$a=4{\cdot}769\pm0{\cdot}002, \quad b=7{\cdot}248\pm0{\cdot}003, \quad c=9{\cdot}756\pm0{\cdot}005$ Å .

Straumanis' values for the iodine coefficients of expansion (Straumanis, 1943) would give

$$a=4{\cdot}777\pm0{\cdot}002, \quad b=7{\cdot}256\pm0{\cdot}003, \quad c=9{\cdot}761\pm0{\cdot}005 \text{ Å}$$
at 16 °C.

These may be compared with the values

$$a = 4{\cdot}7784, \quad b = 7{\cdot}2487, \quad c = 9{\cdot}7704 \text{ Å}$$

obtained by Straumanis using angles up to 84°.

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# On the Bond Lengths of 1:14-Benzbisanthrene

BY MD. ASGAR ALI

*Mathematical Institute, 10 Parks Road, Oxford, England*

The $\pi$-bond orders of the various bonds in 1:14 benzbisanthrene are calculated by the molecular-orbital method within the $\pi$-electron approximation, the molecular orbitals being formed by linear combination of atomic orbitals (l.c.a.o.m.o.). The bond lengths are obtained from the usual curves of $\pi$-bond order *vs.* bond length and compared with experimental values. It is found that the m.o. treatment reproduces the trends in observed bond lengths, but that there is some discrepancy between these two sets of values. The effect of introducing refinements in the calculation is discussed in the light of results obtained for simple molecules like butadiene with this refinements.

Recently Trotter (1958) has determined the bond lengths in 1:14-benzbisanthrene by X-ray diffraction. His results show that the lengths of the central bonds *D*, *C*, *B*, *A* (Fig. 1) increase markedly in that order $(1{\cdot}40 \to 1{\cdot}44 \to 1{\cdot}47 \to 1{\cdot}49$ Å) and that the shortest bond is *V* $(1{\cdot}35$ Å).
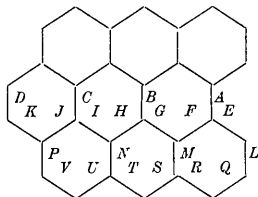


Fig. 1. 1:14-Benzbisanthrene.

Trotter also carried out a simple valence-bond calculation of the bond lengths, taking into account only the thirty unexcited structures. His calculation reproduced nicely the observed trends in the bond lengths, and the calculated values are surprisingly close to the observed. Since it is known that a simple l.c.a.o.m.o. calculation neglecting overlap also predicts

the correct bond lengths in other aromatic hydrocarbons, we were interested in comparing the success of the two methods for 1:14-benzbisanthrene. Pauncz & Berencz (1954) have calculated the $\pi$ bond orders using the molecular-orbital method and have derived bond lengths. We have repeated these calculations and obtained the bond lengths from a smooth order-length curve drawn through these basic points:

|  | $\pi$ Bond order | Bond length |
|---|---|---|
| Diamond corrected to $sp^2$ hybridization | 0 | 1·50 Å |
| Graphite | 0·525 | 1·421 |
| Benzene | 0·667 | 1·39 |
| Ethylene | 1·000 | 1·34 |

Our $\pi$ bond orders and calculated bond lengths (which differ only slightly from those of the previous m.o. calculation) are listed in Table 1 together with the observed distances.

The figure in the third decimal place in the calculated bond lengths has no absolute significance but shows the correct order of the bonds in relation to one another. The Table shows that the trends in bond lengths are reproduced quite accurately in this cal-

Table 1. $\pi$ bond orders and bond lengths

| Bond | $\pi$ Bond order | Calculated bond length | Observed bond length |
|------|-----------------|------------------------|----------------------|
| A | 0·424 | 1·443 Å | 1·49 Å |
| B | 0·489 | 1·427 | 1·47 |
| C | 0·522 | 1·421 | 1·44 |
| D | 0·717 | 1·381 | 1·40 |
| E | 0·634 | 1·398 | 1·36 |
| F | 0·532 | 1·419 | 1·43 |
| G | 0·532 | 1·419 | 1·40 |
| H | 0·551 | 1·415 | 1·41 |
| I | 0·527 | 1·420 | 1·43 |
| J | 0·534 | 1·418 | 1·42 |
| K | 0·565 | 1·412 | 1·39 |
| L | 0·633 | 1·399 | 1·43 |
| M | 0·509 | 1·424 | 1·42 |
| N | 0·496 | 1·426 | 1·44 |
| P | 0·510 | 1·424 | 1·46 |
| Q | 0·703 | 1·384 | 1·37 |
| R | 0·552 | 1·415 | 1·43 |
| S | 0·570 | 1·410 | 1·40 |
| T | 0·626 | 1·400 | 1·37 |
| U | 0·501 | 1·425 | 1·47 |
| V | 0·772 | 1·371 | 1·35 |
| Mean | | 1·412 | 1·418 |

Root mean square error = 0·025.

culation also, but that their absolute values differ from the observed ones. The largest error seems to be in the length of the bond $A$. This is partly due to the uncertainty in the nature of the order-length curve below $\pi$ bond order 0·5 and partly to the simplifying assumption that all resonance integrals are equal, which is far from being true. The root-mean-square of the differences between the calculated lengths and the observed values is 0·025 Å. This might be compared with that for the valence-bond calculation which is 0·01 Å. The mean of our values 1·412 Å compares well with the observed mean 1·418 Å. Probably if we had allowed for the variation of the resonance integral with bond length, or carried out a self-consistent type of calculation as indicated by Pople (1953), assuming the orbitals calculated by the Hückel method as an approximation, we might have obtained a better agreement with observed values. Such a calculation would be very laborious and hence was not undertaken. But we could reasonably expect the same type of improvements in the results as in the case of smaller molecules like butadiene.

In butadiene, with the approximation of equal resonance integral for all the bonds, the l.c.a.o.m.o. calculation yields 0·894 and 0·447 as the $\pi$ bond orders of the end bonds and the central bond. The corresponding bond orders by a self-consistent calculation done by Pople (1953) are 0·9604 and 0·2790. The above figures show that the change in bond order of the central bond is more than that of the end bonds. In fact, this refinement shortens the smaller bond lengths a little but lengthens the longer bond considerably. Hence, with this type of refinement, we can expect that the refined bond order of $D$ will be slightly higher, and that of $A$ considerably less, than the simple bond orders calculated on l.c.a.o.m.o. approximation. Hence the new bond lengths will correspond more closely to the observed values.

There is one point which might be made here. The variation of bond length along the central bonds $D \to C \to B \to A$ seems to be of quite general occurrence in this type of aromatic hydrocarbon. Such a variation also occurs in the central bonds of 1:12-benzoperylene (Pauncz & Berencz, 1953; 1954), which are shown below.
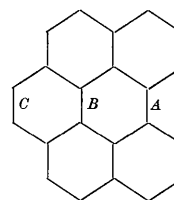


Fig. 2. 1:12-Benzoperylene.

| Bond | $\pi$ Bond order |
|------|-----------------|
| A | 0·427 |
| B | 0·519 |
| C | 0·734 |

These bond orders might be compared with those for similar bonds in 1:14-Benzbisanthrene.

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