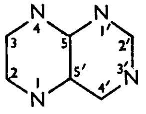
693. *Calculated Bond Lengths in Some Cyclic Compounds. Part IV.** *Pteridine and Melamine, and a Correlation Curve for* C–N *Bonds.*

By T. H. GOODWIN and A. L. PORTE.

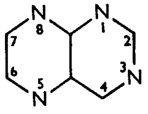
Energy levels, π-electron distributions, and mobile bond orders have been deduced for pteridine and melamine. The results for melamine have been used with those for other compounds, the crystal structures of which have been accurately determined, to establish a curve correlating π-bond order and bond length for C–N bonds in conjugated systems of six-membered rings. This has then been applied to the bond orders obtained for pteridine to permit comparison of the interatomic distances thus expected with those measured by Hamor and Robertson.[1]

HAMOR and ROBERTSON [1] have recently investigated the interatomic distances in pteridine, their values having a standard deviation of about 0·03 Å. The work reported in this paper began as an attempt to predict the bond lengths in this substance by the method of molecular orbitals, but prediction became more difficult as the uncertainties in the curve correlating bond order and bond length were realised. We have therefore developed a new correlation curve and from it have derived bond lengths for comparison with those measured.

Calculations on Pteridine.—In pteridine (I), the atoms of which are here numbered as in the foregoing paper, each of the six carbon and four nitrogen atoms contributes one p_z electron to the π-molecular-orbital system, the secular equations for which were set up in the usual way, the Coulomb integral of carbon being written α and that of nitrogen $\alpha + \frac{1}{2}\beta$. The resonance integrals for C–C and C–N were, as usual, taken to be equal, *viz.*, β, and the overlap integrals were neglected. It was assumed that the molecule is planar although, as the discussion given by Hamor and Robertson [1] suggests, it seems just possible that this is not quite correct. We had completed the first section of the calculations on pteridine before the *X*-ray results were available, though not before the possibility had been mooted by Albert.[2] We believed, however, that the molecule would be shown by the *X*-ray work to be flat.



(I) Numbering used in this paper.



(I) Usual chemical numbering.

TABLE 1. *π-Electron molecular-orbital energy levels (E_i) in pteridine in order of increasing energy.*

i	E_i	i	E_i	i	E_i	i	E_i
1	$\alpha + 2·48377\beta$	4	$\alpha + 1·10302\beta$	7	$\alpha - 0·90997\beta$	9	$\alpha - 1·45460\beta$
2	$\alpha + 1·84220\beta$	5	$\alpha + 0·91874\beta$	8	$\alpha - 1·07655\beta$	10	$\alpha - 2·15775\beta$
3	$\alpha + 1·58342\beta$	6	$\alpha - 0·33221\beta$				

TABLE 2. *π-Electron distribution (q_r) in the ground state of pteridine.*

r	1	2	3	4	5	1'	2'	3'	4'	5'
q_r	1·126	0·905	0·872	1·166	0·891	1·224	0·829	1·194	0·831	0·962

The determination of the energy levels E_i was carried out as described in Part I [3] of this series and Table 1 gives their values. By using each of these energy levels in turn the

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* Part III, *J.*, 1955, 4451.

[1] Hamor and Robertson, preceding paper.

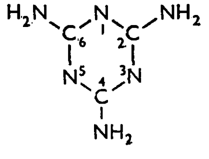
[2] Albert, *Quart. Rev.*, 1952, **6**, 197.

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

π-electron distribution q_r and the π-bond orders p_{rs} were calculated. They are given in Tables 2, 5, and 6.

To convert the bond orders into bond lengths a correlation curve is necessary. For the C–C bonds this has already been established in Part I [3] but for the C–N bonds the position is much less satisfactory. In Parts I and II [4] the linear correlation curve given by Cox and Jeffrey [5] was used. As the flavanthrone considered in those papers contains only two C–N bonds out of the twenty bonds in the asymmetric unit of the molecule it seemed unnecessary to seek a more accurate correlation. In pteridine eight of the eleven bonds are between carbon and nitrogen atoms. Further, Davies [6] has pointed out that the melamine bond orders used to establish Cox and Jeffrey's curve are at fault. We have therefore recalculated them.

Calculations on Melamine.—In melamine, 2 : 4 : 6-triamino-*s*-triazine (II), each of the ring carbon and nitrogen atoms contributes one p_z electron to the molecular-orbital system but each of the amino-nitrogen atoms contributes two. Thus nine molecular orbitals accommodate twelve electrons.



(II)

The molecule has D_{3h} symmetry and examination of the character table shows that the π-electron energy levels must be $3E'' + 3A_2''$, the E'' being doubly degenerate. In evaluating them the Coulomb integral for the ring nitrogen atoms was again set at $\alpha + \frac{1}{2}\beta$ but that for the amino-nitrogen atoms at $\alpha + \beta$. Because in the rest of this paper inductive effects of the nitrogen atoms on the Coulomb integrals of carbon atoms have been neglected we did not at first include them for melamine, but at the suggestion of a Referee we have done so. The results are included under the primed symbols E'_i, q'_r, p'_{rs}. Table 3 gives the energy levels for melamine, the first six being (doubly) occupied in the ground state. The π-electron distribution is then found to be: carbon $q = 0{\cdot}800$, $q' = 0{\cdot}827$; ring N $q = 1{\cdot}430$, $q' = 1{\cdot}417$; amino-N $q = 1{\cdot}770$, $q' = 1{\cdot}754$. The bond orders are ring $p = 0{\cdot}563$, $p' = 0{\cdot}571$; side-chain C–N $p = 0{\cdot}520$, $p' = 0{\cdot}521$. The inductive effects of the nitrogen atoms thus make only a small change in the charge distribution and practically no change in the bond orders.

TABLE 3. *π-Electron molecular-orbital energy levels (E_i) for melamine in order of increasing energy.*

i	Symmetry	$E_i - \alpha$	$E_i' - \alpha$	i	Symmetry	$E_i - \alpha$	$E_i' - \alpha$
1	A_2''	$2{\cdot}5697\beta$	$2{\cdot}6800\beta$	5, 6	E''	$0{\cdot}7274\beta$	$0{\cdot}7349\beta$
2, 3	E''	$1{\cdot}8733\beta$	$1{\cdot}9666\beta$	7, 8	E''	$-1{\cdot}1007\beta$	$-0{\cdot}9514\beta$
4	A''	$0{\cdot}8924\beta$	$0{\cdot}8946\beta$	9	A''	$-1{\cdot}9622\beta$	$-1{\cdot}8247\beta$

The C–N *Correlation Curve.*—Our bond orders for melamine are quite different from those given by Cox and Jeffrey who regarded the nine C–N bonds as equivalent and deduced a value of 0·658 for p. Their conclusion about the equivalence of the bonds was based on the *X*-ray results of Hughes [7] who, estimating that his measurements were not in error by more than 0·05 Å, gave lengths for the ring bonds which averaged 1·343 Å, and for the extracyclic C–N linkages which averaged 1·353 Å.

In comparing these with the calculated bond orders it is desirable to make a small correction for the effect on the bond lengths of the net charges on the atoms. When reasonable values of the dielectric constant and the force constants in the bonds are taken, a contraction of 0·007 Å in the ring bonds and a stretching of 0·004 Å in the side linkages are deduced; thus the measured lengths must be increased and decreased respectively by these amounts in order to obtain the lengths appropriate to bonds between neutral atoms. If this is done the lengths of the bonds become 1·350 (ring) and 1·349 (extracyclic C–N) though to apply corrections of 0·007 Å and 0·004 Å when the experimental uncertainty is reported as 0·05 Å seems rather naïve. We are forced, therefore, to ignore these

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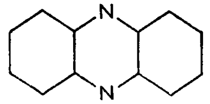
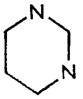
[4] Goodwin, *J.*, 1955, 1689.
[5] Cox and Jeffrey, *Proc. Roy. Soc.*, 1951, *A*, **207**, 110.
[6] Davies, *Trans. Faraday Soc.*, 1955, **51**, 449.
[7] Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

corrections, recognising that the points for melamine are still not as reliable as we should like.

There is, however, a number of other compounds containing accurately measured C–N linkages. These, and the results for them, are listed in Table 4. Only for *s*-triazine is the charge correction to the bond length as great as 0·003 Å; it has therefore been neglected in all cases.

(III)





(IV)

The extremities of the single bond–double bond range are not very satisfactory. Cox and Jeffrey give, for the pure single bond a length of 1·475 Å, but in all the compounds they quote the hybridisation as sp^3 whereas sp^2 hybridisation is involved in the condensed-ring compounds considered here. Since Coulson [8] has shown that the length of 1·54 Å for the tetrahedral C–C becomes 1·50 Å in the trigonal hybrid we suggest that a similar shortening is to be expected in C–N although the data for its calculation are not available. We have therefore taken 1·435 Å for the sp^2 C–N bond of order zero.

TABLE 4. *Mobile orders and lengths of some* C–N *bonds.*

Compound	α_N	p_{C-N}	Bond lengths	Method of measurement
Melamine (II)	See text	0·563 *	1·343 ± 0·05	*X*-Ray [7]
		0·520 *	1·353 ± 0·05	
s-Triazine	$\alpha + 0{\cdot}5\beta$	0·654 * [6]	1·319 ± 0·005	*X*-Ray [a]
α-Phenazine (III)	$\alpha + 0{\cdot}6\beta$	0·603 †	1·345 ± 0·009	*X*-Ray [b, c]
Pyrimidine (IV)	$\alpha + 0{\cdot}6\beta$	0·656 [14]	1·33	*X*-Ray ‡
Pyridine	$\alpha + 0{\cdot}5\beta$	0·654	1·340	Micro-wave [d]

* This paper or unpublished work of present authors.
† Personal communication by Pullman quoted in ref. *c*.
‡ Predicted by Clews and Cochran (*Acta Cryst.*, 1948, **1**, 4) on the basis of their and other data (Pitt, *ibid.*, p. 168; cf. Clews and Cochran, *ibid.*, 1949, **2**, 46).
[a] Wheatley, *Acta Cryst.*, 1955, **8**, 224. [b] Herbstein and Schmidt, *ibid.*, p. 399. [c] *Idem*, *ibid.*, p. 406. [d] Bak, Hansen, and Rastrup-Andersen, *Acta Chem. Scand.*, 1955, **9**, 1355.

For the pure bond of π-order 1, Cox and Jeffrey select 1·28, and the covalent radii values of Stevenson and Schomaker,[9] with the electro-negativity correction according to Gordy,[10] give 1·27 Å. We have adopted another method to determine this value. Of the six intermediate points listed above, five are fairly self-consistent but that for pyridine stands apart. Any reasonable order–length curve among the rest must pass through or very near (0·600, 1·336). We have therefore taken this point as a datum for developing our order–length curve. In the C–C correlation curve established in Part I (Fig. 1, *J.*, 1955, 1687) the ordinates corresponding to orders 0 and 0·6 are 1·50 and 1·406 Å. We have therefore displaced and proportionally compressed the C–C curve so that it passes through (0, 1·435) and (0·600, 1·336). The curve shown results and passes through the points (0·1, 1·431), (0·2, 1·425), (0·3, 1·418), (0·4, 1·407), (0·5, 1·375), (0·6, 1·336), (0·7, 1·312), (0·8, 1·291), (0·9, 1·277), and (1·0, 1·267). The last of these gives the length of the pure double bond and agrees closely with the values deduced from the results of Stevenson and Schomaker and of Gordy. The justification for this procedure is first that since the range of C–N bond orders likely to be met is from 0·5 to 0·7 it is this part of the curve which is the most important. Over this range, and within the limits of accuracy of the calculations and measurements the curve drawn is a perfectly reasonable one. Secondly, the C–C curve of Part I has given quite reliable information in all cases to which it has been applied

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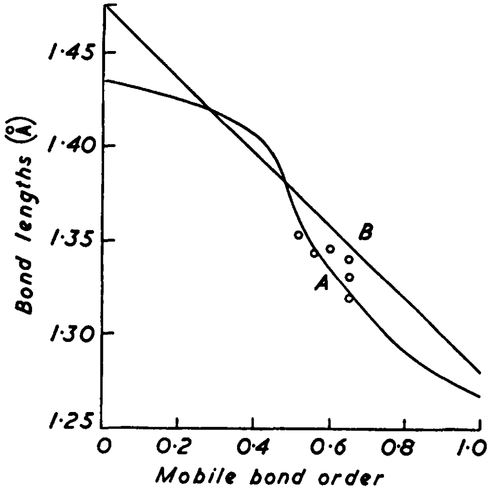
[8] Coulson, Victor Henri Memorial Volume, " Contribution à l'étude de la structure moléculaire," Desoer, Liège, 1948, p. 15.
[9] Stevenson and Schomaker, *J. Amer. Chem. Soc.*, 1941, **63**, 37.
[10] Gordy, *J. Chem. Phys.*, 1947, **15**, 81.

and it is reasonable to suppose that a curve of similar shape will be required for C–N bonds. The difference between our curve and that of Cox and Jeffrey over the technically important range is due chiefly to the more accurately calculated bond orders which we have used.

Two further points remain to be noted. The first is that, bearing in mind the estimated experimental errors in the interatomic distances and the uncertainty as to their significance in some cases, it is difficult to decide on the limits of uncertainty to be attached to lengths read off from our curve, but we believe it to be at most ±0·02 Å, and perhaps less. The second is that, although Coulson[8] points out that the hybridisation ratio and therefore the atomic radius depends on the angle between the bonds, our calculations (which will be described elsewhere) show that in the compounds which we have been discussing here the correction necessary is only +0·005 Å (in the atomic *radius*) if the valency angle is 114°, and –0·002 Å if it is 124°. Since the angles at the ends of any C–N bond tend to be one smaller and one larger than 120° the corrections tend to offset each other (although they are not proportional to the angle), giving total corrections of only about 0·002 Å (usually positive). These are clearly not significant. Although we have usually quoted derived bond lengths to three places of decimals we do not believe that they can be relied on to the third figure; they are given in this form to facilitate their use in later work.



Order–length curve for C–N *bonds.*
A, This paper. *B*, Cox and Jeffrey.[5]

TABLE 5. *π-Bond orders with derived and observed bond lengths for* C–C *bonds in pteridine.*

		Bond length		
r–s	p_{rs}	der.	obs.	Δ
2–3	0·590	1·410	1·39	–0·02
5–5′	0·519	1·435	1·35	–0·09
4′–5′	0·549	1·425	1·42	–0·01

TABLE 6. *π-Bond orders* (p_{rs}) *with derived and observed bond lengths for* C–N *bonds in pteridine.*

		Bond length					Bond length		
–s	p_{rs}	der.	obs.	Δ	*r–s*	p_{rs}	der.	obs.	Δ
–2	0·722	1·307	1·36	0·05	5–1′	0·558	1·349	1·40	0·05
1–5′	0·552	1·351	1·39	0·04	1′–2′	0·709	1·310	1·34	0·03
3–4	0·715	1·309	1·32	0·01	2′–3′	0·599	1·337	1·40	0·06
4–5	0·551	1·352	1·41	0·06	3′–4′	0·706	1·311	1·28	–0·03

Bond Lengths in Pteridine.—Tables 5 and 6 include the calculated and the measured interatomic distances in pteridine; in both tables Δ signifies measured length *minus* derived length.

Considering the information in Table 5 first, the agreement for bonds 2–3 and 4′–5′ is excellent, but that for 5–5′ is very poor. This C–C bond has a measured length which is almost that of a pure double link, a value which is, according to molecular-orbital theory, impossible for this type of system. In addition the greater electronegativity of the nitrogen atoms must cause them to draw electrons towards themselves and away from the C–C bonds which should, therefore, all be longer than in naphthalene. This is, of course, reflected in our calculations and in the measurements on bonds 2–3 and 4′–5′. Hamor and Robertson agree that this value of 1·35 Å for the central linkage is too short but point out that a similar, though smaller discrepancy is found in naphthalene (obs.[11] 1·395 Å; calc. 1·424 Å, as quoted by Coulson, Robertson, and Daudel;[12] 1·435 Å from the curve of Part I). The corresponding bridge bonds in anthracene, on the other hand,[13] measure 1·440, within experimental error of the calculated value of 1·430 Å (1·450 from the curve of Part I).

For the results in Table 6, $|\Delta|_{\text{mean}} = 0{\cdot}04$. The derived lengths are almost always greater than the observed, but as Hamor and Robertson point out, their standard deviation of bond length is 0·03 Å, so that the mean discrepancy is within the limits of experimental error. It is of interest, however, that, if the atoms 5 and 5′ are equally displaced along the line joining them so that they become separated by the distance 1·435 Å indicated by our calculations, then the discrepancies in the bonds C_5–N_4, C_5–$N_{1'}$, $C_{5'}$–N_1, $C_{5'}$–$C_{4'}$ are greatly reduced, to 0·04, 0·02, 0·01, and —0·03 Å, respectively.

Again, much the shortest bond measured is 3′–4′ = 1·28 Å, and the fact that nucleophilic substitution takes place at atom 4′ and that this bond breaks on treatment with acid may well be due to the density and distribution of electrons here. These points support the shortness of this linkage [our calculation of the charge distribution throughout the molecule (Table 2) makes $C_{2'}$ and $C_{4'}$ equally deficient in electrons though Chalvet and Sandorfy,[14] by algebraic superposition of results for compounds with a single nitrogen atom in different positions, find $C_{4'}$ the more deficient] but 1·28 is almost, if not quite, the limit for a pure double bond between carbon and nitrogen, again impossible in this type of compound. If this linkage were lengthened to, say, our calculated value by a procedure similar to that indicated for C_5–$C_{5'}$ bonds, then the bonds 4′–5′ and 2′–3′ would again be shortened and agreement with our calculations improved. With two bonds in the structure apparently so very much shorter than expected we postpone further discussion.

The authors gratefully acknowledge many useful discussions with Professor J. M. Robertson, F.R.S., and Mr. T. A. Hamor, B.Sc., during this work.

CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW. [*Received, April 3rd,* 1956.]

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[11] Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 233, 238.
[12] Coulson, Robertson, and Daudel, *Proc. Roy. Soc.*, 1951, *A*, **207**, 306.
[13] Mathieson, Robertson, and Sinclair, *Acta Cryst.*, 1950, **3**, 245, 251.
[14] Chalvet and Sandorfy, *Compt. rend.*, 1949, **228**, 556.