534. *Some Abnormally Long Carbon–Carbon Bonds.*

By C. A. Coulson and P. N. Skancke.

The aromatic hydrocarbons perylene (I), terrylene (II), and quaterrylene (III), have been studied by the simple molecular-orbital method. The main purpose of the investigation was to consider the long, quasi-single, bonds observed in an *X*-ray analysis of compounds (I) and (III), and by magnetic-susceptibility measurements of (I). Calculations have been made of bond orders, and of steric overcrowding of non-bonded hydrogen atoms. Neither variation of the resonance integral β with bond length, nor configuration interaction, allows a satisfactory prediction of the lengths of these *peri*-bonds.

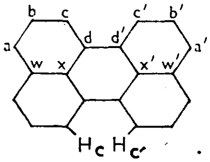
By means of an *X*-ray investigation of perylene (I) Robertson *et al.*[1] have found that the bonds connecting the two naphthalene units—the *peri*-bonds—are significantly longer than the usual aromatic C–C bond. They report a value 1·50 Å for these two bonds

---

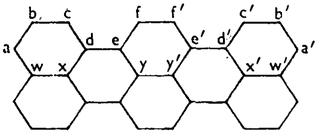
[1] Donaldson, Robertson, and White, *Proc. Roy. Soc.*, 1953, *A*, **220**, 311.

(dd′ in I). More recently Shrivastava and Speakman [2] have carried out a similar investigation of quaterrylene (III). Their conclusion is that in this molecule also there are pairs of unusually long *peri*-bonds (de and hh′ in III). The mean length for all six *peri*-bonds was 1·53 Å.

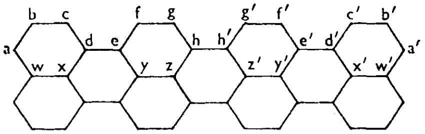
The uncertainty in the determination of these bond distances is comparatively large, on account of unresolved electron-density peaks in the Fourier maps. The reported limits of error are 0·03 Å for the *peri*-bonds in perylene, and 0·01 Å for the corresponding bonds in quaterrylene. However, even with these large uncertainties, these bonds are definitely longer than would be expected in aromatic systems, where measured and calculated bond distances usually lie within the limits 1·38—1·44 Å.



(I)



(II)



(III)

The existence of long, quasi-single, bonds in perylene (I) is supported by some magnetic susceptibility measurements by Hazato [3] and by Shiba and Hazato.[4] These authors showed that the susceptibility for perylene was equal to the sum of the susceptibilities of two naphthalene molecules, less the susceptibility of two hydrogen atoms. This situation argues against any significant double-bond character in the connecting *peri*-bonds.

No experimental structure data are published for terrylene (II). But by analogy with (I) and (III) we should expect a similar situation. We have therefore included it in our calculations. Molecules (I) and (III) are observed to be planar within the uncertainty of the measurements. We assume the same to be true for (II).

In a recent paper Goodwin [5] has published calculated values for the bond orders and bond lengths in these hydrocarbons (I), (II), and (III). His calculations were within the framework of the Hückel approximation, but included allowance for the variation of the resonance integral β with bond length R. He paid special attention to the *peri*-bonds, which are characterized by very low bond orders ($p < 0{\cdot}4$). For these long bonds he found agreement with experiment provided that he used an order–length relationship [6] differing from the analytical expression introduced by Coulson [7a], and designed to fit certain formally single bonds in benzanthrone. This new order-length curve was obtained from Coulson's [7b] " best correlation curve " of 1951 which was then extended for small p and bent over in such a way that it passed through the point $p = 0$, $R = 1{\cdot}50$ Å. With this new curve Goodwin was able to predict lengths for the *peri*-bonds in good agreement with the experimental values.[5]

Despite this success we have felt unhappy about the empirical order–length relation and have preferred to continue with the older curve, for which some theoretical justification can be given and which leads to very satisfactory agreement for nearly all aromatic C–C bonds. Now when this old relation is used for the *peri*-bonds it leads to lengths 0·06—0·09 Å shorter than those observed. We must therefore look for some other explanation. There are three additional factors that we have studied. They are (i) steric repulsions between the hydrogen atoms in *ortho*-positions to the *peri*-bonds, (ii) invalidity of the order–length curve at high or low bond orders through an inadequate relation for the

---

[2] Shrivastava and Speakman, *Proc. Roy. Soc.*, 1960, *A*, **257**, 477.
[3] Hazato, *Bull. Chem. Soc. Japan*, 1949, **22**, 151.
[4] Shiba and Hazato, *Bull. Chem. Soc. Japan*, 1949, **22**, 92.
[5] Goodwin, *J.*, 1960, 4851.
[6] Goodwin and Vand, *J.*, 1955, 1683.
[7] Coulson, (*a*) *Proc. Roy. Soc.*, 1939, *A*, **169**, 413; (*b*) *ibid.*, 1951, *A*, **207**, 91.

compression energy of the underlying σ-bond, and (iii) configuration interaction between the lowest configuration and higher ones of the same total symmetry, but with different bond orders. There are yet other factors discussed in detail by Coulson, Daudel, and Robertson,[8] but we have not considered them here, since there are no reasons for supposing that they would influence the *peri*-bonds in a manner very different from all the other bonds.

In all our calculations we have used the simple Hückel-type approximation, but allowed β to vary with R according to the functional relation suggested by Longuet-Higgins and Salem,[9]

$$\beta(R) = \beta_0 e^{-(R - R_0)/a}, \tag{1}$$

where $a = 0{\cdot}3106$ Å, and β_0 and R_0 are chosen to refer to the benzene molecule. Bond orders are calculated by the Coulson formula,[7a] and bond distances are estimated from mobile bond orders by the Coulson equation

$$R(p) = s - \frac{s - d}{1 + K\left(\frac{1-p}{p}\right)}. \tag{2}$$

Here s and d are the single- and double-bond distances between sp^2 trigonally hybridized carbon atoms, and K is a constant chosen to make the curve (2) pass through the points where $(R,p) = (1{\cdot}517,0), (1{\cdot}337,1)$, and $(1{\cdot}208,2)$. The second and third of these points correspond to ethylene and acetylene, and require no comment (except that we shall later show that if the triple-bond length is increased to allow for a change of hybridization from sp to sp^2 there are small resultant changes in the predicted bond lengths; but these changes are small and are all in the direction of reducing the calculated value; our problem is in no sense simplified by such a change). The pure single-bond length of 1·517 Å has been chosen because this seems to fit best with certain calculated shortenings [10] in the covalent radius as a result of changes in hybridization. Several writers, especially Dewar and Schmeising,[11] have suggested smaller values of s. But if we accept a smaller value we find even greater difficulties in these *peri*-bonds, since the smaller our value of s, the shorter shall we estimate the length of these bonds. With regard to the order–length relation we have preferred the form (2) to the linear relation suggested by Longuet-Higgins and Salem.[9] But the differences are not large, and by no means crucial for our present purposes.

First, let us neglect any possible correction factors to the conventional Hückel treatment. We proceed by iteration and start by setting all β's equal. We then calculate bond orders. This is the first cycle, and it leads to new bond lengths R (using equation 2) and hence, from equation (1), to new β's. We now proceed with further cycles until iteration leads to no significant changes. We then possess self-consistent bond orders and lengths. It is found that four iterations are sufficient for this purpose.

Table 1 presents values for bond orders and bond lengths for the *peri*-bonds obtained after the first and the fourth cycle of iteration. We do not show the results for the other bonds because they present no problem, being in good agreement both with the experimental values [1,2] and with the values calculated by Goodwin [5]; such differences as there are in these other bonds are within the uncertainty of the X-ray measurements, and are not therefore significant.

Table 1 shows that there is a difference Δ between the final calculated and observed lengths of these *peri*-bonds where Δ is in the range 0·06—0·09 Å. This is much too large to be due to errors in the parameters in (1) and (2), and we therefore turn to the three possible corrections (i)—(iii) previously suggested.

[8] Coulson, Daudel, and Robertson, *Proc. Roy. Soc.*, 1951, *A*, **207**, 306.

[9] Longuet-Higgins and Salem, *Proc. Roy. Soc.*, 1959, *A*, **251**, 172.

[10] Coulson, Victor Henri Memorial Volume, " Contribution a l'Étude de la Structure moléculaire,' 1948, Desoer, Liége, p. 15.

[11] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166.

TABLE 1.

Mobile bond orders (p) and bond lengths (R in Å) for the *peri*-bonds in perylene (I; bond dd′), terrylene (II; bond de), and quaterrylene (III; bonds de and hh′).

Molecule	First cycle p	First cycle R	Fourth cycle p	Fourth cycle R	Exp. value R (in Å)	Difference Δ (in Å)
Perylene (I)	0·414	1·435	0·360	1·445	1·50	0·055
Terrylene (II)	0·426	1·432	0·376	1·442	—	
Quaterrylene (III) de	0·429	1·432	0·381	1·441	1·53	0·090
Quaterrylene (III) hh′ ...	0·440	1·430	0·397	1·438		

(i) *Steric Forces.*—If we assume that these molecules are planar, with all valency angles 120°, the distance between the hydrogen atoms in *ortho*-positions to the carbon atoms joined by the *peri*-bonds, is only 1·75 Å (this assumes the C–H length to be 1·08 Å, a value that can hardly be more than 0·01 Å wrong). Now, in paraffin crystals the shortest H • • • H distances between adjacent molecules are 2·48—2·50 Å. So we may expect a repulsive interaction between the "*ortho*"-hydrogens in (I)—(III), which could lead to a distortion of the molecule. If it is distorted, the equilibrium conformation will be such as to minimize the total potential function. This function will be due to the van der Waals steric forces and the internal restoring forces of the molecule.

We need to consider several possible types of deformation. The following possibilities have been considered for all three molecules (I)—(III): (*a*) a "propeller-twist" of one half of the molecule relative to the other half, around an axis passing (see I) through wxx′w′; (*b*) a bending of the "*ortho*"-C–H bonds, but keeping them within the molecular plane; (*c*) an angular distortion of the carbon skeleton, still maintaining planarity; and (*d*) a stretching of the *peri*-bonds.

In order to write down the potential function we need the H • • • H potential and the appropriate molecular force constants. The correct H • • • H van der Waals potential is not known. We have therefore used four different estimates, due to Mason and Kreevoy,[12] Hill,[13] Barton,[14] and Haigh.[15] These are characterized by decreasing "hardness" of the hydrogen atoms. As for the molecular force constants, we have used benzene values [16] for the in-plane deformations, and the Coulson–Senent [17] potential for the out-of-plane deformations. The four possibilities (*a*)—(*d*) were each considered separately, as if each one alone were solely responsible. A more real picture of the true situation would be obtained if all four possibilities were considered simultaneously. However, our results (Table 2) show that except for the hardest H • • • H potential, due to Mason and Kreevoy,[12] this would make little difference.

Table 2 shows the displacements corresponding to minimum total potential energy for all four types of distortion (*a*)—(*d*) and all four van der Waals forces. Table 3 gives the corresponding energies. The calculations refer to perylene, and in this Table R = distance between "*ortho*"-hydrogen atoms in propeller twist (*a*), when the total potential energy has its minimum value, δ = increase in angle $\mathrm{dcH_c}$ in the bending displacement (*b*), α = decrease in angle cdx in angular distortion (*c*), β = increase in angle wxd in angular distortion (*c*), γ = increase in angle bcd in angular distortion (*c*), E = total strain energy (kcal./mole), including both the van der Waals repulsion energy E_w and the deformation energy E_d. "No overcrowding" (abbreviated to N.O.) means that the total potential energy has its minimum for a value of R which does not significantly exceed the value 1·75 Å corresponding to an undistorted molecule. It is not strictly accurate to say that there is absolutely no overcrowding because of a theorem due to Haigh,[15] which states that when the total energy is minimized with respect to in-plane degrees of freedom there will

---

[12] Mason and Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 5808.
[13] Hill, *J. Chem. Phys.*, 1948, **16**, 399.
[14] Barton, *J.*, 1948, 340.
[15] Haigh, unpublished work.
[16] Cyvin, *Acta Chem. Scand.*, 1957, **11**, 1499.
[17] Coulson and Senent, *J.*, 1955, 1813.

always be some distortion, however small; but for an out-of-plane mode, deformation will only occur when the van der Waals curve is " harder " than a certain initial value.

In Table 2, for the deformations of type (*b*) and (*c*) we have also given those values of R which correspond to the angular displacements for these deformations.

TABLE 2.

Equilibrium distortions for perylene.

Type of deformation	Mason and Kreevoy [12]	Hill [13]	Barton [14]	Haigh [15]
(*a*)	$R = 2{\cdot}12$ Å	N.O.	N.O.	N.O.
(*b*)	$\delta = 5{\cdot}0°$, $R = 1{\cdot}91$ Å	$\delta = 1{\cdot}2°$ $R = 1{\cdot}79$ Å	N.O.	N.O.
(*c*)	$\alpha = 0{\cdot}9°$, $\beta = 0{\cdot}5°$ $\gamma = 0{\cdot}5°$, $R = 1{\cdot}79$ Å	N.O.	N.O.	N.O.
(*d*)	N.O.	N.O.	N.O.	N.O.

TABLE 3.

Distortion energies (kcal./mole) for perylene.

Type of deformation	Mason and Kreevoy [12]			Hill [13]			Barton [14]			Haigh [15]		
	E_d	E_w	E	E_d	E_w	E	E_d	E_w	E	E_d	E_w	E
(*a*)	9·55	8·70	18·3	0	2·64	2·64	0	2·09	2·09	0	2·22	2·22
(*b*)	4·32	17·28	21·6	0·26	1·94	2·20	0	2·09	2·09	0	2·22	2·22
(*c*)	0·97	22·16	23·1	0	2·64	2·64	0	2·09	2·09	0	2·22	2·22
(*d*)	0	28·24	28·2	0	2·64	2·64	0	2·09	2·09	0	2·22	2·22

The results in Tables 2 and 3 refer to perylene, but it is clear that they would apply, with very trivial changes, to terrylene (II) and quaterrylene (III).

We may conclude from these results that the overcrowding of the hydrogen atoms cannot be responsible for the experimentally observed increases in the *peri*-bonds. We may also note that hydrogen atoms appear to be more " soft " with respect to mutual penetration than is usually supposed. This is in agreement with unpublished calculations by C. W. Haigh,[15] and suggests that Pauling's value [18] for the van der Waals radius in hydrogen (1·2 Å) is too large for situations of this intramolecular kind.

(ii) *Incorrect Order–Length Relation.*—We now turn to the second possible explanation of the long *peri*-bonds. This is that we have used a Hooke's law potential for the stretching of single and double bonds, whereas we should have used a Morse potential. If $E_d(x)$ and $E_s(x)$ are the energies of single and double bonds at length x, then the energy of a bond of mobile bond order p will be

$$\begin{aligned} E &= pE_d(x) + (1-p)E_s(x) \\ &= pE^0{}_d[e^{-2a(x-d)} - 2e^{-a(x-d)}] + (1-p)E^0{}_s[e^{-2a'(x-s)} - 2e^{-a'(x-s)}], \end{aligned} \tag{3}$$

where $E^0{}_d$ and $E^0{}_s$ are the energies of double and single bonds at their respective equilibrium distances d and s; and where a and a' are constants connected with the curvatures of $E_d(x)$ and $E_s(x)$, and therefore simply related to the force constants for bond stretching.

The bond length R appropriate to bond order p will now be that value of x which minimizes (3). This gives

$$e^{-a(R-d)}[1 - e^{-a(R-d)}] + \frac{1-p}{p}\frac{E^0{}_s}{E^0{}_d}\frac{a'}{a}\, e^{a'(s-R)}[1 - e^{a'(s-R)}] = 0. \tag{4}$$

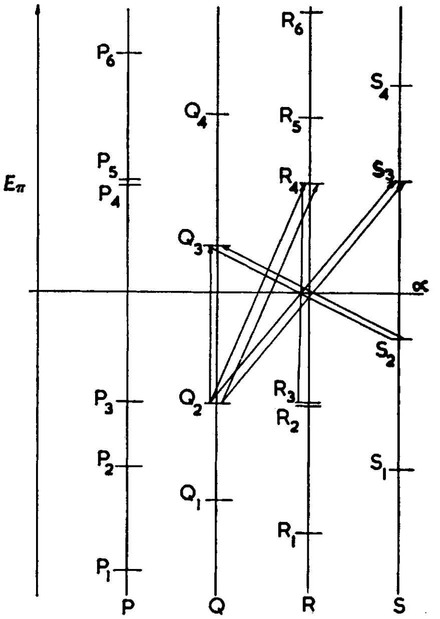
We now put $E^0{}_s = 83{\cdot}6$ kcal./mole, $E^0{}_d = 148{\cdot}4$ kcal./mole, $a' = 2{\cdot}028$ Å^{-1}, $a = 2{\cdot}189$ Å^{-1}, $s = 1{\cdot}517$ Å, $d = 1{\cdot}337$ Å, and solve equation (4) numerically. At the end points where $p = 0$ and 1, $R = s$ and d. Numerical solution of (4) shows that the use of a Morse potential leads to a value of R which is slightly larger than the previous Hooke's law

---

[18] Pauling, " The Nature of the Chemical Bond," 3rd edn., 1960, Cornell Univ. Press, Ithaca, N.Y., p. 260.

potential. This difference has its maximum value 0·0012 Å at $p = 0{\cdot}3$. So, since the greatest change that is brought about by this refinement is only 1/50 of the required increase, we see that we need not consider this refinement any further.

There is one other possible change in the order–length relation (2). When choosing K so that this curve passed through the observed values for single, double, and triple bonds, we made a correction to the single bond (from 1·54 to 1·517 Å) to allow for the hydridization change $sp^3 \longrightarrow sp^2$. But we did not make such a change for the triple bond where the value 1·208 Å refers to sp-hybridization. With sp^2-hybridization here the length would be greater. We have roughly estimated 1·230 Å. This changes the value of K, and hence of calculated bond lengths. But the changes are always in the direction of shortening the bonds, and are therefore of no help to us. They are also small, being nowhere greater than 0·005 Å. We do not therefore pursue this matter any further.



Energies of allowed molecular orbitals for perylene grouped according to their four possible symmetry types. The four pairs of arrows denote the excitations involved in the lower configurations that may interact with the lowest configuration of all.

(iii) *Configuration Interaction.*—It has been pointed out by many people (see *e.g.*, Jacobs[19]) that in any description of the electronic structure of polynuclear aromatic molecules we must expect configuration interaction to play an important part. The corresponding changes introduced into the bond orders have been discussed by Coulson, Daudel, and Robertson.[8] Their conclusion was that configuration interaction would chiefly have the effect of a small, approximately equal, decrease in all bond orders. But they considered only molecules such as naphthalene and anthracene where no *peri*-bonds existed. It might happen that in the latter situations the coefficients of mixing of certain of the higher configurations would be larger and lead to a considerable change in bond order. We have therefore made some simple studies for the case of perylene.

The Figure shows the calculated energies of the allowed molecular orbitals for perylene. The letters P, Q, R, S for the individual orbitals refer to the symmetry notation introduced by Coulson[20] (full group-theory labels are b_{3u}, b_{2g}, b_{1g}, a_{1u}). In the lowest configuration all levels below the horizontal line $E_\pi = \alpha$ are doubly occupied, all the other levels being empty. In calculating the energies of these molecular orbitals we have made the assumption that Hückel orbitals may be employed; and we have supposed, as is usual in such

---

[19] Jacobs, *Proc. Phys. Soc.*, 1949, **62**, *A*, 710.

[20] Coulson, *Proc. Phys. Soc.*, 1948, **60**, 257.

work, that all resonance integrals have the same value. A more complete discussion would allow for different resonance integrals, and would then improve upon the Hückel coefficients. Since, however, we shall show that likely changes in bond lengths do not exceed 0·005 Å, it does not seem worthwhile to make these more elaborate calculations.

Configuration interaction has the effect of mixing into the ground-state wave function excited configurations in which one or more electrons are placed in previously empty molecular orbitals. Most of these one-electron excitations lead to a final wave function of different symmetry, so that no mixing will occur. As for the others, as Miss Jacobs[19] showed for the case of naphthalene, the weights are smaller than for two-electron excitations. If we had used self-consistent molecular orbitals, these one-electron excitations would have been even less important, since, by Brillouin's theorem, they have no interaction with the ground configuration. We have therefore only considered double excitations, such as (1) $S_2^2 \longrightarrow Q_3^2$, (2) $Q_2^2 \longrightarrow S_3^2$, (3) $Q_2^2 \longrightarrow R_4^2$, where the upper index 2 denotes a double excitation. There are many other excited configurations that we would have chosen. Some of them, such as $S_2^2 \longrightarrow S_2S_3$ and $R_3^2 \longrightarrow R_3R_4$, were considered, but did not give any substantial change in *p*-values. Thus the change in *p*-value in the *peri*-bonds in passing from the ground configuration by $S_2^2 \longrightarrow S_2S_3$, is only $-0{\cdot}035$. Since the weight of this configuration must be less than unity, we see that this configuration may be neglected. Similarly the configuration $R_3^2 \longrightarrow R_3R_4$ gives a change $\Delta p = 0{\cdot}0002$, and is therefore entirely unimportant. The three configurations (1)—(3) listed above were those which had the greatest influence in lowering the bond order of the *peri*-bonds, while at the same time not lying energetically much higher than the lowest configuration. Further consideration shows that the excited configuration (1) increases the *peri*-bonds order: both (2) and (3) decrease it.

We now consider the effect of interaction of the lowest configuration with each of the three excited ones, taking each separately in turn. Ideally we should consider the full interaction scheme at once, but it is instructive to see the effect of each alone, and to a first approximation their effects will be additive. We ought also to consider other configurations. But we have not done so because (1)—(3) are the most favourable from the energy point of view. Furthermore, the excitations (2) and (3) both lead to considerably lower orders for the *peri*-bonds in which we are interested. In fact, the configuration (2) gives a total mobile bond order approximately zero for these bonds. It is conceivable that other higher-energy configurations play a significant part. But since, when using perturbation theory to estimate their weight, we see that the weights are proportional to $(\Delta E)^{-2}$, where ΔE is the energy difference of the configurations, we believe that it is unlikely that they are as important as those which we have considered. In order to verify this conclusion we have considered one further configuration (4) arising from the double excitation $P_1^2 \longrightarrow R_6^2$. This new configuration is that particular, doubly-excited one for which the bond order of the *peri*-bonds is as low as possible. If it can be shown that neither the low-energy configurations (1)—(3), nor the higher-energy configuration (4), is able to modify the *peri*-bond lengths appreciably, we can feel fairly confident that a complete configuration-interaction calculation would lead to the same conclusion.

Calculations of configuration interaction can only be made when the full Hamiltonian, including the r_{12}-terms, is used. Our own calculations of the mixing were based on full anti-symmetrized wave functions, and followed the conventional Pariser–Parr–Pople method[21,22] (neglect of differential overlap). The necessary interatomic Coulomb integrals were calculated by using the uniformly charged sphere approximation suggested by Parr.[23]

The results are shown in Table 4, where the changes Δp in bond order and ΔR in bond

---

[21] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466.
[22] Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.
[23] Parr, *J. Chem. Phys.*, 1952, **20**, 1499.

length are shown for each of the three configuration-interaction problems. The indices on Δp and ΔR refer to the particular interaction considered.

These calculations are very approximate. But they show that so far as the *peri*-bonds dd′ are concerned the effect of configuration interaction will be expected to be quite small (less than 0·005 Å) and may even lead to a shorter, rather than a longer, bond. We conclude that this refinement is totally unable to explain the discrepancy between calculated and measured lengths for these bonds.

TABLE 4.

Changes in bond orders (Δp) and bond lengths (ΔR in Å) for perylene (I) by configuration interaction.

Bonds	a–b	b–c	c–d	d–d′	a–w	w–x	d–x
$\Delta_1 p$	−0·021	+0·019	−0·029	+0·027	0	0	0
$\Delta_2 p$	−0·009	+0·001	−0·020	−0·011	0	0	0
$\Delta_3 p$	−0·005	+0·003	−0·012	−0·008	0	0	0
$\Delta_4 p$	−0·002	−0·002	−0·005	−0·008	0	0	−0·008
$\Delta_1 R$	+0·004	−0·003	+0·005	−0·005	0	0	0
$\Delta_2 R$	+0·002	0	+0·004	+0·002	0	0	0
$\Delta_3 R$	+0·001	0	+0·002	+0·001	0	0	0
$\Delta_4 R$	0	0	+0·001	+0·001	0	0	+0·001

Our conclusion is a negative one, for none of the three possible explanations that we have considered appears to be effective. We can see no others with any reasonable likelihood of success. These considerations do, however, suggest that further experimental work on these molecules would be very desirable. A three-dimensional analysis would avoid the overlapping of atoms which limits the present accuracy of bond-length determination. But until the experimental situation really is confirmed, there does not seem to be much point in further theoretical discussion.

One of us (P. N. S.) is grateful to the Norges Tekniske Högskole, Trondheim, and to the Norges Almenvitenskapelige Forskningsråd for a grant which made this research possible. We are both grateful to Drs. J. S. Rollett and T. H. Goodwin, and to Mr. C. W. Haigh, for the benefit of discussion and other help in computing.

MATHEMATICAL INSTITUTE, OXFORD.
[Present address of P. N. S.: ROYAL INSTITUTE OF TECHNOLOGY,
STOCKHOLM 70, SWEDEN.]

[*Received, October 25th,* 1961.]