Short Communications

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Acta Cryst. (1963). **16**, 929

Note on the bond lengths of 1,14-benzbisanthrene.

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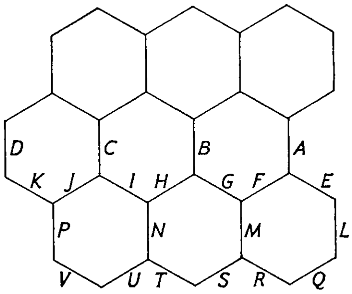
(*Received* 15 *January* 1963)

In an earlier paper (Ali, 1959), the bond lengths in 1,14 benzbisanthrene (I) were calculated by the simple Hückel molecular orbital method and compared with experimental results (Trotter, 1958). In the simple molecular orbital calculation it is assumed that all resonance integrals between nearest neighbours have the same value β. As the calculated lengths show, this assumption is far from correct. So ideally one should allow for the variation of β with length of the bond and get a set of self-consistent bond orders such that the length derived from the bond order is consistent with the β assumed for the bond. This is done by an iterative technique, the length and β for a bond being derived from the bond orders calculated from the solutions of the secular equation of the previous stage. But for this purpose the dependence of β on length has to be known. We assume the simple relation suggested by Longuet-Higgins & Salem (1959):



(I)

$$\beta(r) = -B\exp\left(-r/a\right) \quad (a = 0{\cdot}3106\ \text{Å})$$

such that β (1·40 Å) $= -25{\cdot}56$ kcal.mole^{-1}. The constant a was determined from the breathing vibration of benzene. By an iterative technique starting from the bond orders obtained from the calculation assuming all β's to be equal, we arrive at the self-consistent stage when we find that further iterations make no appreciable change in the bond order. The results of two iterations beyond the first stage are given in Table 1.

We have used the linear relation

$$l = (1{\cdot}50 - 0{\cdot}15p)\ \text{Å}$$

suggested by Longuet-Higgins and Salem (1959) for deriving bond lengths from bond order. The nomenclature of the bonds is as shown in (I). The bond lengths in the second column are the recalculated values using the linear relationship of Longuet-Higgins & Salem.

Table 1. *Bond orders and lengths*

	1st iteration		2nd iteration		3rd iteration	
Bond	Bond order	Length (Å)	Bond order	Length (Å)	Bond order	Length (Å)
A	0·424	1·436	0·3950	1·441	0·3872	1·442
B	0·489	1·427	0·4748	1·429	0·4698	1·430
C	0·522	1·422	0·5202	1·422	0·5208	1·422
D	0·717	1·392	0·7227	1·392	0·7211	1·392
E	0·634	1·405	0·6535	1·402	0·6611	1·401
F	0·532	1·420	0·5300	1·421	0·5272	1·421
G	0·532	1·420	0·5350	1·420	0·5345	1·420
H	0·551	1·417	0·5642	1·415	0·5691	1·415
I	0·527	1·421	0·5185	1·422	0·5131	1·423
J	0·534	1·420	0·5471	1·418	0·5520	1·417
K	0·565	1·415	0·5662	1·415	0·5690	1·415
L	0·633	1·405	0·6189	1·407	0·6124	1·408
M	0·509	1·424	0·5137	1·423	0·5181	1·422
N	0·496	1·426	0·4920	1·426	0·4926	1·426
P	0·510	1·424	0·4812	1·428	0·4713	1·429
Q	0·703	1·395	0·7157	1·393	0·7210	1·392
R	0·551	1·417	0·5454	1·418	0·5422	1·419
S	0·570	1·415	0·5663	1·415	0·5642	1·415
T	0·626	1·406	0·6480	1·403	0·65444	1·402
U	0·501	1·425	0·4699	1·430	0·4595	1·431
V	0·772	1·384	0·7993	1·380	0·8077	1·379

From Table 1 we see that the self-consistency in β improves the result, although not very much. But it is interesting to note that the order of bond length variation in the central part of the molecule is still correctly predicted. It is also seen that the convergence in this β variation procedure is quite rapid and two or three variations are sufficient for achieving consistency of 0·001 Å in the bond length. The bond lengths calculated by this refined procedure are appreciably different from measured ones, so a refined experimental investigation would be desirable in view of the fact that the refined bond lengths in naphthalene and anthracene are predicted by simple molecular orbital theory to about 0·01 Å (Cruickshank & Sparks, 1960; Cruickshank, 1962).

The author would like to express his sincere thanks to Prof. C. A. Coulson, F.R.S., for guidance throughout the work.

References

Ali, M. A. (1959). *Acta Cryst.* **12**, 445.
Cruickshank, D. W. J. & Sparks, R. A. (1960). *Proc. Roy. Soc.* A, **258**, 270.
Cruickshank, D. W. J. (1962). *Tetrahedron*, **17**, 155.
Longuet-Higgins, H. C. & Salem, L. (1959). *Proc. Roy. Soc.* A, **251**, 172.
Trotter, J. (1958). *Acta Cryst.* **11**, 423.