522. *Calculated Bond Lengths in Some Cyclic Compounds. Part VI.** 2 : 3-8 : 9-*Dibenzoperylene.*

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The calculations here reported were carried out early in 1956,[1] when the crystal structure of 2 : 3-8 : 9-dibenzoperylene, under examination [2] in these laboratories, was showing rather unexpected deviations from a truly planar configuration. Although the hydrogen atoms forming the " horns " of the phenanthrene " bays " are somewhat overcrowded and it would not have been surprising if their carbon atoms had been displaced from the mean ring plane by one or two hundredths of an Ångström unit, the *X*-ray examination did not, at that stage, reveal a significant distortion of the molecule in this sense. It did, however, point to one of about 0·07 Å in the atoms *J* † and *L* which are displaced the one above and the other below the mean ring plane by this amount. It was hoped that the bond lengths derived in these present calculations might throw some light on the experimental results.

The calculations were effected by the methods described [3] in Part I of this series, the molecule, for this purpose, being supposed planar with an axis of symmetry perpendicular to the molecular plane. The energies, $(E - \alpha)$, of the occupied orbitals are as follows: (*a*) symmetrical: 2·3749β, 1·9788β, 1·6446β, 1·2474β, β (twice), 0·6965β; (*b*) antisymmetrical: 2·6366β, 2·0713β, 1·6135β, 1·3236β, 1·1824β, 0·7590β, 0·3557β. These lead to the bond lengths L_{GW} given in the Table. The column headed L_{LRR} contains the final observed bond lengths [2] while Δ gives $(L_{\text{LRR}} - L_{\text{GW}})$. The mean value of $|\Delta|$ is 0·017 Å and its greatest value 0·05 Å.

Bond	L_{LRR}	L_{GW}	Δ	Bond	L_{LRR}	L_{GW}	Δ
AB	1·48	1·450	+0·03	FG′	1·42	1·409	+0·01
AC′	1·45	1·426	+0·02	GH	1·46	1·462	0·00
AG	1·38	1·424	−0·04	HI	1·40	1·408	−0·01
BC	1·48	1·471	+0·01	HM	1·38	1·430	−0·05
BN	1·41	1·381	+0·03	IJ	1·41	1·379	+0·03
CD	1·39	1·397	−0·01	JK	1·40	1·400	0·00
DE	1·38	1·393	−0·01	KL	1·38	1·377	0·00
EF	1·39	1·382	+0·01	LM	1·41	1·418	−0·01
				MN	1·41	1·432	−0·02

Hall [4] had submitted, after our calculations had been completed,[1] bond lengths which differ from ours to a scarcely significant extent (having been based on a slightly different curve correlating bond order and bond length) but it was ours which were used [2] for comparison with the measured bond lengths.

There is no doubt about the distortion of the crystal molecules, though it is much less than in compounds such as 3 : 4-5 : 6-dibenzophenanthrene [5] which may be said to show internal overcrowding. In 2 : 3-8 : 9-dibenzoperylene there seems to be a measure of " external overcrowding " but it causes an out-of-plane displacement of only 0·067 Å at atoms *L* and *J*, and only 0·036 Å at atoms I and M. We are not concerned here with the origin of this but we are concerned with its possible effect on the validity of bond-length calculations based on a flat molecule.

For each of the tertiary carbon atoms we may compare its displacement from the mean molecular plane with the mean of the displacements of the atoms attached to it. Only

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* Part V, *J.*, 1958, 3893.

† See ref. 2 for lettering of atoms.

[1] Watson, B.Sc. Thesis, University of Glasgow, 1956.

[2] Lipscomb, Robertson, and Rossmann, *J.*, 1959, 2601.

[3] Goodwin and Vand, *J.*, 1955, 1683.

[4] Hall, *Trans. Faraday Soc.*, 1957, **53**, 573.

[5] McIntosh, Robertson, and Vand, *J.*, 1954, 1661.

for atoms C (0·019 Å) and M (0·010 Å) do these differ by amounts which are possibly significant. Even in the first of these cases the difference represents angles of only $\sin^{-1} 0{\cdot}019/1{\cdot}44 \sim 0{\cdot}7°$ for the angular displacement of the bonds *CA'*, *CB*, *CD*, from the plane of *A'*, *B*, and *D*. This in turn means that the normal sp^2 hybridisation of a flat molecule is only slightly modified in the direction of perfect sp^3 hybridisation, in which this angular displacement is 19½°. Hence it is not surprising that, as Lipscomb, Robertson, and Rossmann say, " The non-planarity appears to have little effect on the bond lengths."

Since these workers have not located the hydrogen atoms it is impossible to say anything about the small distortions of bond angles observed at atoms such as *N*, *M*, *F*, *I'*, though it is curious that atom M is an ordinary " *peri* "-carbon with no hydrogen atom attached.

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