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The Determination of Absolute Structure. II. Absolute Configurations from the Cambridge Crystallographic Data Centre Files for 1982.*

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Abstract

A survey of 102 structures flagged with 'absolute configuration' in the Cambridge Crystallographic Data Centre files for 1982 reveals many unsatisfactory features in the original publications. These are associated with data collection (lack of Friedel opposites and of absorption corrections), misinterpretation of the term 'absolute configuration' (claimed for achiral molecules and space groups), methods used to determine absolute configuration (over-optimistic interpretation of discriminatory tests) and presentation of results (little experimental detail, no prominent statement that an absolute configuration was assigned, no clear description of the methods used). Some confusion arises because of unintentional flagging of absolute configurations determined by solely chemical means.

Introduction

The determination of absolute structure (Jones, 1984) and, in particular, of absolute configuration by X-ray crystallographic measurements is of fundamental importance in many areas of chemistry and biochemistry. The assignment of absolute structure is usually based on analysis of small (Bijvoet) differences in measured intensities of Friedel opposite reflections (hkl and $\bar{h}\bar{k}\bar{l}$, or suitable equivalents); such assignments for key compounds often form the basis for the discussion of a wide range of related compounds. It is thus essential that published reports of absolute structures contain sufficient detail, both as regards methods and results, to be easily understood and judged as to reliability.

Rogers & Allen (1979) presented comments and recommendations regarding publication of absolute configurations; they noted 'unfortunate errors or misleading presentation of results' and were concerned that 'reports ... tend increasingly to be hidden in the body of a paper, accompanied by minimal experimental results'. Had their suggested guidelines been followed, assignments of absolute configuration would today be either obviously correct or, in suspicious cases, easy to check. It therefore seemed worth while to inspect more recent reports of absolute structures to see if the situation had improved. This paper reviews such reports from the year 1982.

Methods of determining absolute structure

Although the principles involved should be well known, it may be useful to recapitulate some of the special features associated with the measurement of non-centrosymmetric structures. We may distinguish two cases: (i) the sole or major objective is the determinatin of absolute structure; and (ii) the determination of absolute structure is incidental to the chemical or other interest, but may be necessary to avoid systematic errors in the least-squares parameters (see below).

Case (i)

In addition to the usual goals of maximum precision and minimum systematic errors (attained perhaps by low-temperature measurements), the intensity differences between hkl and $\bar{h}\bar{k}\bar{l}$ should be maximized; thus a long-wavelength radiation may be more appropriate (although a common exception is furnished by Br, which shows a much higher f_i'' for Mo $K\alpha$ than for Cu $K\alpha$ – see below) and $2\theta_{\max}$ should be as high as is consistent with the scattering power of the crystal (the heavy-atom scattering, which includes the major anomalous scattering, dominates at high 2θ; in addition, f_i'' values are insensitive to 2θ, thus becoming more important relative to f at high 2θ). It should go without saying that Friedel opposites should be collected and, for extremely accurate work, several sets of equivalents aslo. Since the presence of good anomalous scatterers is usually associated with moderate to severe absorption, particularly if Cu $K\alpha$ radiation is used, and since absorption effects are generally much greater than the small Friedel differences, an absorption correction is often essential. It is unrealistic to expect a reliable absolute structure if major systematic errors in the measured intensities remain uncorrected. Finally, measuring hkl

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* Part I: Jones (1984).

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at 2θ, ω, χ, φ followed immediately by $\bar{h}\bar{k}\bar{l}$ at -2θ, $\omega-2\theta$, χ, φ will minimize not only residual absorption and other errors associated with differing path lengths (given a crystal with centrosymmetric *shape*) but also errors in Friedel differences caused by crystal decay or medium-term fluctuations in primary-beam intensity. This method, programmed by Dr W. Clegg, was adopted for compounds (1) and (2) of the preceding paper (Jones, 1984).

The data sets thus obtained, which we may denote as 'primary data sets', are solved and refined in the usual way and then subjected to one or more of the discriminatory tests (Hamilton, 1965; Rogers, 1981; Flack, 1983) to distinguish between the alternative absolute structures. In borderline cases, it is often necessary, after solving the structure, to calculate which reflections are most sensitive to anomalous scattering effects.* This subset is then either extracted from the primary data set and its intensities compared with those calculated for the two possible models, or re-collected extremely accurately, giving a secondary data set which may be used for the same comparisons. See Rabinovich & Hope (1980) for a detailed discussion experimental methods applied to a specific borderline case ($C_{17}H_{16}O$).

Case (ii)

In such cases it is advisable to collect Friedel opposites if the compound contains anomalous scatterers and is known to be non-centrosymmetric. It is likely that no other special precautions will be taken. However, every attempt should be made to assign an absolute structure, since otherwise systematic errors in atom positions may result (Cruickshank & McDonald, 1967).

Data centres and absolute structure

The two main crystallographic data centres (Cambridge and Bonn) adopt different attitudes to the flagging of absolute structure (Kennard, 1984; Bergerhoff, 1984). The Bonn data centre has flagged only five structures, although an attempt is to be made by the author to provide a more thorough analysis. The Cambridge Crystallographic Data Centre (CCDC) flags only absolute *configurations* determined crystallographically. (They have also included some structures where internal comparison with centres of known chirality, *e.g.* tartrate, camphorsulphonate, in turn determined by X-ray methods, was possible.) A search of the CCDC files for structures thus flagged and published in 1982 revealed 108 references. Of these, six were abstracts only; the remaining set of 102 forms the basis for the following discussion.

General comments

There are a number of unsatisfactory featues, almost all of which can be attributed to the authors rather than the CCDC; the task of abstracting crystal structures is arduous and many of the reports were couched in extremely unclear terms. The problems noted by Rogers & Allen (1979) remain and their eminently sensible recommendations are often ignored. The current tendency to drastic abbreviation of published crystal-structure determinations extends also to determinations of absolute configuration; in one extreme case, *all* crystallographic details were relegated to supplementary material (Theopold, Becker & Bergman, 1982). The following detailed discussion is based solely on primary published material.

Achiral structures

Two structures allegedly involving absolute configuration were in the achiral space group $Pna2_1$ (Bianchini, Meli & Orlandini, 1982; Ghilardi, Midollini & Orlandini, 1982). In these cases the general term 'absolute structure' would have been appropriate, if less precise than 'determination of polar-axis direction'. (The CCDC, in flagging the term 'absolute configuration', not unreasonably accepts the authors' claims in this respect; a discussion of the advisability or otherwise of extending this flag to 'absolute strucuture' is outside the scope of this article.) One further achiral structure (in $Aba2$) was flagged with 'absolute configuration', although the authors do not seem to have claimed that the latter was determined (Nirkova, Kuz'mina, Struchkov & Temkin, 1982).

The fact that a compound crystallizes in a chiral space group does not necessarily mean that it is itself chiral. Particularly for metal complexes with polydentate ligands, it may not be immediately obvious whether the compound is chiral (*e.g.* the 11-coordinate $Eu(NO_3)_3(C_{10}H_{20}O_5)$; Bünzli, Klein, Chapuis & Schenk, 1982). At least in one case, some confusion has arisen; thus Venable, Sinn & Grimes (1982) claim to have determined an absolute configuration for a compound $C_{10}H_{28}B_9Co$ in $P2_12_12_1$, yet state that it possesses 'virtual m symmetry'. Again, the use of 'absolute structure' would have been more suitable. (The presence of a proper rotation axis does not, however, rule out chirality; see Becker, Gutekunst & Witthauer, 1982.)

Lack of information

In addition to the extreme case noted above, nine more publications gave either no details of the method

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* Various 'sensitivity formulae' have been used. In the minicomputer program system *SHELXTL* in our laboratory, the 'HKLF−5' command calculates a sensitivity $Q = |F_+^2 - F_-^2|/[F_+^2 + F_-^2]^{0.5}$, which, compared to the simpler fractional sensitivity, upweights strong reflections (because they are generally easier to measure accurately) (Sheldrick, 1984).

used to determine absolute configuration or merely a passing reference to 'use of anomalous dispersion'; in one of these the only mention of absolute configuration was in the title (Roques, Bertrand, Labruyère, Declercq & Germain, 1982).

Use of solely chemical methods

Eight absolute configurations were determined by chemical means, *viz* analogy to, or derivation from, a compound of known absolute configuration. In most cases the authors recognized this distinction with appropriate statements, though not all were clearly worded; one abstract was (doubtlessly unintentionally) somewhat misleading in stating that a compound was 'configurationally determined by X-ray structural analysis' (Boche & Schrott, 1982). Two of the eight structures were flagged 'absolute configuration by internal comparison', although a known steroid configuration was *assumed* in each case (Hashimoto, Kato, Shiro, Takahashi, Jinbo & Satoh, 1982).

Use of English

In many publications it is possible that lack of familiarity with English has led to confusing statements; thus Kamwaya *et al.* (1982) seem to indicate that the correct absolute configuration had a *worse* R than the false one, while Nasini, Merlini, Andreeti, Bocelli & Sgarabotto (1982) seem to have compared refinement of the *same* absolute configuration for two data sets. Yamada *et al.* (1982) seem to have established an absolute configuration opposite to the one refined, yet not to have repeated the refinement with the new configuration; it is thus not clear whether the tables correspond to the correct enantiomer. The same is true of Okuyama, Nakamura, Naganawa, Takito, Umezawa & Iitaka (1982), who state that 'the structure should be described by a coordinate system inverted from that adopted for the intensity measurements'. In such cases one must have sympathy for the abstractors.

Reported methods

A statistical breakdown is as follows: comparison of R values, including Hamilton's (1965) test in most cases, 53; comparison of sensitive reflections, 17; collection of secondary data set (see above), 15; others, 9. (For some structures more than one method was employed.)

R/Hamilton. For many structures a clear difference in R values made Hamilton's test a formality. However, ten structures showed a high R value ($>$ 0·07), which decreases confidence in the accuracy and reliability of the measurements; the highest value for a primary data set was 0·102 (Bilton, 1982). Eleven structures showed a difference in R values $\leq 0{\cdot}1\%$, which, in view of the doubts cast on the validity of Hamilton's test in borderline cases by Rogers (1981) & Marsh (1981), must be considered of limited significance despite the calculated probabilities. (However, it was twice pointed out that a Hamilton test gave the correct, known, absolute configuration even with such a small R difference; Bosch, Jung & Winter, 1982; Bosch, Brückner, Jung & Winter, 1982).

Comparison of sensitive reflections. This method was often used in addition to the Hamilton test. In two cases for which it alone was used, the R value was high [0·088, Fujita, Takeda, Shingu, Kido & Taira (1982) and 0·102, Okuyama *et al.* (1982)]. The choice of sensitive reflections was sometimes severely restricted; thus Bünzli *et al.* (1982) used only $hk0$ reflections in $P3_1$, and Shimojima, Hayashi, Ooka, Shibukawa & Iitaka (1982) seem to have collected very little, if any, more than a quadrant in $P2_1$.

Collection of secondary data. This should be the most reliable, if time-consuming, method. Can the sensitive reflections be relied upon to give the correct absolute configuration, however, when the primary dataset only achieves an accuracy corresponding to R 0·113 (Moser, Rihs & Sauter, 1982)? Do four reflections constitute a large enough set (Ohba, Ito & Saito, 1982)? Is the agreement between observed and calculated Bijvoet differences convincing in those few cases where the details are published (Bláha *et al.*, 1982)?

Other methods. These were made up of: Rogers's (1981) η method, then in its infancy, 2; comparison of chemically equivalent bond lengths (Weber, Mujica & von Schnering, 1982); refinement of f_i'' or changing its sign, 4; comparison of 'goodness of fit' (no further details; Tranqui, Durif, Nasr Eddine, Lieto, Rafalko & Gates, 1982); and change of crystal morphology on adding impurities (Berkovitch-Yellin, Addadi, Idelson, Leiserowitz & Lahav, 1982).

The collection of (in)adequate data

In view of the criteria discussed above, it is interesting to analyse the accounts of data collection with particular respect to (i) collection of Friedel opposites and (ii) absorption corrections.

(i) *Friedel opposites*

Excluding those cases where sensitive reflections were utilized, there remain 72 structures for which some form of refinement was used to determine absolute configuration. Of these, only 14 data sets contained a full set of Friedel opposites and a further six a partial set (to limited $2\theta_{\max}$). No fewer than 44 contained none or very few, and in eight cases the necessary information was not given [$2\theta_{\max}$ would have enabled the number of reflections in a sphere to be calculated by

$$N=(32\pi V/3\lambda^3)\sin^3\theta_{\max}.]$$

The absence of Friedel opposites must make the determination of absolute configuration more difficult; combined with a low $2\theta_{\max}$, it will also lead to an unsuitably low data/parameters ratio [*e.g.* 487 reflections for 17 refined atoms, $2\theta_{\max}$ not given, Bilton (1982); 1875 reflections for 59 atoms, $2\theta_{\max}$ 36° (Mo $K\alpha$), Tranqui *et al.* (1982); 588 reflections for 32 atoms, $2\theta_{\max}$ 40° (Mo $K\alpha$), Carré, Cerveau, Colomer & Corriu (1982)].

There appears to be no general agreement as to what constitues 'all independent/unique reflections'. Some authors use this expression to mean 'all independent/unique reflections assuming Friedel's law holds'; this can clearly be misleading in describing structures with anomalous scatterers (*e.g.* Howard, Fenical, Donovan & Clardy, 1982). Similarly, expressions such as 'a hemisphere of data' are ambiguous if the particular hemisphere (or quadrant *etc.*) is not specified; are Friedel opposites or merely exact equivalents implied? For one structure, the data collected included three sets of equivalents but no Friedel opposites (Gahn, hambley, Sargeson & Snow, 1982).

(ii) *Absorption corrections*

It is impossible to specify a value of μ (or μr) above which an absorption correction may be regarded as essential; similarly, it is not clear to what extent Friedel differences are affected by lack of absorption corrections. Nonetheless, it *is* clear that, for the degree of experimental accuracy required to determine absolute structure, systematic errors should be avoided wherever possible; this must apply *a fortiori* to secondary data sets.

Taking $\mu = 3\text{ mm}^{-1}$ as an arbitrary dividing line (a value often attained by, for example, halogenated derivatives), there were 38 strongly absorbing materials. (In the majority of cases, μ was not given and had to be calculated.) Of these, only 12 were definitely subjected to an absorption correction; 14 were not corrected and no information was given for a further 12. For materials such as $C_{12}H_{17}Br_3Cl_2O_2$ ($\mu = 7{\cdot}0\text{ mm}^{-1}$; Katayama, Ina, Nozaki & Nakayama, 1982), $C_{20}H_{26}INO_2$ ($\mu = 13{\cdot}2\text{ mm}^{-1}$; Kaiser *et al.*, 1982) or $C_{20}H_{32}N_4O_5CoI$ ($\mu = 15{\cdot}3\text{ mm}^{-1}$; Bilton, 1982), the lack of an adequate absorption correction must lead to serious errors in measured intensities (although the latter author thought the 'paucity of data' was responsible for the poor R value). The comments of Bosch, Brückner, Jung & Winter (1982) and Arndt (1984) as to choice of radiation are recommended reading in this respect.

High R values. Nineteeen structures showed $R > 0{\cdot}07$; this was generally attributable to lack of absorption corrections.

Space groups

The space groups $P2_12_12_1$ (50 structures) and $P2_1$ (26) predominated; the only other occurring more than twice was $P1$ (4). Five structures were in enantiomorphous space groups.

Recommendations

Reports of determination of absolute structure continue to be unsatisfactory in many respects. Firstly, not enough effort is made to ensure good-quality data; Friedel opposites should be collected (for primary data sets) and absorption corrections applied. Secondly, important details of data collection are often omitted; the guidelines of *Acta Crystallographica*'s *Notes for Authors* might well be followed in this respect, where space permits, irrespective of journal; even if space is limited, $2\theta_{\max}$, μ, and details of Friedel opposites and absorption corrections (if any) should always be given. The impression sometimes arises that the authors are trying to conceal facts from the reader; it is welcome but rare that authors point out possible imperfections in their data (Byrne *et al.*, 1982) or admit that the indication of absolute configuration is not conclusive and that confirmation is necessary (Pettit, Herald, Doubek, Herald, Arnold & Clardy, 1982). Thirdly, a clear statement that an absolute structure has been assigned should appear in a prominent place in any publication, and sufficient detail of the method used should be included (*cf.* the suggested guidelines of Rogers & Allen, 1979). Fourthly, results of statistical or other tests should not be interpreted too optimistically. Fifthly, absolute configuration should not be claimed for achrial compounds or space groups ('absolute structure' is then a suitable general term: Jones, 1984). Finally, editors and referees must adopt a more critical attitude.

Can an improvement be expected? Even well into 1983, reports of absolute structure continue to indicate a failure to take elementary precautions. The compound $C_{11}H_{17}BrO_2S$ ($P2_12_12_1$, Cu $K\alpha$, $\mu = 6\text{ mm}^{-1}$) was investigated using a needle-shaped crystal, yet no absorption correction was applied; no, or very few, Friedel opposites were collected (judged from the quoted number of reflections). This must cast some doubt on the validity of the Hamilton test, performed on alternative models with closely similar R values ($0{\cdot}0622$, $0{\cdot}0628$), despite the calculated probability of $0{\cdot}005$ that the lower R could fail to correspond to the correct model (Dossena, Marchelli, Armani, Fava & Belicchi, 1983).

Very few crystallographically assigned absolute configurations have had to be revised following reinvestigations (although much evidence against an assignment would have to be collected to prompt such a check).* It should be stressed that the author is *not* suggesting that many of the 1982 absolute configurations were incorrect. However, in view of the imperfections noted, it is far from impossible that one or two were incorrect. It is frustrating to consider that any confusion thus arising (*e.g.* in detailed stereochemical correlations constructed from X-ray absolute configurations regarded as totally reliable: Klyne & Buckingham, 1978) could have been avoided by taking a little more care.

The CCDC provides an excellent service in all but one respect; the frequency with which absolute configurations determined by chemical, not crystallographic, methods are flagged. Some confusion has also arisen from the use of the flag 'absolute configuration by internal comparison'; thus in addition to the two apparent misuses noted above, at least one good candidate (a D-tartrate salt of a cationic chiral cobalt complex: Tada, Kushi & Yoneda, 1982) was omitted. To clarify this situation, the CCDC has decided to remove this flag and discontinue its use (Kennard, 1984).

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* One such case was provided by the mitomycin antibiotics, the absolute configuration of which was determined in 1967 for an *N*-bromotosylate derivative (Tulinsky & van der Hende) and revised in 1983 using an *N*-bromobenzyl derivative (Shirahata & Hirayama). The earlier authors noted high anisotropy or possible disorder of the bromine and sulphur atoms, *viz* of precisely the anomalous scatterers used to assign the absolute configuration, and it may well be that the incorrect assignment was associated with these problems (rather than merely with the high *R* value, as suggested by Shirahata & Hirayama). This may perhaps be a warning against the automatic use of *p*-bromobenzoate or similar derivatives, which are liable to display unusual thermal motion, to determine absolute configuration.

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Anharmonic Potentials and Pseudo Potentials in Ordered and Disordered Crystals

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Abstract

An extension of existing structure-factor formalisms for anharmonic thermal motion in crystals and the corresponding one-particle potentials is presented and applied to ordered and disordered structures. A generalized probability density function (joint p.d.f.) is introduced and it is first shown that anharmonic temperature factors ('thermal motion') and split positions ('disorder') are mathematically equivalent in describing electron or nuclear densities. When probability densities are interpreted in terms of an effective one-particle potential, however, ordered and disordered structures show different behaviour. For ordered structures the effective one-particle potentials are found to be almost independent of temperature; for disordered structures one obtains a temperature-dependent pseudo potential. The different temperature dependence can be used to distinguish between order and disorder. Pseudo potentials are calculated for several types of disorder and compared with potentials derived from X-ray or neutron diffraction experiments.

Introduction

Anharmonic thermal motion of atoms (or ions) in crystals can be studied with the aid of accurate elastic X-ray or neutron diffraction. The measured intensities contain information about the average distribution of atoms around their equilibrium positions (*i.e.* the probability density function p.d.f.) and allow the determination of the effective one-particle potential (OPP) in which the atoms are moving (Dawson, Hurley & Maslen, 1967; Willis, 1969; Willis & Pryor, 1975; Mair, 1980; Zucker & Schulz, 1982*a*).

A particularly interesting group of materials with high anharmonic thermal motion is formed by ionic conductors, which have been extensively studied in recent years [*e.g.* AgI (Cava, Reidinger & Wuensch, 1977), Li_3N (Zucker & Schulz, 1982*b*), Ag_3SI (Perenthaler, Schulz & Beyerle, 1981), $RbAg_4I_5$ (Kuhs, 1983)]. The OPPs allow estimation of the potential barrier for ionic motion and it compares well with the activation energy of conductivity. Thus one has for this special type of material another experimental test for the potential derived from a diffraction experiment.

For some ionic conductors, however, we found a great difference between the activation energy and, in addition, a strongly temperature dependent potential. This result cannot be understood using the usual concepts of a p.d.f. and the corresponding OPP. The necessary extensions of these concepts include the effects of disorder and will be presented hereafter.

The joint probability density function (PDF)

For an isolated atom vibrating around a given equilibrium position, the one-particle p.d.f. is the average in space and time of the probability of finding the atom in a volume element around its equilibrium position. The p.d.f. is then the Fourier transform of the temperature factors (harmonic or anharmonic) associated with this position which are obtained from the measured intensities (Willis, 1969; Johnson & Levy, 1974). This definition of the p.d.f. is only meaningful if different p.d.f.s do not overlap so that electron or nuclear densities can uniquely be assigned to one position, *i.e.* if the p.d.f.s are immeasurably small between two positions.

In some cases the amplitudes of thermal motion become comparable with the distance between two positions. Examples are ionic conductors with a continuous distribution of mobile ions along the

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