From these measurements it seems that a dramatic improvement in accuracy of structure factor determination may well result from the effective correction or experimental removal of extinction errors. It is also evident that a successful theoretical correction must take account of quite complicated anisotropic extinction in view of Fig. 3.

Thanks are due to Dr J. K. Mackenzie for useful discussion in planning this series of measurements and to Dr A. McL. Mathieson for suggesting the project, and discussing its results.

References

ABRAHAMS, S. C., ALEXANDER, L. E., FURNAS, T. C., HAMILTON, W. C., LADELL, J., OKAYA, Y., YOUNG, R. A. & ZALKIN, A. (1967). *Acta Cryst.* **22**, 1.

ABRAHAMS, S. C., HAMILTON, W. C. & MATHIESON, A. MCL. (1970). *Acta Cryst.* A**26**, 1.

BEARDEN, J. A. (1928). *Proc. Nat. Acad. Sci. U.S.* **14**, 539.

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.

DAVIES, D. A., DENNE, W. A., HAINES, P. D., MACKENZIE, J. K. & MATHIESON, A. MCL. (1972). To be published.

DENNE, W. A. (1970*a*). *Acta Cryst.* A**26**, 154.

DENNE, W. A. (1970*b*). *Acta Cryst.* A**26**, 666.

DENNE, W. A. (1971). *J. Appl. Cryst.* **4**, 60.

HART, M. (1969). *Acta Cryst.* A**25**, 134.

JENNINGS, L. D. (1969). *J. Appl. Phys.* **40**, 5038.

KATO, N. (1969). *Acta Cryst.* A**25**, 119.

MACKENZIE, J. K. & MASLEN, V. W. (1968). *Acta Cryst.* A**24**, 628.

MACKENZIE, J. K. (1972). To be published.

MATHIESON, A. MCL. (1969). *Acta Cryst.* A**25**, 264.

MARSH, R. E. (1958). *Acta Cryst.* **11**, 654.

RENNINGER, M. (1969). Proceedings of the IX I.U.Cr. Congress, Stony Brook.

SUDARSANAN, K. & YOUNG, R. A. (1969). *Acta Cryst.* B**25**, 1534.

WHEELER-ROBINSON, B. (1933). *Proc. Roy. Soc.* A**142**, 422.

WILLIS, B. T. M. (1961). U. K. A. E. A. Research Group Report, AERE-R3692

WOLLAN, E. O. (1928). *Proc. Nat. Acad. Sci. U. S.* **14**, 864.

Acta Cryst. (1972). A**28**, 201

Anomalous Scattering by Oxygen: Measurements on (+)-Tartaric Acid

BY HÅKON HOPE AND ULRICH DE LA CAMP

Department of Chemistry, University of California, Davis, California 95616, *U.S.A.*

(*Received* 6 *September* 1971)

The structure of (+)-tartaric acid has been used as a test case to study the feasibility of absolute configuration determinations of compounds in which oxygen is the heaviest atom. Based on about 1100 Ni-filtered Cu $K\alpha$ reflections $(-7\le k\le 7)$ measured on a Picker automatic diffractometer the $(2R,3R)$ and $(2S,3S)$ configurations could be refined to $R=0{\cdot}0228$ and $R=0{\cdot}0231$ respectively. 94 selected enantiomer sensitive reflections gave $R(2R,3R)=0{\cdot}0336$ and $R(2S,3S)=0{\cdot}0374$ $(\Delta f''_O=0{\cdot}032)$. Among the 38 most sensitive Bijvoet differences only one had the incorrect sign. A value of 0·041 (4) for $\Delta f''_O$ (Cu $K\alpha$) was derived from 36 observed Bijvoet differences. Similar measurements with Cr $K\alpha$ radiation also permitted the unequivocal assignment of the correct absolute configuration; however, Cr $K\alpha$ radiation was not found to offer any overall advantage over Cu $K\alpha$ radiation. The cell dimensions used in this study are $a=7{\cdot}7291$ (5), $b=6{\cdot}0069$ (2), $c=6{\cdot}2118$ (3) Å, $\beta=100{\cdot}147$ (2)° (space group $P2_1$; $Z=2$).

Introduction

In a recent study of (+)-methyl-*p*-tolyl sulfoxide (De la Camp & Hope, 1970) the two enantiomeric structures were refined to $R=0{\cdot}034$ and $R=0{\cdot}044$ for the correct and the incorrect enantiomer respectively. This large difference in R indices caused by the anomalous scattering of Cu $K\alpha$ radiation by sulfur $(\Delta f''_S\simeq 0{\cdot}6)$ suggested to us that oxygen in a carbon–hydrogen environment might give rise to measurable anomalous scattering effects, assuming the value of $\Delta f''_O$ to lie in the range 0·03 (Zachariasen, 1965) to 0·10 (*International Tables for X-ray Crystallography*, 1962).

Based on available literature data (+)-tartaric acid seemed a reasonable choice for a test case. The molecule is relatively small, the structure was well determined (Okaya, Stemple & Kay, 1966), there was no doubt about the absolute configuration (Bijvoet, Peerdeman & van Bommel, 1951) and good crystals could be easily obtained. As it turned out the crystals were not as stable under X-ray irradiation as expected, thereby giving rise to some undesirable effects which, however, were not serious enough to thwart a successful outcome.

Preliminary accounts of this work have been given earlier (Hope & de la Camp, 1969; Hope, de la Camp & Thiessen, 1969).

Experimental

From the outset we planned both to investigate the feasibility of absolute configuration determinations based on anomalous scattering from oxygen, and to establish methods which would in practice permit the determination of unknown absolute configurations. For these reasons we intended to collect diffraction data of very high quality, without departing significantly from standard, automated measuring techniques.

(+)-Tartaric acid crystallizes in the monoclinic space group $P2_1$. Because this is a polar space group we decided to collect data for a full hemisphere $(-7 \leq k \leq 7)$. Crystals were obtained by evaporation of an aqueous solution. In order to facilitate absorption correction the specimens used for intensity measurements were carefully ground to spheres (estimated eccentricity < 1 %). For reasons given below we collected two different Cu $K\alpha$ data sets using a freshly prepared crystal for each set. In addition, we obtained Cr $K\alpha$ data from a third crystal.

A survey of results from this laboratory had indicated that our most satisfactory data sets had been obtained with crystals containing a total of about 5.10^{18} electrons. For tartaric acid this corresponds to a sphere about 0·35 mm in diameter. For the two Cu data sets spheres of 0·375 and 0·300 mm diameter were chosen. The crystals were mounted with arbitrary orientation on a Picker diffractometer equipped with a full-circle goniostat. Intensity data were collected with the diffractometer in automatic mode. Approximate monochromation was attained with a nickel filter (in the diffracted beam for the first data set) and a pulse height analyzer in conjunction with a scintillation detector. The θ–2θ scan technique was employed with a scan speed (2θ) of 1° min^{-1} and a scan range of $[2\theta(\alpha_1)-0{\cdot}9^\circ]$–$[2\theta(\alpha_2)+0{\cdot}9^\circ]$. Stationary background counts of 40 sec duration were taken at each end of the scan. In order to reduce coincidence losses, attenuation filters were inserted in the diffracted beam when the count rate exceeded 10^4 cps. (Without attenuation some peak count rates would have reached about $3{\cdot}10^5$ cps.)

For the first data set the reflections were recorded in the order: positive k ($2\theta < 133^\circ$) first, then all reflections with $2\theta > 133^\circ$ (diffractometer in asymmetric mode) and last, negative k ($2\theta < 133^\circ$). Three monitor reflections were measured at 6–8 hr intervals. Two of these ($2\theta \simeq 40^\circ$) showed no systematic variation, whereas the third ($2\theta = 129^\circ$) showed a gradual decline which became discernible about halfway into the data collection, and amounted to nearly 4 % at the time of the final measurements. 1170 reflections were recorded. Absorption corrections were applied in conjunction with a standard Lorentz and polarization data reduction. We did not attempt to correct for the decay; because the effect varied so much with 2θ we found no reasonable way of treating it. Careful inspection of the raw data also indicated a minor asymmetry in some scan ranges for which 2θ exceeded 145°, the asymmetry presumably being caused by small errors in the cell dimensions. (For this data set the cell dimensions and setting parameters had been determined from angular measurements with $2\theta < 133^\circ$.)

Even though a refinement based on this first data set proceeded in a satisfactory manner (see below), the two known flaws (decay and missetting) just described led us to collect a second set of data. In order to avoid the missetting problem, cell dimensions were obtained from reflections (12 *hkl* sets) with 2θ ranging from 140 to 160°. The results are given in Table 1. Decay was diminished by placing the Ni filter in the incident beam, and a later correction was made possible by first measuring all reflections with $2\theta > 133^\circ$ and the remaining ones in order of increasing 2θ. Otherwise, the data col-

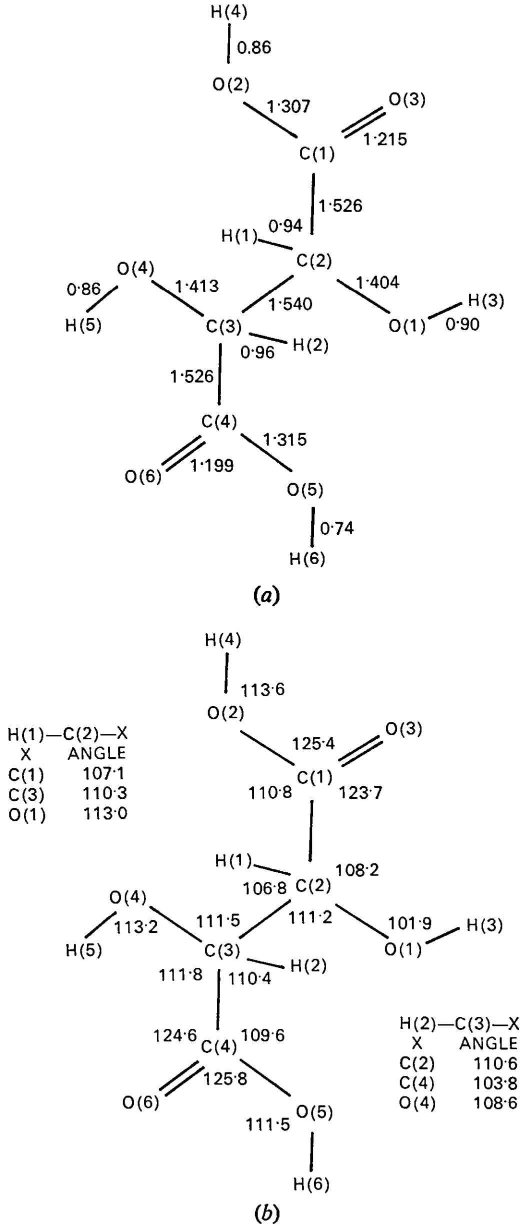

Fig. 1. Molecular geometry. (*a*) Distances. (*b*) Angles. E.s.d. are about 0·002 Å for C–C and C–O, about 0·02 for C–H and O–H, about 0·1° for angles involving only C and O, and about 1–2° for angles involving H.

lection was carried out as for the first set. As before, the low-angle monitor reflections remained stable, whereas the high-angle one showed a gradual decline in intensity. This time, however, the maximum drop amounted to only 2%. As part of the data reduction, in addition to Lp and absorption corrections ($\mu r = 0{\cdot}234$) a decay correction as well as a correction for coincidence losses was applied. Each recorded number of counts, N, was assigned an estimated standard deviation $\sigma(N) = [N + (0{\cdot}009N)^2]^{1/2}$; the factor 0·009 corresponds to the observed variation in monitor reflection intensities. For this data set 1099 unique reflections with $I_o > 3\sigma(I_o)$ were recorded as observed.

Table 1. *Crystallographic data*

Space group: $P2_1$; $Z=2$.
Cell dimensions

a	*b*	*c*	*β*
7·7291 (5) Å	6·0069 (2) Å	6·2118 (3) Å;	100·147° (2)*
7·7290 (1)	6·0004 (1)	6·2126 (1)	100·153 (2)†

$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051$ Å
Absorption coefficients:
$\mu(\text{Cu } K\alpha) = 15{\cdot}6 \text{ cm}^{-1}$
$\mu(\text{Cr } K\alpha) = 49{\cdot}4 \text{ cm}^{-1}$
$d = 1{\cdot}76 \text{ g.cm}^{-3}$

* This work ($t = 24$ °C)
† Abrahams, Hamilton & Mathieson (1970) ($t = 25$ °C)

For the Cr *Kα* data (V-filtered) a sphere of diameter 0·275 mm was used. Data collection was carried out as described for the second Cu data set, resulting in about 370 recorded reflections. The monitor reflections showed no systematic variation during the 35 hr it took to perform the measurements.

Evaluation of data

We will use the subscripts '+' and '−' to refer to the absolute configurations (2*R*,3*R*) and (2*S*,3*S*) respectively. (Absolute configuration notation of Cahn, Ingold & Prelog, 1966). For ease of comparison we have used the atomic numbering system of Okaya *et al.* (1966), with the exception of C(1) and C(2) which had to be interchanged in order to conform with standard chemical numbering (see Fig. 1). The *R* index is defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and the weighted sum of squares of deviations is $S = \sum(|F_o| - |F_c|)^2/\sigma^2(F_o)$. The symbol ΔF_{Bij} denotes the Bijvoet difference $F(hkl)$–$F(\bar{h}\bar{k}\bar{l})$. Atomic form factors for O and C are $f = f^0 + \Delta f' + i\Delta f''$, where f^0 are the values given by Hanson, Herman, Lea & Skillman (1964). For H the bonded form factor of Stewart, Davidson & Simpson (1965) was used.

1*st* Cu *data set*

Even with the knowledge of the minor flaws in the first data set we considered it suitable for further use.

A full-matrix least-squares refinement starting with the parameters of Okaya *et al.* (1966) proceeded smoothly after application of secondary extinction corrections by the method of Zachariasen (1963). The final *R* index was 0·0263. In these calculations we used $\Delta f''_{\text{O}} = 0{\cdot}04$, and ignored $\Delta f''_{\text{C}}$ as well as $\Delta f'$ for both C and O. The value 0·04 was obtained from Hönl's (1933) formula by hand calculation.

A subsequent refinement with $\Delta f''_{\text{O}} = -0{\cdot}04$ was expected to result in a slightly increased *R* index. When the actual value turned out to be lower by 0·0008 we were rather puzzled. However, the difficulty was resolved to our satisfaction when we realized that the coordinates of Okaya *et al.* in a righthanded system correspond to the absolute configuration (2*S*,3*S*), whereas the absolute configuration of (+)-tartaric acid is (2*R*,3*R*) (Bijvoet, Peerdeman & van Bommel, 1951).

The results so far were quite encouraging, but we also felt that a further strengthening of the absolute configuration indication was necessary. For this purpose consideration of only those reflections with the most pronounced anomalous scattering effects has been a commonly used approach. For our data the best criterion for selection of enantiomer sensitive reflections was one based on observability rather than just the magnitude of calculated Bijvoet differences. We chose the function

$$D = (\Delta F_{\text{Bij},c})^2/\sigma^2(F_o)$$

as an index of observability.

For the 150 reflections with $D > 4{\cdot}0$ we obtained $R_+ = 0{\cdot}0328$, $R_- = 0{\cdot}0353$, and $S_-/S_+ = 1{\cdot}28$. For the complete data set the ratio S_-/S_+ is 1·034. It is clear from these results that the anomalous scattering effect of oxygen for Cu *Kα* radiation can be used for the determination of absolute configurations. The minor flaws in the data apparently did not prevent a positive outcome. However, because of the delicate nature of the problem we felt that a more thorough analysis with improved data would be valuable.

2*nd* Cu *data set*

Before refinement of this data set we programmed Hönl's (1933) formula for a PDP-8 computer, obtaining for the various anomalous scattering correction terms: (Cu *Kα*) $\Delta f'_{\text{C}} = 0{\cdot}019$, $\Delta f''_{\text{C}} = 0{\cdot}010$, $\Delta f'_{\text{O}} = 0{\cdot}049$,

Table 2. *Positional parameters for carbon and oxygen*

E.s.d. in parentheses.

	x	*y*	*z*
O(1)	0·33806 (12)	−0·03430	0·51085 (14)
O(2)	0·42983 (12)	0·03227 (26)	−0·02153 (16)
O(3)	0·60928 (10)	−0·00747 (25)	0·30138 (15)
O(4)	0·30636 (11)	−0·41881 (24)	0·23403 (14)
O(5)	−0·07754 (12)	−0·08055 (29)	0·17997 (19)
O(6)	−0·02110 (12)	−0·40779 (30)	0·35026 (19)
C(1)	0·46350 (14)	0·00579 (29)	0·19062 (20)
C(2)	0·29375 (14)	−0·01613 (29)	0·28238 (18)
C(3)	0·20057 (14)	−0·22786 (28)	0·18120 (18)
C(4)	0·02167 (15)	−0·25270 (30)	0·25003 (20)

Table 3. *Coefficients in the anisotropic temperature factor expression* $\exp\,[-(h^2\beta_{11}+\ldots+kl\beta_{23})]\times 10^5$

E.s.d. in parentheses.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	821 (14)	2279 (34)	1080 (22)	−87 (33)	611 (25)	−694 (43)
O(2)	824 (14)	2549 (38)	1365 (22)	−424 (33)	905 (28)	498 (42)
O(3)	522 (12)	2308 (32)	1687 (25)	−188 (32)	494 (26)	−625 (48)
O(4)	680 (12)	1491 (27)	1179 (21)	284 (31)	477 (25)	−130 (39)
O(5)	583 (13)	2566 (35)	2413 (31)	782 (38)	1076 (31)	1698 (53)
O(6)	945 (16)	2399 (36)	2735 (34)	−145 (43)	1534 (37)	1746 (62)
C(1)	571 (16)	973 (32)	1351 (28)	−281 (35)	621 (32)	−291 (48)
C(2)	496 (16)	1277 (34)	1131 (28)	26 (37)	497 (32)	−174 (52)
C(3)	438 (16)	1331 (33)	925 (27)	63 (37)	298 (33)	76 (47)
C(4)	483 (18)	1707 (39)	1034 (26)	−177 (37)	307 (33)	−12 (51)

$\Delta f''_{\mathrm{O}}=0{\cdot}032$; (Cr $K\alpha$) $\Delta f'_{\mathrm{C}}=0{\cdot}036$, $\Delta f''_{\mathrm{C}}=0{\cdot}021$, $\Delta f'_{\mathrm{O}}=0{\cdot}090$, $\Delta f''_{\mathrm{O}}=0{\cdot}070$.

Following correction for secondary extinction [$F_{\mathrm{corr}}=F_o(1+C\beta J_o)^{1/2}$; $C=5{\cdot}3\,.\,10^{-4}$; the symbols are those used by Zachariasen, (1963)] the ($2R$, $3R$) structure refined to $R=0{\cdot}0228$ and the ($2S$,$3S$) to $R=0{\cdot}0231$. The ratio S_-/S_+ is 1·036.

The final parameters for ($2R$,$3R$) are listed in Tables 2, 3 and 4. A comparison of F_o and F_c is given in Table 5.

Table 4. *Positional and thermal parameters for hydrogen*

The isotropic temperature factor is $\exp\,(-B\sin^2\theta/\lambda^2)$. E.s.d. in parentheses.

	x	y	z	B
H(1)	0·2251 (18)	0·1108 (28)	0·2368 (23)	0·78 (25)
H(2)	0·1728 (20)	−0·2151 (36)	0·0249 (30)	2·10 (33)
H(3)	0·2347 (25)	−0·0059 (39)	0·5527 (32)	2·88 (39)
H(4)	0·5222 (27)	0·0346 (38)	−0·0805 (31)	2·44 (36)
H(5)	0·3446 (24)	−0·4330 (37)	0·3720 (35)	2·93 (39)
H(6)	−0·1589 (27)	−0·0784 (42)	0·2279 (32)	2·98 (43)

Enantiomer sensitive reflections were selected as described above. For the 94 reflections with $D>3{\cdot}6$ we obtained $R_+=0{\cdot}0336$, $R_-=0{\cdot}0374$ and $S_-/S_+=1{\cdot}28$. For the 13 reflections with $D>9$ the ratio S_-/S_+ is 1·42. Among the 94 reflections were 38 Bijvoet pairs. Table 6 lists the observed and calculated Bijvoet differences for these pairs. The correlation is generally good, with only one incorrect sign and one $\Delta F_{\mathrm{Bij},o}$ obviously too large. In the first Cu data set there were four incorrect $\Delta F_{\mathrm{Bij},o}$ signs among these same pairs.

At the time of these calculations there were no other theoretical determinations of anomalous scattering terms for first row atoms. It was therefore of interest to attempt a determination of $\Delta f''_{\mathrm{O}}$ from our data. Initially, we adjusted $\Delta f''_{\mathrm{O}}$ to give a minimum for S_+ (in this process we kept the ratio $\Delta f''_{\mathrm{O}}/\Delta f''_{\mathrm{C}}=\lambda^2_{K,\mathrm{C}}/\lambda^2_{K,\mathrm{O}}$ fixed at 3·55; λ_K is the K absorption edge). Instead of modifying our least-squares program to include $\Delta f''$ as one of the variables we carried out usual refinements for each $\Delta f''_{\mathrm{O}}$ value in the set 0·00, 0·02, ...0·10, with $S_{+(\mathrm{min})}$ indicated for $\Delta f''_{\mathrm{O}}=0{\cdot}05$. We also calculated S_+ and S_- for the 94 selected reflections, likewise finding a minimum for $\Delta f''_{\mathrm{O}}\simeq 0{\cdot}05$. However, there were indications that this approach is not quite appropriate.

Inspection of the data in Table 5 reveals the interesting observation that F_o-F_c in general is much larger than the corresponding $\Delta F_{\mathrm{Bij},o}-\Delta F_{\mathrm{Bij},c}$ value. This indicates that there are systematic errors which are the same for both members of a Bijvoet pair. We cannot determine the presence of systematic data errors, but we know that there are errors in the model; actual electron distributions are not spherical, and the ellipsoidal approximation for thermal parameters may not be strictly valid, to mention two effects.

We note that for a structure with one anomalous scatterer (or several with known $\Delta f''$ ratios) the relation

$$F^2_{c,+}-F^2_{c,-}=2\varepsilon_2\Delta f''$$

holds for each Bijvoet pair. (A similar relationship has been used by Parthasarathy, 1962). The structural parameters used to evaluate F_c are those for a ‘neutral, structure ($\Delta f''=0$) and ε_2 is a constant for the reflection considered. For small $\Delta f''$ this also implies

$$F_{c,+}-F_{c,-}=2\varepsilon_1\Delta f'', \text{ or}$$
$$F_{c,+}=F_{c,\mathrm{neutr}}+\varepsilon_1\Delta f'', \text{ and therefore}$$
$$S_+=\sum w(F_o-F_{c,\mathrm{neutr}}-\varepsilon_1\Delta f'')^2$$

which indicates a linear relationship between $S_- - S_+$ and $\Delta f''$. (This linear dependence was exactly satisfied for the S *vs.* $\Delta f''_{\mathrm{O}}$ calculations described above.)

From these considerations we suggest that for small effects, where atomic parameters are not perceptibly affected by $\Delta f''$ values and where systematic errors may be larger than the Bijvoet differences in question the expression $F^2_+-F^2_-=2\varepsilon_2\Delta f''$ (or its near equivalent $F_+-F_-=2\varepsilon_1\Delta f''$) are better suited as a basis for a least-squares determination of $\Delta f''$ than is the complete structure factor expression.

We calculated ε_1 for each of the 36 pairs in Table 6 for which $\Delta F_{\mathrm{Bij},o}$ was not obviously in error, and subsequently minimized the function

$$s=\sum(\Delta F_{\mathrm{Bij},o}-2\varepsilon_1\Delta f''_{\mathrm{O}})^2/2\sigma^2(F_o)$$

with respect to $\Delta f''_O$, obtaining $\Delta f''_O = 0{\cdot}041$ (4), a somewhat better agreement with the calculated value than obtained with the earlier procedures. The minimum corresponds to $s = 35$, indicating that the assigned $\sigma(F_o)$ values are quite reasonable, in contrast to the indication from the structure refinement, where a 'goodness of fit' of 7 suggests seriously underestimated errors. We interpret this discrepancy as indicating that the assigned $\sigma(F_o)$'s are realistic so far as counting statistics are concerned, but that they in no reasonable way reflect the various model errors involved.

Because of the uncertainty in the experimentally determined $\Delta f''_O$ value we found it most appropriate to base the F_c's in Table 5 on the theoretical $\Delta f''$ values quoted above. (The minute differences between our values and those presented by Cromer & Liberman (1970) were deemed insignificant in the present context.)

The Cr *data*

Because of the small number of reflections available the structure could not be successfully refined with the Cr data set. After scaling and secondary extinction correction the parameters from Tables 2, 3 and 4 gave

Table 5. *Observed and calculated structure amplitudes*

The data are listed in groups with common *h* and |*k*|. The columns are *l*, sign of *k*, $100F_o$, $100F_c$, phase angle (°) and $1/\sigma(F_o)$.

H= 0, K= 0				
1	114	127	359	48
2	3410	3467	180	7
3	364	359	180	56
4	2261	2162	0	11
5	367	310	0	45
6	661	694	1	34
7	192	162	181	62
H= 0, K= 1				
1	4239	4282	27	6
1-	4152	4278	153	6
2	1103	1095	60	23
2-	1108	1096	120	23
3	1883	1813	239	14
3-	1868	1812	302	14
4	509	475	212	43
4-	511	475	329	43
5	569	611	275	38
5-	568	609	266	38
6	644	627	308	36
6-	649	626	233	34
7	196	211	91	67
7-	195	212	90	67
H= 0, K= 2				
0	5308	5305	9	5
0-	5331	5306	352	5
1	665	634	185	38
1-	665	633	175	38
2	443	430	256	51
2-	452	430	105	50
3	1528	1500	69	17
3-	1522	1501	292	18
4	1142	1127	8	23
4-	1141	1128	353	23
5-	534	535	215	40
6-	652	644	31	36
7-	136	132	86	67
H= 0, K= 3				
1	2103	2006	45	12
1-	2080	2000	136	12
2	722	691	288	34
2-	738	694	297	34
3	1017	995	262	26
3-	1020	990	279	26
4	395	402	37	48
4-	403	408	144	48
5-	215	228	317	56
6-	376	375	223	50
7-	80	73	283	71
H= 0, K= 4				
0	1951	1918	15	13
0-	1954	1919	345	13
1	656	654	79	37
1-	660	656	282	37
2	442	447	218	45
2-	458	453	142	45
3-	657	659	266	36
4-	932	917	358	27
5-	515	530	245	42
6-	251	252	23	62
H= 0, K= 5				
1-	1746	1684	132	15
2-	453	442	244	43
3-	901	898	314	27
4-	108	95	143	53
5-	192	199	182	62
H= 0, K= 6				
0-	479	468	127	42
1-	459	462	261	41
2-	409	395	335	48
3-	345	331	312	53
4-	74	58	52	56
H= 0, K= 7				
1-	561	549	58	40
3-	337	342	258	62
H= 1, K= 0				
-7	509	506	181	43
-6	25	12	172	17
-5	644	626	1	36
-4	1961	1888	181	13
-3	2078	1992	180	12
-2	981	994	180	27
-1	1172	1167	0	21
0	1075	1027	180	27
1	2256	2431	180	11
2	2392	2403	180	11
3	979	910	0	26
4	700	687	181	34
5	38	38	1	23
6	554	559	181	40
7	193	174	1	67
H= 1, K= 1				
-7	93	88	153	53
-7-	102	94	28	56
-6	140	144	115	53
-6-	138	146	66	53
-5	1055	1091	285	24
-5-	1055	1092	256	24
-4	1381	1325	60	19
-4-	1381	1326	121	19
-3	788	760	251	33
-3-	784	757	290	33
-2	722	711	143	34
-2-	717	707	37	36
-1	1919	1923	169	14
-1-	1943	1925	11	13
0	1550	1632	23	17
0-	1668	1628	157	16
1	2727	2683	315	9
1-	2418	2680	225	9
2	3875	3981	99	8
2-	3814	3982	82	8
3	989	960	159	26
3-	988	960	22	26
4	203	202	301	59
4-	215	200	242	59
5	187	183	60	53
5-	196	188	121	56
6	640	662	83	36
6-	644	666	98	36
7	174	162	161	67
7-	174	161	20	67
H= 1, K= 2				
-7	620	632	204	38
-7-	622	632	158	37
-6	198	206	152	56
-6-	194	204	209	56
-5	311	320	324	50
-5-	315	320	37	50
-4	1496	1453	218	17
-4-	1502	1453	143	17
-3	736	753	183	34
-3-	737	753	197	34
-2	602	596	88	42
-2-	607	599	273	42
-1	1104	1076	209	21
-1-	1107	1077	152	21
0	3505	3592	187	7
0-	3621	3591	173	7
1	2643	2730	267	10
1-	2682	2733	94	10
2	527	503	0	45
2-	530	502	359	45
3	1306	1286	78	20
3-	1309	1290	283	20
4	1419	1396	178	18
4-	1423	1396	182	18
5	713	723	255	33
5-	713	727	106	33
6	68	64	243	40
6-	64	59	120	38
7-	386	387	2	54
H= 1, K= 3				
-7	426	440	147	53
-6	394	398	201	50
-6-	395	399	340	48
-5	558	573	303	38
-5-	561	576	238	38
-4	842	904	29	29
-4-	882	905	152	29
-3	1176	1154	240	22
-3-	1172	1152	301	22
-2	809	816	65	31
-2-	810	818	116	31
-1	1233	1223	150	21
-1-	1238	1225	11	21
0	604	623	94	40
0-	590	619	87	42
1	1438	1393	240	18
1-	1424	1397	300	19
2-	757	754	72	33
3	648	633	41	37
3-	652	634	140	37
4	633	624	58	36
4-	628	671	123	36
5	1001	990	179	25
5-	993	988	2	25
6	486	465	145	63
6-	478	461	37	45
7-	139	142	225	91
H= 1, K= 4				
-6	565	579	157	40
-6-	567	580	204	40
-5	440	438	238	45
-5-	443	438	123	45
-4	806	808	242	30
-4-	802	806	99	30
-3	314	329	197	50
-3-	318	330	144	50
-2	444	450	68	45
-2-	442	450	293	45
-1	311	288	316	56
-1-	307	285	24	56
0	1349	1409	192	19
0-	1409	1409	169	18
1	1693	1692	263	18
1-	1689	1699	98	16
2	477	480	202	43
2-	474	479	159	43
3	552	556	105	40
3-	599	561	256	37
4	437	446	37	45
4-	436	445	324	45
5	579	575	294	38
5-	582	576	68	38
6-	454	471	173	45
H= 1, K= 5				
-6	69	66	293	77
-5	246	254	119	62
-5-	243	253	63	62
-4	561	541	8	38
-4-	567	562	173	38
-3	995	1008	265	25
-3-	996	1002	276	25
-2	340	318	167	50
-2-	325	315	13	50
-1	1009	1017	134	25
-1-	1018	1017	47	25
0-	1079	1095	124	24
1	461	452	284	41
1-	470	449	257	43
2	673	676	260	34
2-	679	677	281	34
3	671	671	175	34
3-	674	672	6	34
4	622	624	90	37
4-	624	623	91	37
5-	156	145	59	71
H= 1, K= 6				
-4-	30	21	245	25
-3	199	193	355	59
-3-	194	189	6	59
-2	471	479	337	43
-2-	480	478	24	43
-1-	521	525	121	40
0-	1051	1047	171	24
1-	233	216	34	56
2	584	575	11	38
2-	596	575	350	37
3	209	221	241	62
3-	204	217	121	59
4-	190	188	192	71
H= 1, K= 7				
-3-	231	242	280	77
-1-	384	391	96	53
0-	198	192	90	67
2-	626	412	244	50
H= 2, K= 0				
-7	398	403	1	50
-6	47	35	180	29
-5	881	878	1	29
-4	328	322	1	58
-3	1987	1979	0	12
-2	811	796	180	31
-1	158	158	0	77
0	1361	1353	0	17
1	1717	1865	0	15
2	734	692	0	34
3	453	445	1	50
4	1279	1296	181	21
5	201	228	0	58
6	451	445	1	45
7	342	323	181	59
H= 2, K= 1				
-7	324	334	12	56
-7-	329	339	168	56
-6	765	772	279	31
-6-	758	770	262	31
-5	453	443	273	45
-5-	455	446	268	43
-4	824	858	118	30
-4-	830	859	62	30
-3	2146	2184	84	12
-3-	2191	2186	97	11
-2	3467	3522	288	7
-2-	3641	3520	253	7
-1	1218	1239	273	21
-1-	1243	1238	248	21
0	1368	1387	253	19
0-	1401	1383	288	17
1	971	974	349	24
1-	976	976	191	24
2	860	816	240	30
2-	869	821	301	30
3	614	612	59	38
3-	607	607	122	40
4	1662	1669	281	16
4-	1657	1667	260	16
5	297	292	324	53
5-	298	290	216	53
6	313	315	269	53
6-	318	315	274	53
7	156	150	144	77
7-	155	147	35	77
H= 2, K= 2				
-7	187	192	48	67
-7-	182	188	319	67
-6	573	585	39	38
-6-	576	589	322	38
-5	1097	1101	340	23
-5-	1097	1098	21	23
-4	496	491	293	43
-4-	500	498	69	43
-3	1324	1283	56	20
-3-	1332	1281	305	20
-2	1605	1617	111	16
-2-	1638	1617	250	16
-1	1005	996	306	26
-1-	1019	999	55	26
0	755	722	39	34
0-	758	720	322	34
1	2160	2277	352	12
1-	2217	2275	9	11
2	1173	1149	8	22
2-	1167	1150	353	22
3	821	809	137	30
3-	816	804	224	31
4	1498	1518	190	17
4-	1509	1519	171	18
5	568	571	2	38
5-	565	572	359	38
6	994	985	16	25
6-	998	986	345	25
7-	222	209	169	77
H= 2, K= 3				
-7	339	331	168	59
-6	541	550	249	40
-6-	546	550	292	40
-5	668	672	358	34
-5-	664	671	183	34
-4	290	279	145	53
-4-	292	284	36	53
-3	679	677	79	36
-3-	671	675	102	36
-2	1550	1508	317	17
-2-	1558	1508	228	17
-1	734	710	289	34
-1-	731	711	252	34
0	2066	2016	205	13
0-	2081	2015	335	13
1	487	493	30	45
1-	489	491	151	45
2	1059	1048	324	24
2-	1052	1040	217	25
3	1738	1752	15	15
3-	1742	1752	166	15
4	1113	1111	251	23
4-	1111	1112	290	23
5	887	874	213	28
5-	892	874	328	28
6	84	90	5	56
6-	79	87	176	56
H= 2, K= 4				
-6	443	453	125	48
-6-	448	451	237	48
-5	589	586	305	38
-5-	585	585	57	38
-4	625	636	346	36
-4-	624	635	15	36
-3	742	741	101	32
-3-	742	740	260	32
-2	1160	1185	105	22
-2-	1165	1184	256	22
-1	1453	1443	347	18
-1-	1463	1442	14	18
0	119	112	33	53
0-	116	112	328	53
1	365	353	235	50
1-	362	351	126	50
2	346	345	143	50
2-	345	342	218	50
3	474	483	80	43
3-	472	480	281	43
4	323	322	1	50
4-	321	322	0	50
5	269	274	325	56
5-	271	274	36	56
6-	257	268	194	71
H= 2, K= 5				
-6	66	76	19	83
-5	275	271	74	59
-5-	277	269	108	59
-4	471	479	226	43
-4-	477	482	316	43
-3	397	400	318	48
-3-	400	402	223	45
-2	221	226	44	53
-2-	215	226	137	53
-1-	542	542	153	40
0-	216	213	307	53
1	414	409	350	45
1-	416	409	191	45
2	430	460	264	45
2-	434	462	278	45
3	426	450	39	45
3-	428	448	143	45
4	298	294	270	56
4-	302	292	271	56
5-	452	452	223	50
H= 2, K= 6				
-4-	397	407	294	53
-3	451	455	196	45
-3-	451	454	165	45
-2-	80	87	159	43
-1-	543	551	355	40
0-	376	394	249	48
1	200	205	76	56
1-	208	212	285	56
2	79	65	44	45
2-	82	68	317	48
3	261	262	196	62
3-	249	263	144	62
4-	100	104	197	77
H= 2, K= 7				
-3-	83	72	138	83
2-	219	210	121	71
H= 3, K= 0				
-7	707	711	141	33
-6	369	362	180	48
-5	1171	1175	180	22
-4	639	645	0	37
-3	1271	1347	0	20
-2	1231	1253	180	21
-1	5787	5889	180	4
0	3208	3170	0	8
1	395	377	1	54
2	854	822	180	30
3	97	81	182	50
4	1274	1270	0	20
5	770	776	180	31
6	302	300	180	54
7	206	195	0	83
H= 3, K= 1				
-7	538	525	332	42
-7-	534	523	209	42
-6	718	707	129	33
-6-	716	701	52	33
-5	980	994	135	24
-5-	974	996	46	26
-4	535	560	248	42
-4-	533	558	292	42
-3	960	975	19	27
-3-	973	979	142	27
-2	1955	1973	56	13
-2-	2031	1974	125	12
-1	2469	2507	128	10
-1-	2584	2508	53	10
0	1337	1348	194	19
0-	1360	1345	346	19
1	503	505	345	48
1-	501	505	195	48
2	1358	1379	102	19
2-	1356	1374	79	19
3	387	370	131	50
3-	379	368	50	50
4	1034	1049	70	24
4-	1038	1052	111	24
5	585	582	87	38
5-	594	584	94	37
6	408	403	233	50
6-	410	406	308	50
H= 3, K= 2				
-7	91	89	146	59
-7-	91	89	181	59
-6	731	725	335	32
-6-	732	721	26	32
-5	1182	1200	178	22
-5-	1194	1201	183	22
-4	897	902	225	28
-4-	903	907	135	28
-3	615	627	43	38
-3-	625	630	318	38
-2	613	620	316	40
-2-	607	616	45	40
-1	2639	2703	177	10
-1-	2805	2704	188	9
0	1891	1860	30	14
0-	1988	1858	330	12
1	355	328	319	56
1-	359	329	42	56
2	1448	1486	249	18
2-	1438	1487	112	18
3	727	728	156	33
3-	730	727	205	33
4	1016	1013	11	25
6-	1012	1013	350	25
5	537	538	96	60
5-	538	540	265	40
6	155	158	348	67
6-	153	157	18	67
H= 3, K= 3				
-7	169	176	210	83
-7-	169	178	330	83
-6	542	543	137	42
-6-	552	549	44	40
-5	629	640	77	36
-5-	633	645	104	34
-4	534	523	238	40
-4-	525	520	303	40
-3	277	287	283	58
-3-	285	292	258	53
-2	1341	1332	58	19
-2-	1356	1332	123	19
-1	1560	1557	166	17
-1-	1603	1558	15	16
0	1546	1534	180	17
0-	1576	1534	1	17
1	1412	1425	83	18
1-	1442	1424	119	18
2	566	561	86	40
2-	571	563	135	40
3	658	654	237	36
3-	658	651	304	36
4	588	588	131	38
4-	585	587	50	38
5	725	727	129	32
5-	737	729	52	32
6-	254	254	149	67
H= 3, K= 4				
-6	450	452	270	48
-5	954	953	143	26
-5-	963	953	179	26
-4	363	350	266	48
-4-	362	348	96	48
-3	431	452	60	45
-3-	435	456	300	45
-2	609	602	307	37
-2-	610	603	55	37
-1	566	586	170	40
-1-	553	584	191	40
0	122	115	242	53
0-	120	114	118	50
1	485	443	182	43
1-	492	442	178	43
2	601	608	250	37
2-	605	612	111	37
3	402	391	68	45
3-	410	396	293	45
4	912	918	0	27
4-	925	920	1	27
5	611	609	151	38
5-	609	605	210	38
H= 3, K= 5				
-5-	435	442	25	50
-4	727	726	236	32
-4-	720	724	305	32
-3	472	493	330	43
-3-	478	492	210	42
-2	983	1000	72	26
-2-	990	1002	109	25
-1-	776	776	359	30
0	690	723	198	33
0-	698	723	343	33
1	806	806	81	30
1-	816	808	100	29
2	99	92	295	48
2-	107	94	244	50
3	703	680	230	33
3-	712	680	311	33
4	254	274	79	59
6-	286	276	102	59
5-	450	452	88	48
H= 3, K= 6				
-4-	660	655	140	37
-3	187	190	278	62
-3-	198	188	83	62
-2-	705	714	20	33
-1-	502	518	284	42
0-	462	477	144	43
1	255	261	184	56
1-	255	258	178	56
2	126	138	257	62
2-	129	140	104	59
3-	118	128	287	67
H= 3, K= 7				
-2-	211	210	60	77
1-	521	489	76	43
H= 4, K= 0				
-7	806	795	181	30
-6	620	609	180	37
-5	1846	1906	1	14
-4	1114	1147	0	23
-3	657	672	180	37
-2	1977	1943	180	11
-1	224	242	0	71
0	290	329	0	56
1	105	110	0	59
2	171	184	181	62
3	728	700	1	33
4	1158	1168	181	22
5	479	466	181	43
6	128	122	142	67
H= 4, K= 1				
-7	147	136	29	67
-7-	148	135	151	67
-6	557	554	188	40
-6-	552	551	353	40
-5	1932	2015	260	14
-5-	1959	2019	282	13
-4	822	835	22	30
-4-	820	833	159	30
-3	745	774	33	33
-3-	745	771	147	33
-2	499	482	326	45
-2-	504	484	215	45
-1	1662	1617	233	16
-1-	1689	1618	307	15
0	914	926	268	29
0-	925	927	273	29
1	2819	2810	279	9
1-	2853	2809	242	9
2	1038	1027	101	25
2-	1040	1026	80	25
3	533	524	82	42
3-	533	524	99	42
4	757	781	315	31
4-	749	779	226	32
5	841	869	267	28
5-	887	869	274	28
6	321	328	165	50
6-	318	325	16	50
H= 4, K= 2				
-7	105	111	207	71
-7-	117	108	44	71
-6	424	416	103	48
-6-	425	415	259	48
-5	725	734	26	32
-5-	728	734	336	32
-4	814	812	276	30
-4-	814	812	85	30
-3	423	432	248	48
-3-	420	433	113	48
-2	593	577	92	40
-2-	594	578	269	40
-1	863	883	27	29
-1-	871	884	333	29
0	1301	1336	132	20
0-	1323	1337	229	20
1	1123	1114	264	23
1-	1130	1118	97	23
2	860	877	282	29
2-	869	875	79	29
3	347	347	60	50
3-	346	348	302	50
4	933	919	157	27
4-	939	919	204	26
5	250	247	291	56
5-	247	248	70	59
6-	59	41	103	59
H= 4, K= 3				
-7	135	135	136	91
-7-	139	136	45	91
-6	244	234	295	62
-6-	241	230	284	62
-5	886	894	292	24
-5-	889	892	249	24
-4	717	723	48	33
-4-	716	719	133	33
-3	626	649	215	37
-3-	634	656	326	34
-2	957	942	324	26
-2-	968	964	217	26
-1	804	828	297	31
-1-	804	820	243	31
0	744	747	18	33
0-	752	788	143	32
1	841	827	265	29
1-	862	830	277	29
2	318	343	186	50
2-	316	342	355	50
3	149	156	0	53
3-	151	156	182	53
4	671	682	349	38
4-	667	681	192	38
5	524	517	272	42
5-	523	517	270	42
H= 4, K= 4				
-6	620	623	140	38
-5	598	581	32	38
-5-	599	583	329	38
-4	948	948	340	26
-4-	943	943	21	26
-3	522	527	212	40
-3-	522	529	149	40
-2	854	876	171	29
-2-	855	872	190	29
-1-	607	609	1	37
0	558	550	91	38
0-	589	587	270	37
1	582	592	302	38
1-	574	589	60	38
2	364	362	279	48
2-	365	363	82	48
3	406	426	186	45
4	530	505	160	42
4-	527	502	202	42
5-	334	309	72	62
H= 4, K= 5				
-5-	396	394	327	53
-4	808	800	47	30
-4-	813	799	134	30
-3	471	474	350	43
-3-	464	465	191	43
-2	503	513	295	42
-2-	511	515	246	42
-1	638	682	235	36
-1-	650	683	306	36
0	518	518	26	40
0-	528	521	156	40
1	152	182	16	53
1-	156	182	165	56
2	198	210	315	56
2-	198	209	227	56
3	29	12	249	24
3-	19	14	304	15
4-	392	374	176	56
H= 4, K= 6				
-4-	135	135	20	83
-3-	73	82	178	53
-2-	169	176	291	62
-1-	248	249	8	59
0	247	251	182	59
0-	256	250	180	59
1	239	233	302	62
1-	244	233	60	62
2-	226	209	7	67
3-	386	383	163	56
H= 4, K= 7				
-1-	194	202	217	83
H= 5, K= 0				
-7	93	71	2	67
-6	40	50	182	27
-5	285	290	0	50
-4	648	682	181	36
-3	935	905	1	27
-2	277	303	0	59
-1	79	73	357	50
0	372	358	0	53
1	193	65	178	62
2	200	232	1	56
3	1250	1291	1	21
4	92	82	182	45
5	128	139	181	56
6	415	426	1	53
H= 5, K= 1				
-7	461	464	98	50
-7-	463	463	88	50
-6	475	468	154	45
-6-	472	464	28	45
-5	159	157	86	53
-5-	158	155	96	53
-4	158	144	323	53
-4-	145	139	217	53
-3	1699	1735	92	15
-3-	1727	1737	89	15
-2	331	368	260	54
-2-	336	370	280	56
-1	819	844	112	31
-1-	816	840	68	31
0	779	809	123	32
0-	785	813	58	32
1	733	705	61	33
1-	743	711	120	31
2	664	704	245	34
2-	645	703	296	34
3	455	453	85	43
3-	453	449	96	43
4	78	54	27	42
4-	62	54	156	37
5	500	508	103	43
5-	502	505	78	43
H= 5, K= 2				
-7	341	380	12	62
-7-	345	339	349	62
-6	382	373	97	50
-6-	382	378	265	50
-5	537	524	194	40
-5-	536	524	167	40
-4	954	980	223	26
-4-	967	985	138	26
-3	1272	1293	5	21
-3-	1289	1292	356	20
-2	1212	1229	46	22
-2-	1234	1237	315	21
-1	278	281	234	54
-1-	275	281	126	58
0	924	945	155	28
0-	932	940	205	27
1	35	40	141	23
1-	31	38	217	20
2	768	818	353	31
2-	764	815	7	31
3	951	974	15	26
3-	955	974	347	26
4	210	219	195	56
4-	216	221	166	56
5-	103	106	193	62
H= 5, K= 3				
-6	244	248	109	62
-6-	251	247	73	62
-5	534	533	69	42
-5-	536	533	112	42
-4	1035	1046	189	24
-4-	1047	1047	352	24
-3	809	816	161	30
-3-	803	809	21	30
-2	956	975	4	28
-2-	967	978	176	26
-1	1307	1337	34	20
-1-	1322	1336	146	20
0	1284	1233	164	21
0-	1238	1236	17	21
1	1002	1018	153	25
1-	1006	1011	29	25
2	771	792	229	31
2-	773	789	312	31
3	902	932	28	27
3-	898	932	157	28
4	278	286	39	50
4-	274	285	142	56
5-	326	332	25	62
H= 5, K= 4				
-6	494	494	88	48
-6-	494	496	274	48
-5	156	146	313	67
-5-	147	143	48	62
-4	370	381	270	50
-4-	373	384	91	50
-3	479	475	190	43
-3-	482	476	171	42
-2	667	665	132	34
-2-	686	666	230	33
-1	1062	1056	1	24
-1-	1076	1056	0	24
0	683	696	41	33
0-	660	694	320	34
1	310	311	158	50
1-	306	310	202	50
2	372	376	197	48
2-	348	374	164	48
3	192	180	14	59
3-	192	181	348	59
4-	305	314	343	62
H= 5, K= 5				
-5	667	686	89	36
-5-	681	685	92	36
-4-	162	161	6	67
-3	384	403	281	50
-3-	387	401	240	50
-2	373	371	199	50
-2-	376	368	350	50
-1	295	297	111	53
-1-	296	295	70	53
0	369	377	150	50
0-	371	381	31	48
1	370	377	79	50
1-	374	380	103	50
2	287	312	225	59
2-	285	311	316	59
3-	246	232	150	67
H= 5, K= 6				
-3-	146	150	219	83
-1-	391	379	356	53
0-	106	109	173	62
1-	241	241	162	67
2-	87	92	252	43
H= 6, K= 0				
-7	570	572	181	42
-6	13	6	351	11
-5	361	355	181	50
-4	110	87	181	50
-3	192	185	1	56
-2	535	553	1	42
-1	2462	2464	181	11
0	300	305	0	53
1	157	164	0	53
2	560	570	180	38
3	828	842	181	29
4	516	507	1	42
5	148	133	181	59
H= 6, K= 1				
-6	408	415	247	50
-6-	410	415	275	50
-5	108	106	278	53
-5-	108	105	266	50
-4	483	526	278	43
-4-	485	528	265	42
-3	659	678	264	36
-3-	659	679	277	36
-2	220	194	21	56
-2-	208	187	161	56
-1	683	695	102	38
-1-	677	682	79	38
0	653	639	285	36
0-	635	626	255	37
1	1258	1280	297	21
1-	1253	1275	284	21
2	504	541	118	42
2-	506	542	63	42
3	523	532	181	40
3-	520	532	0	40
4	107	106	358	58
4-	114	110	183	59
5-	322	322	143	62
H= 6, K= 2				
-6	315	302	304	59
-6-	316	302	57	59
-5	537	548	151	42
-5-	539	547	210	42
-4	259	261	282	53
-4-	258	259	79	53
-3	517	558	5	38
-3-	521	555	355	40
-2	768	748	300	31
-2-	771	770	62	31
-1	2510	2628	190	10
-1-	2609	2630	171	10
0	619	630	133	37
0-	623	627	229	37
1	984	1020	23	24
1-	998	1025	337	24
2	722	720	305	32
2-	718	714	58	33
3	1131	1158	190	23
3-	1135	1161	171	22
4	340	358	233	56
4-	343	361	127	56
5-	201	181	225	83
H= 6, K= 3				
-6	476	472	277	48
-6-	476	471	245	48
-5	126	124	253	62
-5-	128	123	288	62
-4	550	546	202	40
-4-	534	546	339	40
-3	384	389	279	48
-3-	380	384	263	48
-2	1513	1542	18	18
-2-	1525	1537	163	17
-1	242	241	347	53
-1-	245	243	198	53
0	1480	1496	226	18
0-	1497	1496	315	18
1	290	301	236	53
1-	294	303	305	53
2	796	833	58	30
2-	792	834	123	30
3	131	129	2	59
3-	130	128	178	59
4-	159	178	273	71
H= 6, K= 4				
-5	121	116	116	77
-5-	124	117	246	77
-4	320	324	255	56
-4-	322	323	106	56
-3	449	446	177	45
-3-	455	445	185	45
-2	583	584	278	38
-2-	589	587	84	33
-1	185	198	181	56
-1-	238	201	180	56
0	203	197	66	56
0-	211	200	294	56
1	131	127	84	56
1-	132	130	298	53
2	639	622	255	36
2-	645	627	107	36
3-	593	593	147	40
H= 6, K= 5				
-4-	79	78	287	67
-3-	292	286	284	62
-2	392	401	88	50
-2-	385	396	117	50
-1	300	291	268	56
-1-	305	293	274	56
0	785	789	275	32
0-	748	745	246	32
1	440	419	57	48
1-	448	422	125	48
2-	611	603	99	38
H= 6, K= 6				
-1-	283	294	188	67
0-	346	341	128	62
H= 7, K= 0				
-6	457	445	181	50
-5	296	311	1	56
-4	255	244	1	56
-3	389	322	1	48
-2	323	346	1	50
-1	1474	1561	1	18
0	317	301	1	50
1	1018	1022	180	25
2	489	504	180	42
3	1620	1438	1	18
4	515	503	0	45
H= 7, K= 1				
-6	1252	1214	95	20
-6-	1255	1215	87	20
-5	522	511	241	43
-5-	525	513	300	42
-4	207	179	294	58
-4-	216	180	247	58
-3	282	306	158	53
-3-	282	306	24	53
-2	188	160	92	56
-2-	186	158	90	53
-1	176	172	35	53
-1-	174	174	147	53
0	1183	1209	63	22
0-	1193	1212	118	22
1	763	761	283	31
1-	765	759	259	31
2	794	810	214	30
2-	789	809	327	30
3	352	359	180	53
3-	345	354	2	53
4-	538	546	160	43
H= 7, K= 2				
-6	249	257	84	77
-6-	255	261	279	77
-5	753	742	76	32
-5-	753	739	285	32
-4	223	238	304	59
-4-	221	237	18	59
-3	515	506	302	42
-3-	521	506	60	42
-2	165	171	171	56
-2-	181	171	189	56
-1	839	845	3	29
-1-	840	845	358	29
0	909	904	67	27
0-	917	908	294	27
1	157	157	74	56
1-	166	157	287	56
2	253	252	254	56
2-	258	255	108	56
3	501	494	358	43
3-	506	496	4	43
4-	187	187	242	83
H= 7, K= 3				
-5	246	248	227	71
-5-	246	248	315	71
-4	467	471	75	45
-4-	467	471	107	45
-3	314	312	154	53
-3-	317	314	28	53
-2	390	386	334	48
-2-	393	388	207	48
-1	429	434	245	45
-1-	442	434	296	45
0	669	659	93	34
0-	667	654	89	34
1	103	119	21	53
1-	96	115	159	59
2	308	314	273	54
2-	303	308	268	54
3-	149	151	305	77
H= 7, K= 4				
-4-	310	306	9	62
-3	137	145	265	67
-3-	141	146	97	67
-2	361	357	132	53
-2-	368	359	277	53
-1	916	917	9	27
-1-	927	917	353	27
0	539	542	76	42
0-	553	545	286	40
1	427	419	182	50
1-	432	418	178	48
2-	136	119	104	77
H= 7, K= 5				
-3-	45	38	2	67
-2-	241	236	262	71
-1-	302	305	303	62
0-	679	639	129	34
1-	305	317	88	67
H= 8, K= 0				
-5	20	50	188	22
-4	650	683	181	37
-3	290	309	1	56
-2	195	225	1	56
-1	688	675	181	34
0	807	788	181	30
1	416	421	181	48
2	55	36	355	43
3	615	599	1	37
H= 8, K= 1				
-5	300	296	256	67
-5-	305	299	285	62
-4	637	653	247	37
-4-	636	651	275	37
-3	674	654	108	36
-3-	684	658	74	34
-2	71	59	27	42
-2-	86	58	159	48
-1	452	460	37	45
-1-	450	459	144	45
0	170	174	253	56
0-	156	173	258	56
1	282	298	120	56
1-	275	293	63	56
2	512	510	192	43
2-	511	511	347	43
3-	304	298	105	67
H= 8, K= 2				
-5	239	249	149	77
-5-	239	250	213	77
-4	867	831	205	29
-4-	848	830	157	29
-3	321	323	302	56
-3-	324	325	60	56
-2	113	99	76	54
-2-	116	109	285	56
-1	607	613	220	38
-1-	609	618	142	37
0	404	390	178	48
0-	407	381	184	48
1	144	133	76	62
1-	144	136	285	62
2-	113	105	148	71
H= 8, K= 3				
-4	258	245	216	71
-4-	260	247	326	71
-3-	804	747	13	31
-2	75	79	166	53
-2-	75	76	14	53
-1	603	594	16	38
-1-	600	593	164	38
0	344	338	251	56
0-	349	339	291	56
1-	221	220	96	67
2-	293	302	354	67
H= 8, K= 4				
-3	77	81	273	83
-3-	82	82	92	83
-2-	618	598	181	40
-1-	518	506	117	45
0-	195	180	131	77
H= 9, K= 0				
-4	24	19	178	33
-3	324	309	180	59
-2	985	990	1	26
-1	101	84	181	62
0	221	197	1	62
1	155	126	1	77
H= 9, K= 1				
-4	347	336	49	62
-4-	352	338	132	62
-3	662	640	278	37
-3-	658	636	264	37
-2	792	787	275	31
-2-	796	789	246	31
-1	359	347	102	56
-1-	350	344	80	56
0-	469	470	82	48
1-	494	495	256	48
H= 9, K= 2				
-3	313	316	81	67
-3-	320	318	281	62
-2	1230	1205	354	21
-2-	1242	1204	7	20
-1-	312	308	95	62
0-	199	201	222	77
1-	400	393	278	56
H= 9, K= 3				
-2	568	558	326	42
-2-	574	559	215	42
-1-	584	559	149	42

an R index of 0·057. Among the 68 reflections with $D>4$ were 28 Bijvoet pairs. Four of the observed Bijvoet differences had the incorrect sign; however, all pairs with $D>8$ gave the correct sign indication, and also in magnitude the agreement was fairly good.

With Cr $K\alpha$ radiation the Bijvoet differences (in $|F|$) are about twice as large as for Cu $K\alpha$; in a few cases ΔF_{Bij} amounts to about 10% in $|F|$, which of course is quite readily observable.

The molecular structure

The molecular geometry determined by Okaya *et al.* (1966) is in excellent agreement with ours (see Fig. 1). The largest difference in an interatomic distance, in terms of their e.s.d.'s, corresponds to about 2σ, and most of the differences in bond angles are negligible.

The thermal parameters, however, show larger relative discrepancies. Part of the difference most likely results from the use of different form factors. In addition, the absorption corrections employed by Okaya *et al.* seem to have been based on an incorrect value of μr (0·8 instead of 0·4), which would also give rise to a systematic difference in the temperature factors.

Comparison with the parameters from an 'Intensity measurement project' (Hamilton & Abrahams, 1970) does not seem appropriate, since those results were based on incomplete data.

Conclusions

This study has demonstrated conclusively that absolute configurations can be reliably determined from the anomalous scattering effects of oxygen, using either Cu $K\alpha$ or Cr $K\alpha$ radiation. Assuming diffractometer data of good quality, we feel that it will often be possible to obtain the absolute configuration with no measurements in addition to those required for the structure determination (*e.g.* Neidle & Rogers, 1970; Thiessen & Hope, 1970).

Cr $K\alpha$ radiation in general does not offer any particular advantage over Cu $K\alpha$ radiation; drawbacks associated with the relatively small number of reflections available (about one-third of the Cu $K\alpha$ sphere) and the absorption problems encountered tend to cancel the benefits of the potentially more pronounced effects.

The method used by us for determination of $\Delta f''_{\mathrm{O}}$ from observed ΔF_{Bij} seemed the most convenient for our data. However, if only a relatively small number of Bijvoet pairs have been measured, the use of $\Delta I_{\mathrm{Bij}}/I$ ratios (Parthasarathy, 1962; Zachariasen, 1965) as the basis for a least-squares calculation may be safer, particularly where absorption corrections have not been made, since it essentially eliminates scaling problems.

Table 6. *Observed and calculated ΔF_{Bij}*

Two pairs marked with * were not used in the evaluation of $\Delta f_{\mathrm{O}}''$ (see text).

			$100\Delta F_{\mathrm{Bij}}$					$100\Delta F_{\mathrm{Bij}}$					$100\Delta F_{\mathrm{Bij}}$	
h	|k|	l	obs	calc	h	|k|	l	obs	calc	h	|k|	l	obs	calc
0	4	2	-16	-6	3	3	-6	-10	-6	5	3	-3	6	7
1	1	-7	-9	-6	3	3	-5	-4	-5	5	4	-5	9	6
1	1	5	-9	-6	3	3	-3	-8	-5	6	1	-2	12	7
1	6	-3	5	4	3	4	-3	-4	-4	6	2	4	-3	-3
1	6	3	5	4	3	4	3	-8	-5	6	4	0	-8	-3
2	1	-7	-5	-5	*4	2	-7	-12	3	6	5	-2	7	5
2	1	3	7	5	4	3	-6	5	4	7	1	3	7	5
2	1	7	1	3	4	3	-3	-8	-7	7	2	-6	-6	-4
2	2	-7	5	4	*4	4	0	-31	-7	7	3	1	7	4
2	3	-4	-2	-5	4	5	-3	7	9	7	3	2	5	6
2	3	2	6	8	5	1	-4	13	5	8	1	-5	-5	-3
2	3	6	5	3	5	1	-2	-5	-4	8	1	1	7	5
2	6	1	-8	-7	5	1	1	-10	-6					

The present data clearly are not precise enough to provide a good test of the accuracy of the calculated $\Delta f''_{\mathrm{O}}$ value. However, with very careful measurements of Bijvoet differences for a set of selected reflections it should be possible to lower the e.s.d. in $\Delta f''_{\mathrm{O}}$ from the present 0·004 to, say, 0·001, although for the results to be meaningful at this level it will also be necessary to eliminate most of the systematic errors in the evaluation of the temperature factors, since the magnitude of $\Delta F_{\mathrm{Bij},c}$ depends on these parameters.

Presumably the most accurate determinations of Bijvoet differences can be obtained from measurements of hkl–$\bar{h}\bar{k}\bar{l}$ pairs. Our main reason for measuring hkl and $h\bar{k}l$ rather than exact Friedel pairs was one involving setting efficiency for the diffractometer.

Moncrief & Sims (1969) have developed an experimental method for relative absorption correction of individual reflections, which may be necessary for instruments which do not permit the observation of both hkl and $\bar{h}\bar{k}\bar{l}$ reflections with one crystal mounting. Ordinarily, however, for instruments with full 3- or 4-circle geometry this complication can of course be avoided.

The dependence of S_-/S_+ on the magnitude of $\Delta f''$ poses an intriguing question regarding the use of Hamilton's (1965) R ratio significance test. It seems that unless one is certain about the accuracy of the $\Delta f''$ values used the significance of a given R ratio may be somewhat dubious.

In order to determine whether the absolute configuration of a molecule containing only C, N and H could be established by X-ray methods we performed a model calculation, assuming a formula $C_7N_3H_6$ and the same $\sigma(F)$ as in the second Cu data set. The results strongly suggest that a number of observable Bijvoet differences sufficient for a satisfactory result can be expected. In a similar way we have found that the determination of the absolute configuration of a hydrocarbon with present methods is beyond reach.

This work has been supported through grants from the National Science Foundation.

References

Abrahams, S. C., Hamilton, W. C. & Mathieson, A. McL. (1970). *Acta Cryst.* A**26**, 1.

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* **168**, 271.
CAHN, R. S., INGOLD, C. K. & PRELOG, V. (1966). *Angew. Chem.* Int. Ed. **5**, 358.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891.
DE LA CAMP, U. & HOPE, H. (1970). *Acta Cryst.* B**26**, 846.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
HAMILTON, W. C. & ABRAHAMS, S. C. (1970). *Acta Cryst.* A**26**, 18.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
HÖNL, H. (1933). *Ann. Phys. Lpz.* **18**, 625.
HOPE, H. & DE LA CAMP, U. (1969). *Nature, Lond.* **221**, 54.
HOPE, H., DE LA CAMP, U. & THIESSEN, W. E. (1969). *Acta Cryst.* A**25**, S78.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
MONCRIEF, J. W. & SIMS, S. P. (1969). *Chem. Commun.* p. 914.
NEIDLE, S. & ROGERS, D. (1970). *Nature, Lond.* **225**, 376.
OKAYA, Y., STEMPLE, N. R. & KAY, M. I. (1966). *Acta Cryst.* **21**, 237.
PARTHASARATHY, R. (1962). *Acta Cryst.* **15**, 41.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
THIESSEN, W. E. & HOPE, H. (1970). *Acta Cryst.* B**26**, 554.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.
ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 714.

Acta Cryst. (1972). A**28**, 207

Theoretical Determination of the Geometrical Form of the Crystal of Anthracene

BY A. I. KITAIGORODSKY AND N. A. AHMED

Institute of Elemento-Organic Compounds, Academy of Sciences of the USSR, Moscow

(*Received* 13 *October* 1971)

The form of a crystal of anthracene was determined by calculating from the atom–atom potentials the surface energies of all planes having simple indices and by drawing out a Wulff plot. Good agreement is obtained between the theoretical form and that of real crystals grown from solution.

Introduction

The relationship between the internal structure of a crystal and its external habit was first expressed by A. Bravais, who emphasized the importance of crystal planes of high density. The significance of the atomic array in determining crystal habit was then shown by Kossel (1928), Stranski (1928), Hartman (1958) and others. There were also several attempts at correlating crystal habit with surface free energy when plotted in spherical coordinates [Wulff's plot or 'γ plot' (Wulff, 1901; Yamada, 1924; Herring, 1950)]. Hartman & Perdok (1955) introduced the periodic bond chain method which serves as a preliminary investigation before an exact calculation of surface energy is carried out. Wulff & Gualtieri (1962) showed that differences between experimental and derived habits yield specific information with regard to the nature of adsorption, surface lattice deformation, and the character of bonding. In all this work there was no possibility of the calculation of exact values of surface energy since a method of calculating the internal forces was lacking. The introduction in chemical organic crystallography of the method of atom–atom potentials made possible the calculation of several properties (Kitaigorodsky, 1970). In this work the exact values of surface energy have been calculated and the geometrical form of the crystal of anthracene has been derived. Anthracene was chosen as it has a simple molecule containing only carbon and hydrogen atoms, the interactions of which are known. Moreover the structure is known to a high degree of accuracy.

Calculation of the potential energy of nucleation

Any crystallization operation can be considered to consist of three steps:

(1) achievement of supersaturation.
(2) formation of crystal nuclei,
(3) growth of crystals,

The formation of crystal nuclei is a difficult process: not only do the constituent molecules have to coagulate, resisting the tendency to redissolve, but they have to become orientated into a fixed lattice. Most probably, the mechanism of nucleation is as follows: minute structures are formed, first from the collision of two molecules, then from that of a third with the pair, and so on. Short chains or flat monolayers may be formed initially and eventually the lattice structure is built up. The most probable factor that influences the choice of molecules for coagulation is the binding energy.

For simplicity of calculating the potential energy of nucleation, the following model was assumed.

(*a*) The initial state is an ideal gas.
(*b*) Molecules are arranged from the very beginning according to the crystal lattice but not necessarily