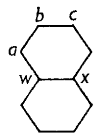
943. *Calculated Bond Lengths in Some Cyclic Compounds. Part VII.* The Series Naphthalene, Perylene, Terrylene, Quaterrylene, and the Lengths of Low-order Bonds.*

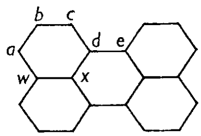
By T. H. Goodwin.

The series of compounds naphthalene (I), perylene (II), terrylene (III), and quaterrylene (IV) has been studied with special reference to the orders and lengths of the *peri*-bonds. The great lengths of these bonds in (IV), as measured by *X*-rays, lead to a reappraisal of the correlation between order and length when the order is particularly low.

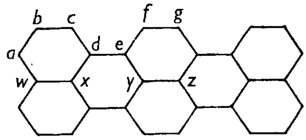
It is generally found that good *X*-ray measurements on cyclic hydrocarbons and careful wave-mechanical calculations of bond order lead to agreement to within 0·02 Å in the bond lengths, the uncertainties in measurements and calculations usually lying within the same limits ±0·02 Å. To convert orders into lengths, use must be made of a correlation curve and although various curves have been proposed they usually differ only slightly for bonds of mobile order $0{\cdot}5 < p < 1{\cdot}0$. In Part I [1] of this series we developed a correlation which, for $p \geqslant 0{\cdot}46$, accepted that obtained by Coulson [2] in 1951 from the generally very accurate measurement of thirty-six bonds in nine hydrocarbons and the corresponding orders calculated by the simplest (Hückel) molecular-orbital approximation. Bonds of lower order are rare but the limits of the curve are of interest and many workers have supposed that the bond of zero mobile order between two carbon atoms each having sp^2-hybridisation



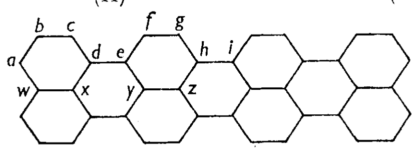
(I)



(II)



(III)



(IV)

(which we shall hereafter refer to simply as the " zero-order bond ") is 1·50 Å long (Coulson,[3] Goodwin and Vand,[1] etc.). Dewar and Schmeising,[4] however, have recently claimed that it is only 1·47 Å long, while others, supposing such a zero-order bond to be unrealisable (*i.e.*, between sp^2-carbon atoms) have worked with a correlation based on ethane or diamond (sp^3-carbon), ethylene (sp^2), and acetylene (sp), sometimes, following an earlier study by Coulson,[5] giving an analytical expression for the curve.

There is, however, a relatively small number of hydrocarbons for which certain bonds are found to be of uncommonly low order, *e.g.*, perylene (II), terrylene (tribenzo[*de, kl, rst*]-pentaphene †) (III), and quaterrylene (benzo[1,2,3-*cd*:4,5,6-*c'd'*]diperylene) (IV). In the last of these, Shrivastava and Speakman [2] find the mean length of the six *peri*-bonds

* Part VI, *J.*, 1959, 2625.

† The letters used to denote ring fusion are not to be confused with the (arbitrary) lettering of atoms adopted in this paper.

[1] Goodwin and Vand, *J.*, 1955, 1683.
[2] Coulson, *Proc. Roy. Soc.*, 1951, *A*, **207**, 95.
[3] Coulson, " Victor Henri Memorial Volume," " Contribution a l'Étude de la Structure Moléculaire," Desoer, Liége, 1948, p. 15.
[4] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166.
[5] Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413.

(*de*, *hj*, etc.) to be 1·53 ± 0·01 Å, and so it is clear that theory must allow bonds longer than 1·47 or 1·50. *de* and *hj* are bonds which must be represented as single if only unexcited (Kekulé) structures are included in the valency bond canonical set, *i.e.*, they must be of zero order.

In molecular-orbital theory p may be low, but cannot be zero since the p_z-orbitals on neighbouring atoms must always overlap even if only feebly. The lowest realisable order and greatest realisable length then become interesting questions.

The calculations forming the basis of this paper were started before the X-ray work on quaterrylene (IV) was complete. Perylene (II) had already been studied both by X-rays [7] and by wave-mechanics,[8,9] but as the computations on quaterrylene were carried through three iterative cycles it seemed desirable to treat perylene similarly and then to extend the

TABLE 1. *Ground state energies for naphthalene, perylene, terrylene, and quaterrylene in terms of* $x = (E - \alpha)/\beta$. *Unoccupied levels of orbitals of symmetries* A_1 *and* A_2 *have energies given by* $-1 \times$ *energies of corresponding occupied levels of* B_1 *and* B_2 *and* vice versa. (*The molecular symmetry of the* π-*orbital system is* C_{2v} *with* C_2 *perpendicular to the molecular plane and the x-axis containing the bond wx.*)

Naphthalene (I) Iteration			Perylene (II) Iteration			Terrylene (III) Iteration			Quaterrylene (IV) Iteration		
1	2	3	1	2	3	1	2	3	1	2	3
Symmetry A_1											
2·3028	2·1341	2·1206	2·5883	2·2878	2·2859	2·6614	2·3451	2·3393	2·6902	2·3530	2·3510
1·0000	0·8942	0·8823	1·5936	1·4412	1·4286	2·1299	1·9771	1·9741	2·3670	2·1160	2·1113
			1·0000	0·9190	0·9069	1·2703	1·1840	1·1873	1·7837	1·5559	1·5447
						1·0000	0·9467	0·9373	1·1004	1·0360	1·0420
						1·0000	0·9306	0·9130	1·0000	0·9551	0·9450
									1·0000	0·9264	0·9119
Symmetry A_2											
0·6180	0·6874	0·7256	1·5321	1·5441	1·5444	1·7709	1·6836	1·6850	1·8649	1·7468	1·7524
			0·3473	0·4129	0·4657	1·1361	1·0266	1·0333	1·4780	1·4889	1·4966
						0·2411	0·2999	0·3492	0·8914	0·8283	0·8457
									0·1846	0·2300	0·2799
Symmetry B_1											
1·3028	1·2543	1·2389	2·1819	2·0181	2·0196	2·4550	2·1972	2·1897	2·5667	2·2644	2·2588
			1·0000	0·9648	0·9811	1·7171	1·5251	1·5070	2·1010	1·9352	1·9418
			1·0000	0·9181	0·9068	1·0000	0·9310	0·9130	1·4377	1·3052	1·3030
						0·8894	0·8603	0·8812	1·0000	0·9580	0·9458
									1·0000	0·9272	0·9120
									0·8359	0·7924	0·8194
Symmetry B_2											
1·6180	1·6224	1·6106	1·8794	1·7674	1·7731	1·9419	1·8102	1·8188	1·9659	1·8254	1·8334
			1·0000	0·9366	0·9510	1·4970	1·5102	1·5146	1·7004	1·6209	1·6253
						0·7092	0·6897	0·7161	1·2053	1·0649	1·0722
									0·5473	0·5429	0·5686

TABLE 2. *Bond orders and lengths* (L *in* Å) *for naphthalene* (I).

	First iteration			Third iteration						
rs	H_{rs}	p_{rs}	L_{rs}	H_{rs}	p_{rs}	L_{rs}	L_M	Δ	L_M'	Δ'
ab	1	0·725	1·372	1·081	0·784	1·363	1·361	−2	1·358	−5
aw	1	0·555	1·423	0·854	0·509	1·439	1·425	−14	1·420	−19
bc	1	0·603	1·405	0·885	0·526	1·432	1·421	−11	1·395	−37
wx	1	0·518	1·435	0·879	0·589	1·409	1·410	1	1·395	−14

study to terrylene which has never been thoroughly examined by X-rays, and to naphthalene [10] (I), since these compounds (II), (III), and (IV) can be regarded as polynaphthalenes.

[6] Shrivastava and Speakman, *Proc. Roy. Soc.*, 1960, *A*, **257**, 477.
[7] Donaldson, Robertson, and White, *Proc. Roy. Soc.*, 1953, *A*, **220**, 311.
[8] Syrkin and Dyatkina, *Acta Physicochim., U.R.S.S.*, 1946, **21**, 921; Baldock, Berthier, and Pullman. *Compt. rend.*, 1949, **228**, 931.
[9] Paunez and Wilheim, *Acta Chim. Acad. Sci. Hung.*, 1957, **11**, 63.
[10] Hückel, *Z. Physik*, 1932, **76**, 628; Lennard-Jones and Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811.

At all stages the overlap integrals were neglected and, for the first iteration on each compound, the usual Hückel assumptions were made.

The π-electron energies, the L.C.A.O.M.O. coefficients, and the bond orders, as well as,

TABLE 3. *Bond orders and lengths (L in Å) for perylene* (II).

rs	Fist iteration			Third iteration				
	H_{rs}	p_{rs}	L_{rs}	H_{rs}	p_{rs}	L_{rs}	L_M	Δ
ab	1	0·707	1·376	1·066	0·762	1·366	1·381	15
aw	1	0·552	1·422	0·857	0·516	1·436	1·376	−60
bc	1	0·629	1·398	0·931	0·563	1·419	1·453	34
cd	1	0·644	1·393	1·033	0·725	1·373	1·383	10
de	1	0·414	1·473	0·714	0·310	1·485 *	1·499	14
dx	1	0·529	1·430	0·841	0·504	1·442	1·448	6
wx	1	0·526	1·432	0·876	0·581	1·413	1·445	32

* L_N = 1·56 Å.

by way of check, the charge distributions (which must be uniform in these alternant hydrocarbons) were all deduced by methods which differ from those described in the earlier papers of this series in that the problem was treated as one in matrix algebra and solved on the English Electric DEUCE in the Computing Department of this University. The energies $x = (E - \alpha)/\beta$ were determined as latent roots of the matrix of secular equations $\boldsymbol{A} - \boldsymbol{I}\boldsymbol{x} = 0$, the Givens method for symmetrical matrices being used. The DEUCE programmes LL21 and NPL150, for matrices up to 30 $\times$ 30 and 60 $\times$ 60 respectively, also give as latent vectors the molecular-orbital coefficients corresponding to the various roots obtained. After these had been normalised to $\sum_i C^2_{ri} = 1$, they were used as data in a series of programmes operated under the control of the General Interpretative Programme ZCO1/3 to evaluate the partial and total π-bond orders p and charge densities q. From the orders p, the bond lengths were first obtained by means of the correlation curve described in Part I.

TABLE 4. *Bond orders and lengths (L in Å) for terrylene* (III).

rs	First iteration			Third iteration		
	H_{rs}	p_{rs}	L_{rs}	H_{rs}	p_{rs}	L_{rs}
ab	1	0·704	1·377	1·061	0·757	1·366
aw	1	0·552	1·423	0·857	0·519	1·435
bc	1	0·633	1·394	0·940	0·570	1·416
cd	1	0·635	1·394	1·026	0·715	1·375
de	1	0·426	1·471	0·718	0·323	1·484 *
dx	1	0·529	1·432	0·852	0·507	1·439
ef	1	0·622	1·398	1·006	0·692	1·380
ey	1	0·526	1·433	0·847	0·513	1·437
fg	1	0·664	1·387	0·982	0·611	1·403
wx	1	0·526	1·433	0·878	0·577	1·414
yz	1	0·534	1·430	0·878	0·570	1·416

* L_N = 1·550 Å.

TABLE 5. *Bond orders and lengths (L in Å) for quaterrylene* (IV).

rs	First iteration			Third iteration				
	H_{rs}	p_{rs}	L_{rs}	H_{rs}	p_{rs}	L_{rs}	L_M	Δ
ab	1	0·702	1·378	1·057	0·753	1·367	1·378	11
aw	1	0·552	1·423	0·860	0·521	1·434	1·400	−34
bc	1	0·634	1·394	0·944	0·574	1·415	1·419	4
cd	1	0·632	1·396	1·020	0·710	1·376	1·401	25
de	1	0·429	1·469	0·720	0·329	1·484 *	1·534	50
dx	1	0·529	1·433	0·844	0·508	1·440	1·413	−27
ef	1	0·616	1·402	0·995	0·683	1·382	1·365	−17
ey	1	0·526	1·434	0·844	0·515	1·437	1·403	−34
fg	1	0·671	1·385	0·995	0·624	1·399	1·398	−1
gh	1	0·612	1·403	0·990	0·678	1·383	1·391	8
hj	1	0·441	1·466	0·725	0·345	1·482 †	1·524	42
hz	1	0·526	1·434	0·844	0·514	1·437	1·406	−31
wx	1	0·526	1·434	0·870	0·574	1·415	1·432	17
yz	1	0·535	1·430	0·880	0·568	1·417	1·430	13

* L_N = 1·545 Å. † L_N = 1·535 Å.

It will be obvious that the values of exchange (and overlap) integrals must depend on internuclear distance and hence that equating all H_{rs} between orbitals on neighbouring atoms is unjustified, especially in a series of compounds containing formal single bonds. (There are eighty-one canonical Kekulé forms of quaterrylene and, in all these, all six *peri*-bonds must be single.) Mulliken, Rieke, and Brown,[11] following Lennard-Jones,[12] have given a table showing the variation of H_{rs} with bond length. By using this table, values of L_{rs} obtained in the first iteration could be applied to give values of H_{rs} for a second. The reduction of H_{rs} for a low-order bond will, of course, reduce the order still further and hence call for yet further reduction. It is not claimed that this is a simple self-consistent field technique, but we believe that the results of the second and the third iteration are more reliable and useful than the simple Hückel approximation. The real difficulty is knowing where to stop. We have stopped at the third iteration because the total π-electron energy in the first iteration of quaterrylene is at $40\alpha + 57{\cdot}44\beta$ but falls (numerically) to $40\alpha + 53{\cdot}94\beta$ at the second and then only to $40\alpha + 53{\cdot}12\beta$ at the third. (These and corresponding figures for a number of other compounds form the basis of the next paper in this series, now in progress.) This shows that most of the " slack " is taken up in the second iteration and very little more in the third. This procedure was applied twice (three iterations) and the results are given in Tables 1—5. In these, all H_{rs} are expressed in terms of the value, β, for a length of 1·39 Å, and only Table 1 (energies) contains results for all three iterations. From Tables 2—5 information relating to the second iteration has been omitted to save space, but Tables 2, 3, and 5 also include the measured bond lengths L_M for compounds (I), (II), and (IV), and $\Delta = 1000(L_M - L_{rs})$. For naphthalene the " measured " lengths are those derived by Cruickshank [13] from the observations of Abrahams, Robertson, and White.[14] For perylene the figures are taken from Donaldson's work [15] and are for average bond lengths between resolved atoms, except for the bond *wx*, in neither version of which is resolution of both atoms achieved. This bond length *wx* is taken from the published paper of Donaldson, Robertson, and White and is based on estimated positions of unresolved atoms; there is no reason to suppose it to be far wrong, but these workers only claim to have determined the interatomic distances to within 0·04 Å for the reasons given and because even for the resolved atoms the centres were not always well defined. The values of L_M for quaterrylene (IV) are again averages between resolved atoms (32 out of the 40) and are from the paper by Shrivastava and Speakman.[6]

Discussion

Naphthalene.—The agreement between L_M and L_{rs} for the third iteration is remarkably good and seems to call only for the comment that Cruickshank's figures lead to much better agreement with this third round of calculations than do the lengths L_M' given by Abrahams, Robertson, and White.

Perylene.—For four of the seven chemically and symmetrically distinguishable bonds agreement between L_M and L_{rs} is very satisfactory Of the remainder, *wx* is the bond between atoms which are not satisfactorily resolved and so a discrepancy of only 0·03 Å cannot be considered significant. The bond *bc* is also in agreement within the authors' estimated experimental error of 0·04 Å. The measured value of *aw* is remarkably short when compared (Table 7) with the lengths of corresponding bonds in the other compounds considered here and one suspects that it is in error.

Quaterrylene.—Shrivastava and Speakman estimate the standard deviation of their bond lengths as 0·02 Å for bonds in the direction of the greatest molecular length, and

[11] Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 48.
[12] Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280.
[13] Cruickshank, *Acta Cryst.*, 1958, **10**, 507.
[14] Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 238.
[15] Donaldson, Ph.D. Thesis, University of Glasgow, 1952, p. 67.

0·03 Å for other bonds. The values of Δ in Table 5 are, therefore, generally very satisfactory, for though the bonds *de* and *hj* differ from the calculated values by amounts approaching twice the standard deviation these are the bonds which are formally single in the Kekulé formulæ. We discuss them below. The bonds *aw, dx, ey, hz* are 0·034, 0·027, 0·034, 0·031 Å shorter than calculated and this systemmatic deviation seems significant; it is almost certainly connected with the anomaly of the *peri*-bonds.

General.—Quaterrylene can also be regarded as a bisperylene or as a tetrakisnaphthalene. In Table 6 the third iteration results and measured lengths L_M of Table 5 have been averaged as for bisperylene and tetrakisnaphthalene; they may be compared with the figures for compounds (I) and (II) in Tables 2 and 3. These results are not quite the same as would be obtained by supposing that no delocalisation can occur across the bonds uniting the naphthalene or perylene fragments; such a situation is, however, implicit in the comparison of the four compounds in Table 7, where, so that the experimental data

TABLE 6. *Calculated and measured bond lengths (in Å) in quaterrylene (IV) averaged as for " bisperylene " and " tetrakisnaphthalene."*

	Quaterrylene			Bisperylene			Tetrakisnaphthalene		
rs	L_{rs}	L_M	Δ	L_{rs}	L_M	Δ	L_{rs}	L_M	Δ
ab	1·367	1·378	11	1·375	1·385	10	1·377	1·387	10
aw	1·434	1·400	−34	1·436	1·403	−33	1·437	1·406	−31
bc	1·415	1·419	4	1·407	1·410	3	1·407	1·410	3
cd	1·376	1·401	25	1·378	1·388	10			
de	1·545 *	1·534	−11	1·545 *	1·534	−11	1·542 *	1·531	−11
dx	1·440	1·413	−27	1·439	1·408	−25			
ef	1·382	1·365	−17						
ey	1·437	1·403	−34						
fg	1·399	1·398	−1						
gh	1·383	1·391	8						
hj	1·535 *	1·524	−11	1·535 *	1·524	−11			
hg	1·437	1·406	−31						
wx	1·415	1·432	17	1·423	1·431	8	1·423	1·431	8
yz	1·417	1·430	13						

* L_N.

TABLE 7. *Comparison of calculated and measured bond lengths (in Å).*

	Naphthalene (I)			Perylene (II)			Terrylene (III)	Quaterrylene (IV)		
rs	L_{rs}	L_M	Δ	L_{rs}	L_M	Δ	L_{rs}	L_{rs}	L_M	Δ
ab	1·363	1·358	−5	1·366	1·38	14	1·366	1·367	1·378	11
aw	1·439	1·420	−19	1·436	1·375	−61	1·435	1·434	1·400	−34
bc	1·432	1·395	−37	1·419	1·45	31	1·416	1·415	1·419	4
cd				1·373	1·38	7	1·375	1·376	1·401	25
de				1·560 *	1·50	−60	1·550 *	1·545 *	1·534	−11
dx							1·439	1·440	1·413	−27
cf							1·380	1·382	1·365	−17
ey							1·437	1·437	1·405	−34
fg							1·403	1·399	1·398	−1
gh								1·383	1·391	8
hj								1·535 *	1·524	−11
hz								1·437	1·406	−31
wx	1·409	1·395	−14	1·442	1·45	8	1·414	1·415	1·432	17
yz				1·413	1·445	32	1·416	1·417	1·430	13

* L_N.

for naphthalene (I) may be more nearly comparable with those for compounds (II) and (IV), they are those of Abrahams, Robertson, and White. The near-identity of the results for corresponding bonds in these four compounds as shown in Table 7 points itself to the low order of the *peri*-bond.

The most interesting feature is, of course, the discrepancy in *peri*-bonds, and the definite establishment of their great length in quaterrylene calls for a re-appraisal of the lengths of low-order bonds between trigonally hybridised carbon atoms. The simplest course is to adopt the extrapolation of Coulson's 1951 correlation curve. This is necessarily somewhat subjective, but if the locus of (p,L) given in Part I as (1·000, 1·340), (0·900, 1·351), (0·800, 1·361), (0·700, 1·378), (0·600, 1·406), (0·500, 1·443) is extended reasonably it passes through (0·400, 1·499) and (0·325, 1·550) and gives for the lengths of the bonds *de* and *hj* of quaterrylene (IV), which have p equal to 0·329 and 0·345, $L_{de} = 1{\cdot}545$ and $L_{hj} = 1{\cdot}535$ quoted as L_N in the footnotes to Tables 3, 4, 5. These are each only 0·011 Å greater than observed and, although Shrivastava and Speakman do not regard the difference between these bond lengths 1·534 and 1·524 as significant, we feel that it is since their difference is exactly in the sense of our conclusions. At the same time it would be unwise to consider that this agreement establishes our extrapolation unequivocally. In the first place, in perylene, $p_{de} = 0{\cdot}310$ and our extended curve would give $L_{de} = 1{\cdot}56$. This is 0·06 Å greater than the measured value, but the experimental error of 0·04 Å makes this less significant. Secondly, the adoption of this " new " view from the outset would have modified the subsequent values of β_{de} and β_{hj} and therefore the subsequent values of p for these and (as a second-order effect) for other bonds. As these calculations were started before the final measurements by Shrivastava and Speakman were available it was not thought necessary to repeat them. Thirdly, Coulson's 1951 curve [2] used bond orders calculated by the Hückel approximations. The bond orders we have just been discussing are third-iteration results. This possible source of inconsistency is being looked into but a complete revision of Coulson's bond orders is still under way. The first iteration (Hückel) orders for bonds *de* and *hj* of quaterrylene (IV) are 0·429 and 0·441, which, by the new extrapolation lead to $L_{de} = 1{\cdot}481$ and $L_{hj} = 1{\cdot}473$; these are both 0·05 Å shorter than observed and so cannot be correct. As we have pointed out, the extrapolated Coulson curve differs only from the curve of Part I for orders less than $p = 0{\cdot}46$ and so no other bonds in this series of compounds are affected by this revision.

Two other points need comment. The first is that we do not, and cannot, indicate a maximum length for a bond between sp^2-hybridised carbon atoms, much less suggest a length for the zero-order bond. Overlap may be small, but it cannot be eliminated. At some stage, however, it will become too feeble to dominate distorting agencies in crystal packing and molecular configuration as in the biphenyls. Perhaps biphenyl itself represents the limit for, though there is evidence [16] (the bimolecular unit cell of space group $P2_1/a$) that the crystal has a planar molecule, Bastiansen's electron-diffraction study [17] of the vapour points to a twisting of the benzene rings about the central bond. Unfortunately neither method has yet given unequivocal bond lengths and angles. In the perylene series the long bonds occur in pairs and so maintain the planarity of the molecules.

Finally attention should be called to the paper of Pauncz and Wilheim [9] on the compounds (II), (III), and (IV) in which, by the Hückel approximation (the present first iteration) but by a different correlation curve, they derive bond lengths. These differ by *ca.* ±0·01 from the first iteration results of Tables 3, 4, 5, except for the *peri*-bonds which are invariably at least 0·02 Å shorter than in our first iterations (old correlation), about 0·09 Å shorter than our third iterations (new correlation), and 0·06—0·09 Å shorter than measured.

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[16] Dahr, *Indian J. Phys.*, 1932, **7**, 43.
[17] Bastiansen, *Acta Chim. Scand.*, 1949, **3**, 408.