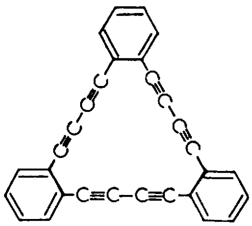
791. *Calculated Bond Lengths in Some Cyclic Compounds. Part V.* 1 : 2-7 : 8-13 : 14-Tribenzo*cyclo*octadeca-1 : 7 : 13-triene-3 : 5 : 9 : 11 : 15 : 17-hexayne and Diphenyldiacetylene.*

By T. H. Goodwin.

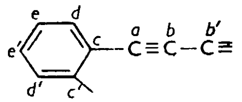
Energy levels, bond orders, and bond lengths in these compounds have been derived by the molecular-orbital technique, corrections being applied, by successive approximations, to the exchange integrals H_{rs} for their dependence on bond length.

The results for diphenyldiacetylene suggest that a further study of bond orders and lengths in conjugated acetylenes is called for.

The preparation of a yellow highly crystalline substance tentatively described as the novel macrocycle 1 : 2-7 : 8-13 : 14-tribenzo*cyclo*octadeca-1 : 7 : 13-triene-3 : 5 : 9 : 11 : 15 : 17-hexayne (I) has been recorded recently by Eglinton and Galbraith [1] although, owing to its instability, final establishment or denial of the postulated structure is proving difficult.[2] *X*-Ray examination is being carried out in this department by Dr. J. C. Speakman and Mr. W. K. Grant, and a calculation of the expected bond lengths in (I), subsequently referred to as " the triangle," is of great interest in anticipation of their results. Especially interesting are the lengths of the formal single bonds in the butadiyne arms of the triangle because a number of similarly situated single bonds have been found to be remarkably short. For example, the central link in diacetylenedicarboxylic acid dihydrate measures [3] 1·33 ± 0·02 Å, and so is even shorter than the double bond in ethylene found by Pauling and Brockway [4] to be 1·34 ± 0·02 and by Galloway and Barker [5] to be 1·353 ± 0·01 Å. In the same way the middle bond in diacetylene itself is reported [6] as 1·36 ± 0·03 Å.



(I)



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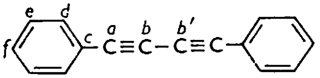

(III)

Bond lengths have now been calculated for " the triangle " by the molecular-orbital technique, group theoretical methods being used to simplify the calculations. These fall into three parts because the p_z-electrons on the carbon atoms of the butadiyne chains interact with each other and with the p_z-electrons on the carbon atoms of the benzene rings and so form a π-molecular orbital system spreading over all thirty carbon atoms of " the triangle." The p_y-electrons of the atoms in the butadiyne chains are, on the other hand, confined to these chains since the remaining valency-shell orbitals of the benzenoid carbon atoms are engaged in sp^2-hybridisation and the formation of σ-bonds and so cannot react appreciably with them. Thus the p_y- and p_z-atomic orbitals, giving rise to π_y- and π_z-molecular orbitals, must be handled separately and then combined to derive the interatomic distances.

π_z-Molecular Orbitals.—The molecule has D_{3h} symmetry and consideration of the

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* Part IV, *J.*, 1956, 3595.

[1] Eglinton and Galbraith, *Proc. Chem. Soc.*, 1957, 350.

[2] Dr. A. Eglinton, personal communication.

[3] Dunitz and Robertson, *J.*, 1947, 1145.

[4] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1223.

[5] Galloway and Barker, *J. Chem. Phys.*, 1942, **10**, 88.

[6] Pauling, Springall, and Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927.

character table[7] shows that the π_z-molecular orbital energy levels must be $10E'' + 5A_1'' + 5A_2''$, the E'' levels being doubly degenerate. Thus the thirtieth-order secular determinant breaks down into two (identical) tenth- and two (different) fifth-order ones.

To avoid begging the question we must begin by assuming that all exchange integrals H_{rs} between orbitals on neighbouring atoms *r*, *s* are equal. This is done in spite of the fact that one expects $H_{\mathrm{H-C}}$ and $H_{\mathrm{H\equiv C}}$ to be respectively smaller and larger than $H_{\mathrm{ar-ar}} = \beta$, the integral between neighbouring orbitals on carbon atoms (taken as 1·39 Å apart) in benzene, since the interatomic distances are in the order pure single bond > benzene bond > pure triple bond. All other exchange integrals and all overlap integrals are assumed to be zero.

With these approximations the energy levels $E - \alpha$ (α being the Coulomb integral for carbon) for this first iteration were obtained (Table 1) by well-established methods, and hence the total π_z-bond orders p_z were calculated.* These are given in Table 2 for the seven distinctly different bonds of the molecule which, for greater convenience of reference, are indicated as in (II), the repeat pattern of the molecule.

TABLE 1. *Energy levels of π-orbitals in "the triangle." (Only occupied levels are given and these are numbered within each symmetry class in order of increasing energy in the third iteration.)*

Symmetry class	Orbital number	$E - \alpha$ 1st Iteration	$E - \alpha$ 2nd Iteration	$E - \alpha$ 3rd Iteration	Symmetry class	Orbital number	$E - \alpha$ 1st Iteration	$E - \alpha$ 2nd Iteration	$E - \alpha$ 3rd Iteration
(i) π_z-Orbitals					(i) π_z-Orbitals				
A_2''	1	2·3028 β	2·4089 β	2·3529 β	E''	3	1·3591 β	1·4142 β	1·4444 β
E''	1	2·2504 β	2·3184 β	2·2593 β	E''	4	β	0·9990 β	1·0036 β
E''	2	1·7321 β	2·0063 β	2·0152 β	A_2''	3	β	0·9234 β	0·9489 β
A_2''	2	1·6180 β	1·8288 β	1·8425 β	A_1''	2	0·6180 β	0·8476 β	0·9057 β
A_1''	1	1·3028 β	1·4235 β	1·4587 β	E''	5	0·3287 β	0·5890 β	0·7214 β
(ii) π_y-Orbitals					(ii) π_y-Obitals				
A_u	1	1·6180 β	2·1747 β	2·0964 β	B_g	1	0·6180 β	1·1047 β	1·2364 β

TABLE 2. *Exchange integrals (β_{rs}), partial (p_z and p_y) and total (p) mobile bond orders, and lengths (L) in "the triangle."*

Bond	Iteration	β_{rs}	p_z	p_y	p	L	Bond	Iteration	β_{rs}	p_z	p_y	p	L
ab	1	1	0·7463	0·8943	1·6406	1·230	*cd*	1	1	0·5905		0·5905	1·410
	2	1·55	0·8895	0·9453	1·8348	1·214		2	0·93	0·6279		0·6279	1·397
	3	1·61	0·9296	0·9661	1·8957	1·209		3	0·97	0·6370		0·6370	1·394
ac	1	1	0·4887		0·4887	1·449	*de*	1	1	0·6898		0·6898	1·380
	2	0·80	0·3160		0·3160	1·485		2	1·03	0·6905		0·6905	1·380
	3	0·71	0·2590		0·2590	1·489		3	1·03	0·6855		0·6855	1·381
bb′	1	1	0·5436	0·4473	0·9909	1·369	*ee′*	1	1	0·6286		0·6286	1·396
	2	1·07	0·3390	0·3263	0·6652	1·432		2	0·97	0·6312		0·6312	1·395
	3	0·86	0·2763	0·2580	0·5343	1·441		3	0·98	0·6407		0·6407	1·393
cc′	1	1	0·5197		0·5197	1·436							
	2	0·85	0·6024		0·6024	1·406							
	3	0·94	0·6290		0·6290	1·396							

π_y-Molecular Orbitals.—The three sets of p_y-atomic orbitals of the butadiyne chains must, with the many other atomic orbitals which are symmetrical about the plane of the nuclei, conform collectively to the D_{3h} symmetry of the whole molecule. However, the non-interaction of these two groups of orbitals makes it very much easier to consider the butadiyne sets separately from the start than to factorise them out later, so this has been done. In this first iteration, there are, therefore, three sets of π_y-molecular orbitals which

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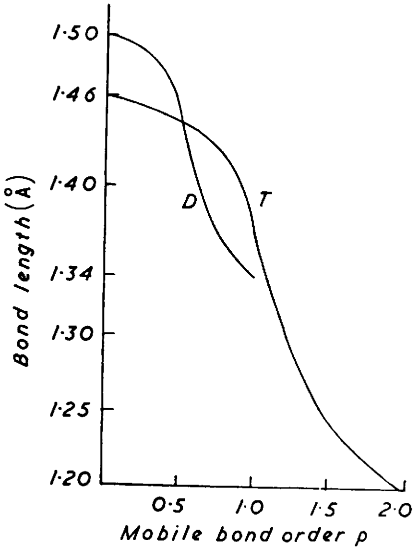
* It is customary to use p (with or without subscript) as symbol for atomic orbitals of quantum number $l = 1$ as well as for bond orders, but care has been taken to make clear which is implied in each case.

[7] Herzberg, "Infra-red and Raman Spectra," van Nostrand Co., New York, 1945, p. 117.

are identical with the π-orbitals of butadiene as calculated with equal exchange integrals between neighbouring atomic orbitals. Their energies are included in Table 1 and the corresponding total π_y-bond orders p_y in Table 2.

Total Bond Orders and Derived Bond Lengths.—The total mobile bond orders for all electrons are given as $p = p_y + p_z$. To convert these into bond lengths two correlation curves have been used. The first was established in Fig. 1 of Part I[8] and is shown as curve D in the Figure of the present paper. This has been used for all C–C bonds except ab and bb'. For these a new curve has been derived as follows. In a system such as "the triangle" the π_y- and π_z-orbitals cannot interact but do intersect in the line of the butadiyne carbon nuclei. Hence what are essentially two butadiene systems are superposed in each of these regions and so the correlation curve should be, not one based on the extrapolation of curve D to a point appropriate to acetylene ($p = 2$, $L = 1{\cdot}20$ Å), but one, T, obtained by doubling the mobile order scale ($0 < p < 2$) and extending and displacing the length scale to cover the range $1{\cdot}46 > L > 1{\cdot}20$ Å. The graph then passes through the points (0, 1·46), (0·2, 1·455), (0·4, 1·447), (0·6, 1·437), (0·8, 1·420), (1·0, 1·367), (1·2, 1·307), (1·4, 1·262), (1·6, 1·234), (1·8, 1·216), (2·0, 1·20). The value 1·46 Å for the pure single bond ($p = 0$) formed by sp-hybridised orbitals results from the argument that, just as the pure single bond formed by sp^3-hybrids is shortened[9] by 0·04 Å when the hybridisation becomes sp^2, so a similar further shortening is to be expected on passing to sp-hybridisation. A comment is made later on the value 1·20 Å for C≡C in a pure triple bond.



It might be objected that this is a rather arbitrary technique for converting bond orders into bond lengths since it implies that, however p is made up from p_y and p_z, the same bond length is obtained. This is so, but the same criticism is applicable to the combination of the partial (one-electron) bond orders which make up p_y and p_z and could only be overcome by applying a self-consistent field technique. In any case it would be impracticable to derive bond lengths L_y and L_z from p_y and p_z and then combine them to obtain substantially shorter lengths L for the complete multiple bond.

From curve T, then, are obtained lengths L for the bonds ab and bb', while curve D is used for all other C–C bonds. These lengths are given in Table 2 and suggest that the formal single bonds ac and bb' are much shorter than might have been expected (1·50 and 1·46 Å, respectively), the triple bond ab rather longer (1·20 Å) than, and the benzene ring bonds not much different from expectation (1·39 Å) apart from cc' which seems surprisingly large and distorts the hexagon appreciably. However, these deviations are all attributable to the naïve assumption that all H_{rs} between neighbour orbitals are equal to β. To try to correct for this the bond lengths L obtained in the first iteration were used to give improved integrals H_{rs} by means of the table given by Mulliken, Rieke, and Brown.[10] These are recorded in Table 2 as multiples of β.

Second and Third Iterations.—Energy levels, bond orders and lengths for the second iteration were obtained as before (Tables 1 and 2). The new bond lengths are more realistic. The links comprising the benzene rings are now approximately equal though

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

[9] Coulson, Victor Henri Memorial Volume, Contribution a l'Étude de la Structure Moléculaire Desoer, Liège, 1948, p. 15.

[10] Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 48.

cc' is still slightly longer than the rest. The formal triple bonds are of about the expected length though the " diacetylene single bond " *bb'* is much longer than originally, having now a mobile order of only 0·665 from both π_y- and π_z-orbitals. Increasing H_{ab} must, of course, decrease the order and increase the length of both *ac* and *bb'* but it is perhaps surprising that the former has gone up to 1·485 Å in length. In fact, the results as a whole should warn against confidence in calculations in which all exchange integrals are equalised in spite of differences in bond type.

Since the second iteration made so great a difference to the estimated bond lengths, a third cycle of operations was carried out to give the further energies, orders, and lengths recorded in Tables 1 and 2, the H_{rs} values being obtained from the lengths given by the second cycle.

The interatomic distances obtained in this iteration differed so little from those obtained in the second that they were supposed now to have converged to the ultimate values appropriate to this type of calculation. Although they are given to a third decimal place, it is not suggested that they are reliable beyond the second; the third is given to facilitate their use in later work.

When this type of calculation is carried out on aromatic condensed-ring hydrocarbons the derived bond lengths agree with good *X*-ray measurements to within ±0·02 Å. There are fewer acetylenic compounds on which *X*-ray measurements and molecular-orbital calculations have been made, but it seems likely that the present bond lengths in the benzene rings should be within ±0·02 Å of the experimental values when available, and the remaining inter-carbon bonds within about ±0·04 Å. However, to permit comparison with a closely similar compound on which experimental measurements have been made, calculations corresponding to the foregoing have now been made on diphenyldiacetylene and are described later. Anticipating these results, we may say that the above conclusions about the reliability of the calculations on " the triangle " seem justified.

Ultraviolet Absorption Spectrum.—The ultraviolet spectrum [1] of the yellow compound shows rather more than twenty peaks, many of which must represent vibrational structure. Although this spectrum cannot be adduced as conclusive confirmation of the structure (I), yet it is consistent with it, as can be seen by correlating it with the calculated transition energies. Above 250 mμ there appear to be three separate electronic transitions with their origins near 23,000 ($\varepsilon_{\max.}$ 1600), 27,800 ($\varepsilon_{\max.}$ 10,500), and 33,170 ($\varepsilon_{\max.}$ 234,400) cm.$^{-1}$. From simple considerations these should involve the promotion of one electron from one of the highest occupied degenerate pair ($5e''$) of orbitals to one of the lowest unoccupied degenerate pair ($6e''$). This promotion gives rise to three excited electronic states $E'' \times E'' = A_1' + A_2' + E'$. Transitions from the ground state A_1' to the states A_1' and A_2' are forbidden in absorption, while the transition to the state E' is allowed and should occur with high intensity. On this basis, the intense band at 33,170 cm.$^{-1}$ would mark the allowed transition $A_1' \longrightarrow E'$ which is polarised in the plane of the molecule. The bands at lower frequency may represent the forbidden transitions $A_1' \longrightarrow A_1'$ and $A_1' \longrightarrow A_2'$ intensified by transfer from the allowed transition. Whether the 27,800 cm.$^{-1}$ transition belongs to $A_1' \longrightarrow A_2'$ and the 23,300 cm.$^{-1}$ transition to $A_1' \longrightarrow A_1'$ or *vice versa* is a matter for further calculations, but it is noteworthy that the calculated transition energy of $2 \times 0{\cdot}72\beta$ corresponds to *ca.* 28,800 cm.$^{-1}$ (if $\beta \approx 20{,}000$ cm.$^{-1}$), which is almost exactly the *average* energy of the three transitions (28,100 cm.$^{-1}$); if, however, allowance of 5000 cm.$^{-1}$ is to be made [11] for singlet–triplet splitting, β would have to be 16,000 cm.$^{-1}$. This, though rather low, is still of the correct order of magnitude. Further, the intensity of the putative forbidden transitions can be explained by using a matrix element for intensity transfer of about the same size as that deduced from the spectrum of benzene.

Diphenyldiacetylene.—Partly to check the remarkable change in length of the bond

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[11] Platt, *J. Chem. Phys.*, 1951, **19**, 1418.

bb′ of " the triangle " between the first and the second iteration, and partly to provide an estimate of the likely deviation between observed and calculated lengths, the interatomic distances in diphenyldiacetylene (III) were calculated for comparison with Wiebenga's measurements.[12] The π-orbital energies are shown in Table 3 for each of the three iterations, and the exchange integrals, bond orders, and bond lengths are given in Table 4, all being determined by the methods described for " the triangle." Table 4 also includes Wiebenga's measurements (all of which he claims to be accurate to $\pm 0{\cdot}03$ Å) and the discrepancy $\Delta = L_{\text{obs.}} - L_{\text{calc.}}$ At all stages the computations on both (I) and (III) ran closely parallel, thereby confirming both the arithmetic and the technique of successive approximations.

TABLE 3. *Energy levels of π-orbitals in diphenyldiacetylene. (Only occupied levels are given, and these are numbered within each symmetry class in order of increasing energy in the third iteration.)*

			$E - \alpha$					$E - \alpha$	
Symmetry	Orbital number	1st Iteration	2nd Iteration	3rd Iteration	Symmetry	Orbital number	1st Iteration	2nd Iteration	3rd Iteration
(i) π_y-Orbitals					(i) π_y-Orbitals				
B_{3u}	1	2·1829 β	2·3297 β	2·2899 β	B_{1g}	1	β	1·0200 β	β
B_{2g}	1	2·1227 β	2·0516 β	2·0834 β	A_u	1	β	1·0200 β	β
B_{3u}	2	1·6673 β	1·9018 β	1·9029 β	B_{3u}	3	β	0·9511 β	0·9913 β
B_{2g}	2	1·3417 β	1·4104 β	1·4412 β	B_{2g}	3	0·3859 β	0·6905 β	0·7995 β
(ii) π_z-Orbitals					(ii) π_z-Orbitals				
B_{2u}	1	1·6180 β	2·1578 β	2·0964 β	B_{3g}	1	0·6180 β	1·1278 β	1·2364 β

TABLE 4. *Exchange integrals, partial and total mobile bond orders, and lengths in diphenyldiacetylene.*

Bond	Iteration	β_{rs}	p_z	p_y	p	L	$L_{\text{obs.}}$	Δ
ab	1	1	0·7814	0·8943	1·6757	1·227		
	2	1·56	0·9042	0·9496	1·8538	1·214		
	3	1·61	0·9331	0·9661	1·8992	1·209	1·18	−0·03
ac	1	1	0·4442		0·4442	1·467		
	2	0·76	0·2871		0·2871	1·487		
	3	0·70	0·2470		0·2470	1·490	1·44	−0·05
bb′	1	1	0·5127	0·4473	0·9600	1·381		
	2	1·03	0·3384	0·3134	0·6518	1·433		
	3	0·86	0·2740	0·2580	0·5320	1·441	1·39	−0·05
cd	1	1	0·5962		0·5962	1·408		
	2	0·93	0·6337		0·6337	1·395		
	3	0·98 *	0·6456		0·6456	1·391		
de	1	1	0·6827		0·6827	1·383		
	2	1·02	0·6807		0·6807	1·382		
	3	1·02 *	0·6709		0·6709	1·385		
fe	1	1	0·6552		0·6552	1·390		
	2	1·00	0·6585		0·6585	1·388		
	3	1·00	0·6640		0·6640	1·387		

* Assumed = 1·00 although derived as stated.

Agreement between observed and calculated interatomic distances is, not surprisingly, excellent in the benzene rings.

The discrepancy Δ_{ab} for the acetylenic links is well within the limit admitted both experimentally and theoretically. Its negative sign is probably due either to the selection of acetylene as the standard triple bond or to the use of *X*-ray crystallography for the measurement of diphenyldiacetylene, for there is a marked tendency (Table 5) for spectroscopic methods to give interatomic distances of about 1·20 Å in $C{\equiv}C$ while *X*-ray investigations lead to slightly shorter lengths though dimethyltriacetylene is exceptional in this respect. It is usual to suggest that the inter-carbon distance in acetylene may be slightly

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[12] Wiebenga, *Z. Krist.*, 1940, **102**, 193.

too great for a pure triple bond by reason of the small negative charges which incipient ionisation of the hydrogen atoms would confer on the carbons. A similar repulsion between negatively charged carbon atoms might apply to symmetrical dihalogenoacetylenes as a result of the high electronegativity of the halogen atoms. Again, in the symmetrical compounds studied by *X*-rays, the central bonds whether triple or single will be slightly elongated as a result of the net changes which any hetero-atoms in the system will induce, though these elongations may well be too small to take into account in any theoretical estimate of bond length. However, multiple bonds in conjugated systems must be longer than in isolation other things being equal, and so the *X*-ray results suggest that curve *T* should perhaps have been drawn to a point $p = 2$, $L = 1{\cdot}17$ Å (say); it is unfortunate that the central bond of di-*tert*.-butylacetylene has never been measured. Further, while spectroscopic measurements lead to internuclear distances, *X*-ray studies give distances between centres of electron density; these are not necessarily the same, and correlation curves between order and length should relate to one experimental method only. Work is therefore planned to investigate this matter further. Meanwhile, for want of a better, curve *T* must be used.

TABLE 5. *Lengths of some* C≡C *bonds.*

[M.W. = Microwave; Sp = spectroscopic measurements; E.D. = electron diffraction; E.D.S. = electron diffraction sector technique; X.R. = *X*-ray measurements on crystals.]

Compound	Length (Å)	Method	Ref.
Chloroacetylene	1·211 ± 0·001	M.W.	14
Acetylene	1·207 ± 0·002	Sp.	13
Methylacetylene	1·2073	M.W.	15
,,	1·207 ± 0·002	M.W.	16
Cyanoacetylene	1·203	M.W.	17
Methylcyanoacetylene	1·203	M.W.	18
Dibromoacetylene	1·20 ± 0·03	E.D.	19
Dimethyldiacetylene	1·20 ± 0·02	E.D.	5
Dimethyltriacetylene	1·199 ± 0·01	X.R.	20
Dichloroacetylene	1·195	E.D.S.	21
Diacetylene	1·19 ± 0·03	E.D.	5
Acetylenedicarboxylic acid dihydrate	1·19 ± 0·02	X.R.	22
Tolan	1·19 ± 0·02	X.R.	23
Diacetylenedicarboxylic acid dihydrate	1·185 ± 0·02	X.R.	2
Diphenyldiacetylene	1·18 ± 0·03	X.R.	12
Di-iodoacetylene	1·18	E.D.	19

The formal single bonds *ac* and *bb'* as determined in the first iteration are respectively 0·03 Å longer and 0·01 Å shorter than observed. These deviations are within the experimental error indicated by Wiebenga, but it is impossible to believe that all exchange integrals between neighbouring atomic orbitals are the same, and so this agreement between observed and calculated interatomic distances must be ignored. In the third iteration, $\Delta = -0{\cdot}05$ Å for each of these links and this seems rather large. The calculations may be at fault in the correlation of bond length with either (*a*) exchange integral, though from the method of derivation [10] this does not seem likely to be serious, or (*b*) bond order. There have been very few correlations of bond order and bond length in acetylenes

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[13] Herzberg, *op. cit.*, p. 398.

[14] Westenberg, Goldstein, and Wilson, *J. Chem. Phys.*, 1949, **17**, 1319.

[15] Thomas, Sherrard, and Sheridan, *Trans. Faraday Soc.*, 1955, **51**, 623.

[16] Trambarulo and Gordy, *J. Chem. Phys.*, 1950, **18**, 1613.

[17] Westenberg and Wilson, *J. Amer. Chem. Soc.*, 1950, **72**, 199.

[18] Sheridan and Thomas, *Nature*, 1954, **174**, 798.

[19] Brockway, *Rev. Mod. Phys.*, 1936, **8**, 231.

[20] Jeffrey and Rollett, *Proc. Roy. Soc.*, 1952, *A*, **213**, 86.

[21] Finbak and Hassel, *Arch. Math. Naturv.*, 1941, **44**, No. 3; Hassel and Taarland, *Tidsskr. Kjemi Bergvesen Met.*, 1941, **1**, 172.

[22] Dunitz and Robertson, *J.*, 1947, 148.

[23] Robertson and Woodward, *Proc. Roy. Soc.*, 1938, *A*, **164**, 436.

which have taken account of the variation of H_{rs} with interatomic distance and further investigations of this are proposed. There is, of course, the third possibility that the *X*-ray measurements, carried out nearly twenty years ago, are rather less accurate than was supposed.

Dr. G. Eglinton is thanked for helpful discussion, and Dr. J. C. D. Brand for helpful discussions and for his correlation of the ultraviolet absorption spectrum of the yellow substance with the molecular-orbital energy levels of " the triangle."

CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW. [*Received, June* 16*th*, 1958.]