order of reflection. Clearly at least three orders of reflection are required in order to decide which of the two types of distortion broadening theory is applicable to the data.

Thus for size broadening, two quite different (but precisely defined) parameters may be obtained from integral breadth methods and from the Fourier transform method. When lattice distortions are the only cause of broadening, different results, which are not all compatible, will be obtained from the different analyses. Clearly the situation is further complicated by the simultaneous presence of both size and distortion broadening.

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The crystal structure of terpyridylzinc chloride: a refinement.

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The crystal structure of terpyridylzinc chloride has been reported by Corbridge & Cox (1956). The monoclinic space group of the form investigated was $P2_1/a$ with a = 16·21, b = 8·25, c = 10·97 Å and β = 93·5°. Each zinc atom was shown to be at the centre of a distorted trigonal bipyramidal group of three nitrogen and two chlorine atoms. The published atomic coordinates, particularly those of carbon and nitrogen atoms, were however of low precision, having been determined directly from three-dimensional electron density maps. The exact configuration of the terpyridyl ligand was therefore uncertain. In conjunction with a structure analysis of the tin(IV) complex $[Sn(CH_3)_2Cl_2]_2$. terpyridyl (Fergusson, Roper & Wilkins, 1965) we wished to know these details and therefore have carried out a least-squares refinement of the data of Corbridge & Cox.

Refinement commenced with the published atomic coordinates and, of the 554 listed structure factors, all were used except one thought to be affected by extinction and four others for which $F_{\rm obs}$ was indicated as uncertain. The block-diagonal least-squares procedure was used (the program being that written for the IBM 1620 computer by G. A. Mair) and each atom was assigned an independent isotropic thermal parameter. Least-squares weights were as follows: $\sqrt{W}=10/F_{\rm obs}$ for $F_{\rm obs}>10$; $\sqrt{W}=F_{\rm obs}/10$ for $F_{\rm obs}<10$. Unobserved reflexions were assigned a value of 0·6, all these numbers referring to the original scale. Self-consistent field model scattering factors were used for all atoms except zinc, for which anomalous dispersion 'in phase' corrections were applied to the Thomas–Fermi–Dirac scattering factors (*International Tables for X-ray Crystallography*, 1962).

Table 1. *Atomic coordinates and isotropic thermal parameters*

	x/a	y/b	z/c	B
Zn	0·1181	0·0955	0·2171	2·09 Å^2
Cl(1)	0·2383	0·0239	0·1389	2·90
Cl(2)	0·1318	0·3226	0·3342	2·03
N(1)	0·1169	−0·101	0·359	1·0
N(2)	−0·0059	0·027	0·224	1·5
N(3)	0·0520	0·203	0·058	1·4
C(1)	0·1893	−0·162	0·415	2·5
C(2)	0·1805	−0·286	0·505	2·8
C(3)	0·1099	−0·334	0·543	4·0
C(4)	0·0321	−0·260	0·480	2·0
C(5)	0·0468	−0·147	0·391	1·7
C(6)	−0·0291	−0·070	0·325	1·0
C(7)	−0·1118	−0·094	0·343	1·5
C(8)	−0·1699	−0·016	0·266	2·3
C(9)	−0·1504	0·089	0·175	2·1
C(10)	−0·0647	0·101	0·155	1·5
C(11)	−0·0325	0·200	0·060	4·1
C(12)	−0·0834	0·279	−0·030	2·1
C(13)	−0·0466	0·360	−0·122	2·1
C(14)	−0·0421	0·372	−0·120	2·4
C(15)	0·0921	0·290	−0·026	2·6

After two preliminary refinement cycles during which only zinc and chlorine positions and an overall scale factor were varied, seven further cycles were computed during which all positional and thermal parameters were allowed to vary. During this refinement, which was aided by an acceleration procedure (Hodgson & Rollett, 1963), the discrepancy index R decreased from 0·24 to 0·14. The final

Table 2. *Interatomic distances and angles*

Zn–Cl(1)	2·25 Å	σ = 0·01 Å	(2·28 Å)*
Zn–Cl(2)	2·27	0·01	(2·29)
Zn–N(1)	2·24	0·04	(2·19)
Zn–N(2)	2·09	0·04	(2·11)
Zn–N(3)	2·18	0·04	(2·34)

Cl(1)ZnCl(2)	112°	(111°)
Cl(1)ZnN(1)	97	
Cl(1)ZnN(2)	143	
Cl(1)ZnN(3)	101	
Cl(2)ZnN(1)	102	
Cl(2)ZnN(2)	105	
Cl(2)ZnN(3)	98	
N(1)ZnN(2)	74	(79)
N(1)ZnN(3)	145	
N(2)ZnN(3)	73	(72)

N(1)C(1)	1·38 Å	N(3)C(15)	1·36 Å
N(1)C(5)	1·27	N(3)C(11)	1·37
N(2)C(6)	1·43	N(2)C(10)	1·32
C(1)C(2)	1·44	C(14)C(15)	1·44
C(2)C(3)	1·30	C(13)C(14)	1·44
C(3)C(4)	1·53	C(12)C(13)	1·38
C(4)C(5)	1·37	C(11)C(12)	1·41
C(6)C(7)	1·38	C(9)C(10)	1·42
C(7)C(8)	1·38	C(8)C(9)	1·37
C(5)C(6)	1·53	C(10)C(11)	1·45

* Values in parenthesis are those reported by Corbridge & Cox (1956).

Table 3. *Coefficients of least-squares planes**

	A	*B*	*C*	*D*	Maximum deviation	Mean deviation
Equatorial plane	−0·18337	0·56199	0·80655	0·00180	0·006 Å	0·003 Å
Ring *A*	0·02614	−0·71935	−0·69414	−0·00209	0·024	0·014
Ring *B*	0·00456	0·78510	0·61934	0·00171	0·037	0·023
Ring *C*	0·03580	−0·82270	−0·56733	−0·00173	0·031	0·019

* The equation of the plane is $AX'+BY+CZ'+D=0$ where $X'=X+Z\cos\beta$ and $Z'=Z\cos\beta$. X, Y, Z are monoclinic unit-cell coordinates expressed in Å.

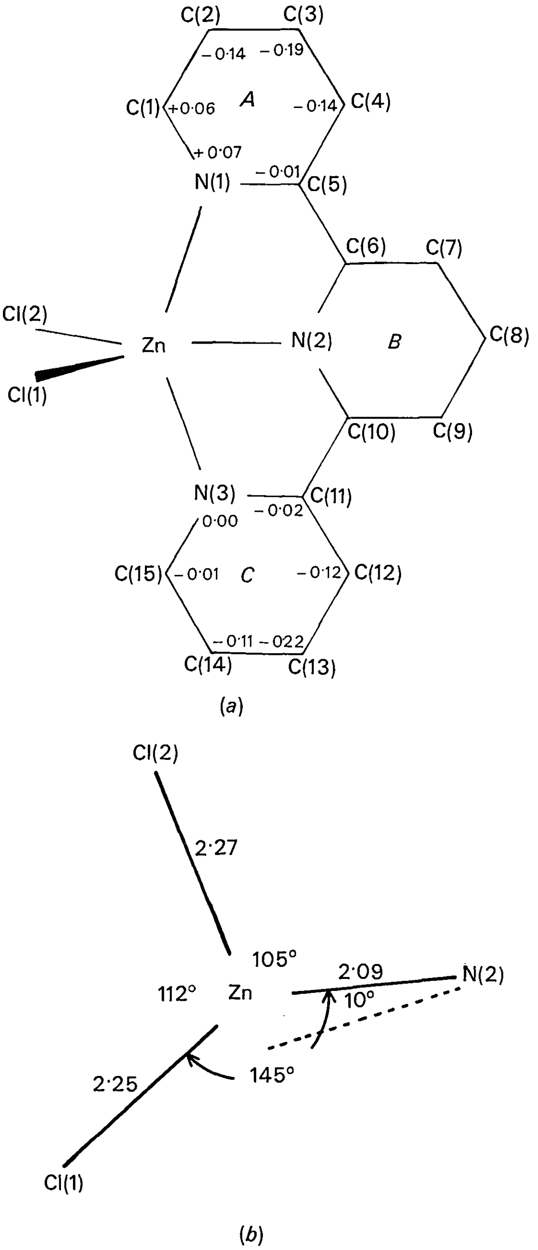

Fig. 1. (*a*) A view of the molecule normal to the terpyridyl plane. Numbers associated with atoms of rings *A* and *C* are perpendicular displacements (Å) from the mean plane of ring *B*. (*b*) The equatorial plane showing interatomic distances (Å) and angles and the orientation of the lone pair of N(2) (broken line).

F_{obs} scale is 91·5 % of the original value. Shifts in zinc and chlorine coordinates were quite small but light atom shifts averaged 0·15 Å with a maximum of 0·45 Å. Final coordinates and thermal parameters are listed in Table 1.

Estimates of the errors in light-atom positions may best be obtained in terms of the agreement with standard values of the lengths of the C–C and C–N bonds in the aromatic rings (Table 2). This indicates a mean standard error of 0·05 Å for an individual C–C or C–N bond, which is in accord with the estimates provided by the least-squares procedure itself. The least-squares estimated standard errors for the Zn–Cl and Zn–N bonds are 0·01 and 0·035 Å respectively. The molecule is illustrated in Fig. 1(*a*) showing the trigonal bipyramidal coordination about the zinc atom as Corbridge & Cox reported. The fact that the refined coordinates, particularly of the light atoms, have much higher precision, enables us to examine profitably the finer features of the stereochemistry. Reference will be made to the least-squares planes, calculated by the method of Schomaker, Waser, Marsh & Bergman (1959), through rings *A*, *B* and *C* of the terpyridyl group and through the equatorial plane of the bipyramid. Coefficients of the equations of these planes, referred to orthogonal axes, are listed in Table 3.

The equatorial plane [Fig. 1(*b*)] containing atoms Zn, Cl(1), Cl(2) and N(2) is well defined and the maximum atomic displacement from it (0·006 Å) is insignificant. Of special interest, however, are the angles about the zinc atom, which deviate significantly from trigonal values. At least a partial explanation for the large difference (38°) between angles Cl(1)ZnN(2) and Cl(2)ZnN(2) is provided by the fact that the least-squares plane through ring *B* (which is at 87° to the equatorial plane) points 0·38 Å to one side of the zinc atom, the side away from Cl(2). If we assume the lone pair of N(2) to lie in the plane of ring *B*, it therefore makes an angle of 10° with the Zn–N(2) vector and is presumably directed so as to make best overlap with one of the vacant zinc orbitals trigonally oriented in the equatorial plane. The indication then is that the Zn–N(2) bond is bent and that the Cl(1)ZnN(2) bond angle is less than the corresponding interatomic angle.

The planes of ring *A* and ring *C* respectively point 0·08 and 0·19 Å to one side of the zinc atom, the side towards Cl(2). Although these two displacements are, of themselves, only possibly significant, considered together with the orientation of ring *B* significantly to the opposite side of the zinc atom, they indicate a systematic departure from planarity of the coordinated terpyridyl group. The exact configuration may best be described in terms of a twisting of rings *A* and *C* with respect to ring *B* about the bonds C(5)–C(6) and C(10)–C(11) respectively, the two angles of twist being 6·0° and 4·4°. This distortion may be associated with the attempt of the three nitrogen atoms to approach as closely as possible one equatorial and two polar positions of the trigonal bipyramid while at the same time maintaining covalent bond distances from the zinc atom. These approaches are aided by in-plane distortions about the same bonds C(5)–C(6) and C(10)–C(11) which make the mean value of the four internal angles of the type N(1) C(5)C(6) 9° smaller than the mean of the four external angles of the type C(4)C(5)C(6). Some distortion of this type is to be expected on account of the non-equivalence of the N–C and C–C bonds within the rings, and has been observed in the dipyridyl molecule (Merritt & Schroeder, 1956). Even with the distortions described, if N(1) and N(3) are to approach the zinc atom to within bonding distances, then N(2) must approach even closer. Hence the shortening of Zn–N(2), although statistically only possibly significant, is probably real.

Although 2,2′,2″-terpyridyl might exist as a *trans* form in isolation it is unlikely that it would coordinate as such because of the strong repulsions which would exist between the coordinated metal atom and the non-bonding C–H groups in the 2-positions. On the assumption then that it is functioning in the *cis* form, 2,2′,2″-terpyridyl will coordinate as a tridentate ligand, or not at all. The preference shown by zinc for tetrahedral coordination must therefore be sacrificed in the present situation and the coordination mode must rather be based on the arrangement of the three nitrogen atoms in the approximately planar ligand. The stoichiometry of the compound then favours 5-coordination with a trigonal bipyramidal arrangement a natural consequence.

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Diamagnetic anisotropies of naphthalene tetrachloride and 1,3,5-triphenylbenzene molecules.

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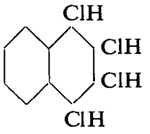
Naphthalene tetrachloride, $C_{10}H_8Cl_4$



The crystal structure has been determined and refined by Lasheen (1952, 1956).

$$a=7{\cdot}925,\ b=10{\cdot}25,\ c=14{\cdot}25\ \text{Å},$$
$$\beta=112{\cdot}6^\circ;\ Z=4;\ I2/c.$$

The unsubstituted ring and the two neighbouring carbon atoms in the molecule are found to be closely planar.

Lasheen (1952) measured the crystal diamagnetic anisotropies and Lasheen & Heddewi (1966) the mean molecular susceptibility (all in 10^{-6} e.m.u./g) $\chi_1-\chi_2=56{\cdot}2$, $\chi_1-\chi_3=2{\cdot}6$, $\chi_3-\chi_2=53{\cdot}6$, $\bar{\chi}_M=-164{\cdot}55$ where χ_3 is along [010] and ψ (angle χ_1: [001], positive in obtuse β)$=0{\cdot}5^\circ$.

Hence $\chi_1=-144{\cdot}95$, $\chi_2=-201{\cdot}15$, $\chi_3=-147{\cdot}55$.

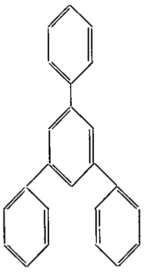
Lonsdale & Krishnan (1936) showed how to calculate molecular susceptibilities from crystal susceptibilities, given the molecular direction cosines, which in this case are:

		a'	b	c
(length)	L	0	1	0
(breadth)	M	−0·1154	0	0·9933
(normal)	N	0·9934	0·0026	0·1149

a' is perpendicular to c in (010). Hence the values given in Table 1.

Table 1 shows that the molecular anisotropy of naphthalene tetrachloride has almost the same value as that of a benzene ring with two hydrogen atoms substituted. Thus the cyclohexane ring has no or very small magnetic anisotropy and hence does not contribute to that of the whole molecule.

1.3.5-**Triphenylbenzene,** $C_{24}H_{18}$



The crystal structure was determined by Farag (1954), who gave: $a=7{\cdot}47$, $b=19{\cdot}66$, $c=11{\cdot}19$ Å; $Z=4$; $Pna2_1$. The molecules, which form an approximately layer arrangement, are not planar, the substituted phenyl groups being twisted about the formal single bonds by (+34°, −27°, +24°)±2° respectively, out of the plane of the central ring. The benzene rings are planar to within ±0·08 Å.

The crystal diamagnetic anisotropies and susceptibilities were measured by Krishnan & Banerjee (1934) and later confirmed by Lonsdale (1937). The crystal susceptibilities are:

$$\chi_a=-313,\ \chi_b=-155,\ \chi_c=-140$$

(all in 10^{-6} e.m.u./g.).