

## The Determination of Absolute Structure. V. The Importance of Absorption Corrections\*

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### Abstract

Thirteen non-centrosymmetric structures with absorption coefficients ranging from 45 to  $0.6 \text{ mm}^{-1}$  were refined using both absorption-corrected and uncorrected data. The absorption was in no case severe, since  $\bar{\mu}_r$  was less than 1 for each structure. In these circumstances, the absolute-structure parameter  $\eta$  could be determined equally clearly in both cases, although its e.s.d. increased somewhat for uncorrected data. More serious were the effects of uncorrected data on the precision of molecular dimensions.

### Introduction

An earlier paper in this series (Jones, 1984*b*) presented a survey of published absolute configurations from the Cambridge Crystallographic Data Centre files for 1982 and noted several unsatisfactory features, in particular the frequent absence of an absorption correction even for large crystals of strongly absorbing materials (absorption coefficients  $\mu$  up to  $15.3 \text{ mm}^{-1}$ ). It was suggested that an absorption correction would often be essential, and that a reliable determination of absolute structure (Jones, 1984*a*) could not be expected if major systematic errors (*i.e.* absorption errors) remained uncorrected.

Absorption and anomalous dispersion are correlated effects, since they have their origin in the same physical phenomenon; they both increase with increasing atomic number in a regular fashion except for large discontinuities at the absorption edges. It has been demonstrated (Jones, 1984*a*) that absolute structure can be routinely determined for organic compounds containing S, P or Cl atoms; such compounds generally exhibit negligible absorption effects ( $\mu < 0.5 \text{ mm}^{-1}$  for Mo  $K\alpha$  radiation). Since anomalous dispersion effects thus become measurable before absorption effects are significant, and they keep more or less in step with increasing atomic number, the above suggestion must be seriously questioned; is an absorption correction perhaps unnecessary when an absolute structure is to be determined? This paper compares results of absolute struc-

ture determinations using data sets both with and without absorption corrections for thirteen compounds.

### Methods

All data sets were measured in profile-fitting mode (Clegg, 1981) on a Stoe-Siemens four-circle diffractometer with monochromated Mo  $K\alpha$  radiation, to a maximum  $2\theta$  compatible with the scattering power of the crystal ( $45\text{--}65^\circ$ ). Because absorption coefficients tend to be small with Mo  $K\alpha$  radiation, these thirteen compounds represent the only non-centrosymmetric structures with fairly high absorption that we have measured (out of several hundred structures in all).

Absorption corrections were applied on the basis of azimuthal scans ( $\psi$  scans) at  $\psi$  intervals of  $30^\circ$  (where accessible). Typically, 50 reflections (including equivalents) provided 400 measurements. The absorption correction program XEMP (G. M. Sheldrick, unpublished) assumes an ellipsoidal crystal, which is a reasonable approximation in most cases except for extremely thin plates.

Refinement was based on  $F$  values, the 'unobserved' threshold being set at  $4\sigma(F)$ . Weighting schemes  $w^{-1} = \sigma^2(F) + gF^2$  were applied;  $g$  values were optimized to obtain a flat variance analysis with respect to  $F$  for the absorption-corrected data. Unchanged  $g$  values were used for the uncorrected data; although much larger values would often have been necessary to flatten out the variance analysis, this had little effect on the refined parameters. The absolute structures were determined by  $\eta$  refinement (Rogers, 1981). More details can be found in the individual publications or on request from the authors.

### Results and discussion

Results are summarized in Table 1. Much to our surprise, the assignment of absolute structure based on uncorrected data was in each case unambiguous although the e.s.d. of  $\eta$  generally increased slightly. We must therefore concur with the conclusion of Bernardinelli & Flack (1985) that the bias in the value

\* Part IV: Jones (1986).

Table 1. *Refinements with and without absorption corrections*

Compound	Space group	$\mu$ (mm <sup>-1</sup> )	Corrected data				Uncorrected data			
			$R_{\text{int}}$	$R$	$\eta$	$S$	$R_{\text{int}}$	$R$	$\eta$	$S$
(1) Au <sub>2</sub> Sr(OH) <sub>8</sub>	<i>I</i> 422	46.5	0.026	0.027	1.00 (13)	1.09	0.026	0.030	0.99 (15)	1.27
(2) C <sub>20</sub> H <sub>18</sub> AuO <sub>2</sub> P	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	8.0	no equivs.	0.028	1.04 (2)	1.27	—	0.040	1.04 (3)	1.80
(3) C <sub>15</sub> H <sub>8</sub> Br <sub>2</sub> O <sub>6</sub>	<i>P</i> 2 <sub>1</sub>	5.7	0.028	0.046	1.03 (3)	1.31	0.031	0.075	1.06 (6)	2.25
(4) CuAlCl <sub>4</sub>	<i>P</i> 42 <i>c</i>	5.5	0.031	0.039	1.04 (20)	1.21	0.052	0.041	0.97 (22)	1.24
(5) C <sub>4</sub> AgAsF <sub>6</sub> N <sub>4</sub> S <sub>8</sub>	<i>P</i> 4	3.7	0.014	0.037	1.05 (6)	1.87	0.062	0.063	1.06 (9)	2.90
(6) C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> F <sub>4</sub> P <sub>2</sub> W	<i>F</i> dd2	3.7	no equivs.	0.021	1.04 (2)	1.26	—	0.036	1.01 (3)	2.18
(7) C <sub>66</sub> H <sub>48</sub> F <sub>10</sub> P <sub>4</sub> Pd <sub>2</sub> PtS <sub>6</sub>	<i>P</i> 3 <sub>2</sub> 21	2.8	0.017	0.060	1.045 (15)	1.57	0.028	0.062	1.046 (16)	1.61
(8) C <sub>27</sub> H <sub>31</sub> CoINO <sub>3</sub> P <sub>2</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	1.8	0.016	0.041	1.07 (4)	1.36	0.016	0.048	1.05 (5)	1.61
(9) C <sub>32</sub> H <sub>33</sub> CoINO <sub>2</sub> P	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	1.7	0.023	0.058	1.05 (6)	1.27	0.023	0.060	1.05 (6)	1.32
(10) C <sub>28</sub> H <sub>34</sub> BrNO <sub>5</sub>	<i>P</i> 2 <sub>1</sub>	1.5	0.015	0.046	1.00 (2)	1.50	0.020	0.047	1.00 (2)	1.50
(11) C <sub>25</sub> H <sub>29</sub> MoN <sub>2</sub> O <sub>2</sub> Rh	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	1.2	0.025	0.028	1.10 (7)	1.22	0.057	0.029	1.12 (7)	1.24
(12) C <sub>28</sub> H <sub>27</sub> MoN <sub>2</sub> O <sub>2</sub> Rh	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	1.2	0.021	0.038	1.06 (8)	1.47	0.021	0.038	1.07 (9)	1.50
(13) C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> Mo	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	0.7	0.016	0.029	1.18 (7)	1.25	0.016	0.030	1.17 (7)	1.29

References: (1) Jones & Sheldrick (1984); (2) Jones (1984c); (4) Hildebrandt, Jones, Schwarzmann & Sheldrick (1982); (5) Roesky, Gries, Schimkowiak & Jones (1986); (6) Roesky, Seseke, Noltemeyer, Jones & Sheldrick (1986); (7) Forniés, Usón, Gil & Jones (1986); (10) Hoppe, Gonschorrek, Egert & Schmidt (1985); (11), (13) Brunner, Wachter, Schmidbauer, Sheldrick & Jones (1986); all others unpublished work from this Institute.

of the absolute-structure parameter arising from neglect of absorption is small [(Flack (1983) uses a different method and associated parameter  $x$  to determine absolute structure, but the  $x$  and  $\eta$  methods are similar in philosophy]. This conclusion should however be subject to the following important qualifications:

(i) The size of the crystals (1)–(13) was restricted to ensure that  $\overline{\mu r}$  was in each case less than 1, even for compound (1) where  $\mu = 46.5 \text{ mm}^{-1}$ . With higher values of  $\overline{\mu r}$  the absorption errors may become intractable; an earlier data set for (1) was accidentally collected with a larger crystal (*ca* 0.2 mm) because of a wrongly calculated microscope magnification and the structure proved to be unrefinable (heavy atoms 'non-positive-definite', light atoms not located).

(ii) For many of the crystals, the Friedel opposites  $\overline{hkl}$  were measured at  $-2\theta$ ,  $\omega - 2\theta$ ,  $\chi$ ,  $\varphi$  (referred to  $hkl$  at  $2\theta$ ,  $\omega$ ,  $\chi$ ,  $\varphi$ ), which reduces absorption errors for crystals of centrosymmetric shape (the transmission factors are identical). Similarly, in many cases several equivalents were collected and merged; this also reduces absorption errors.

(iii) It is seldom the case that the sole object of a crystal structure analysis is the determination of absolute structure. The neglect of absorption effects *does* have a serious effect on other parameters, as is well known (Jones, 1984d). A general decrease in precision is reflected in higher  $R$  and  $S$  values [most severe for compound (3), a plate-shaped crystal]. We wish to stress that we consider absorption corrections to be a necessary precaution to avoid these unwanted

effects; we routinely perform such corrections for all structures with  $\mu > ca 1 \text{ mm}^{-1}$ .

An observation unconnected with absorption effects is that the  $\eta$  values in Table 1 are almost all greater than 1; is it possible that  $f''$  values in the literature are systematically slightly too small?

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