bonding orbitals of the metal are utilized at least to some extent in stabilizing the molecule.

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A Note On Self Consistent Bond Lengths for Tetracene and Pentacene

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Approximate self-consistent bond lengths have been calculated for tetracene and pentacene. The agreement with recent experimental results, obtained from X-ray crystallography, is reasonable.

Method and results

Brown & Bassett (1958) have described a very quick method for determining the first-order eigenvector when a perturbation is applied to a system which has a real symmetric Hamiltonian matrix. Subsequently, Coulson & Gølebiewski (1961) have applied Brown & Bassett's result in the development of a simple and approximately self-consistent method for calculating the bond lengths of conjugated systems.

Table 1. *Comparison of calculated bond lengths with experimental results for tetracene and pentacene*

See Fig. 1 for labelling of bonds

	Tetracene (Fig. 1(*a*))			Pentacene (Fig. 1(*b*))		
Bond	Calculated bond length	Experimental result	Deviation	Calculated bond length	Experimental result	Deviation
A	1·413 Å	1·40 Å	+0·013 Å	1·408 Å	1·39 Å	+0·018 Å
B	1·400	1·39	+0·010	1·416	1·40	+0·016
C	1·429	1·42	+0·009	1·399	1·38	+0·019
D	1·375	1·38	−0·005	1·430	1·42	+0·010
E	1·423	1·46	−0·037	1·375	1·35	+0·025
F	1·431	1·42	+0·011	1·424	1·43	−0·006
G	1·434	1·46	−0·026	1·432	1·44	−0·008
H				1·436	1·45	−0·014

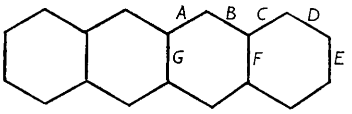
The experimental result is an average of two or four measurements for each bond length; the r.m.s. deviation is of the order of 0·02 Å for the experimental measurements.

The following equations were employed for the relationships between the bond length R, the π bond order p and the resonance integral β

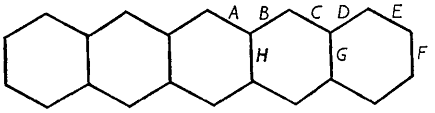
$$R = 1{\cdot}517 - 0{\cdot}18p \quad (R \text{ in Å})$$

$$\beta = \beta_0 \exp\left[-2{\cdot}683R\right].$$

For butadiene, naphthalene and anthracene Coulson & Gølebiewski obtained excellent results; in view of recent experimental measurements (Robertson *et al.*, 1961) it seemed worthwhile to make a Coulson–Gølebiewski calculation for tetracene and pentacene. The calculated and experimental results for tetracene and pentacene are shown in Table 1. The experimental bond lengths, which are quoted, are the results of a small revision which was made on the crystal structures of tetracene and pentacene (Robertson *et al.*, 1961).



(*a*) tetracene



(*b*) pentacene

Fig. 1. (*a*) Tetracene, (*b*) pentacene.

A comment should be added about the validity of the approximate self-consistent method employed in the present calculations. Exact self-consistent calculations exist for the bond lengths of diphenylene (Ali, Asgar & Coulson, 1960). The Coulson & Gølebiewski approximate self-consistent method was applied to diphenylene; the agreement between approximate and exact self-consistent bond lengths is 0·001 Å. Thus, for all practical purposes, the Coulson & Gølebiewski method is self-consistent.

Discussion

The agreement between experimental and calculated bond lengths, although not perfect, is reasonable since at the present stage of refinement the experimental results are reliable to only 0·02 Å. It is exceedingly difficult to obtain good crystals of tetracene and pentacene and the agreement is as good as we can expect at present.

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