

- KANNAN, K. K. (1965). Thesis, Indian Institute of Science, Bangalore.
- LINDLEY, P. F. & WOODWARD, P. (1966). *J. Chem. Soc. (A)*, p. 123.
- LINDQVIST, I. & ROSENSTEIN, R. (1960). *Acta Chem. Scand.* **14**, 1228.
- LONG, R. E. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 448.
- LOW, B. W., HIRSHFELD, F. L. & RICHARDS, F. M. (1959). *J. Amer. Chem. Soc.* **81**, 4412.
- MARSH, R. E. (1958). *Acta Cryst.* **11**, 654.
- MITANI, S. (1964). *J. Phys. Soc. Japan*, **19**, 481.
- MOHANA RAO, J. K. (1968). *Indian J. Pure Appl. Phys.* **6**, 51.
- NARAYANAN, P. & VENKATARAMAN, S. (1970). *Curr. Sci.* **39**, 147.
- NARAYANAN, P. S. & WARRIER, A. V. R. (1967). *Proc. Int. Conf. Spectrosc. Bombay*, **2**, 312.
- NARAY-SZABO, ST. V. & POCZA, J. (1942). *Z. Kristallogr.* **104**, 28.
- PAULING, L. (1960). *The Nature of Chemical Bond*. Chapter 7, pp. 224, 256. Ithaca: Cornell Univ. Press.
- PEPINSKY, R., OKAYA, Y., EASTMAN, D. P. & MITSUL, T. (1957). *Phys. Rev.* **107**, 1538.
- PEPINSKY, R., VEDAM, K., HOSHINO, S. & OKAYA, Y. (1958). *Phys. Rev.* **111**, 430.
- PEPINSKY, R., VEDAM, K. & OKAYA, Y. (1958). *Phys. Rev.* **110**, 1309.
- PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.
- SABROWSKY, H. & HOPPE, R. (1968). *Z. anorg. allgem. Chem.* **358**, 241.
- SATO, S. (1968). *J. Phys. Soc. Japan* **25**, 185.
- STOSICK, A. J. (1945). *J. Amer. Chem. Soc.* **67**, 365.
- TIWARY, H. V., DEVANARAYANAN, S. & NARAYANAN, P. S. (1969). *Ind. J. Pure Appl. Phys.* **7**, 655.
- TOMITA, K. & NITTA, I. (1961). *Bull. Chem. Soc. Japan* **34**, 286.
- VISWAMITRA, M. A. (1971). To be published.
- VISWAMITRA, M. A. & KANNAN, K. K. (1962). *J. Sci. Instrum.* **39**, 318.
- WARRIER, A. V. R. & NARAYANAN, P. S. (1967). *Proc. Ind. Acad. Sci.* **66 A**, 46.
- WYCKOFF, R. W. G. (1965). *Crystal Structures*, Vol. 1, 2nd ed. pp. 10, 331.

Acta Cryst. (1972). **B28**, 1496

The Determination of Absolute Configuration and $\Delta f''$ Values for Light-Atom Structures*

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The absolute configurations of 7 compounds containing only C, H and O atoms have been determined by careful measurement of about 20 Bijvoet differences for each compound using Cu $K\alpha$ radiation. A highly significant indication was obtained even in unfavourable cases with poorly refined structures ($R > 10\%$) or structures with very low oxygen content. A comparison of R values for the two enantiomers without considering the Bijvoet differences did not give significant indications. The generally weak intensities were measured with high precision using an alternating procedure and were corrected for absorption. Multiple diffraction was identified as an important cause of systematic errors. A value of 0.0182 ± 0.0008 for the quantity $\Delta f_{O:C}$ was deduced from the measurements. Values of $n = 2.78 \pm 0.06$ and $C = 4.66 \pm 0.25$ were calculated for the parameters in the empirical relation

$$\Delta f'' = C(\lambda/\lambda_K)^{n-1}$$

using the above result and Zachariasen's data on quartz. $\Delta f''$ values obtained from the above equation agree well with Cromer's values calculated from atomic wave functions assuming $n = 2.75$ for the K shells. The importance of obtaining further experimental values of $\Delta f''$ is stressed.

Introduction

The determination of absolute configuration by X-ray methods has recently been extended to light-atom structures using the very small anomalous scattering power of oxygen (Hope & de la Camp, 1969; Thiessen

& Hope, 1970; Moncrief & Sims, 1969; Neidle & Rogers, 1970). The methods used were the 'Bijvoet method' (measurement of Bijvoet differences) and the ' R method' (see Hamilton, 1965, example 4) modified by limiting the R -value comparison of the two enantiomers to a set of 'sensitive' reflexions.

In this paper the techniques of measurement and statistical evaluation developed during the course of an investigation of 7 substances are reported. The refined method is now capable of producing significant results in unfavourable (practical) cases. The power of

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the Bijvoet and R methods are critically compared for the structures determined.

There was some doubt as to the values of $\Delta f''$ for light atoms. Hope, de la Camp & Thiessen (1969) used theoretical values, $\Delta f''_{\text{O}}=0.032$ and $\Delta f''_{\text{C}}=0.010$, and obtained generally good agreement between observed and calculated Bijvoet differences. Moncrief & Sims (1969) estimated 0.05 for oxygen atoms. More accurate experimental $\Delta f''$ values have now been deduced from our measurements. A preliminary account of part of this work has already been published (Engel, Zechmeister, Röhr, Brandl, Narayanan & Hoppe, 1971).

Theory

Theoretical values of $\Delta f''$

The atomic form factor is written

$$f^t = f + i\Delta f'' = f(1 + i\delta) \quad (1a)$$

where

$$\delta = \Delta f''/f. \quad (1b)$$

The term f includes the real part $\Delta f'$ of the anomalous contribution: δ is the anomalous phase rotation.

Comprehensive calculations of the anomalous scattering factors have been made by Cromer (1965) using new atomic wave functions to calculate the virtual oscillator strengths g_K associated with the electronic transitions. The analysis depends on the oscillator density distribution deduced from empirical knowledge of the frequency dependence of the (photoelectric) absorption coefficient $\mu (= \sum \mu_K)$:

$$\mu_K = \begin{cases} A_K \lambda^n K & \text{for } \lambda < \lambda_K \\ 0 & \text{for } \lambda > \lambda_K \end{cases} \quad (2)$$

μ_K is the contribution of the K th shell to μ and λ_K the wavelength of the relevant absorption edge. The resulting expression for $\Delta f''$ is

$$\Delta f'' = \sum_K \frac{\pi}{2} (n_K - 1) g_K (\lambda/\lambda_K)^{n_K - 1}. \quad (3)$$

As Cromer points out, a defect of this analysis is that equation (2) is only an approximation. Firstly, n_K may vary slightly with wavelength (more terms necessary) and with atomic number. The best value of n for each shell is not known accurately. James (1958, p. 160) gives equations for $\Delta f'$ and $\Delta f''$ for the K shell due to Hönl, which are derived from an oscillator density function corresponding to a value of about 2.7 for n . $\Delta f''$ values from Hönl's equation are rather lower than Cromer's values as the contributions of higher shells are neglected. Cromer uses the value 11/4 for the K shell recommended by Parratt & Hempstead (1954). Middleton & Gazzara (1967) have recently determined a value of 2.8 for the K shell from absorption measurements. Secondly, there is considerable fine structure in the absorption spectra especially near the absorption edges. The approximations made in Cromer's analysis could thus lead to significant errors in the value of $\Delta f''$. As the fine structure in the absorp-

tion spectra varies with the electronic state of the atom concerned, $\Delta f''$ could also vary from compound to compound, indeed even among like atoms in different chemical environments in the same crystal.

The effect of $\Delta f''$ on the structure factors

The effect of the anomalous scattering factors on the structure-factor amplitudes is expressed as the Bijvoet difference, which is defined here for convenience as

$$B_{\text{H}} = (Q_{\text{H}} - 1)/\frac{1}{2}(Q_{\text{H}} + 1) \quad (4)$$

where Q_{H} is the quotient of the structure factors $|F_{\text{H}}|/|F_{\bar{\text{H}}}|$. A comparison of the signs of the measured and calculated B 's yields the absolute configuration. A comparison of their magnitudes provides information on the magnitude of $\Delta f''$. As pointed out by Parthasarathy (1962a) the relationship is linear if B is not too large.

$$\Delta f''_{\text{ex}}/\Delta f''_{\text{th}} = B_{\text{ex}}/B_{\text{th}} (= \text{DEL}). \quad (5)$$

$\Delta f''_{\text{th}}$ is the value used in calculating the B_{th} . The exact definition of B is not important as long as it is adhered to throughout.

For a crystal containing two atomic species, O and C say, the structure factor is written

$$F_{\text{H}} = (f_{\text{C}} + i\Delta f''_{\text{C}})S_{\text{C}} + (f_{\text{O}} + i\Delta f''_{\text{O}})S_{\text{O}}$$

where $S_j = \sum_k \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_k\}$, the sum being taken over all atoms of type j . This can be rearranged

$$F_{\text{H}} = (f_{\text{C}}S_{\text{C}} + f_{\text{O}}S_{\text{O}}) + i \frac{\Delta f''_{\text{C}}}{f_{\text{C}}} (f_{\text{C}}S_{\text{C}} + f_{\text{O}}S_{\text{O}}) + i(\Delta f''_{\text{O}} - \Delta f''_{\text{C}} \cdot f_{\text{O}}/f_{\text{C}})S_{\text{O}}. \quad (6)$$

The first term is the 'normal' contribution to the structure factor. The second term is perpendicular to the first and merely rotates the phase of the structure factor by an angle δ_{C} producing a negligible change in its magnitude. The third term is perpendicular to the normal O contribution and therefore defines an 'effective imaginary anomalous scattering factor' for O relative to C, for which we introduce the notation $\Delta f''_{\text{O:C}}$ or $\Delta f''_{\text{eff}}$:

$$\Delta f''_{\text{O:C}} = \Delta f''_{\text{O}} - \Delta f''_{\text{C}} \cdot f_{\text{O}}/f_{\text{C}}. \quad (7)$$

Dividing through by f_{O} gives the equivalent relation,

$$\delta_{\text{O:C}} = \delta_{\text{O}} - \delta_{\text{C}}.$$

The magnitude of the Bijvoet differences will depend on $\Delta f''_{\text{eff}}$ (or δ_{eff}) and it is this quantity that can be deduced from equation (5). Individual values of $\Delta f''$ cannot be obtained directly. Generalizing equation (6) for a structure containing n atomic species shows that one can in principle only determine $\Delta f''_{\text{eff}}$ for $n-1$ species relative to the n th species (cf. Zachariasen, 1965).

Equation (7) can be solved for the individual $\Delta f''$ values if we make the following assumption about their ratio. For atomic species that do not differ too

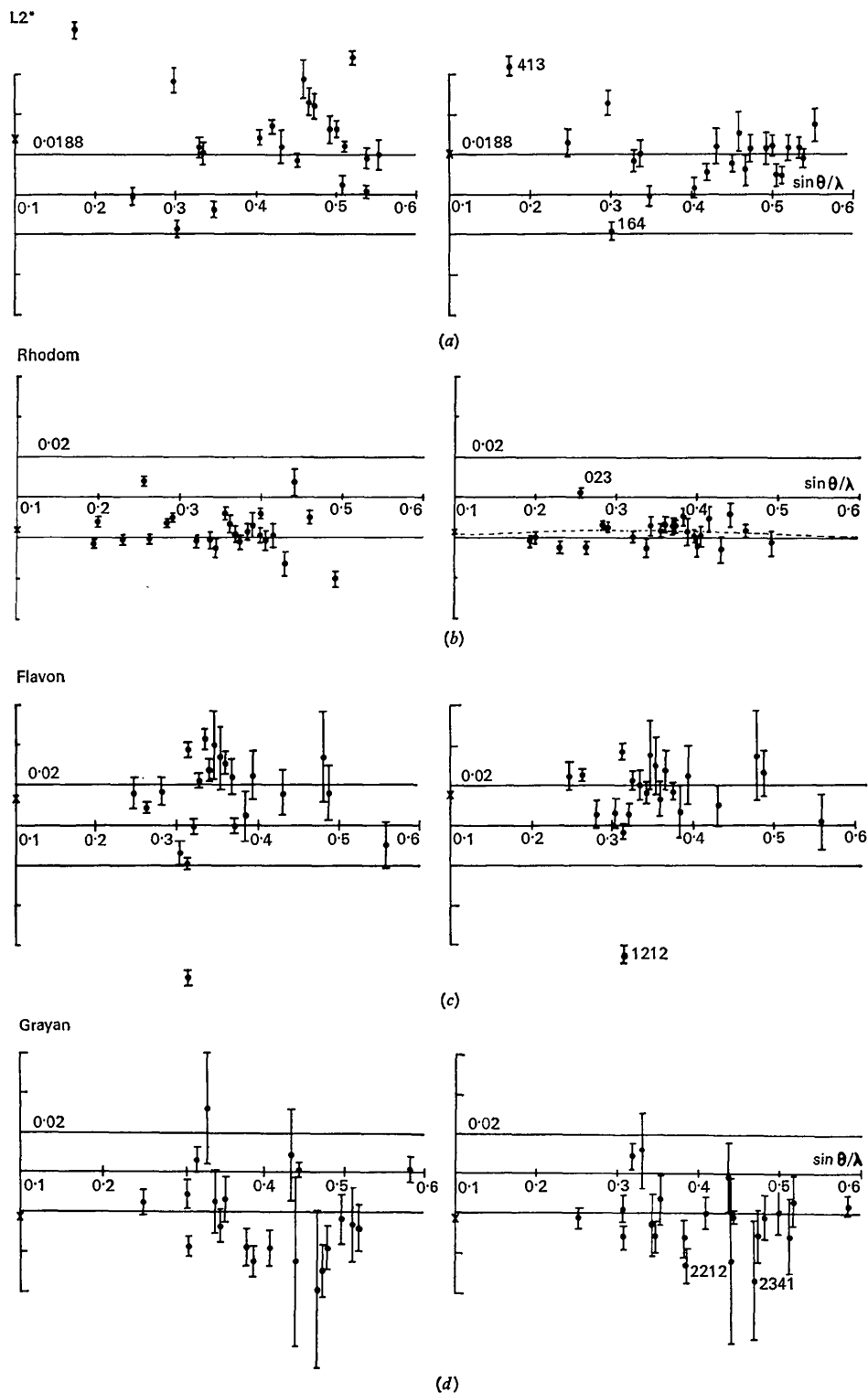


Fig. 1. Plots against $\sin \theta/\lambda$ of the experimental values of $\Delta f''_{o:c}$ calculated from equation (5) (left hand diagrams, before absorption correction) and from equation (12) (right-hand diagrams, after absorption correction). The bars indicate 1σ values. The crosses on the vertical axes indicate the mean values. Lines corresponding to DEL (DELA) = ± 1 are shown. The scale factor for $\Delta f''_{o:c}$ is 0.02 for all diagrams except (a) ($L2^*$) for which it is 0.0188. The dashed curve in (b) gives the value of $\Delta f''_{o:c}$ obtained using $\Delta f''_o = 0.0322$ and $\Delta f''_c = 0.0098$ (Hönl values). The specially marked reflexions are those omitted in calculating the best mean values.

evaluation of his measurements on quartz but used a poor value of $n=3$. Equation (9) should, of course, only be used for similar atoms. If one atomic species is heavy and the other light, it is better to assume a rough theoretical value of $\Delta f''$ for the light atom and to calculate $\Delta f''$ for the strong anomalous scatterer directly from equation (7).

$\Delta f''$ values vary very little with $\sin \theta/\lambda$. Even if they are assumed constant, $\Delta f''_{\text{eff}}$ still varies slightly as f_o/f_c is not constant. Assuming $\Delta f''_o=0.0322$ and $\Delta f''_c=0.0098$ (calculated from HönI's equation for Cu $K\alpha$ radiation) $\Delta f''_{o:c}$ varies between 0.019 and 0.016 for $\sin \theta/\lambda \leq 0.6$. This means that the largest structure-factor differences for the weaker reflexions will be

about 2% (intensity differences of 4%) for light atom (C-H-O) compounds.

Experimental determination of $\Delta f''$ in the literature

Roof (1961) estimated values of $\Delta f'$ and $\Delta f''$ using powder samples of the oxides of Th, U and Pu and obtained qualitative agreement with theory. Cromer, Larson & Roof (1964), however, failed in an attempt to determine $\Delta f''_U$ by allowing it to vary as a parameter in the refinement of a centrosymmetric structure. Really reliable $\Delta f''$ values can, of course, only be obtained by careful measurement of selected Bijvoet differences.

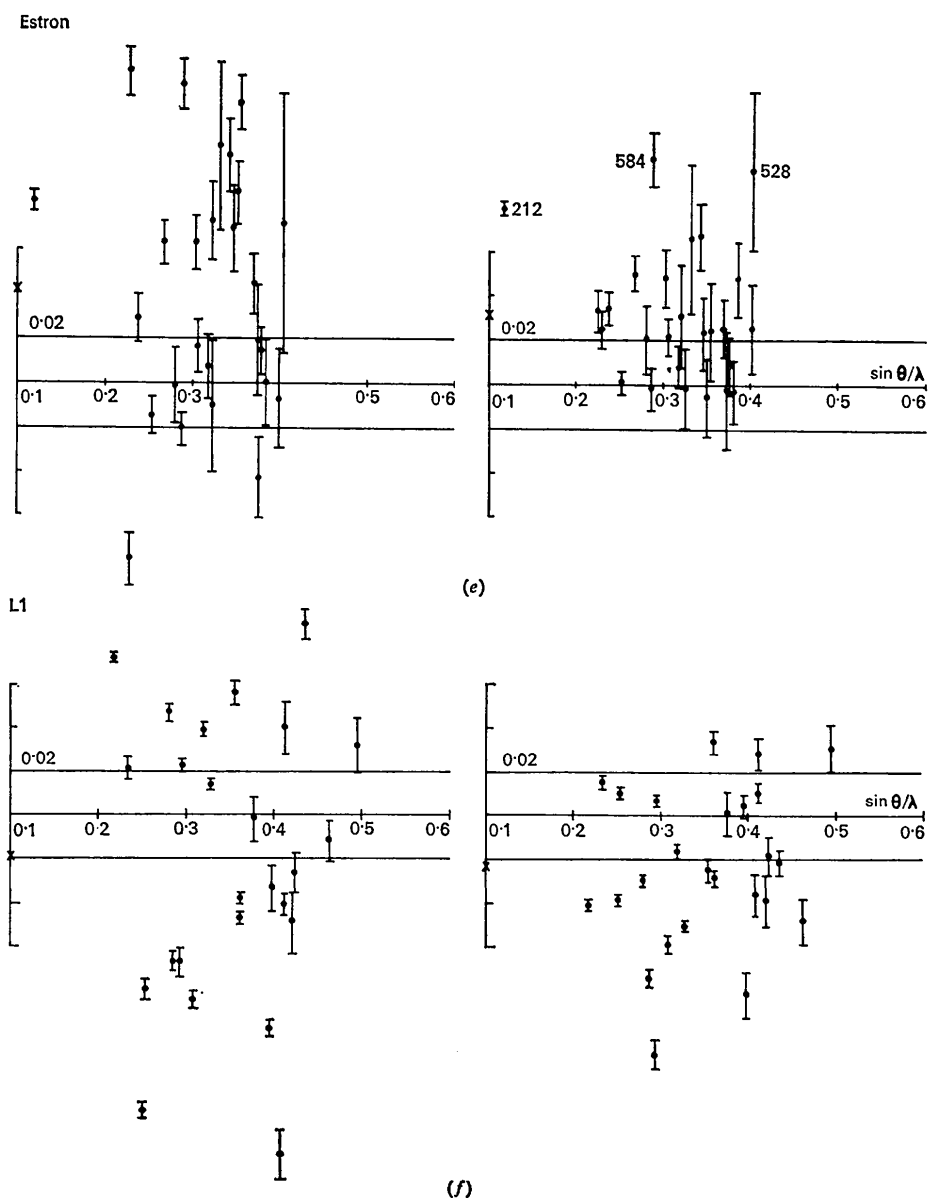
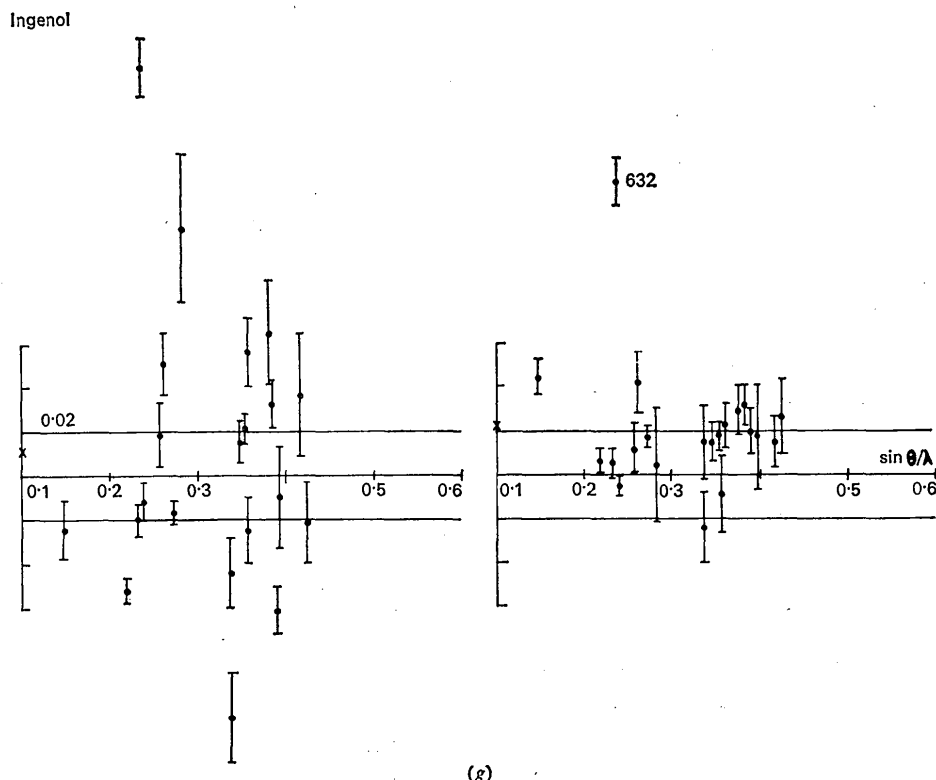


Fig. 1 (cont.)

(g)
Fig. 1 (cont.)

Parthasarathy (1962a) was the first to do this and estimated a value of $\Delta f''_{C1} = 0.67 \pm 0.05$ for Cu $K\alpha$ radiation. This is in actual fact a $\Delta f''_{\text{eff}}$ value. For the compound $C_9O_3NH_{11}.HCl$ one can insert average values $f_L = 6.5$ and $\Delta f''_L = 0.016$ for the light atoms into equation (7) obtaining $\Delta f''_{C1} = 0.71$. Using values of the scattering factors for $\sin \theta/\lambda = 0.5$ gives $\Delta f''_{C1} = 0.73$. Cromer's theoretical value is 0.72.

Hall & Maslen (1966) determined $\Delta f''_I$ for Cu $K\alpha$ radiation from measurements on $C_{34}H_{51}O_6I$ and were also able to estimate a fall-off with $\sin \theta/\lambda$. They obtained $\Delta f''_I = 6.3$ and $6.0 (\pm 0.3)$ for $\sin \theta/\lambda = 0$ and 0.5 respectively. Again inserting $\Delta f''_L = 0.013$ for the light atoms in equation (7) one obtains the values 6.4 and 6.2. Hall & Maslen measured the intensities photographically and used all the reflexions including the 'insensitive' ones in their calculations. Nevertheless their value agrees well with Cromer's theoretical one of 6.68.

Zachariasen's (1965) careful analysis of quartz will be discussed later.

Experimental

The measurements were made with Ni-filtered Cu $K\alpha$ radiation on a Siemens off-line 4-circle diffractometer using the standard 5-value measuring procedure.

Absorption correction

As the intensity differences are very small, small

absorption errors will be very critical. These can, however, be corrected experimentally by measuring a neighbouring Bijvoet pair for which B_{th} is small. As the X-ray paths are very similar for neighbouring reflexions the absorption error for the two quotients will be similar. The corrected structure factor quotient is then Q_{H1}/Q_{H2} where the subscript 1 refers to the main Bijvoet pair and 2 to the neighbouring absorption pair. Moncrief & Sims (1969) have applied a similar absorption correction. The corrected Bijvoet difference is

$$BA = (Q_{H1}/Q_{H2} - 1)^{1/2} (Q_{H1}/Q_{H2} + 1) \quad (11)$$

[cf. equation (4)]. The correction will be most accurate if a neighbouring reflection is chosen along the shortest reciprocal axis.

This absorption correction is not restricted to a neighbouring reflexion with small B_{th} . Indeed, the sensitivity of the measurement can be increased considerably if an absorption pair is chosen for which B_{th} is also large and of opposite sign to that of the main pair. Equation (11) still holds for this 'Bijvoet double difference' and observed and calculated values of BA can be used in equation (5) giving

$$\Delta f''_{\text{ex}}/\Delta f''_{th} = BA_{\text{ex}}/BA_{th} (= \text{DELA}). \quad (12)$$

If the reflexion to be measured has index 1 along the shortest reciprocal axis (b say) then it is best to measure the Bijvoet pair along this axis if possible ($h1l$, $h\bar{1}l$).

For this pair the absorption error will be very small and need not be corrected.

The experimental absorption correction should be able to correct for geometrical errors as well. If for example part of the reflexion is cut off as a result of crystal misalignment or of peak broadening due to poor crystal quality or thermal diffuse scattering, the error will be in the same sense for neighbouring reflexions.

Choice of reflexions

For each compound a structure-factor calculation 'FC with dispersion correction' (Stewart, 1967) was performed with $\Delta f''_{\text{O}}=0.02$ and $\Delta f''_{\text{C}}=0.00$. This corresponds to the rounded off theoretical value of $\Delta f''_{\text{eff}}$ for oxygen atoms in a matrix of carbon atoms. In order to calculate the theoretical Bijvoet difference the structure factor of the Bijvoet partner $|F_{\bar{h}}|$ was calculated directly from the information available on F_{h} using

$$|F_{\bar{h}}| = \{(2a-c)^2 + (2b-d)^2\}^{1/2}$$

where a (b) is the real (imaginary) part of the structure factor without dispersion correction applied and c (d) the real (imaginary) part corrected for dispersion. This expression is only valid if the $\Delta f'$ values are not applied explicitly as dispersion corrections. They can be applied directly to the form factor tables if required. This short cut eliminates further unnecessary structure-factor calculations.

The most sensitive Bijvoet reflexions and their best absorption neighbours were chosen by computer using as criteria the magnitudes of F and BA_{th} and the distance between the neighbouring reflexions in reciprocal space.

Alternating procedure

Good counting statistics were obtained for the weak reflexions by measuring over a long period of up to 4 hr for a Bijvoet pair. In order to correct for apparatus

Table 3. Summary of the results of the Bijvoet measurements

R , RE etc. are residuals (given in %) for the calculated and observed Bijvoet differences [equations (13), (14) and (15)]. A + in the column headed Enantiomer indicates that the configuration assumed in calculating the B_{th} is correct. A - indicates the mirror image. The values of $\Delta f''_{\text{O:C}}$ and $\Delta f''_{\text{O}}$ are unweighted means. σ_{ex} and σ_{th} are their standard deviations ($\times 10^4$). A second set of values was calculated for most substances omitting a few reflexions with very large systematic errors.

	n	Before absorption correction			After absorption correction			Enantiomer
		R	RE	RTH	RA	RAE	$RTHA$	
L2*	22	3.15	6.27	0.65	2.28	5.06	0.74	+
	20	2.34	5.91	0.64	1.21	4.73	0.74	
Rhodom	24	4.59	1.16	0.47	4.92	0.88	0.54	-
	23	4.68	1.03	0.48	5.01	0.76	0.55	
Flavon	22	2.41	4.24	0.96	2.07	4.33	1.00	+
	21	1.76	4.22	0.98	1.25	4.34	1.02	
Grayan	21	5.63	2.18	2.42	5.87	1.95	2.43	-
	19	4.76	1.83	1.21	4.92	1.48	1.24	
Estron	26	5.07	7.14	1.88	3.77	7.21	2.22	+
	23	4.42	6.25	1.79	2.33	5.79	2.14	
L1	25	5.94	4.81	0.55	6.69	4.02	0.70	-
Ingenol	21	4.51	4.79	1.12	2.72	4.79	1.27	+
	20	3.71	3.53	1.13	1.60	3.82	1.28	

	n	Before absorption correction			After absorption correction					
		$\Delta f''_{\text{O:C}}$	σ_{ex}	σ_{th}	$\Delta f''_{\text{O:C}}$	σ_{ex}	σ_{th}	$\Delta f''_{\text{O}}$	σ_{ex}	σ_{th}
L2*	22	0.0263	49	11	0.0188	33	13	0.0375	68	26
	20	0.0259	43	12	0.0185	23	14	0.0369	47	27
Rhodom	24	-0.0163	22	8	-0.0169	14	9	-0.0356	28	18
	23	-0.0173	20	8	-0.0176	11	9	-0.0374	23	19
Flavon	22	0.0125	56	21	0.0147	45	22	0.0310	97	46
	21	0.0167	39	22	0.0185	26	23	0.0392	54	48
Grayan	21	-0.0218	49	38	-0.0223	35	34	-0.0454	73	69
	19	-0.0186	49	30	-0.0196	33	26	-0.0402	70	54
Estron	26	0.0417	112	40	0.0317	60	34	0.0676	127	72
	23	0.0345	117	37	0.0237	45	34	0.0512	98	74
L1	25	-0.0199	127	14	-0.0232	73	13	-0.0497	156	27
Ingenol	21	0.0100	140	37	0.0212	66	29	0.0450	142	62
	20	0.0011	114	38	0.0156	37	30	0.0328	77	64

instability the measurement was subdivided and the reflexions hkl and $\bar{h}kl$ measured alternately 10 times.

The best observed value of the quotient Q_{ex} [for use in equations (4) or (11)] was taken as the mean of the 10 individual quotients $|F_{\text{H}}|/|F_{\bar{\text{H}}}|$. This procedure corrects for long term instability. Short term instability is also partially neutralized as it is unlikely that it would influence all 10 quotients in the same sense. The standard deviation of Q_{ex} was determined from the distribution of the 10 quotients from the mean (SGMEX) and compared with the standard deviation expected from counting statistics (SGMTH) – see Table 2, columns 9 and 10. These were generally found to be similar and the larger value was used for the subsequent error calculations.

The general formulae used throughout in calculating standard deviations of the mean \bar{x} of n individual values x_i are

$$\sigma_{\text{ex}} = \left\{ \sum (x_i - \bar{x})^2 / n(n-1) \right\}^{1/2}$$

$$\sigma_{\text{th}} = \left[\sum \{ \sigma(x_i) \}^2 \right]^{1/2} / n.$$

Results

Table 1 gives crystallographic details for the 7 structures whose absolute configurations have been determined. The R values are those of the refinement stage at which the B_{th} were calculated. The final R values are given in brackets where necessary. The crystal size refers to the one used for the Bijvoet measurement. In the case of L2*, Rhodom, Flavon and L1 this was the crystal used in the structure analysis. For Grayan and Estron a different crystal was used. In the case of Ingenol the crystal could not be identified with certainty.

The detailed results for Rhodom are shown in Table 2 in order to give an indication of the magnitudes involved. $\Delta f''_{\text{O}}$ was calculated from each value of $\Delta f''_{\text{O};\text{C}}$ using equation (10). The results for all 7 substances are summarized in Fig. 1. For the first measurement (L2*) the structure-factor calculation was performed with $\Delta f''_{\text{O}} = 0.1$ and $\Delta f''_{\text{C}} = 0.0$ (values for Cu $K\alpha$ radiation from *International Tables for X-ray Crystallography*, 1962). The mean value obtained for DELA [equation (12)] was 0.188. Fig. 1(a) was therefore scaled up by this factor. This result gave an indication of the order of magnitude of $\Delta f''_{\text{O};\text{C}}$ and all further structure factor calculations were therefore performed with $\Delta f''_{\text{O}} = 0.02$ and $\Delta f''_{\text{C}} = 0.00$.

The experimental values of $\Delta f''_{\text{O};\text{C}}$ obtained for each substance (unweighted means of the individual values) are given in Table 3 before and after absorption correction. As described for the 10 quotients in the alternating measuring procedure, σ_{ex} and σ_{th} are standard deviations calculated from the distribution of the individual values and from counting statistics. The sign of $\Delta f''_{\text{O};\text{C}}$ indicates the correct enantiomer. An equivalent indication is given by the residuals, R and RE , between the measured Bijvoet differences and those calculated for the assumed structure and for its enantiomer

$$R = \left\{ \sum (B_{\text{ex}} - B_{\text{th}})^2 / n \right\}^{1/2} \quad (13)$$

$$RE = \left\{ \sum (B_{\text{ex}} + B_{\text{th}})^2 / n \right\}^{1/2} \quad (14)$$

$$RTH = \left\{ \sum [\sigma(B_{\text{ex}})]^2 / n \right\}^{1/2}. \quad (15)$$

RTH is the residual expected from counting statistics. The expressions for RA , RAE and $RTHA$, the values after absorption correction, are as above with BA substituted for B . (In the evaluation of the L2* measurement the B_{th} values were scaled up by the factor 0.188 before calculating these residuals.)

The improvement of the results due to the absorption correction is immediately obvious. Whereas the σ_{th} values increase slightly owing to the contribution of the absorption measurement to the statistical error, the σ_{ex} values decrease strikingly. RTH increases while R for the correct enantiomer decreases. The fact that σ_{ex} is in most cases still well above σ_{th} after absorption correction, indicates that systematic errors are present either in the observed or in the calculated Bijvoet differences.

In calculating the mean values for $\Delta f''_{\text{O};\text{C}}$ the individual values for each reflexion were not weighted, as the large systematic errors are just as likely to occur for the more precisely as for the less precisely measured values. The distribution of the values about the mean for each substance, however, does give a meaningful indication of its accuracy. A mean for the 7 substances can, therefore, now be calculated weighting the individual values as $1/\sigma_{\text{ex}}^2$ giving $\Delta f''_{\text{O};\text{C}} = 0.0182 \pm 0.0008$. The weighted mean of the individual values of $\Delta f''_{\text{O}}$ for each substance is 0.0380 ± 0.0018 . It is again stressed that the value for $\Delta f''_{\text{O};\text{C}}$ is a purely experimental value while the values for $\Delta f''_{\text{O}}$ were calculated making a theoretical assumption [equation (9)]. A best value for $\Delta f''_{\text{O}}$ will be derived later.

Discussion

A description of the absolute configurations of the substances investigated here is given by Engel, Zechmeister & Hoppe (1972) with references to the crystal-structure analyses and to previous stereochemical investigations. In order to document the calculations unambiguously an extract of the set of atomic coordinates from which the B_{th} were calculated is given for each substance (Table 4). Reference to Table 3 then reveals whether the absolute configuration corresponds to these coordinates relative to a right-handed or a left-handed system. The coordinates of the final refinements, some not yet published, may differ slightly from these and may refer to a different molecule in the unit cell.

Analysis of systematic errors

The use of an inaccurate value for $\Delta f''_{\text{O};\text{C}}$ in calculating the B_{th} does not affect the accuracy with which the experimental value can be determined. The small variation (15%) of $\Delta f''_{\text{O};\text{C}}$ with $\sin \theta/\lambda$ is also

Table 4. Extracts from the sets of atomic coordinates used in calculating the B_{th}

Ingenol	x	y	z
C(8)	0.32943	0.31123	0.48452
C(13)	0.27301	0.41471	0.41746
C(14)	0.34486	0.37479	0.40014
C(15)	0.34558	0.43239	0.52670
L1			
C(8)	0.10164	0.94844	0.54946
C(13)	0.16130	0.94031	0.30203
C(14)	0.13035	1.00074	0.42275
C(15)	0.18146	1.01410	0.42884
Rhodom			
C(116)	-0.23044	-0.13791	0.48944
C(118)	-0.23060	-0.18735	0.41889
C(117)	-0.07807	-0.20301	0.37871
C(115)	-0.03331	-0.17637	0.18084
Estron			
C(12)	0.92993	0.18183	0.11619
C(13)	0.86270	0.21226	0.05357
C(14)	0.74705	0.20727	0.08487
C(17)	0.88094	0.25429	0.09084
L2*			
C(8)	0.11112	0.16855	0.29721
C(13)	0.05245	0.23373	0.50313
C(14)	0.06577	0.24983	0.37088
C(15)	0.10339	0.32456	0.45724
Grayan			
C(1)	0.08440	0.36122	0.11735
C(2)	0.03780	0.41311	0.22555
C(5)	0.06721	0.33121	0.89324
C(10)	0.13205	0.43416	0.15015
Flavon			
C(6)	0.36558	0.19536	0.16851
C(7)	0.39322	0.30847	0.18740
C(8)	0.43925	0.32261	0.33874
O(1)	0.33732	0.37903	0.20895

insignificant. Other possible sources of error in the B_{th} are therefore now discussed.

1. *Atomic coordinates.* Errors in the atomic coordinates and temperature parameters will cause errors in the B_{th} . The residual electron-density distribution that is not adequately described by ellipsoidal atoms is a further source of errors. In order to gain an idea of the order of magnitude of these effects, structure factors were recalculated for L2* with atomic parameters corresponding to two different stages of the refinement, $R=10.6$ and 5.4% . The largest change in B_{th} for the set of sensitive reflexions measured was 30% . No B_{th} changed its sign. This result is significant as it means that the Bijvoet method for determining the absolute configuration is not limited to accurately refined structures. Parthasarathy (1962a,b) has attempted to estimate the errors in B_{th} from the standard deviations of the atomic parameters.

2. *Influence of the H atoms.* The calculation of B_{th} as performed here using $\Delta f''_O=0.02$, $\Delta f''_C=0.00$ and $\Delta f''_H=0.00$ is not strictly valid. More accurate B_{th} would have

been obtained with the set of values (0.038, 0.013, 0.000) for example. An indication of the magnitude of the errors incurred can be gained by comparing the contribution of each atomic species to B_{th} in terms of its $\Delta f''_{eff}$ value relative to carbon, *i.e.* relative to the atomic species with the largest normal contribution to the structure factors. Equation (7) gives $\Delta f''_{O:C}=0.018$, $\Delta f''_{C:C}=0.000$ and $\Delta f''_{H:C}=-0.002$. These $\Delta f''_{eff}$ would yield the same B_{th} values as would the true $\Delta f''$, and our B_{th} calculations ignored this effective H contribution.

Of the compounds investigated Estron ($C_{19}H_{24}O_3$) contained the most H relative to O. The average anomalous contribution to $|F|$ is $n^{1/2}\Delta f''_{eff}$, where n is the number of atoms of a particular species in the molecule. (Strictly, the whole unit cell should be considered but the relative values are the same for the molecule.) The values for the expression are 0.031 and 0.010 for O and H respectively. The average H contribution to the Bijvoet differences is thus one third as large as the average O contribution. The reflexions measured were, however, chosen for their large O:C contributions and it is unlikely that these same reflexions would also have large C:H contributions. Errors of at most 10% would be expected for these reflexions and considerably smaller errors for the other compounds. This estimate was roughly confirmed by a test calculation on L1.

The errors in B_{th} discussed here are small compared with the discrepancies revealed in Fig. 1 and Table 3. Errors in B_{ex} are therefore now investigated.

3. *Multiple diffraction.* The reflexions which exhibited large deviations from the means and which were omitted in calculating the best means for $\Delta f''_{O:C}$ and $\Delta f''_O$ are marked in Fig. 1. As all the reflexions measured were very weak, multiple diffraction should manifest itself as an increase in their intensities. For the reflexions Flavon (12,1,2), Ingenol (632), Estron (212 and 528) and L2* (164 and the absorption neighbour of 413), F_{obs} was significantly greater than F_{calc} in the original crystal-structure analysis showing that they had probably been in error there as well. For the first three reflexions the occurrence of multiple diffraction was verified explicitly by following the intensity change on azimuthal rotation. (The reflexions Grayan (22,1,2 and 23,4,1) were omitted because of their large standard deviations, and Rhodom (023) and Estron (584) were omitted because of their large deviations from the mean alone.)

Multiple diffraction increases the intensities of both Bijvoet partners, but the magnitude of the intensity contribution depends on absorption effects and on geometrical factors such as the exact crystal orientation. Differences here can completely mask the Bijvoet effects even when the contribution due to multiple diffraction is quite small. A useful additional criterion for choosing which Bijvoet reflexions to measure might therefore be that F_{obs} is not very much greater than F_{calc} . As several reflexions are seen to be

seriously in error due to multiple diffraction, it is very likely that this effect is also responsible for many less noticeable errors.

4. *Further sources of error.* The contribution of residual errors to the standard deviation is

$$\sigma_r = (\sigma_{ex}^2 - \sigma_{th}^2)^{1/2}. \quad (16)$$

The contribution to the residual errors which is removed by the absorption correction is

$$\sigma_{abs} = (\sigma_{r1}^2 - \sigma_{r2}^2)^{1/2} \quad (17)$$

where the subscripts 1 and 2 refer to σ_r before and after application of the absorption correction. Table 5 shows the standard deviations for the 7 determinations. The absorption correction reduces σ_r strikingly for all substances, especially for Estron and Ingenol. In general, the larger the improvement (σ_{abs}) due to absorption correction, the larger is the residual error σ_{r2} . This trend may be due in part to the inherent inaccuracy of an absorption correction which uses a single neighbouring reflexion as reference.

Table 5. *Error analysis*

σ_{ex} and σ_{th} are the standard deviations ($\times 10^4$) of $\Delta f''_{O:C}$ omitting poor reflexions (see Table 3). σ_{r1} , σ_{r2} and σ_{abs} are defined in equations (16) and (17). In Tables 5 to 8 the structures are given in order of increasing σ_{ex} after absorption correction.

	Before absorption correction			After absorption correction			σ_{abs}
	σ_{ex}	σ_{th}	σ_{r1}	σ_{ex}	σ_{th}	σ_{r2}	
Rhodom	20	8	18	11	9	6	17
L2*	43	12	41	23	14	18	37
Flavon	39	22	32	26	23	12	30
Grayan	49	29	39	33	26	20	34
Ingenol	114	38	107	37	30	22	105
Estron	117	37	111	45	34	29	107
L1	127	14	126	73	13	72	104

For L1, however, there is an unusually large residual σ_{r2} . It is difficult to find an explanation for this. The crystal-structure refinement appears to be as good as the others. The Bijvoet reflexions showing the largest discrepancies were investigated for the effects of multiple diffraction by azimuthal rotation, but no intensity changes were observed. It is possible that the crystal itself was at fault. A small disoriented crystallite, for example, reflecting only 5% of the total intensity would easily be overlooked and could cause large errors in the Bijvoet differences if its contribution were registered for a reflexion but not for its Bijvoet partner. The absorption correction should, however, have been able to deal more successfully with errors of this kind. No really plausible explanation can, therefore, be put forward for the large residual error in this measurement.

The systematic errors due to absorption, multiple diffraction and crystal imperfection should all have been smaller if smaller crystals had been used. Large

crystals (usually those used for the structure analysis) were purposely chosen in order to obtain good counting statistics. In view of the large systematic errors encountered, however, it may be wiser to sacrifice some counting precision and use smaller crystals. The systematic errors were smallest for the Rhodom measurement for the following probable reasons. (1) The crystal was very thin (0.04 mm) so that the absorption correction and therefore its error were very small for all the reflexions measured. (2) The crystal was not mounted about a symmetry axis and therefore an important type of systematic multiple diffraction could not occur (see Burbank, 1965). All the other crystals were orthorhombic. (3) For a thin crystal the effects of (chance) multiple diffraction are smaller, as the X-ray paths are shorter.

Suitability of the structures

Large Bijvoet differences can only result if the O and C contributions to the structure factor are roughly equal. This will occur most often for structures with the optimal constitution

$$(n_o/n_c)_{opt} = (f_c/f_o)^2 (=0.46).$$

n_j is the number of atoms of type j in the molecule. An average value for the ratio of the scattering factors over the range $\sin \theta/\lambda \leq 0.6$ is used.

If the unit cell is large the intensities are generally weaker and it will be more difficult to measure the Bijvoet differences accurately. The average intensity is (in arbitrary units)

$$I = \sum_c f_j^2 / V^2 \quad (18)$$

where the sum is taken over the unit cell and V is its volume. In Table 6 n_o/n_c and I are listed for the various substances.

Table 6. *Suitability of the structures for enantiomer determination*

n_o/n_c is the O:C atomic ratio. All structures have a ratio smaller than the optimum value of 0.46. N is the number of molecules in the unit cell. $\sum_m f_j^2$ is the sum over one molecule using for simplicity values of f for $\sin \theta/\lambda = 0$. V is the volume of the unit cell in \AA^3 . I is an indication of the average intensity [see equation (18)].

	n_o/n_c	N	$\sum_m f_j^2$	V	I ($\times 10^4$)
Rhodom	0.35	4	1186	1602.7	18.5
L2*	0.31	4	1484	2561.4	9.1
Flavon	0.29	4	1334	2088.2	12.2
Grayan	0.32	4	1277	2042.5	12.2
Ingenol	0.31	4	1482	2567.7	9.0
Estron	0.16	12	900	4986.1	4.3
L1	0.25	4	1704	3038.4	7.4

Rhodom is seen to be the most suitable substance in terms of both constitution and average intensities. This is confirmed by the fact that the Rhodom measure-

ments yielded the lowest standard deviation σ_{th} . This low σ_{th} and the low level of residual errors (σ_{r1}) together make this measurement the most accurate one by far. Estron on the other hand is the least suitable substance both in terms of constitution (only 3 oxygen atoms against 19 carbon) and cell size (3 molecules in the asymmetric unit). Estron does indeed have the highest standard deviation σ_{th} . The crystal also possesses a fairly high overall temperature factor (5.3 \AA^2) which further reduces the intensities. The fact that a significant enantiomer indication was obtained for Estron in spite of these three unfavourable circumstances shows how effective the Bijvoet method can be.

Significance of the enantiomer indication

The significance with which the absolute configuration has been determined is the same as that for the sign of the $\Delta f''_{O:C}$ value obtained in each case. To estimate this significance the quantity t is calculated,

$$t = |\bar{x} - m|/s \quad (19)$$

[see *International Tables for X-ray Crystallography*, 1959, p. 90, equation (1)]. \bar{x} is the mean value ($\Delta f''_{O:C}$) obtained from n individual measurements, m the unknown true value, and s the estimated standard deviation (σ_{ex}). The probability P that the sign of $\Delta f''_{O:C}$ has been wrongly determined can be estimated by putting $m=0$. P is a function of t and n which has been tabulated (e.g. *International Tables for X-ray Crystallography*, 1959, p. 94). Table 7 shows the significance P for each determination, i.e. the probability that the absolute configuration has been wrongly determined. As the true value of $\Delta f''_{O:C}$ is now known with confidence to be 0.018, larger values of t and higher significance could be deduced by putting $m = -0.018$ in equation (19). In view of the large systematic errors in the measurements, however, the more conservative estimate of the significance with $m=0$ is probably better. An equivalent estimate of the significance can be obtained by using Hamilton's (1965) R -value tables to compare the residuals of the observed and calculated Bijvoet differences for the two enantiomers. Such a comparison is not to be confused with the original 'R method' which relies on a comparison of structure-

Table 7. Significance of the enantiomer indications

The values of $\Delta f''_{O:C}$ and σ_{ex} are those after absorption correction and omitting poor reflexions (see Table 3). n is the number of individual values (reflexions). t is defined in equation (19). P is the probability that the enantiomer indication is incorrect.

	n	$\Delta f''_{O:C}$	σ_{ex}	t	P
Rhodom	23	-0.01775	0.00110	16.13	$\ll 0.001$
L2*	20	0.01853	0.00227	8.16	$\ll 0.001$
Flavon	21	0.01850	0.00257	7.20	$\ll 0.001$
Grayan	19	-0.01960	0.00328	5.98	$\ll 0.001$
Ingenol	20	0.01557	0.00367	4.24	< 0.001
Estron	23	0.02372	0.00451	5.26	$\ll 0.001$
L1	25	-0.02316	0.00727	3.18	< 0.01

factor residuals without its being necessary to measure Bijvoet differences.

In order to compare the effectiveness of the Bijvoet method and the R method (applied to the structure factors), the latter was tested on the structures determined here. It was not attempted to optimize the criteria for choosing the limited set of reflexions, but 2 or 3 different sets were investigated for each substance. The significance obtained was very poor (only Rhodom gave a result with $P < 0.05$ for a set of 82 reflexions with an R value ratio of 1.022) and the indication was wrong in about half of the cases! This result shows that the Bijvoet method is very much more sensitive than the R method, a conclusion to which the other groups that have worked on light-atom structures (using either method) have also come. As pointed out earlier this superiority is due to the fact that the Bijvoet differences usually give a correct enantiomer indication even at high values of R , while the differences between F_{obs} and F_{calc} are very large and very often give a wrong indication. A further advantage of the Bijvoet method is that it permits the use of a specialized and highly accurate absorption correction. Finally, there is some doubt about how to apply Hamilton's (1965) significance tables to a limited set of reflexions.

Summing up, it would appear that the R method is suitable for structures with heavier atoms or for light-atom structures when the intensity measurements and the refinement are very accurate ($R \approx 3\%$). For normal light-atom structures where it is not intended or not feasible to perform extreme refinement (because of poor crystal quality for example) one will still have to resort to the careful measurement of Bijvoet differences.

Individual $\Delta f''$ values

As described above, $\Delta f''_O$ was calculated from the experimental values of $\Delta f''_{O:C}$ using a theoretical assumption [equation (9) with $n=2.75$, $X=0.333_s$]. The weighted means were $\Delta f''_{O:C}=0.0182$ and $\Delta f''_O=0.0380$. These values are now substituted into equation (10) giving a mean value for f_O/f_C of 1.562 for all 7 sets of measurements. This can now be substituted back into equation (10) to calculate a value of $\Delta f''_O$ for various values of the parameter n without having to repeat the full evaluation of all the measurements.

Zachariasen (1965) has calculated values of $\Delta f''_{Si:O}$ from Cu $K\alpha$ measurements of Bijvoet differences on α -quartz. Assuming $n=3$ [equation (9)] he deduced $\Delta f''_{Si:O}=0.31 \pm 1$ and $\Delta f''_O=0.028$. Average values of $\Delta f''_{Si:O}=0.24_3$ and $\Delta f''_{Si:O}=0.31_6$ can be calculated from his Table 2. Substitution in equation (10), together with the value $X=0.09$ used by Zachariasen, gives an average f_{Si}/f_O of 2.58. Using equations (9) and (10) the value of n can now be adjusted until Zachariasen's results and those reported here yield the same value for $\Delta f''_O$ ($\lambda_{KSi}=6.745 \text{ \AA}$, Kaelble, 1967). This is the case for $n=2.77_6$ and $\Delta f''_O=0.037_3$. Taking the experimental errors into account the values

$$n = 2.78 \pm 0.06$$

$$\Delta f''_{\text{O}} = 0.037 \pm 0.002$$

$$\Delta f''_{\text{Si}} = 0.34 \pm 0.02$$

$$\Delta f''_{\text{C}} = 0.0122 \pm 0.0007$$

are obtained for Cu $K\alpha$ radiation. The parameter C [equation (8)] is 4.66 ± 0.25 . Cromer's value for $\Delta f''_{\text{Si}}$ is 0.36. The value obtained using equation (20) (with $\mu/\rho = 60.4 \text{ cm}^{-1}$) is 0.32₄. The new semi-empirical value lies between these two, 1σ from either value. The value for n agrees with those quoted earlier (2.75 and 2.8).

While equation (8) is only an approximation, the restriction to two parameters is probably valid within the accuracy of 6% claimed here. A small set of $\Delta f''$ values for light atoms is therefore given in Table 8. (The value for H is not very meaningful, as this atom only has one electron and this is involved in the chemical bond.) The values in Table 8 agree with those of Cromer where they overlap. If Cromer's table were extended to lighter atoms the values would also agree, as Cromer assumes a value of 11/4 for the K shell which provides the main contribution to $\Delta f''$.

Table 8. $\Delta f''$ values calculated from equation (8) with $n = 2.77_6$ and $C = 4.66$

The accuracy is about 6% for Cu $K\alpha$ radiation between C and Si and somewhat poorer for other atomic species and wavelengths.

	Z	λ_K	Cr $K\alpha$	Fe $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
H	1	918	2.29092	1.93728	1.54178	0.71069
He	2	504	0.00011	0.00008	0.00005	0.00001
Li	3	226.953	0.00032	0.00024	0.00016	0.00004
Be	4	106.9	0.00133	0.00099	0.00066	0.00017
B	5	64.6	0.00506	0.00376	0.00250	0.00063
C	6	43.767	0.0124	0.00919	0.00613	0.00155
N	7	31.052	0.0247	0.0184	0.0122	0.00309
O	8	23.367	0.0455	0.0338	0.0225	0.00569
F	9	18.05	0.0754	0.0560	0.0373	0.00943
Ne	10	14.19	0.119	0.0885	0.0590	0.0149
Na	11	11.48	0.183	0.136	0.0905	0.0229
Mg	12	9.512	0.266	0.198	0.132	0.0333
Al	13	7.956	0.372	0.276	0.184	0.0465
Si	14	6.745	0.511	0.379	0.253	0.0639
P	15	5.787	0.685	0.508	0.339	0.0857
S	16	5.018	0.899	0.667	0.445	0.112
Cl	17	4.397	1.16	0.860	0.573	0.145
A	18	3.871	1.46	1.09	0.725	0.183
K	19	3.437	1.84	1.36	0.909	0.230
Ca	20	3.070	2.27	1.68	1.12	0.284
			2.77	2.06	1.37	0.347

Measurement with Cr $K\alpha$ radiation

Our first Bijvoet measurement was made on Ingenol with Cr $K\alpha$ radiation. The structure factors were calculated using $\Delta f''_{\text{O}} = 0.2$ and $\Delta f''_{\text{C}} = 0.1$ (*International Tables for X-ray Crystallography*, 1962). While these values simulate the true value of $\Delta f''_{\text{O:C}}$ (≈ 0.04) very well, the value of $\Delta f''_{\text{C:H}}$ is 5 times too high and the resulting B_{th} values were badly in error. The enantiomer indication was correct but the significance was poor ($P < 0.05$) and a poor value of $\Delta f''_{\text{O:C}}$ was re-

ported for this radiation by Engel *et al.* (1971). Re-evaluation of the measurement using the structure factors calculated with $\Delta f''_{\text{O}} = 0.02$ and $\Delta f''_{\text{C}} = 0.00$ yielded a value of $\Delta f''_{\text{O:C}} = 0.035 \pm 0.007$ and a very significant enantiomer indication ($P \ll 0.001$). A comparison of this value with that obtained with Cu $K\alpha$ radiation gives $n = 2.7 \pm 0.5$, roughly confirming the value of n obtained above.

In view of the experience here, it is concluded that if true $\Delta f''$ values are not known fairly accurately it may be better to calculate the Bijvoet differences using a single value of $\Delta f''_{\text{eff}}$ and not individual $\Delta f''$ values. This holds for the determination of absolute configuration as well as $\Delta f''$ values.

Concluding remarks

Absolute configuration with still lighter atoms

In view of the high significance of the results obtained here the determination of absolute configuration may also be feasible for structures containing only C and H atoms. The value of $\Delta f''_{\text{C:H}}$ is quite large enough (0.012), but the normal H contribution to the structure factor is extremely small. The optimum atomic ratio would be $n_{\text{H}}/n_{\text{C}} = 36$, while values usually lie between 1 and 2. Thus very few reflexions will have large Bijvoet differences.

Cr $K\alpha$ radiation is considered less suitable than Cu $K\alpha$ for compounds containing O, as fewer reflexions are measurable and as the absorption correction is larger. For compounds without O, however, the absorption correction is less important. Further, as the form factor for H falls off more rapidly with $\sin \theta/\lambda$ than for C, the sensitive reflexions will probably all be accessible to Cr $K\alpha$. Thus the higher value for $\Delta f''_{\text{C:H}}$ of 0.024 should be a genuine advantage here.

The value of $\Delta f''_{\text{N:C}}$ is small (0.007 for Cu $K\alpha$) but the atomic ratios found in practice are nearer the optimum value of $n_{\text{N}}/n_{\text{C}} \approx 0.7$. The presence of N will thus certainly improve the chances of obtaining a significant enantiomer indication.

Determination of $\Delta f''$

It is surprising how few values for $\Delta f''$ have been determined experimentally. All the determinations found in the literature have been described above. Yet the determination of at least a $\Delta f''_{\text{eff}}$ value is easy if attention is concentrated on the sensitive reflexions (see Parthasarathy, 1962a; Zachariasen, 1965). In the present paper it has been shown how Bijvoet differences can be measured with high accuracy ($< 1\%$) giving $\Delta f''_{\text{O:C}}$ with an accuracy of 5%. It should thus certainly be possible to determine values for heavier atoms with an accuracy of about 1%. Large values of $\Delta f''$ in the neighbourhood of absorption edges would be of particular interest in order to check Cromer's (1965) values, e.g. Fe and Co with Cu $K\alpha$, Ni $K\alpha$ and Co $K\alpha$ radiation, Br, U and Th with Mo $K\alpha$ etc.

Experimental $\Delta f''$ values could, further, be used to

calculate more accurate values of absorption coefficients (and also oscillator densities) using the relation

$$\Delta f'' = \frac{mc^2 A}{2e^2 \lambda N} \cdot \left(\frac{\mu}{\rho}\right) \quad (20)$$

where A is the atomic weight, N Avogadro's number and μ/ρ the photoelectric part of the mass absorption coefficient. μ/ρ is difficult to measure accurately although an accuracy of better than 1% is claimed for recent measurements on metals (see Deslattes, 1969). A far wider choice of elements is, however, available for $\Delta f''$ determinations. In order to ensure a good determination, a number of points must be borne in mind. Firstly, a crystal containing the relevant element must be chosen, whose non-centrosymmetric structure has been well determined without systematic errors (see Cruickshank & McDonald, 1967). Secondly, in evaluating the result a valid correction must be made for the influence of the other elements in the crystal. Thirdly, for large values of $\Delta f''$ particular attention will have to be paid to the absorption correction. There is, however, such a wide spectrum of structures available – metallo-organic complexes, heavy-atom derivatives of organic substances and light-atom salts such as nitrates and carbonates – that it should be possible to fulfil the above conditions.

General absorption correction for Bijvoet differences

The absorption correction applied here can be adapted to the case where anomalous scattering is to be used to help solve an unknown structure. In this case a complete set of Bijvoet differences is measured. The relative absorption correction for the Bijvoet pair, $F_{\mathbf{H}}$ and $F_{\bar{\mathbf{H}}}$, (the individual absorption corrections need not be known so accurately) can then be approximated by the average value of all Bijvoet quotients (Q_{ex}) for the lattice points in a small sphere in reciprocal space centred on \mathbf{H} . The sphere should contain sufficient points so that the average value of the true Bijvoet quotients is near 1. The sphere should, however, be small enough so that the change of the absorption factor inside it is still linear. If $|B|$ is the average magnitude of the Bijvoet difference and if n reflexions are used to scale each point, the standard deviation of the scale factor is $|B|/\sqrt{n}$. For $n=25$ this implies 20% absorption errors for the average Bijvoet differences. If only the strongest 25 in a sphere containing 50 reflexions are used for scaling, the error will be still less. This sphere should thus fulfil the statistical condition and for crystals with large unit cells (proteins) the linearity condition as well.

This correction factor is more direct and probably more accurate than other experimental or theoretical corrections and requires no extra measurements. It could also be applied to scale the structure-factor differences obtained with two different wavelengths. The only modification here is that the theoretical scale factor is not exactly 1 but $\{\sum f_j^2(\lambda_1)/\sum f_j^2(\lambda_2)\}^{1/2}$.

Influence of light atoms in phase determination

Anomalous scattering is often used in the phase determination for proteins. De Vries (1970) has, therefore, attempted to estimate the effect (usually neglected) on the Bijvoet differences of the atoms in the native protein. His estimates for the light atoms were too high because of uncertainty in the $\Delta f''$ values. De Vries's calculations can now be repeated with the experimentally determined values.

Table 9 gives the anomalous contributions to the structure factors for each atomic species in Hg-haemoglobin for Cu $K\alpha$ radiation. These contributions, however, still give a false impression of the influence on the Bijvoet differences. A better estimate is obtained using $\Delta f''_{\text{eff}}$ values relative to the atomic species with the largest normal contribution to the structure factors, namely C. Table 9 shows the effect of this modification. The contributions of Hg, Fe and S in terms of $\Delta f''_{\text{eff}}$ have hardly altered their values. The effect of the light atoms on the other hand has been halved. De Vries's conclusion that Fe and S influence the Bijvoet differences appreciably thus remains valid; the influence of O, C and N is, however, very small.

Table 9. Contributions of the various atomic species in a Hg derivative of haemoglobin for Cu $K\alpha$ radiation

The columns give the number of atoms in the half-molecule, the normal form factor, the anomalous form factor, the effective anomalous form factor relative to C, and the average contributions of these three form factors to the structure factors.

	n	f	$\Delta f''$	$\Delta f''_{\text{eff}}$	$\sqrt{\sum f^2}$	$\sqrt{\sum \Delta f''^2}$	$\sqrt{\sum \Delta f''_{\text{eff}}^2}$
H	2000	1	0.000	-0.002	45	0.00	0.09
C	1580	6	0.012	0.000	238	0.48	0.00
N	397	7	0.023	0.008	139	0.46	0.16
O	439	8	0.037	0.021	168	0.78	0.44
S	7	16	0.57	0.54	43	1.51	1.43
Fe	2	26	3.45	3.40	37	4.88	4.80
Hg	0.65	80	7.04	6.88	52	4.58	4.47

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Note added in proof: Cromer & Liberman (1970) have recently recalculated anomalous scattering factors computing the photoelectric absorption theoretically instead of using the empirical equation (2). For Cu $K\alpha$ radiation they give $\Delta f''_{\text{O}}=0.032$ and $\Delta f''_{\text{C}}=0.009$. They quote unpublished measurements by Zachariasen of $\Delta f''$ for K and P. Further experimental values of $\Delta f''$ have been measured by Marezio (1965a,b) for Ga, Al and O. Marezio gives $\Delta f''_{\text{O}}=0.028 \pm 0.005$.

References

- BURBANK, R. D. (1965). *Acta Cryst.* **19**, 957.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
 CROMER, D. T., LARSON, A. C. & ROOF, R.B., JR (1964). *Acta Cryst.* **17**, 272.
 CROMER, D. T. & LIBERMAN D. (1970). *J. Chem. Phys.* **52**, 1891.
 CRUICKSHANK, D. W. J. & McDONALD, W. S. (1967). *Acta Cryst.* **23**, 9.
 DESLATTES, R. D. (1969). *Acta Cryst.* **A25**, 89.
 ENGEL, D. W., ZECHMEISTER, K., RÖHRL, M., BRANDL, F., NARAYANAN, P. & HOPPE, W. (1971). *Nature Physical Science*, **229**, 28.
 ENGEL, D. W., ZECHMEISTER, K. & HOPPE, W. (1972). *Tetrahedron Letters*. In the press.
 HALL, S. R. & MASLEN, E. N. (1966). *Acta Cryst.* **20**, 383.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
 HOPE, H. & DE LA CAMP, U. (1969). *Nature, Lond.* **221**, 54.
 HOPE, H., DE LA CAMP, U. & THIESSEN, W. E. (1969). *Acta Cryst.* **A25**, S78.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JAMES, R. W. (1958). *The Optical Principles of the Diffraction of X-rays*. London: Bell.
 KAEUBLE, E. F. (1967). *Handbook of X-rays*, 1–12. New York: McGraw-Hill.
 MAREZIO, M. (1965a). *Acta Cryst.* **19**, 284.
 MAREZIO, M. (1965b). *Acta Cryst.* **19**, 396.
 MIDDLETON, R. M. & GAZZARA, C. P. (1967). *Acta Cryst.* **23**, 712.
 MONCRIEF, J. W. & SIMS, S. P. (1969). *Chem. Commun.* p. 914.
 NEIDLE, S. & ROGERS, D. (1970). *Nature, Lond.* **225**, 376.
 PARRATT, L. G. & HEMPSTEAD, C. F. (1954). *Phys. Rev.* **94**, 1593.
 PARTHASARATHY, R. (1962a). *Acta Cryst.* **15**, 41.
 PARTHASARATHY, R. (1962b). *Acta Cryst.* **15**, 855.
 ROOF, R. B., JR (1961). *Acta Cryst.* **14**, 934.
 STEWART, J. M. (1967). *X-ray 67. Program System for X-ray Crystallography*. Technical report 67-58. Computing Science Center, Univ. of Maryland.
 THIESSEN, W. E. & HOPE, H. (1970). *Acta Cryst.* **B26**, 554.
 VRIES, A. DE (1970). In *Crystallographic Computing*, p. 160. Edited by F. R. AHMED. Copenhagen: Munksgaard.
 ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 714.

Acta Cryst. (1972). **B28**, 1509

The Crystal and Molecular Structure of a Dimer of 1*H*,4*H*-Naphtho[1,8]diselenepine

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The crystal and molecular structure of a dimer of 1*H*,4*H*-naphtho[1,8]diselenepine has been determined. The data used were 1350 reflexions measured on a Picker four-circle diffractometer. The crystals are monoclinic with space group *C2/c* and cell dimensions $a=22.907$, $b=5.1459$, $c=18.091$ Å and $\beta=97.97^\circ$. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares to $R=0.029$. The molecule has a twofold axis of symmetry. The naphthalene rings are inclined at 46.2° to the *ac* plane while the Se atoms lie roughly in a plane parallel to the *ac* plane. Within the molecule there is a short (1.96 Å) H–H contact causing the molecule to be somewhat distorted. The Se–Se bond has the length 2.315 Å, the Se–C bonds are 1.991, the C(*sp*³)–C(*sp*²) bonds are 1.491 and the C(*sp*²)–C(*sp*²) bonds 1.396 Å. The dihedral angle at the Se–Se bond is 88.1° .

Introduction

In connexion with work on ring systems containing sulphur or selenium Biezais-Zirnis & Fredga (1971) obtained a product which they considered to be a dimer of the intended product 1*H*,4*H*-naphtho[1,8]diselenepine. The molecular weight of the compound could not be determined, neither could the absorption spectra be recorded due to low solubility. A single-crystal analysis was undertaken to clarify the situation.

Experimental

The crystals used were small pale yellow needles crystallized from boiling xylene. Preliminary cell dimensions were obtained from Weissenberg photographs which also showed the space group to be *Cc* or *C2/c*. A crystal with the dimensions $0.024 \times 0.024 \times 0.26$ mm was mounted along the needle axis (*b* axis) and used for data collection on a Picker FACS-1 automatic four-circle diffractometer. Cu *K* α radiation