13189.898	10276.366	-2913.532
2.0	2.069	-13187.228	10273.708	-2913.520
4.0	2.117	-13176.507	10263.041	-2913.467
6.0	2.196	-13158.829	10245.481	-2913.348

Table 5. *Effect of scaling the experimental distortion vector*

Geometry	H–H Distance (Å)	Electronic energy (eV)	Nuclear energy (eV)	Total energy (eV)
s 0.1	1.801	−13178.044	10264.865	−2913.180
s 0.3	1.857	−13180.425	10267.087	−2913.338
s 0.8	1.986	−13187.512	10273.974	−2913.538
s 1.0	2.052	−13190.800	10277.265	−2913.535
s 1.2	2.109	−13194.321	10280.838	−2913.483
s 1.7	2.249	−13204.213	10291.091	−2913.123
s 2.0	2.334	−13210.868	10298.130	−2912.738

Table 6. *Effect of scaling the Coulson Haigh in-plane distortion*

Geometry	H–H Distance (Å)	Electronic energy (eV)	Nuclear energy (eV)	Total energy (eV)
$\varrho = 0.0$	1.818	−13262.762	10349.036	−2913.726
5.0	1.984	−13238.266	10324.621	−2913.646
7.0	2.034	−13230.809	10317.185	−2913.623
10.0	2.109	−13219.855	10306.278	−2913.577
15.0	2.235	−13202.206	10306.740	−2913.466
20.0	2.361	−13185.296	10271.980	−2913.316
25.0	2.487	−13169.101	10255.973	−2913.128

The results of scaling $x - x_0$ by the scale factor s, with x taken from the experimental results, are shown in Table 5. The fact that the minimum energy configuration occurs near $s = 1$ shows that the Coulson-Haigh approach is a valid method, providing only that the relative magnitudes of the components of x can be correctly estimated. If this can be done by prior calculations, the lowest energy conformation of a molecule like phenanthrene can be found by a one-parameter minimization. It would even be feasible to build such a minimization procedure automatically into the molecular orbital calculations by an iterative search method, although this was not done in the present calculations. This points up the importance of further study of such techniques, by which a complete geometry calculation, with a minimum number of artificial constraints, may become feasible.

Table 6 shows the results of scaling the parameter ϱ, with the C–H bond shortening q included.

The results show no minimum in the range of potentials studied, the minimum energy occuring for the basic undeformed geometry given by x_0. Repeating the calculations above without the C–H shortening (q), and again with undistorted bond lengths taken from the X-ray data, give slightly different energy values, but identical trends. This indicates that the force-constant values chosen by Coulson and Haigh in calculating the distortion vector x as a function of dU/dR are not sufficiently precise to yield an energy minimum over the range

Table 7. *Energy as a function of the* C–C–H *dihedral angle*

Geometry	H–H Distance (Å)	Electronic energy (eV)	Nuclear energy (eV)	Total energy (eV)
118.0°	1.931	−13195.067	10281.547	−2913.520
119.0°	1.9656	−13193.834	10280.303	−2913.531
119.5°	1.981	−13193.231	10279.696	−2913.534
120.0°	1.998	−13192.636	10279.100	−2913.537
120.5°	2.015	−13192.051	10278.513	−2913.538
121.5°	2.032	−13191.475	10277.937	−2913.537
122.0°	2.066	−13190.349	10276.816	−2913.533
124.0°	2.135	−13188.204	10274.696	−2913.507
126.0°	2.205	−13186.202	10272.741	−2913.461

investigated. In other words, the distortion in Table 6 is not sufficiently realistic to produce an energy lowering.

Table 7 shows the effects of opening up the overcrowded area by varying the angle C(12)–C(4)–H(4) from 118° to 126°.

The lowest energy calculated was for angles of 120°–121°. This is in fairly good agreement with the observed angle of 121.6°, and indicates that in phenanthrene opening up the angle to 126° to relieve the overcrowded area sets up excessive strain in other parts of the molecule.

Conclusion

In conclusion, we can say that the present molecular orbital calculations are in generally good accord with the experimental structure determinations on phenanthrene. The calculations suggest that the isolated molecule geometry of phenanthrene may be planar. The slight aplanarity in the crystal is probably due to crystal forces, although the present method is not the most appropriate for studying possible anisotropic interactions. It is planned to investigate this point further by calculations with a different molecular orbital method.

The Coulson-Haigh formalism appears to have a very great potential for the simplification of energy minimization problems in complex systems. The quantitative performance of this formalism depends strongly on the choice of appropriate values of force constants. More study appears to be needed on this choice, particularly for sites distant from the overcrowded area. One approach might be to derive these values so as to reproduce the experimental distortion vector x for phenanthrene, then apply these values to more complicated systems.

Acknowledgements. The author wishes to thank first Dr. Damask for drawing his attention to this problem, and Dr. M. Kay for making preliminary reports of the neutron diffraction work available, and for many discussions. This work was carried out during a year's visit to the Mathematical Institute, University of Oxford. Many thanks are due to Professor C. A. Coulson for his kind hospitality and keen interest in the work, and to Dr. J. Bailey for advice and much assistance in the use of his efficient CNDO computer program, without which the work would not have been feasible.

References

1. Coulson, C. A., Haigh, C. W.: Tetrahedron **19**, 527 (1963).
2. — Senent, S.: J. chem. Soc. (London) **1955**, 1813, 1819.
3. Trotter, J.: Acta crystallogr. **16**, 605 (1963).
4. — Crystal-structure studies of aromatic hydrocarbons. Royal Institute of Chemistry, Lecture Series, Number 2, 1964.
5. Arndt, R. A., Damask, A. C.: J. chem. Physics **45**, 755 (1966).
6. — — J. chem. Physics **45**, 4627 (1966).
7. Matsumoto, S., Tsukada, R.: Bull. chem. Soc. Japan **38**, 2023 (1965).
8. — Bull. chem. Soc. Japan **39**, 1811 (1966).
9. — Tsuguo, F.: Bull. chem. Soc. Japan **40**, 743 (1967).
10. Kay, M. I., Okaya, Y., Cox, D. T.: Acta crystallogr. (in press).
11. Pritchard, H. O., Sumner, F. H.: Proc. Roy. Soc. (London) A **226**, 138 (1954).
12. Pople, J. A., Segal, G. A.: J. chem. Physics **43**, S 129 (1965).
13. Bailey, J. D.: Ph. D. Thesis, U. of Oxford 1969.

Professor Alec Grimison
Puerto Rico Nuclear Center
Caparra Heights Station
San Juan, Puerto Rico, 00935