

X-RAY RESULTS ON AROMATIC HYDROCARBONS

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Abstract Recent X-ray results for the bond lengths in naphthalene and anthracene agree to about 0.01 Å with the simple MO and Pauling theories. Chrysene and quaterylene are also discussed. The bearing of these results on the controversy about the effects of environment and π -bonding in C—C bonds is considered.

1. INTRODUCTION

A NUMBER of recent discussions, particularly those of Stoicheff and his colleagues,^{1,2} have shown how the measured C—C bond lengths in hydrocarbons with unique classical structures all lie close to values characteristic of the environment of the bond. Thus when each carbon is three-co-ordinated any C—C single bond has a length of about 1.48 Å. Further the bond lengths alter regularly with the co-ordination numbers. The constancy of the bond lengths in particular environments suggests rather strongly that the unique classical structure has a high degree of relevance as a simple picture, so that the central bond in butadiene "really" has little or no π -bond character. This view has been argued^{3,4} especially by Dewar and Schmeising.⁵ On the other hand Mulliken⁶ has argued that, though the simple Hückel theory leads to difficulties, up-to-date MO π -electron resonance theories are consistent with the constancies of the bond lengths in the particular environments. However, even though the more recent MO theories may drop the bond order for the central bond in butadiene to about 0.2, it remains a distinct difficulty to them that the observed length of 1.462 Å in the much-puckered cyclo-octatetraene⁷ is less than the 1.483 Å in butadiene.⁸ The results⁹ for diphenyl and 2,2'-dipyridyl, which does not maintain the sterically unhindered planar *trans* form, also suggest very little π -character in their central C—C bonds.

The aromatic hydrocarbons do not have unique classical structures and their C—C bonds must have partial double-bond character on any theory. Discarding benzene and graphite, in each of which all the bonds are of equal length and which all the theories are arranged to fit, the study of these molecules should be useful in the controversy over the relative effects of π -bonding and environment. In the six-membered rings all carbons are three-co-ordinated and, to the extent to which adjacent links to hydrogen or to carbon have the same effects, the environment of all C—C bonds is the same. The variation of C—C bond lengths within one molecule and in

* It is not important to this paper whether the change in carbon radius with environment is due to hybridization changes^{10,11} or to the effects of intramolecular repulsions.¹²

¹ G. Herzberg and B. P. Stoicheff, *Nature, Lond.* **175**, 79 (1955).

² C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

³ M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).

⁴ M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **11**, 96 (1960).

⁵ L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).

⁶ R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).

⁷ O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).

⁸ A. Almendinger, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12**, 1221 (1958).

⁹ A. Almendinger and O. Bastiansen, *Det Agt. Norske Vid. Selsk. Skrift. No. 4* (1958).

different molecules is thus primarily a reflection of their different π -bond characters and may be used to test the merits of different valence theories without the complications of drastically changing environments. Some years ago it seemed that the experimental results were better fitted by MO theories than by any kind of VB theory, including the simplest Pauling-type theory of the resonance of classical structures. More recent and more accurate X-ray crystallographic results show that both the simple MO theory and the simple Pauling method predict CC lengths in sterically-unhindered aromatic molecules to within about 0.01 Å. Thus the resonating-classical-structures method does almost as well for aromatic molecules as the unique-classical-structure approach does for the non-aromatic hydrocarbons. The present paper discusses these problems in the light of four very recent papers on the crystal structures of aromatic molecules which appeared in *Proc. Roy. Soc. (Ser. A)* in September and October 1960. Cruickshank and Sparks¹⁰ gave results for naphthalene and anthracene, Burns and Iball¹¹ for chrysene, Shrivastava and Speakman¹² for quaterrylene, and Mason¹³ for 1:2:8:9-dibenzaecridine. The paper by Cruickshank and Sparks also included a considerable discussion of the VB and MO theories and their predictions for all these molecules. The present paper, prepared by request for this Symposium and therefore written close on the heels of the Cruickshank and Sparks paper, is partly a summary of points made there and the reader is referred to it for a fuller discussion of many details.

2 NAPHTHALENE AND ANTHRACENE

The new experimental bond lengths for naphthalene and anthracene presented by Cruickshank and Sparks¹⁰ are combinations of several independent refinements of sets of three-dimensional X-ray data. The results for naphthalene are the average of Cruickshank's refinement of the data of Robertson *et al.*¹⁴ by the differential-synthesis method and Sparks' refinement of the same data by the least-squares method. The results for anthracene are a weighted average of the similar refinements of the data of Robertson *et al.* together with Sparks' least-squares refinement of Phillips' high-accuracy proportional-counter data. These refinements all allowed for the anisotropic vibrations of the atoms in the crystals and included corrections for finite series and peak overlapping effects, and also for the apparent atomic displacements caused by the rotational oscillations of the molecules.¹⁵ The results of the various refinements were in satisfactory agreement. The final averaged bond lengths are given in Table 1. Their e.s.d.'s, estimated a little more conservatively than in some earlier work, are approximately 0.005 Å for naphthalene and 0.004 Å for anthracene. The present bond lengths have an r.m.s. difference of 0.016 Å from those found directly from the electron density maps without any corrections by Robertson and his colleagues, and have an r.m.s. difference of 0.011 Å from those given by Ahmed and Cruickshank¹⁶ after application of simple finite series corrections. The successive corrections have brought

¹⁰ D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc. A* **258**, 270 (1960).

¹¹ D. M. Burns and J. C. Iball, *Proc. Roy. Soc. A* **257**, 491 (1960).

¹² H. N. Shrivastava and J. C. Speakman, *Proc. Roy. Soc. A* **257**, 477 (1960).

¹³ R. Mason, *Proc. Roy. Soc. A* **258**, 302 (1960).

¹⁴ naphthalene: S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Cryst.* **2**, 233, 238 (1949)

anthracene: A. McL. Mathieson, J. M. Robertson and V. C. Sinclair, *Acta Cryst.* **3**, 245 (1950), V. C. Sinclair, J. M. Robertson and A. McL. Mathieson, *Acta Cryst.* **3**, 251 (1950).

¹⁵ D. W. J. Cruickshank, *Acta Cryst.* **9**, 757 (1956)

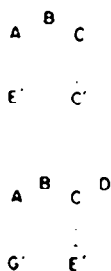
¹⁶ I. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.* **5**, 852 (1952)

small increases in the mean bond lengths of each molecule, but some less regular changes have also occurred. In particular the difference between the corresponding internal bonds CC' in naphthalene and CE' in anthracene has been reduced from 0.045 Å in Robertson's results to 0.010 Å at present. This reduction has removed a source of much theoretical perplexity.

The new X-ray results are in remarkably good agreement with those obtained by Almenningen, Bastiansen and Dyvik¹⁷ in their gas phase electron-diffraction study. The r.m.s. difference is only 0.004 Å, which seems fortuitously small.

TABLE I. BOND LENGTHS (Å) IN NAPHTHALENE AND ANTHRACENE

Bond	Experimental	Pauling superposition	Simple MO
Naphthalene			
AB	1.364	1.375	1.384
BC	1.421	1.421	1.416
CC'	1.418	1.421	1.424
AE'	1.415	1.421	1.406
Anthracene			
AB	1.368	1.365	1.382
BC	1.436	1.434	1.420
CD	1.399	1.397	1.406
CE'	1.428	1.434	1.430
AG'	1.419	1.434	1.410



The comparison of the experimental results with various theoretical results, including several modifications of MO theory, is discussed in some detail in Cruickshank and Sparks' paper. The main point that emerged was that the simplest forms of the MO and VB theories both predict bond lengths for naphthalene and anthracene which correct to about 0.01 Å. These theoretical values are also shown in Table I. The simple MO values given by Coulson *et al.*¹⁸ have r.m.s. differences with experiment of 0.012 Å for naphthalene and 0.011 Å for anthracene, which are no greater than the errors to be anticipated from the known limitations of the method. Some half dozen corrections can be made to the simple MO theory, but none of these has a predominant effect. Inclusion of three of the more important corrections—self-consistency,

¹⁷ A. Almenningen, O. Bastiansen and F. Dyvik, Private Communication.

¹⁸ C. A. Coulson, R. Daudel and J. M. Robertson, *Proc. Roy. Soc. A* **207**, 306 (1951).

variation of σ -bond energy with length, and configuration interaction— gives somewhat better agreement (0.007 Å), though one fears that another correction might worsen it.

The earlier experimental results were in rather poor agreement with those predicted by the simple Pauling method, where the bond orders are given by the proportion of the Kekulé structures in which a particular bond is double. Its agreement with the latest results is excellent. In naphthalene AB has bond order $\frac{3}{4}$ and the other bonds $\frac{1}{4}$. In anthracene AB has order $\frac{3}{4}$, CD $\frac{1}{4}$ and the others $\frac{1}{4}$. These bond orders can be seen immediately to be in general agreement with the experimental results of Table 1, for in naphthalene AB is markedly the shortest bond, while in anthracene AB is again short, CD is intermediate and the other three bonds are long. The lengths shown in Table 1 in the column headed 'Pauling superposition' are those obtained from these π -bond orders p by the Pauling-type formula* for the length

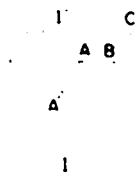
$$r = 1.477 - (1.477 - 1.337) \frac{1.333p}{0.333p + 1}$$

The constants in this formula are determined by the values of 1.337 Å for ethylene (bond order 1), 1.397 Å for benzene (order $\frac{2}{3}$) and 1.421 Å for graphite (order $\frac{1}{3}$). The formula extrapolates to a value of 1.477 Å for a single bond, which is seductively close to the estimates of about 1.48 Å obtained from molecules with unique classical structures, when both carbons are three-co-ordinated. The r.m.s. differences between the experimental results and those given by the Pauling method are only 0.006 Å for naphthalene and 0.007 Å for anthracene.

The change in fortune of the Pauling method offers a warning against undue trust in any but the most thorough experimental analyses. Though the earlier results were obtained by what were then advanced procedures, their accuracy was over-estimated. Similarly the estimates of accuracy of the present results may be falsified if further systematic errors are discovered—a sombre truism which applies to any experimental technique.

3. OTHER AROMATIC MOLECULES

Although many alternant aromatic hydrocarbons have been investigated by X-ray crystallography, very few have been refined to a degree comparable with that for naphthalene or anthracene, which now appears to be the minimum necessary for reliability. Such analyses require three-dimensional data with corrections for finite series, anisotropic vibrations and rotational oscillation effects. The results obtained by Burns and Iball¹¹ for chrysene (I) have e.s.d.'s of about 0.004 Å and are about as



accurate as those given above for anthracene. The r.m.s. discrepancies for the eleven independent CC bonds of chrysene are 0.016 Å for the simple MO theory and 0.015 Å

* The p in the numerator was inadvertently omitted in the printing of Cruickshank and Sparks' paper.¹⁰

for the Pauling method. The chief cause of these larger discrepancies is the value of 1.468 Å measured for the AB bond. This is 0.03–0.04 Å longer than the theoretical values and, as Burns and Iball point out, the reasonable explanation is that this bond is stretched as a consequence of the steric repulsion between the hydrogens attached to atoms C and I'. Other bonds will also be affected and the theories are thus not fully applicable to this slightly overcrowded molecule.

A similar overcrowding between hydrogen atoms seems to be the reason for the long 1.53 Å, 0.01 Å *peri*-bonds connecting the naphthalenic residues in quaterylene¹² (II). Of the 81 Kekulé structures for this molecule, none involve the *peri*-bonds as



double bonds; a length of 1.48 Å is therefore expected and it is reasonable to ascribe the increase to 1.53 Å as due to the overcrowding effect. Strictly this analysis by two-dimensional methods does not at all reach the specified standards of reliability, but as the 1.53 Å is an average for six independent *peri*-bonds, it is probably sufficiently accurate to be regarded as significantly longer than the expected 1.48 Å.

These difficulties of overcrowding can be avoided by replacement of CH by N at appropriate points of the rings. The remaining CC bonds can then be compared experimentally and theoretically. Such comparisons seem justified by the facts that the experimental results for acridine^{19,20} and phenazine²¹ show that their CC lengths are practically the same as the corresponding lengths in anthracene and because the MO bond orders for CC bonds in hydrocarbons and in the N-replaced molecules, with $\alpha_N = \alpha_C = 0.5$, differ very little. Mason's experimental results^{13,22} for 1:2:8:9-dibenz-acridine in which there is no steric hindrance are therefore of potential interest. However the results published in 1960 as the conclusion of the work show an r.m.s. deviation between pairs of chemically equivalent bonds of 0.028 Å, which is almost three times as large as that of the interim results of 1957; one pair now differing by as much as 0.053 Å. Unfortunately the description of the refinement is very brief and no comment is offered on this difficulty: the trouble may be partly due to the fact that the data is only two-dimensional. Only the 1957 results were known to Cruickshank and Sparks, who found r.m.s. discrepancies between theory and experiment for the 12 CC bonds of 0.011 Å for the Pauling method and 0.008 Å for the MO method. In view of the poor internal consistency of the 1960 results it is not surprising that the two discrepancies now rise to 0.015 and 0.014 Å; the relative performance of the two theories at any rate remains similar.

4. COMPARISON OF MO AND PAULING METHODS

The good performance of both the simple MO and Pauling approaches to the determination of bond lengths in polynuclear aromatic hydrocarbons can be traced to

¹⁹ D. C. Phillips, *Acta Cryst.* **9**, 237 (1956).

²⁰ D. C. Phillips, F. R. Ahmed and W. H. Barnes, *Acta Cryst.* **13**, 365 (1960).

²¹ F. L. Hirshfeld and G. M. J. Schmidt, *J. Chem. Phys.* **26**, 963 (1957).

²² R. Mason, *Nature, Lond.* **179**, 465 (1957).

a correlation of the two sorts of bond order. Fig. 1 plots MO bond orders against Pauling bond orders for fifteen representative molecules. To a first approximation there is a roughly linear relation in which as the Pauling π -order p varies from 0 to 1.0 the MO order m varies from 0.4 to 0.85. With appropriate choices for the order/length relations, this general correlation explains why both methods compare similarly with experiment. On more detailed examination striking results emerge if the bonds

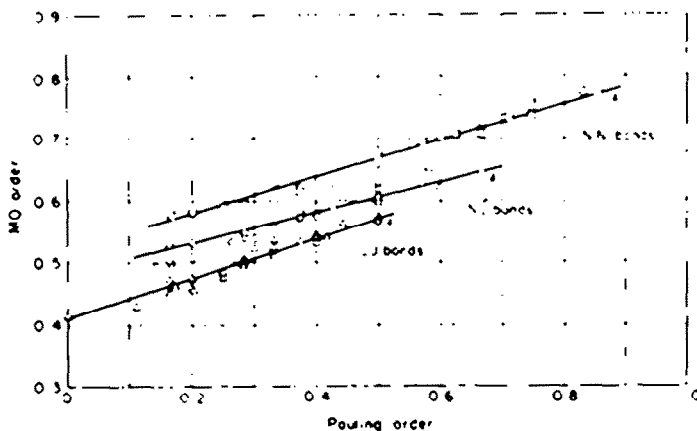


FIG. 1. The correlation of MO and Pauling bond orders. \square , NN bonds; \circ , NJ bonds; \triangle , JJ bonds.
Vertical ordinate: MO bond order
Horizontal ordinate: Pauling bond order

are divided into three classes: NN, in which neither carbon atom is at the junction of two rings; NJ, with one atom at a ring junction; and JJ, with both atoms at junctions. The relations

$$m = 0.52 + 0.30p \text{ (for NN bonds),}$$

$$m = 0.48 + 0.25p \text{ (for NJ bonds),}$$

$$m = 0.41 + 0.33p \text{ (for JJ bonds),}$$

which are shown as straight lines in Fig. 1, then represent the correlation quite well.

For each theory Cruickshank and Sparks examined whether the experimental lengths showed different behaviour for the three classes, but the available results did not permit any unambiguous conclusions. The one evident conclusion from the experimental results was that the simple MO theory would do a little better if the theoretical order/length curve fell more steeply—this would accord with the wider spread of bond orders which more complete MO theories would show.

5. CONCLUDING REMARKS

The remarkably good behaviour of the Pauling or resonating classical-structures method of determining bond lengths in aromatic molecules seems to fit in with the good performance of the unique classical-structure method for non-aromatic hydrocarbons, granted that different standard lengths are used for the various coordination numbers. In view of the general defects of the simple MO method, typified by the excessive bond-order of the central bond in butadiene, it is perhaps surprising that it predicts bond lengths in aromatic molecules to within about 0.01 Å. Its good

performance seems due to the general correlation of its bond orders with the Pauling orders and to the use of a somewhat *S* shaped order/length curve (a more exaggerated *S* would mask the defects still further).

As implied previously, the only moderately accurate results which seem to be available for aromatic molecules free from steric hindrance are those for naphthalene and anthracene. Clearly more such molecules need to be studied; naphthacene, pyrene and coronene would be obvious early choices. The analogue of perylene formed by joining two isoquinoline units centrosymmetrically would also be worth investigation as it also would be free from steric hindrance. The length of its *peri*-bond would be of great interest as it has a bond-order of zero in the Pauling method and of about 0.4 in the simple MO theory, which presumably reduces to about 0.2 in more complete treatments. This length will thus be relevant to the discussion of the long bonds in butadiene, cyclo-octatetraene, diphenyl and 2.2'-dipyridyl, where the present evidence seems unfavourable even to the up-to-date MO theories.

In connexion with future X-ray investigations, it may be remarked that improvements in experimental techniques should make it possible²² to determine bond lengths with e.s.d.'s of about one-third the best values mentioned above and reduced to, say, 0.0013 Å. Such accuracies should be possible in low temperature studies on the automatic counter diffractometers now starting to come into use, which are designed to measure thousands of reflexions quickly and accurately. Results of this precision will provide stringent tests for valence theories (and will cause the crystallographers the same kind of troubles over anharmonicity, etc., as are now experienced by spectroscopists and electron-diffractionists).

A final point can be introduced by way of Trotter's recent X-ray structure determination²⁴ of *p*-benzoquinone (III), in which the various desirable corrections were made. The measured bond lengths are C—O 1.222 ± 0.008 Å, C—C 1.477 ± 0.006 Å, C—C



III

1.322 ± 0.008 Å. These are close to the values expected in the classical structure-method for bonds in these environments. Within experimental error, the value of 1.322 Å is not significantly different from a value of 1.337 Å in ethylene. However recalling that the C—C single bond in the paraffins^{25,26} is of the order of 0.01 Å shorter than the C—C single bond in diamond, these two double bonds are not to be expected to have exactly the same length. This draws attention to the fact that the three reference points used to derive the order/length relation for the Pauling method were for ethylene, benzene and graphite, where each carbon has respectively two, one and no hydrogens as neighbours. In the rings of aromatic molecules no carbon is ever joined as in ethylene to two hydrogens, so that as a start to a more consistent approach it would be most valuable to have a modern redetermination of the C—C length in tetramethylethylene.²⁷

²² D. W. J. Cruickshank, *Acta Cryst.* 13, 774 (1960).

²³ J. Trotter, *Acta Cryst.* 13, 86 (1960).

²⁴ R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Amer. Chem. Soc.* 81, 4765 (1959).

²⁵ D. R. Lide, *J. Chem. Phys.* 33, 1514 (1960).

²⁶ I. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* 59, 1223 (1937).