273. *The Crystal Structure of Cupric Tropolone and the Dimensions of the Tropolone Ring.*

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A two-dimensional crystal analysis of cupric tropolone has been carried out, making use of the phase-determining power of the copper atom. The analysis is practically a direct one from the *X*-ray measurements, and makes only a minimum of reference to the chemical structure. In the final projection, made by the usual Fourier series method, all the atoms (except hydrogen) are clearly resolved, and the bond lengths and angles are worked out. The tropolone ring appears to be an almost regular planar heptagon, with an average carbon–carbon distance of 1·40 A., indicating strong aromatic character. It is possible to differentiate the oxygen atoms as carbonyl and hydroxyl on the basis of bond-length measurements. The central cupric copper is coplanar with its four surrounding oxygen atoms, which lie approximately at distances to be expected for covalent linkages of the dsp^2 type.

The chemistry of tropolone and some of its derivatives has been described by Cook, Gibb, Raphael, and Sommerville (*J.*, 1951, 503) and the infra-red spectrum has been studied by Koch (*J.*, 1951, 512). One point of outstanding interest in these structures which cannot be completely solved by organic chemical methods concerns the fine structure of the seven-membered carbon ring. The evidence available from various chemical and physical methods of approach has been fully discussed in the above references, but no rigorous determination of the molecular geometry has been made. It is obviously desirable to measure the spatial positions of the atoms in these molecules as precisely as possible. The most feasible and indeed the only way of doing this with certainty for structures of this degree of complexity is by means of the *X*-ray crystallographic method. We have, therefore, commenced such investigations on tropolone and a number of its derivatives.

The present paper describes the results obtained for the copper complex, known as cupric tropolone. This derivative was chosen for the initial study for the following reasons. The crystals, although small, are extremely stable. They are monoclinic, and one axis (c) is as short as 3·8 A. It should, therefore, be possible to obtain a clear projection of the whole structure in this direction, as any interleaving of the molecules within this periodicity is clearly ruled out. The copper atoms are also found to lie at symmetry centres in the structure, and, for those *X*-ray reflections to which they contribute, the copper atoms should to a very large extent be phase determining. This opens up the possibility of a perfectly direct approach to the structure, without making use of any of the chemical evidence.

The whole situation is clearly analogous to the metal phthalocyanine crystal structures (Robertson, *J.*, 1935, 615; 1936, 1195; Robertson and Woodward, *J.*, 1937, 219; 1940, 36). In nickel phthalocyanine it was found that the phase constants of 132 of the 152 ($h0l$) reflections were governed by the central nickel atom, while in platinum phthalocyanine all the 302 ($h0l$) reflections were phase determined. As the molecule of cupric tropolone is very much smaller than the nickel phthalocyanine molecule ($C_{14}H_{10}O_4Cu$ as against $C_{32}H_{16}N_8Ni$) it is reasonable to expect that all or nearly all of the corresponding phase constants in the cupric tropolone structure will be determined by the copper atom.

There is, however, one important difference. In the phthalocyanine structures the short axis is the monoclinic symmetry axis b. Consequently, the principal projections, which give practically all the information about the structure and in which all the atoms are resolved, are compounded from the ($h0l$) structure factors, to all of which the central metal atom makes a positive contribution. In projection the metal atom lattice is effectively primitive. In cupric tropolone, however, the short axis is the monoclinic axis c and the principal projection is compounded from the ($hk0$) structure factors. Here the copper atoms only contribute to those structure factors for which the index sum ($h + k$) is even, because in this projection the metal atom lattice is face-centred. For the structure factors with ($h + k$) odd, the contributions from the copper atoms cancel each other out, and consequently these reflections are not phase determined.

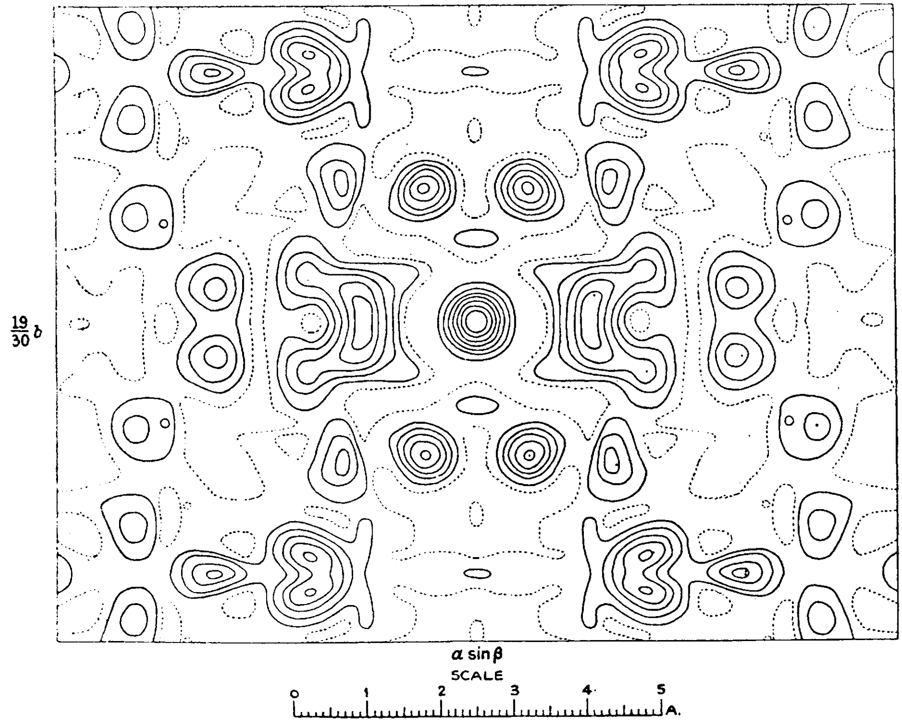
It is, of course, true that these cases are both present in the phthalocyanine structure, but here the a and c projections are of no practical importance because the atoms are not resolved.

Consequently, the problem was not fully studied at that time. (Since then, however, various projections in analogous structures have been studied in some detail; *e.g.*, strychnine sulphate and selenate, Bokhoven, Schoone, and Bijvoet, *Proc. K. Acad. Sci. Amsterdam*, 1947, **50**, 825; 1948, **51**, 990.) Conversely, in cupric tropolone, the projection of the structure along the symmetry axis *b* will be completely phase determined, but this projection is not likely to prove a useful one.

The solution of the cupric tropolone structure, described below, is therefore of some crystallographic interest, as a supplement to the earlier phthalocyanine studies, as well as of chemical interest in relation to the geometry of the molecule.

FIG. 1.

Projection along c, *synthesised from* (h + k)*-even structure factors only. It shows the structure superimposed on its mirror image. The contour scale is arbitrary, but it is reduced by a factor of* 5 *on the central atom.*



The analysis proceeds in two stages. The first is perfectly direct and independent of any chemical information, making use of the phase-determined reflections only. This gives a picture of the structure superimposed on a mirror image of itself (Fig. 1). From the co-ordinates so obtained the phases of the remaining reflections can then be determined, and the analysis carried to completion (Fig. 2). At the beginning of this second stage, it is convenient, but not absolutely essential, to make reference to the expected chemical structure as an aid in separating the molecule from its superimposed mirror image.

As the analysis, limited by the shape and size of the crystals, is at present confined to two dimensions, only two co-ordinates for each atom can be determined directly. It is shown, however, that the projections of the tropolone ring so obtained conform very accurately to the projection of a regular planar heptagon, and on this basis the bond lengths and angles are worked out. The average value of the carbon–carbon bond length in the ring is 1·40 A., and deviations from this value are so small that they may be due to errors in measurement, although there is some evidence of a faint alternation of long and slightly shorter bonds in the ring. These dimensions are typically aromati cin character. The cupric copper atom is coplanar with its four surrounding oxygen atoms which lie approximately in the positions to be expected for covalent linkages of the *dsp*^{2} coplanar type. The oxygen atoms can, however, be differentiated by the lengths of the links which they make to the ring carbon atoms (1·25 and 1·34 A.) as belonging to the carbonyl and the hydroxyl type respectively.

Crystal Data.—Cupric tropolone, $(C_7H_5O_2)_2Cu$; *M*, 305·8; m. p. (decomp.) 300°; *d*, calc. 1·683, found 1·696. Monoclinic prismatic, $a = 11·60 \pm 0·05$, $b = 13·82 \pm 0·02$, $c = 3·80 \pm 0·005$ A., $\beta = 93°$ (approx.). Absent spectra, (*h*0*l*) when *h* is odd (not fully established), (0*k*0) when *k* is odd. Space group, C_{2h}^5–$P2_1/a$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell = 608 A.^{3}. Total number of electrons per unit cell = F(000) = 310.

This copper derivative crystallises in very fine lustrous green needles from benzene or alcohol. The system is monoclinic and the needle axis has been chosen as the *c* axis. A pair of (110) faces are usually well developed, with very small (100) or (010) faces. Small end faces are sometimes visible, but could not be positively identified.

Experimental Measurements.—Copper-*K*α radiation was used ($\lambda = 1·542$ A.), and the reflections were recorded on rotation, oscillation, and moving-film photographs. Owing to the needle-like shape of the crystals, satisfactory moving-film records could only be obtained for the (*hk*0) zone reflections. The principal specimen employed in this case had a width of 0·09 mm., a thickness of 0·05—0·06 mm., and an effective length (limited by the collimator) of about 0·9 mm.; it weighed approximately $6·8 \times 10^{-6}$ g. The intensities of the (*hk*0) reflections were estimated visually by using the multiple-film technique. The small size of the crystal rendered accurate estimation difficult, but at the same time tended to reduce errors due to absorption, for which no corrections were attempted. F values calculated from the intensities by the usual mosaic crystal formulæ are listed in Table IV under " F, meas."

The *a* and *b* periodicities were established by rotation and oscillation photographs, the needle axis being kept approximately perpendicular to the rotation axis. With the crystals available it was not possible fully to establish the (*h*0*l*) halving, but the absence of odd orders of (*h*00) and (0*k*0) was checked as far as 14,0,0 and 0,16,0. Any remaining space-group uncertainty will not affect the main conclusions described below.

Structure Analysis.—As the unit cell contains two copper atoms, these must lie on symmetry centres at (0,0,0), (½,½,0). When $(h + k)$ is even the contributions of the copper atoms will be in phase, and it is safe to assume that these contributions will determine the sign of the total structure amplitude for at least the great majority of these planes. We may, therefore, assume that the (*hk*0) structure factors are of positive sign when $(h + k)$ is even.

However, when $(h + k)$ is odd, the contributions of the copper atoms cancel out. The structure factors observed in this case are therefore due to the contributions of the other atoms, carbon and oxygen, in the molecule, and the sign of these structure factors may be either positive or negative. This is borne out by a survey of the (*hk*0) zone of reflections, which shows that these are generally much stronger when $(h + k)$ is even; 91 of these even-index reflections were observed out of a possible 111 lying within the range of copper radiation (82%), but only 28 odd-index reflections were observed out of a possible 97 (29%). Overall, 119 reflections were observed out of a possible 208 (57%).

The structure analysis was now carried out in the following way. A double Fourier synthesis was first performed with the even-index $(h + k$ even) structure factors as coefficients, with all signs positive, the odd-index structure factors being entirely omitted. It is clear that this operation introduces a false element of symmetry into the resulting projection, which consists of a two-fold axis or plane, parallel to *a* or *b*, passing through the symmetry centres, the effect being to create a face-centred projection. Such a projection must result from the imposed general halving when $(h + k)$ is odd. In this projection the peak density of each atom will be halved and each will be accompanied by its mirror image. To obtain the real structure it will be necessary to select one atom from each of the resulting pairs and reject the other.

The result of this synthesis, from the even-index structure factors alone, is shown in Fig. 1. It is, of course, produced directly from the *X*-ray measurements by application of the usual standard calculations, and involves no knowledge of the chemical structure. No atoms have been assumed to exist in the structure apart from the central metal atom.

The next step, however, is accomplished more easily by making some reference to the known chemical facts.* It is necessary to select one atom from each of the pairs and reject the other, making use of the co-ordinates of the selected atoms to calculate the phase constants of the

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* As a very limited number of well-resolved peaks appear in the projection (Fig. 1), it would seem possible to arrive at the final solution without making use of any chemical information. Different selections of co-ordinates could be made from the pairs of peaks present, and the test of the right selection would be that which gave the best agreement in the structure factor calculations. This would be a possible although tedious process.

odd-index reflections, and so complete the synthesis. There is no difficulty in doing this because in each quadrant of the diagram there is found a ring of seven fairly low peaks which must be due to carbon atoms. Outside this ring and nearer to the central copper atom, there is a higher peak in each quadrant which must represent oxygen. The other oxygen atom and its mirror image coalesce to form an oval near the central copper, but an approximate co-ordinate can readily be assigned. The co-ordinates finally chosen are indicated by small black dots in the lower right-hand quadrant on Fig. 1.

These co-ordinates are listed in Table I, and were then used to calculate all the structure factors, with the results given in Table IV. The overall agreement obtained is quite good, the average discrepancy, obtained by dividing the sum of the individual discrepancies by the total of the measured F values, being only 15·8%. This confirms the selection of atoms taken as being correct. In these structure-factor calculations an averaged atomic *f*-curve for carbon and oxygen was used (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106), the atoms being weighted in the ratio of 6 to 9. For copper an empirical scattering curve was used, of similar shape to the *f*-curve found for nickel in the nickel phthalocyanine structure (Robertson and Woodward, *J.*, 1937, 219). The measured F values were correlated with these calculated values, and so placed on at least an approximately absolute scale.

FIG. 2.

Electron-density projection covering one molecule of cupric tropolone. Contour scale approximately one electron per A.^{2} *per line, the one-electron line being dotted. Scale on the copper atom, five electrons per* A.^{2} *per line.*

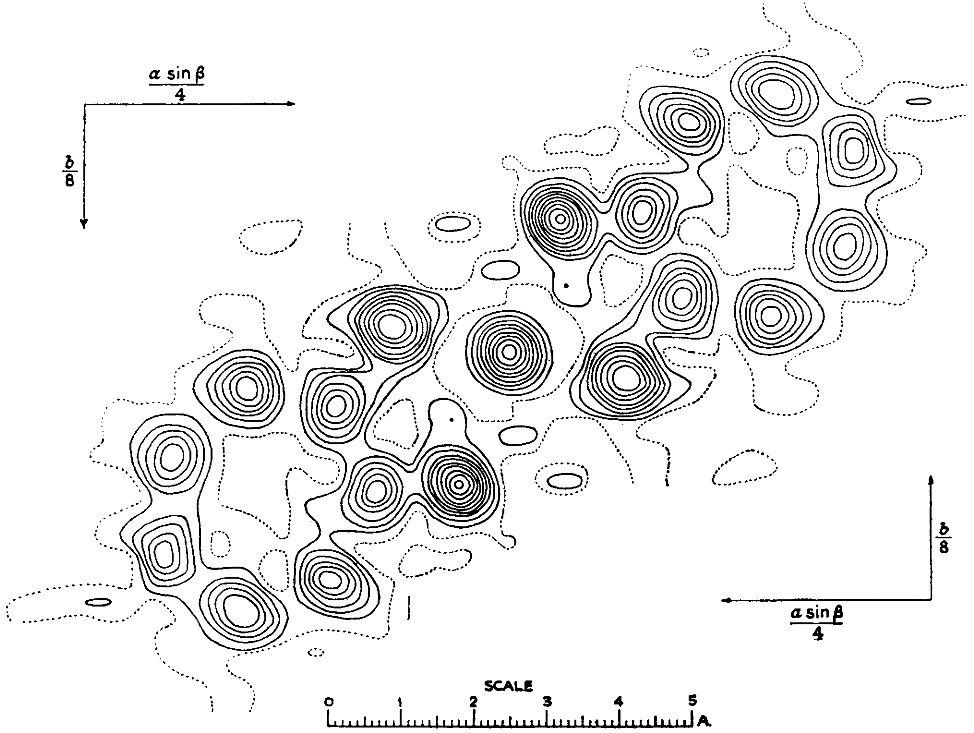


TABLE I.

Co-ordinates derived from the first projection (*Fig.* 1).

Atom.	x/a.	y/b.	X (A.).	Y (A.).	Atom.	x/a.	y/b.	X (A.).	Y (A.).
Cu	0	0	0	0					
O(1)	0·139	−0·028	1·60	−0·38	CH(3)	0·209	0·230	2·40	3·17
O(2)	0·062	0·133	0·71	1·83	CH(4)	0·320	0·251	3·68	3·46
C(1)	0·202	0·050	2·32	0·69	CH(5)	0·410	0·202	4·72	2·78
C(2)	0·165	0·143	1·90	1·97	CH(6)	0·403	0·104	4·64	1·42
					CH(7)	0·315	0·035	3·62	0·48

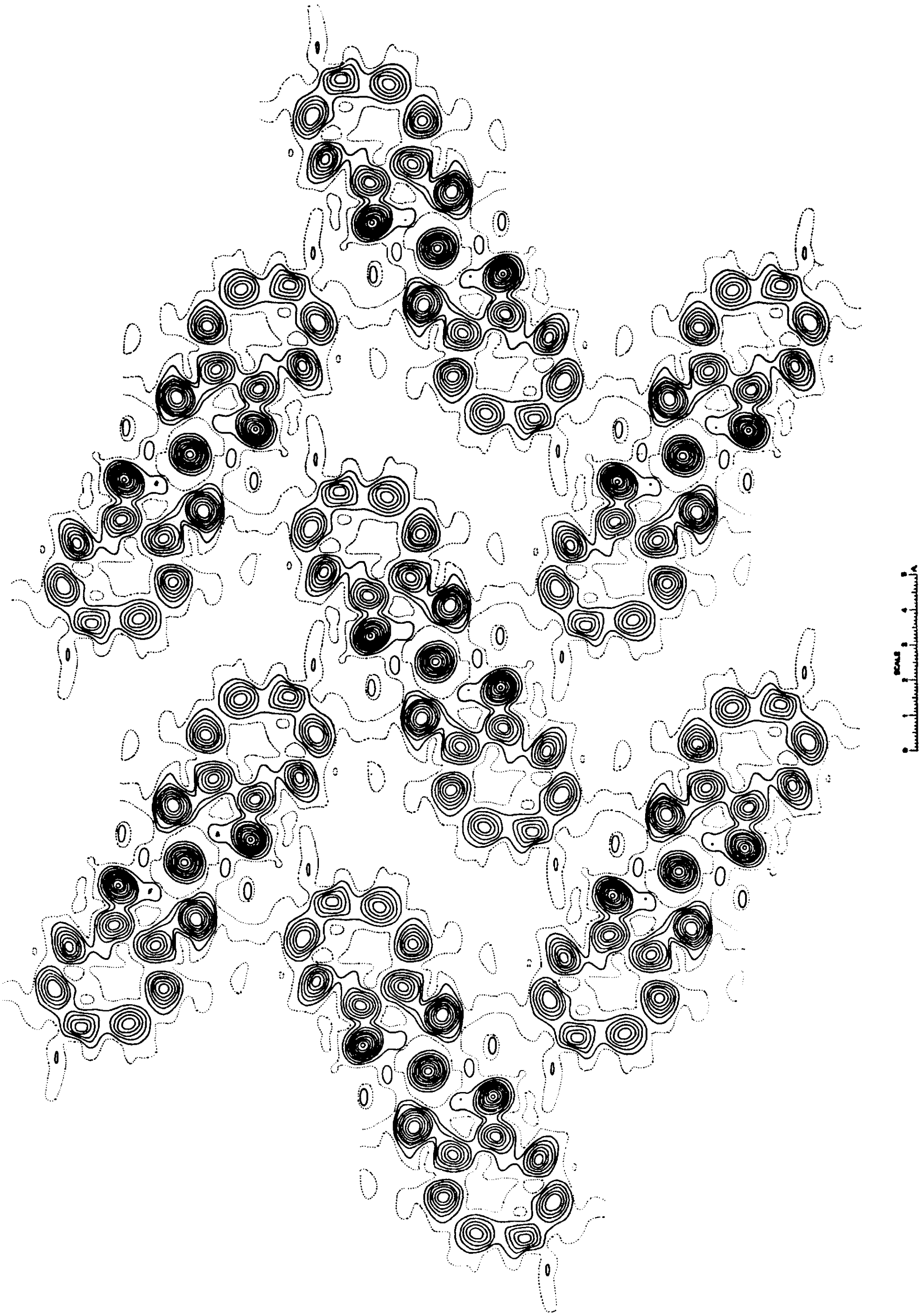


Fig. 3.

Electron-density projection showing the arrangement of several cupric tropolone molecules in the crystal structure.

It will be found that all the $(h + k)$-even structure factors still retain a positive sign in these calculations, which justifies our earlier assumption about the phase-determining power of the copper atom. As the signs of the $(h + k)$-odd structure factors are now known as well, we are in a position to proceed to a complete double Fourier synthesis, employing all the terms, which should give a faithful picture of the true structure.

The result of this calculation, extending over half the unit cell and covering one molecule of the complex, is shown in Fig. 2, and a smaller-scale drawing extending over several molecules is shown in Fig. 3. The Fourier summations were carried out by the 3-figure strip and stencil method (Robertson, *J. Sci. Instr.*, 1948, **25**, 28), the axial sub-divisions being $a/60 = 0·193$ A. and $b/60 = 0·230$ A., and the contour levels were plotted by graphical interpolation.

INTERPRETATION AND DISCUSSION.

Examination of Fig. 2 will show that co-ordinates can now be assigned to all the atoms with considerable accuracy. The atoms are generally spherical in outline, although considerable distortions exist. No special significance can be attached to these distortions and spurious detail which are due in the first place to diffraction effects from the copper atom, where the peak value of the density is 47 as against 6 or 7 on the carbon atoms. (In Fig. 2 the contour scale on the central atom is reduced by a factor of 5 with respect to the rest of the diagram.) In the second place, the intensity estimates at present available are not very accurate. Taking these factors into account, however, it would appear that we can assign co-ordinates to the atoms which should be correct to within about 0·03 or 0·04 A. Table II gives a list of the values obtained.

TABLE II.

Co-ordinates and orientation (calculated from the final projection, Fig. 2).

Atom.	x/a.	y/b.	X (A).	Y (A.).	Atom.	x/a.	y/b.	X (A.).	Y (A.).
Cu	0	0	0	0					
O(1)	0·137	−0·025	1·59	−0·35	CH(3)	0·209	0·229	2·42	3·17
O(2)	0·058	0·134	0·68	1·85	CH(4)	0·317	0·260	3·68	3·59
C(1)	0·203	0·054	2·36	0·75	CH(5)	0·408	0·201	4·73	2·78
C(2)	0·157	0·140	1·82	1·94	CH(6)	0·397	0·104	4·60	1·43
					CH(7)	0·310	0·036	3·59	0·49

Molecular orientation. The normal to the molecular plane makes an angle of 26·5° with the c crystal axis. The line in the molecular plane of zero inclination (perpendicular to c) makes an angle of 29° with the b crystal axis.

At the present stage of the analysis the third co-ordinate of the atoms (z) cannot be directly obtained. From a study of the outstanding features of the projection, however, a very probable assignment can be made from which it is possible to obtain the bond lengths and other data.

It is found that within narrow limits the seven carbon centres in the projection of the tropolone ring (Fig. 2) lie on an ellipse. After several trials with ellipses of different parameters, the result shown in Fig. 4 was obtained. The fit is quite accurate for most of the carbon centres, the deviation in the case of atoms 2 and 6 being not more than about 0·04 A. The circle of which this ellipse is a projection has a radius of 1·61 A., and there is a strong presumption that the atoms in the tropolone ring actually lie on this circle, for the following reasons. The ratio of the major to the minor axis of the ellipse is as 1·115 to 1, which corresponds accurately to the ratio of the length of the c crystal axis of cupric tropolone to the interplanar spacing of graphite (3·80 to 3·40). In all the phthalocyanine structures which have been examined by X-ray analysis, and in a large number of aromatic hydrocarbon structures, it is found that the perpendicular distance between overlying molecular planes is close to the graphite interplanar distance of 3·4 A. Indeed, this fact is often found to govern the crystal structure, and the length of the principal crystal axis depends only on this constant and the inclination of the molecular planes.

These various facts, and above all the regularity of the atomic arrangement in the tropolone ring, suggest very strongly that the carbon atoms must be almost exactly coplanar, and that the inclination of this plane to the c axis is $\cos^{-1}$ (minor axis of ellipse/major axis of ellipse) or $\cos^{-1}$ (3·40/3·80). For the angle of inclination, θ, this gives a value of 26·5°.

The fitting of the ellipse to the projection of the tropolone ring (Fig. 4) also gives the direction of inclination of the molecular plane, and so provides all the data required to calculate the interatomic distances. It is found that the major axis of the ellipse makes an angle of 29° with the b crystal axis. Lines in the projection parallel to this direction will have zero inclination, and perpendicular to this direction (the direction of the minor axis), they will have the maximum inclination, θ (26·5°). In any other direction making an angle, α, with the direction of the minor axis, the angle ψ between a line in the molecular plane and its projection will be given by the relation

$$\tan \psi = \tan \theta \cos \alpha = 0{\cdot}499 \cos \alpha$$

and the true length, R, of a line whose measured length in the projection is r will be given by $R = r/\cos \psi$.

The interatomic distances given in Fig. 5 are calculated on this basis. It is assumed that the two oxygen atoms and the copper atom are coplanar with the tropolone ring. As the copper atom coincides with a centre of symmetry in the structure, it must be exactly coplanar with its four surrounding oxygen atoms. It is not necessary, however, that this plane should coincide with the plane of the tropolone ring. We make this assumption on the chemical evidence and also because it leads to a reasonable interpretation of the bond lengths.

The average value of the carbon–carbon bond length in the tropolone ring is 1·40 A. Deviations from this value are small, and it cannot be said with certainty that they exceed the possible error. The bond C(4)–C(5) at 1·45 A. is exceptionally long, and it is difficult to account for this value. It is not thought that much significance should be attached to this deviation because in this region the atoms are rather distorted and it is possible that the error here will be greater than the average error. There is some evidence of a faint alternation of slightly longer and shorter bonds as we go round the ring, but the bond C(2)–C(3) might be expected to be of the longer type, like C(1)–C(2). This alternation, however, is so slight that very little significance can be attached to it at present. In general, it can be said that the resonance effect appears to stabilise the structure into an almost, if not quite, regular planar heptagon with average carbon–carbon bond length of 1·40 A.

FIG. 4.

Ellipse of major axis 1·61 A. *and minor axis* 1·44 A. *fitted to the carbon centres in the projection of the tropolone ring.*

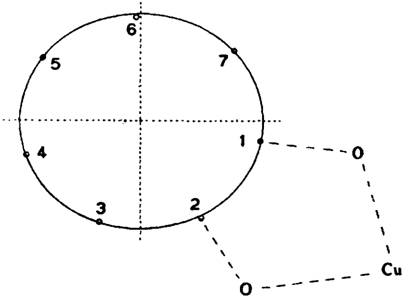
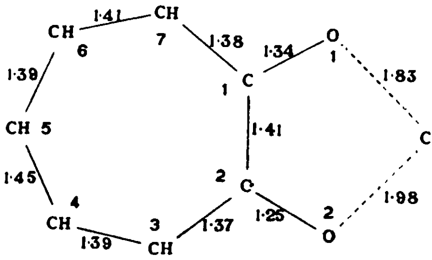


FIG. 5.

Interatomic distances.



Outside the tropolone ring, the bond-length measurements are capable of clearly differentiating the oxygen atoms. The distance of 1·34 A. between C(1) and O(1) corresponds to a hydroxylic link, whereas the distance of 1·25 A. from C(2) to O(2) corresponds to a carbonyl linkage. Further evidence that O(1) is indeed the hydroxylic oxygen is provided by the distance of 1·83 A. found between it and the copper atom, the other copper–oxygen distance being considerably greater at 1·98 A. In such circumstances the planar configuration of cupric copper with the formation of four covalent bonds of the dsp^2 type is to be expected, and recalls the structure of various compounds of copper with β-diketones (Cox and Webster, *J.*, 1935, 731).

The values found for the valency angles are collected with the bond-length measurements in Table III and do not call for much comment. The angles should be accurate to within about 3—4°. The theoretical angle for a regular heptagon is 128·6° and the angles found are all within

TABLE III.

Bond lengths and valency angles.

Cu–O(1)	= 1·83 A.	C(3)–C(4)	= 1·39	O(1)–Cu–O(2)	= 84°	C(7)–C(1)–C(2)	= 131°
Cu–O(2)	= 1·98	C(4)–C(5)	= 1·45	C(1)–O(1)–Cu	= 112°	C(1)–C(2)–C(3)	= 127°
C(2)–O(2)	= 1·25	C(5)–C(6)	= 1·39	C(2)–O(2)–Cu	= 111°	C(2)–C(3)–C(4)	= 131°
C(1)–O(1)	= 1·34	C(6)–C(7)	= 1·41	C(1)–C(2)–O(2)	= 116°	C(3)–C(4)–C(5)	= 129°
C(1)–C(2)	= 1·41	C(7)–C(1)	= 1·38	C(3)–C(2)–O(2)	= 117°	C(4)–C(5)–C(6)	= 125°
C(2)–C(3)	= 1·37			C(2)–C(1)–O(1)	= 118°	C(5)–C(6)–C(7)	= 133°
				C(7)–C(1)–O(1)	= 111°	C(6)–C(7)–C(1)	= 126°

about 4° of this figure. The copper–oxygen bonds deviate somewhat from the expected square configuration, the angle being 84°.

Intermolecular distances have not been worked out in detail, but inspection of Fig. 3 makes it clear that they are all of the usual van der Waals type and are generally greater than 3·5 A.

TABLE IV.

Measured and calculated values of the structure factor.

hkl.	2 sin θ ($\lambda = 1·542$).	F, meas.	F, calc.
200	0·268	9	+14
400	0·536	<6	+12
600	0·804	43	+39
800	1·073	<6	+2
10,0,0	1·341	22	+25
12,0,0	1·609	11	+14
14,0,0	1·877	7	+7
020	0·223	53	+51
040	0·447	65	+59
060	0·670	26	+30
080	0·894	54	+46
0,10,0	1·117	<7	+10
0,12,0	1·341	<7	+5
0,14,0	1·564	<8	+8
0,16,0	1·788	8	+9
110	0·174	74	+77
120	0·260	55	−54
130	0·360	44	+47
140	0·469	<6	+4
150	0·577	32	+36
170	0·794	53	+53
190	1·016	29	+22
1,11,0	1·239	<7	+7
1,12,0	1·350	11	+8
1,13,0	1·460	16	+18
1,15,0	1·689	13	+14
210	0·289	13	+9
220	0·348	39	+43
230	0·430	3	−4
240	0·521	4	+3
250	0·620	37	+35
260	0·723	37	+45
270	0·831	16	+9
280	0·937	30	+28
290	1·045	<6	−3
2,10,0	1·152	37	+36
2,11,0	1·261	13	+13
2,12,0	1·372	17	+15
2,13,0	1·483	16	+13
2,14,0	1·595	15	+17
2,16,0	1·818	12	+12
310	0·416	24	+28
320	0·460	35	−26
330	0·526	37	+37
340	0·602	21	+19
350	0·690	22	+26
360	0·782	35	+26
370	0·883	30	+29
380	0·983	14	+11
390	1·088	23	+25
3,11,0	1·297	26	+25
3,13,0	1·514	6	+10
3,15,0	1·731	15	+13
410	0·547	5	+7
420	0·581	25	+28
430	0·632	<5	−4
440	0·700	34	+36
460	0·860	19	+23
480	1·045	17	+20
490	1·142	15	−17
4,10,0	1·242	16	+16
4,11,0	1·341	<6	0
4,12,0	1·449	23	+18
4,14,0	1·660	13	+15
4,16,0	1·876	7	+13
510	0·683	40	+43
520	0·710	18	−11
530	0·751	9	+16
540	0·810	<5	−3
550	0·876	28	+30
560	0·950	7	−4
570	1·032	7	+10
590	1·211	26	+26
5,11,0	1·401	13	+15
5,13,0	1·607	21	+15
610	0·813	25	−18
620	0·838	41	+40
630	0·873	11	−11
640	0·923	49	+45
650	0·981	4	−5
660	1·050	25	+26
680	1·204	25	+24
6,10,0	1·375	<7	+4
6,12,0	1·569	19	+16
710	0·946	32	+32
720	0·965	<6	−6
730	0·999	37	+34
740	1·042	5	−6
750	1·095	32	+30
770	1·223	26	+22
780	1·300	16	−14
790	1·379	15	+16
7,11,0	1·550	26	+19
7,13,0	1·734	<8	+7
7,15,0	1·927	5	+7
820	1·095	27	+30
830	1·127	<6	−4
840	1·165	26	+23
850	1·211	21	+16
860	1·266	26	+23
880	1·400	13	+11
8,10,0	1·550	26	+22
8,12,0	1·720	14	+13
8,14,0	1·901	5	+9
910	1·210	14	+15
920	1·228	14	+14
930	1·255	37	+31
940	1·289	11	+6
950	1·330	32	+25
960	1·381	16	+12
970	1·439	<7	+6
990	1·570	6	+11
9,11,0	1·721	12	+12
9,13,0	1·901	7	+11
10,1,1	1·346	<7	−3
10,2,0	1·360	15	+13
10,3,0	1·382	11	+9
10,4,0	1·414	26	+22
10,10,0	1·745	13	+13
10,12,0	1·900	5	+10
11,3,0	1·512	13	+13
11,4,0	1·542	<6	−5
11,5,0	1·579	5	+10
11,6,0	1·621	6	−9
11,7,0	1·672	6	+13
11,11,0	1·921	7	+11
12,1,0	1·613	14	+7
12,3,0	1·642	<6	0
12,6,0	1·743	6	+12
12,8,0	1·841	9	+11
12,10,0	1·960	5	+11
13,1,0	1·748	14	+11
13,3,0	1·777	6	+10
13,5,0	1·830	5	+8
13,7,0	1·910	8	+13
14,2,0	1·890	5	+7
14,4,0	1·928	4	+6
14,6,0	1·990	3	+8

It is a pleasure to express my thanks to Professor J. W. Cook and Dr. Raphael who supplied the crystals for this work, and to my two students, Mr. R. B. Campbell and Mr. G. Todd, for valuable assistance with part of the numerical work, and for a density determination.

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[*Received, November 3rd,* 1950.]