High-Speed Single-Crystal X-ray Data Collection with Conventional Diffractometers

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Abstract

A Syntex $P2_1$ diffractometer has been used to collect low-temperature data (140 K) for three structures by the ω-scan technique, allowing 1 s for scan and 0·5 s each for two background measurements for each reflection, yielding about 400 reflections h^{-1}. The compounds studied are: 1,5-dithiacyclooctane–iodine adduct, $C_6H_{12}S_2.2I_2$ (I); 4,4′-bis(2-methoxycarbonyl-ethyl)-3,3′,5,5′-tetramethylpyrromethene hydrochloride, $C_{21}H_{29}N_2O_4^+.Cl^-$ (II); N-[1-(acetylamino)ethylidene]sulfamic acid, $C_4H_8N_2O_4S$ (III). Recognizable solutions were derived without difficulty from each data set. For (II) and (III) all H atoms were located. The results have been compared with those obtained from conventional data (30 s per scan, 15 s each for two backgrounds). In general, the fast data collection resulted in a 50% increase in positional e.s.d.'s. For (I) the crystal was small (3 × 10^{15} unit cells) with anisotropic absorption; the results for C positions are marginally acceptable, with e.s.d.'s of 0·04 and 0·025 Å respectively for the two sets. For (III) (2 × 10^{16} unit cells) the fast data gave very satisfactory results; e.s.d.'s for C or N positions are ~0·003 *vs* ~0·002 Å from the standard data, indicating that virtually no loss of structural information resulted from the high-speed technique. The high-speed results for (II) (8 × 10^{15} unit cells) are also acceptable, with e.s.d.'s in the range 0·01–0·005 Å for C or N positions. Low-temperature data are important for the success of the high-speed method.

Introduction

Since the first structure elucidations based on diffraction data (Bragg, 1913) X-ray crystallography has become established as the ultimate method for the definitive determination of crystal and molecular structures. Yet, it has not gained universal acceptance as a routine analytical tool. Potential beneficiaries often make claims to the effect that X-ray studies are too expensive or too time-consuming or that too much unwanted, detailed information results. Very often such claims have a foundation in reality, and as a consequence less reliable methods of structure elucidation are often used when an X-ray study clearly should be the preferred choice.

Before the advent of contemporary computer-controlled diffractometers, the measurement of a single-crystal X-ray diffraction data set was a large undertaking, making remeasurement of the set highly undesirable. It was therefore reasonable in each project to make an effort to get the best data possible, and lengthy work to extract the maximum amount of information from the data was in order. Most of our current knowledge of intensity measurements, data reduction, refinement models, and reliability tests probably comes from that kind of careful work.

The availability of computer-controlled diffractometers now leaves one with a wider range of data-collection strategies. However, reading of contemporary X-ray structure literature reveals that this flexibility is far from being fully utilized. We also note that with standard refinement of data below sin $\theta/\lambda = 0.65$ Å^{-1}, the uncertainty in the definition ('accuracy') of an atomic position in a light-atom structure can be as high as 0·02 Å. This results from model deficiencies (failure to account for valence-shell asphericity, inadequate thermal-motion model, *etc.*). Documentation of such effects has been presented by Coppens, Sabine, Delaplane & Ibers (1969). Other illuminating examples can be found in many recent papers quoting phenyl C—C distances in the range 1·35 to 1·37 Å with bond-length e.s.d.'s of 0·005 Å or less, even though the C—C bonds in benzene are close to 1·395 Å. In spite of these uncertainties much time and effort is expended both in data collection and subsequent computing on attempts to reach low R indices, or to reduce e.s.d.'s to, say, 2 × 10^{-3} Å for light-atom positions. This in turn often leads to high cost of X-ray studies, without a commensurate yield of reliable or wanted information.

In order to make X-ray crystallography a desirable choice as an analytic tool there is a need for a flexible approach to structure determination. As far as possible it is desirable to tailor data collection and computing effort to the actual needs of the project.

From a procedural point of view potential simplification and time saving can be effected in two distinct phases: in data collection and in data processing. We have undertaken a study aimed at reducing the time spent on data collection to the minimum attainable

with our equipment, without the loss of essential reliability in the determination of atom connectivity and molecular geometry as required by the instigator of the analytical problem, and also without a significant increase in computing cost resulting from low-quality data. We now report some encouraging results of this work.

Procedures

All measurements were carried out on a Syntex $P2_1$/FORTRAN diffractometer equipped with a locally modified Syntex LT-1 low-temperature attachment. The structures of three compounds with different characteristics were used as test cases.
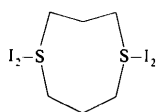
1,5-Dithiacyclooctane–iodine adduct (I)
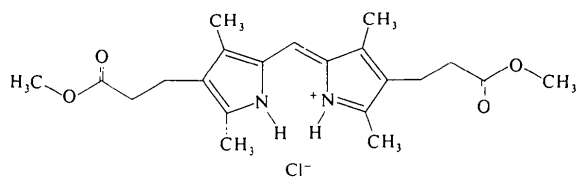
4,4'-Bis(2-methoxycarbonylethyl)-3,3',5,5'-tetramethylpyr-romethene hydrochloride (II)
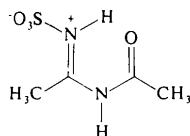
N-|1-(Acetylamino)ethylidene|sulfamic acid (III)

Compound (I) is a relatively small molecule with a large proportion of heavy atoms; compound (II) is a medium-size organic molecule (28 atoms other than H); compound (III) is a small organic molecule.

For each crystal we collected two data sets, one with a 'conventional' scan speed of $2°$ min^{-1}, the other with a speed of $58·6°$ min^{-1} (later referred to as 'slow' and 'fast', respectively). The fast speed is the maximum attainable with our present system. The ω-scan technique, with an ω range of $1°$, was used throughout. Stationary background counts were taken for $0·5$ s each at ω offsets of $+1$ and $-1°$. The peak-optimi-zation feature of the data-collection routine allows for inaccuracies in the orientation matrix, permitting short set-up times. No special treatment to enhance the reliability of weak reflections was used. The crystal temperature was kept near 140 K. In order to ensure proper choice of unit cell and to check crystal quality,

Table 1. *Crystallographic data*

Cell dimensions were measured at 140 K. E.s.d.'s (in parentheses) apply to the least significant digits.

	$C_6H_{12}S_2.2I_2$	$C_{21}H_{29}N_2O_4^+.Cl^-$	$C_4H_8N_2O_4S$
a (Å)	18·255 (5)	8·599 (2)	7·2735 (3)
b (Å)	8·525 (3)	23·254 (4)	10·1196 (8)
c (Å)	19·706 (2)	11·102 (1)	10·4462 (4)
β (°)	104·71 (2)	103·37 (1)	104·164 (3)
Z	8	4	4
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$

Table 2. *Data-collection statistics*

Where two entries are given, the top line refers to the slow data sets, the bottom line to the fast data.

	$C_6H_{12}S_2.2I_2$	$C_{21}H_{29}N_2O_4^+.Cl^-$	$C_4H_8N_2O_4S$
Maximum 2θ	120^a	55^b	55^b
Unit cells/crystal	3×10^{15}	8×10^{15}	2×10^{16}
Number of reflections	4547	5276	1846
$\sum \sigma(F)/\sum (F)$	0·03	0·06	0·02
	0·11	0·16	0·09
% $I/\sigma(I) < 3$	13	28	12
	41	56	30
Final R index ^{c}	0·116	0·097	0·046
	0·128	0·103	0·050

(*a*) Cu $K\alpha$ (graphite monochromator). (*b*) Mo $K\alpha$ (graphite monochromator). (*c*) Observed reflections.

each crystal was examined photographically on the diffractometer; sample ω scans were also recorded and displayed.

Approximate dimensions of the crystals used were: (I) $0·75 \times 0·25 \times 0·05$ mm; (II) $0·475 \times 0·25 \times 0·15$ mm; (III) $0·33 \times 0·25 \times 0·20$ mm. Data for (I) were collected with Cu $K\alpha$ radiation, for (II) and (III) with Mo $K\alpha$.

The slow scan results in about 55 reflections h^{-1}; the fast scan yields 350–500 reflections h^{-1}. The actual number depends on crystal orientation and the size of the reciprocal unit cell.

Crystallographic data and data pertaining to data-collection and refinement results are given in Tables 1 and 2, respectively.

For each compound the structure was independently determined from each of the two data sets. The structures were solved by application of the Sayre (1952) equation, as programmed by Long (1965), and refined by least-squares methods. In structure (I) the S and I atoms were given anisotropic temperature factors, in (II) all atoms were treated as isotropic, and in (III) the SO$_3$-group atoms were given anisotropic temperature factors. Reflections with $I/\sigma(I) < 3$ were not used in refinements.

Structure (I) probably was subjected to the most demanding test as the crystal was small and poorly developed, the C to I ratio is unfavorable, and Cu radiation was used with resulting highly anisotropic absorption. The use of Cu $K\alpha$ instead of Mo $K\alpha$ results in better counting statistics.

Discussion

In all cases the fast data collection led to molecular models fully acceptable for normal chemical purposes. For compounds (II) and (III) all H atoms were unequivocally located from difference Fourier syntheses, and the overall quality of the results for (III) is as good as that of most structures based on more conservative data-collection methods. In general, the e.s.d.'s in positional parameters from fast data increase by about 50% over those from slow data.

Table 3 gives a summary of e.s.d.'s for postional parameters for all data sets, Table 4 gives the results of bond-length comparisons for the pairs of data sets for the three structures. As one would expect, the quality of the results is strongly dependent on counting statistics. In Table 2 we have listed the approximate number of unit cells in each crystal. It appears that one can expect

Table 3. *Estimated standard deviations*

E.s.d.'s (in Å) are given for each type of atom in each compound. The mean e.s.d. ($\times 10^4$, except for H $\times 10^3$) for each type of atom is followed by the range of e.s.d.'s in parentheses. The top line refers to the slow data set, the bottom line to the fast.

$C_6H_{12}S_2.2I_2$		$C_{21}H_{29}N_2O_4^+.Cl^-$		$C_4H_8N_2O_4S$	
I	14 (13–16)	Cl	12 (12–13)	S	6 (5–6)
	22 (20–27)		18 (17–19)		9 (8–10)
S	54 (50–60)	O	40 (35–52)	O	19 (16–27)
	80 (75–104)		53 (48–66)		25 (22–34)
C	230 (220–270)	N	38 (37–38)	N	19 (18–22)
	360 (310–520)		54 (53–57)		27 (26–31)
		C	49 (42–65)	C	24 (21–27)
			66 (58–97)		36 (30–46)
		H	55 (39–127)	H	35 (25–50)
			63 (37–87)		38 (30–46)

Table 4. *Bond-length differences*

The mean difference ($\times 10^3$) between the individual bond lengths (in Å) obtained from the two data sets is given for the classes of bonds as noted. The maximum difference ($\times 10^3$) is given in parentheses.

$C_6H_{12}S_2.2I_2$		$C_{21}H_{29}N_2O_4^+.Cl^-$		$C_4H_8N_2O_4S$	
I–I	4 (8)	$C-X^a$	8 (17)	$S-X^c$	2 (3)
S–I	8 (17)	$H-X^b$	73 (358)	$C-X^a$	5 (11)
S–C	28 (60)			$H-X^b$	20 (68)
C–C	53 (104)				

(a) $X=$ C, N, O. (b) $X=$ C, N. (c) $X=$ N, O.

good results if this number exceeds 10^{16}, and absorption is not excessively anisotropic.

A positive contributing factor is the use of low-temperature techniques. For a crystal with an average thermal parameter, B, of 4 Å² at room temperature, the intensity of a reflection at sin $\theta/\lambda = 0.5$ Å⁻¹ will at 140 K in general be enhanced by a factor of about 3. The low temperature often also obviates the need for an anisotropic thermal-motion model (Cynkier & Hope, 1978).

The two Mo $K\alpha$ data sets extend to $2\theta = 55°$. As shown in Table 2 a large proportion of reflections with $I/\sigma(I) < 3$ resulted from the fast scans. Most of these reflections are found at the higher angles, and further economy results if data are limited to a $2\theta_{max}$ of 45 to 50°. The loss of resolution is usually insignificant, but about a one-third reduction in data-collection time will result.

Given a crystal of sufficient volume, say, 0·05–0·15 mm³, we think that the procedure described here will lead to satisfactory results in practically all cases. The enhancement in speed over that of conventional techniques represents nearly an order of magnitude. The total diffractometer time (including set-up time) for each of the fast data sets for (I) and (II) was about 13 h. With adequate computing facilities at hand structures of this type can thus be conveniently completed within 24 h. The full ω-scan technique used here has the advantage of giving a reasonably consistent estimate of the integrated intensity, even if the crystal is somewhat flawed. In general, we do not recommend the use of the stationary-crystal–stationary-detector method. Even though enhanced counting statistics usually results the demands on crystal quality and accuracy in orientation are much more severe, and serious intensity errors can result from small imperfections.

We also point out that at least 70% of elapsed diffractometer time is spent between intensity measurements. Engineering and programming improvements can conceivably lead to equipment capable of measuring a much larger number of reflections per hour without resorting to position-sensitive detectors or some such solution.

It is clear that the fast data collection leads to some loss of precision, but we emphasize that this need not represent loss of important information. The attainable *precision* will very often be commensurate with the *accuracy* of conventional structure determination. High accuracy is normally only attainable through the use of extensive high-order data, and the high precision often reported for conventional data may therefore not be of particular value. We strongly advocate that the crystallographer assess the real needs of each project, and plan data strategy in accordance with these needs.

The thoughts expressed here are by no means new. Bragg & Bragg (1913) in their paper on the structure of

diamond already had a clearly established philosophy, succinctly expressed in the quote: 'Great precision was not attempted; to attain it would have been needlessly troublesome'. We think the time has come to heed the advice implicit in that statement.

We emphasize, however, that we do not advocate careless work. Reasonable precautions must always be taken to ensure acceptable crystal quality, to detect twinning and other problems, and to obtain data for correct space-group assignments. If this is not done, the gains of fast data acquisition may be offset by subsequent computing problems.

A great proportion of our routine structures will hereafter be based on data collected with techniques similar to those described here. Also, since these results were obtained it has become feasible to introduce crystal structure determination as an undergraduate physical chemistry laboratory exercise in this department. So far about ten such projects have been successfully completed.

The materials used in this study were obtained from the laboratories of Professors W. K. Musker (I), K. M. Smith (II), and C. P. Nash (III). We thank them for their interest. Detailed descriptions of the structures will be published elsewhere.

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Structure of Xanthene-9-spiro-2'-[3',4'-bis(*tert*-butylthio)thiete]

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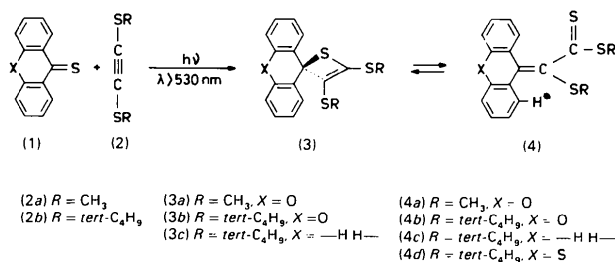*Organisch Chemisch Laboratorium, Rijksuniversiteit, Croesestraat 79, Utrecht, The Netherlands*

Abstract

$C_{23}H_{26}OS_3$ is obtained by irradiating a solution of 9-xanthenethione and bis(*tert*-butylthio)ethyne. The crystals are monoclinic, $P2_1/n$, with $a = 14\cdot890$ (5), $b = 9\cdot296$ (5), $c = 16\cdot342$ (11) Å, $\beta = 101\cdot14$ (5)°, $Z = 4$. The structure was determined from 3427 independent diffractometer intensities with $I > 2\cdot5\sigma(I)$ by the heavy-atom method and refined to $R = 0\cdot054$. Bond lengths and angles in the planar thiete ring indicate appreciable strain; the xanthene system is slightly curved.

Introduction

Brouwer, George, Seykens & Bos (1979) reported the isolation of the red crystalline α,β-unsaturated dithio-

ester (4a) after irradiating a solution of 9-xanthenethione (1) and bis(methylthio)ethyne (2a). The thiete (3a), a (2 + 2) cycloadduct,

(1)   (2)   (3)   (4)

(2a) R = CH₃   (3a) R = CH₃, X = O   (4a) R = CH₃, X = O
(2b) R = tert-C₄H₉   (3b) R = tert-C₄H₉, X = O   (4b) R = tert-C₄H₉, X = O
                            (3c) R = tert-C₄H₉, X = —H H— (4c) R = tert-C₄H₉, X = —H H—
                                                         (4d) R = tert-C₄H₉, X = S

was postulated as an intermediary, giving a rearrangement known to occur for oxetes (Brandsma, Bos & Arens, 1969) which are oxygen analogues of thietes. To investigate the scope of this reaction and to demonstrate the intermediacy of a thiete, we studied the

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