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Structure Determination of Organic Compounds Using an In-Laboratory Rapid X-ray Measurement System – Comparison with Structures Determined by a Four-Circle Diffractometer

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Abstract

A new type of X-ray diffractometer (IPD-WAS) has been recently developed as a rapid X-ray measurement system in the laboratory. This equipment has been closely examined from the viewpoint of a tool for the data collection of organic crystals. Intensities of two stable compounds [I: bis(2,4,6-trimethylthiobenzoic) thioanhydride; II: dimethyl 1,2-di-*tert*-butyl-3,6-dimethyl 4,5-dicarboxylate] and one unstable compound (III: tri-4-methylphenylbismuth dichloride) were measured with Mo $K\alpha$ radiation, with the total time for the intensity measurement being 2 or 3 h for each compound. 1995, 2360 and 2502 independent reflections of 3520, 5238 and 5397 measured reflections were used for structure determination for (I), (II) and (III), respectively. The structures were solved successfully by conventional direct methods and the Patterson method. The final R values were 0.055, 0.050 and 0.067 for (I), (II) and (III), respectively. For (I) and (II), intensities were also measured with a four-circle diffractometer using the same specimens, the final R values being 0.058 and 0.055 for 2733 and 3224 reflections for (I) and (II), respectively. The agreement between the two sets of structural geometry, obtained from the IPD-WAS and the four-circle diffractometer, was quite satisfactory. Accurate intensities of the unstable (III) could not be obtained by the four-circle diffractometer.

1. Introduction

Rapid collection of X-ray intensity data is especially important for determining structures of unstable compounds. In order to obtain an intensity data set from a single crystal within several hours, a new type of X-ray diffractometer, IPD-WAS (Kamiya, Iwasaki, Tanaka & Katayama, 1990; Kamiya, Iwasaki & Tanaka, 1993; Kamiya & Iwasaki, 1995), was recently developed for time-resolved data collection of intermediate states of crystalline-phase reactions. IPD-WAS consists of a rotating anode generator and a focusing monochromator, a chamber containing a Weissenberg camera with multi-screens which are automatically adjustable to any desired layer lines for lowering background level, two cylindrical imaging plates (Amemiya & Miyahara, 1988; Sonoda, Takano, Miyahara & Kato, 1983) as two-dimensional detectors, which are used alternately to reduce effective readout time for each imaging plate, and a rotating laser optics newly designed for the readout of the cylindrical

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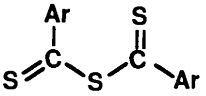
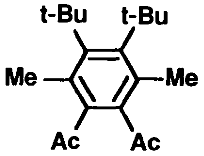
imaging plate. This equipment allowed us to measure intensities from a single crystal within a few hours in the laboratory.

Taking only 2 or 3 h to collect an intensity data set is very attractive for the ordinary structure analysis, especially of unstable crystals. In expecting the use of IPD-WAS for the routine structure analysis, we thought it necessary to carry out a close examination of the performance of this equipment, because it was at first uncertain whether this machine is capable of giving intensity data adequate for the direct method in spite of the restriction of $2\theta_{\max}$ (45° on the equator for this equipment). It is also necessary that quantity and quality of the intensity data obtained with this system must be comparable to those obtained by a four-circle diffractometer. With this purpose structure analyses of two stable compounds (I and II) and one unstable compound (III) were carried out. After the structure analyses were successfully completed, the intensity data for (I) and (II) were measured with a four-circle diffractometer using the same specimens in order to compare the structural geometry and the accuracy of the results.



Ar = 2,4,6-tri-Me-Ph-

(I)



Ac = -COOMe

(II)

$(Tol)_3BiCl_2$

(III)

2. Experimental

2.1. *Analysis of stable crystals* (I) *and* (II) *using IPD-WAS*

Compound (I) was synthesized by Kato (1990) and its blue crystals were obtained from a CH_2Cl_2–hexane mixed solution. Compound (II), synthesized by Nakayama (1991), was recrystallized from a hexane solution for X-ray works. Crystal data, details of data collection and structure refinement are listed in Table 1. Lattice constants employed in the structure analyses of (I) and (II) were those measured by a four-circle diffractometer. Intensity data were collected using the IPD-WAS at RIKEN with Mo$K\alpha$ radiation (50 kV, 200 mA) with a graphite monochromator. 1995 and 2360 independent reflections of 3520 and 5238 measured reflections were obtained for (I) and (II), respectively. The total time for the intensity measurement was 2 or 3 h for each compound. No absorption corrections were applied. The structures of (I) and (II) were solved successfully by direct methods with the program *MULTAN78* (Main *et al.*, 1978), in spite of the lack of reflections with high 2θ angles. The positions of all the H atoms could be obtained from the D-maps. The final refinement with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms was carried out by the block-diagonal least-squares. The final R values were 0.055 and 0.050 for (I) and (II), respectively. $\Sigma w(|F_c| - k^{-1}|F_o|)^2$ was minimized, where $w = 1$ for (I) and $w = 1/(1.01635 - 0.10418|F_o| + 0.00308|F_o|^2)$ for (II). The atomic positions of the non-H atoms obtained from IPD-WAS are listed in Tables 2 and 3 for (I) and (II), respectively.

2.2. *Analysis of stable crystals* (I) *and* (II) *using a four-circle diffractometer*

A four-circle diffractometer (Rigaku AFC-5R, hereafter abbreviated as 4-C) was used to measure intensities with the same specimens of (I) and (II). An absorption correction was applied numerically for (I), but not for (II). Structures were solved and refined independently from the structures obtained using IPD-WAS. Six H atoms for (I) and 16 for (II) could not be located from the D-maps. The calculated positions of these H atoms were included in the refinement. The final R values were 0.058 and 0.055 for 2733 and 3224 observed reflections of (I) and (II), respectively.[*] $w = 1/(1.1076 - 0.0211|F_o| + 0.0007|F_o|^2)$ and $1/[\sigma(F)^2 + 0.00169|F_o|^2]$ for (I) and (II), respectively.

2.3. *Analysis of unstable crystals* (III) *using IPD-WAS*

Crystal (III) was unstable under the exposure of X-rays and gradually decomposed during the data collection by the four-circle diffractometer. The structure analysis with intensity data measured on 4-C failed because of the poor quality of data. Therefore, intensity data were remeasured using IPD-WAS, taking advantage of its rapid measurement. The total measurement time was 3 h. Lattice constants were obtained from each imaging plate and averaged values with e.s.d.'s were calculated over these imaging plates. 2502 independent reflections of 5397 measured reflections were obtained. No absorption corrections were applied. Before the structure analysis, (III) was assumed to be $Bi(tol)_3O_5$, because the compound was obtained from oxidation of tri-p-tolylbismuth with ozone (Ogawa & Suzuki, 1991). Positions of the Bi atom and three tolyl groups were obtained by the Patterson method. Further refinement of the structure revealed that the structure had two high peaks at the apical positions instead of the expected structure with five O atoms. Two peaks were assigned Cl atoms from

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[*] Lists of structure factors, anisotropic thermal parameters, atomic parameters, H-atom coordinates and complete geometry for 4-C, and an *ORTEP* drawing of (II), including those of 4-C, have been deposited with the IUCr (Reference: AS0654). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

	(I) IPD-WAS	(I) 4-C	(II) IPD-WAS	(II) 4-C	(III) IPD-WAS
Crystal data					
Chemical formula	$C_{20}H_{22}S_3$	$C_{20}H_{22}S_3$	$C_{20}H_{30}O_4$	$C_{20}H_{30}O_4$	$C_{21}H_{21}BiCl_2$
Chemical formula weight	358.59	358.59	334.46	334.46	553.28
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$C2/c$
a (Å)	8.520 (2)	8.520 (2)	10.885 (1)	10.885 (1)	15.410 (14)
b (Å)	12.434 (2)	12.434 (2)	10.169 (1)	10.169 (1)	19.748 (8)
c (Å)	18.790 (3)	18.790 (3)	17.597 (2)	17.597 (2)	15.415 (2)
β (°)	100.91 (2)	100.91 (2)	104.82 (1)	104.82 (1)	117.36 (5)
V (Å^3)	1954.7 (6)	1954.7 (6)	1883.1 (3)	1883.1 (3)	4166 (8)
Z	4	4	4	4	8
D_x (Mg m^{-3})	1.219	1.219	1.180	1.180	1.764
D_m (Mg m^{-3})	1.220	1.220	1.184	1.184	1.777
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71069
No. of reflections for cell parameters	25	25	25	25	741
θ range (°)	13.1–17.1	13.1–17.1	12.6–17.35	12.6–17.35	2.0–12.5
μ (mm^{-1})	0.361	0.361	0.075	0.075	8.698
Temperature (K)	297.2	297.2	293	293	293
Crystal form	Needles	Needles	Plates	Plates	Plates
Crystal size (mm)	0.48× 0.23× 0.20	0.48× 0.23× 0.20	0.56× 0.50× 0.17	0.56× 0.50× 0.17	0.10× 0.10× 0.10
Crystal color	Blue	Blue	Colorless	Colorless	Colorless
Data collection					
Diffractometer	IPD-WAS	Rigaku AFC-5*R*	IPD-WAS	Rigaku AFC-5*R*	IPD-WAS
Data collection method	Weissenberg	ω–2θ	Weissenberg	ω–2θ	Weissenberg
Rotation axis	*a*	–	*b*	–	*a*
$\Delta\varphi$ (°)	120	–	180	–	240
Screen setting mode*	II	–	II	–	II
No. of repetition of photographing*	1	–	1	–	1
Number of IPs	6	–	5	–	6
Measurement time (h)	3	72	2.5	72	3
Absorptiom correction	None	Numerical integration	None	None	None
$T_{\min}$	–	0.918	–	–	–
$T_{\max}$	–	0.943	–	–	–
No. of measured reflections	3520	5072	5238	4828	5397
No. of independent reflections	2271	4487	2523	4364	2825
No. of observed reflections	1995	2733	2360	3224	2502
Criterion for observed reflections	$\|F_o\| > \sigma(F)$	$\|F_o\| > 3\sigma(F)$	$\|F_o\| > \sigma(F)$	$\|F_o\| > 3\sigma(F)$	$\|F_o\| > \sigma(F)$
$R_{\rm int}$	0.043	0.028	0.043	0.021	0.044
$\theta_{\max}$ (°)	24.7	27.5	24.7	27.5	24.7
Range of h, k, l	$-6 \rightarrow h \rightarrow 6$ $-13 \rightarrow k \rightarrow 13$ $-20 \rightarrow l \rightarrow 20$	$-11 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 16$ $0 \rightarrow l \rightarrow 24$	$-11 \rightarrow h \rightarrow 11$ $-8 \rightarrow k \rightarrow 8$ $-18 \rightarrow l \rightarrow 18$	$0 \rightarrow h \rightarrow 15$ $0 \rightarrow k \rightarrow 14$ $-23 \rightarrow l \rightarrow 23$	$-18 \rightarrow h \rightarrow 18$ $-21 \rightarrow k \rightarrow 21$ $-19 \rightarrow l \rightarrow 19$
No. of standard reflections	–	3	–	3	–
Frequency of standard reflections	–	Every 50 reflections	–	Every 50 reflections	–
Intensity decay (%)	–	0.8	–	1.7	–
Refinement					
Refinement on	*F*	*F*	*F*	*F*	*F*
R	0.055	0.058	0.050	0.055	0.067
wR	0.048	0.065	0.043	0.085	0.078
S	1.085	1.067	1.048	1.440	1.305
No. of reflections used in refinement	1995	2733	2360	3224	2502
No. of parameters used	296	296	337	337	301
H-atom treatment	From *D*-map refinement	From *D*-map and calculation refinement	From *D*-map refinement	From *D*-map and calculation refinement	From calculation refinement
Weighting scheme	See text	See text	See text	See text	See text
$(\Delta/\sigma)_{\max}$	0.052	0.091	0.087	0.025	0.107
$\Delta\rho_{\max}$(e Å^{-3})	0.319	0.526	0.190	0.229	1.465
$\Delta\rho_{\min}$(e Å^{-3})	−0.403	−0.597	−0.151	−0.206	−1.320
Extinction correction	None	None	None	None	None
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)				

Table 1 (*cont.*)

	(I) IPD-WAS	(I) 4-C	(II) IPD-WAS	(II) 4-C	(III) IPD-WAS
Computer programs					
Data collection	*WELMS* (Tanaka, Yao, Kamiya & Iwasaki, 1994)	*AFC5* (Rigaku Corporation, 1990)	*WELMS* (Tanaka, Yao, Kamiya & Iwasaki, 1994)	*AFC5* (Rigaku Corporation, 1990)	*WELMS* (Tanaka, Yao, Kamiya & Iwasaki, 1994)
Cell refinement	*AFC5* (Rigaku Corporation, 1990)	*AFC5* (Rigaku Corporation, 1990)	*AFC5* (Rigaku Corporation, 1990)	*AFC5* (Rigaku Corporation, 1990)	*WELMS* (Tanaka *et al.*, 1994)
Data reduction	*SSM* (Tanaka, 1990)	*UNICSIII* (Sakurai & Kobayashi, 1979)	*SSM* (Tanaka, 1990)	*UNICSIII* (Sakurai & Kobayashi, 1979)	*SSM* (Tanaka, 1990)
Structure solution	*MULTAN78* (Main *et al.*, 1978)	*MULTAN78* (Main *et al.*, 1978)	*MULTAN78* (Main *et al.*, 1978)	*MULTAN78* (Main *et al.*, 1978)	*SHELXS86* (Sheldrick, 1985)
Structure refinement	*UNICSIII* (Sakurai & Kobayashi, 1979)	*UNICSIII* (Sakurai & Kobayashi, 1979)	*UNICSIII* (Sakurai & Kobayashi, 1979)	*UNICSIII* (Sakurai & Kobayashi, 1979)	*UNICSIII* (Sakurai & Kobayashi, 1979)
Preparation of material for publication	House program	House program	House program	House program	House program

* Kamiya & Iwasaki (1995).

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I) *using IPD-WAS*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S(1)	0.26342 (17)	0.10524 (9)	0.36305 (6)	5.39 (4)
S(2)	0.2382 (2)	−0.08948 (10)	0.26282 (7)	7.78 (6)
S(3)	0.3276 (3)	0.31244 (11)	0.31313 (8)	9.69 (7)
C(1)	0.2371 (5)	−0.0316 (3)	0.3388 (2)	4.49 (14)
C(2)	0.2914 (6)	0.1878 (3)	0.2908 (2)	5.27 (15)
C(11)	0.2144 (5)	−0.0915 (3)	0.4055 (2)	4.16 (13)
C(12)	0.0617 (5)	−0.1002 (3)	0.4224 (2)	4.39 (13)
C(13)	0.0472 (6)	−0.1583 (4)	0.4831 (2)	5.19 (15)
C(14)	0.1716 (6)	−0.2082 (3)	0.5268 (2)	5.15 (15)
C(15)	0.3207 (6)	−0.1977 (3)	0.5095 (2)	5.30 (15)
C(16)	0.3470 (6)	−0.1396 (3)	0.4496 (2)	4.73 (14)
C(17)	−0.0841 (6)	−0.0520 (4)	0.3753 (3)	6.38 (18)
C(18)	0.1458 (8)	−0.2753 (5)	0.5911 (2)	8.0 (2)
C(19)	0.5127 (7)	−0.1299 (4)	0.4345 (3)	6.86 (19)
C(21)	0.2883 (5)	0.1464 (3)	0.2165 (2)	4.24 (13)
C(22)	0.4315 (5)	0.1175 (3)	0.1954 (2)	4.65 (14)
C(23)	0.4244 (6)	0.0854 (4)	0.1254 (2)	5.55 (16)
C(24)	0.2840 (6)	0.0812 (4)	0.0749 (2)	5.24 (15)
C(25)	0.1451 (6)	0.1083 (4)	0.0980 (2)	5.24 (15)
C(26)	0.1421 (5)	0.1407 (3)	0.1679 (2)	4.64 (14)
C(27)	0.5892 (7)	0.1131 (5)	0.2480 (3)	7.4 (2)
C(28)	0.2794 (8)	0.0445 (5)	−0.0021 (3)	8.4 (2)
C(29)	−0.0151 (7)	0.1632 (5)	0.1896 (3)	7.2 (2)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II) *using IPD-WAS*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O(1)	−0.06503 (14)	0.37340 (16)	0.24348 (8)	4.96 (5)
O(2)	0.09565 (13)	0.24498 (16)	0.30549 (7)	4.60 (5)
O(3)	−0.24661 (13)	0.1867 (2)	0.07689 (10)	6.62 (6)
O(4)	−0.12110 (12)	0.09937 (15)	0.18546 (8)	4.35 (5)
C(1)	0.1193 (2)	0.2683 (2)	0.0217 (1)	2.96 (5)
C(2)	0.2202 (2)	0.2881 (2)	0.0902 (1)	2.87 (5)
C(3)	0.1861 (2)	0.3128 (2)	0.1619 (1)	3.02 (6)
C(4)	0.0668 (2)	0.2783 (2)	0.1688 (1)	2.94 (5)
C(5)	−0.0206 (2)	0.2196 (2)	0.1058 (1)	3.21 (6)
C(6)	0.0036 (2)	0.2165 (2)	0.0319 (1)	3.29 (6)
C(11)	0.1215 (2)	0.3216 (2)	−0.0620 (1)	3.73 (6)
C(12)	0.2194 (2)	0.4317 (3)	−0.0559 (1)	5.09 (8)
C(13)	0.1398 (2)	0.2177 (3)	−0.1224 (1)	5.28 (8)
C(14)	−0.0067 (2)	0.3919 (3)	−0.0977 (1)	4.96 (8)
C(21)	0.3639 (2)	0.2584 (2)	0.0962 (1)	3.76 (6)
C(22)	0.4058 (2)	0.1616 (3)	0.1659 (1)	5.46 (8)
C(23)	0.4556 (2)	0.3764 (3)	0.1088 (2)	6.15 (9)
C(24)	0.3827 (2)	0.1757 (3)	0.0270 (1)	4.93 (8)
C(31)	0.2716 (2)	0.3905 (3)	0.2289 (1)	4.61 (7)
C(41)	0.0245 (2)	0.3058 (2)	0.2420 (1)	3.53 (6)
C(42)	0.0550 (2)	0.2628 (3)	0.3771 (1)	5.83 (9)
C(51)	−0.1423 (2)	0.1686 (2)	0.1186 (1)	4.00 (6)
C(52)	−0.2317 (2)	0.0602 (3)	0.2113 (2)	6.08 (9)
C(61)	−0.0912 (2)	0.1445 (3)	−0.0333 (1)	4.80 (7)

the peak heights. H atoms were located from the calculation. The structure was refined successfully by block-diagonal least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. The final R was 0.067 for 2502 observed reflections; $w = 1/[\sigma(F)^2 + 0.00174|F_o|^2]$.

All computations were performed on an IBM3090-180S Computer of the Information Processing Center of the University of Electro-Communications.

3. Comparison of the structures obtained from IPD-WAS and 4-C

3.1. *Comparison of atomic parameters and structures*

ORTEP drawings (Johnson, 1976) of molecular structures of (I) obtained by IPD-WAS and 4-C are compared in Fig. 1, with atom numbering. As can be readily seen, the molecular structures of (I) obtained by IPD-WAS and 4-C are in remarkable agreement with each other. Selected molecular dimensions obtained by IPD-WAS are listed in Table 4. The r.m.s. and average values of Δ/σ [$= (x_{\rm IP} - x_{\rm 4C})/\sigma$ *etc.*] and the maximum values of $|\Delta|/\sigma$ for non-H atoms, as well as those for bond lengths and angles, are listed in Table 5. No significant differences among x, y and z parameters are observed, although the largest value of index h obtained by IPD-WAS is smaller than that of 4-C. The atomic parameters, bond lengths and angles of non-H atoms obtained from the two data sets agree quite well with each other, within twice the e.s.d.'s, except a few atoms. It is remarkable that e.s.d.'s of the atomic parameters and

Table 4. *Selected bond lengths* (Å), *angles* (°) *and torsion angles of non*-H *atoms of* (I) *obtained by IPD-WAS*

S(1)—C(1)	1.765 (4)	S(3)—C(2)	1.620 (4)
S(1)—C(2)	1.754 (5)	C(1)—C(11)	1.502 (6)
S(2)—C(1)	1.600 (4)	C(2)—C(21)	1.483 (6)
C(1)—S(1)—C(2)	113.2 (2)	S(3)—C(2)—C(21)	123.0 (4)
S(1)—C(1)—S(2)	130.0 (3)	C(1)—C(11)—C(12)	120.0 (4)
S(1)—C(1)—C(11)	107.0 (3)	C(1)—C(11)—C(16)	119.2 (4)
S(2)—C(1)—C(11)	123.1 (4)	C(2)—C(21)—C(22)	119.7 (4)
S(1)—C(2)—S(3)	114.0 (3)	C(2)—C(21)—C(26)	119.1 (4)
S(1)—C(2)—C(21)	123.0 (4)		
C(2)—S(1)—C(1)—S(2)	1.2 (3)	S(1)—C(1)—C(11)—C(12)	86.4 (4)
C(2)—S(1)—C(1)—C(11)	−179.9 (3)	S(2)—C(1)—C(11)—C(12)	−94.5 (4)
C(1)—S(1)—C(2)—S(3)	−176.1 (2)	S(1)—C(2)—C(21)—C(22)	−94.1 (4)
C(1)—S(1)—C(2)—C(21)	1.7 (4)	S(3)—C(2)—C(21)—C(22)	83.5 (4)

Table 5. *Comparison of atomic parameters, bond lengths and angles obtained by IPD-WAS and 4-C*

		$\lvert\Delta x\rvert/\sigma$	$\lvert\Delta y\rvert/\sigma$	$\lvert\Delta z\rvert/\sigma$	$\lvert\Delta B_{eq}\rvert/\sigma$	$\lvert\Delta l\rvert/\sigma$	$\lvert\Delta\theta\rvert/\sigma$
(I)	Maximum	4.1	4.0	5.3	17.0	2.8	2.9
	r.m.s.	2.0	2.0	2.1	6.0	1.2	1.4
	Mean*	−0.3	0.0	0.4	5.1	0.4	−0.2
(II)	Maximum	5.5	4.0	5.0	10.2	3.5	1.7
	r.m.s.	2.3	1.9	1.9	6.9	4.5	2.0
	Mean*	−0.7	0.0	−0.2	6.8	0.0	−0.2

* Mean = $[\sum \Delta_{(IP-4C)}/\sigma]/n$.

Table 6. *Selected bond lengths* (Å), *angles* (°) *and torsion angles of non*-H *atoms of* (II) *obtained by IPD-WAS*

O(1)—C(41)	1.198 (3)	C(2)—C(3)	1.426 (3)
O(2)—C(41)	1.338 (2)	C(2)—C(21)	1.570 (3)
O(2)—C(42)	1.449 (3)	C(3)—C(4)	1.380 (3)
O(3)—C(51)	1.198 (2)	C(3)—C(31)	1.523 (3)
O(4)—C(51)	1.340 (3)	C(4)—C(5)	1.397 (2)
O(4)—C(52)	1.447 (3)	C(4)—C(41)	1.500 (3)
C(1)—C(2)	1.422 (2)	C(5)—C(6)	1.390 (3)
C(1)—C(6)	1.418 (3)	C(5)—C(51)	1.493 (3)
C(1)—C(11)	1.576 (3)	C(6)—C(61)	1.521 (3)
C(41)—O(2)—C(42)	115.3 (2)	C(5)—C(4)—C(41)	117.7 (2)
C(51)—O(4)—C(52)	116.8 (2)	C(4)—C(5)—C(6)	119.9 (2)
C(2)—C(1)—C(6)	117.6 (2)	C(4)—C(5)—C(51)	118.6 (2)
C(2)—C(1)—C(11)	123.4 (2)	C(6)—C(5)—C(51)	121.4 (2)
C(6)—C(1)—C(11)	118.2 (2)	C(1)—C(6)—C(5)	119.8 (2)
C(1)—C(2)—C(3)	117.1 (2)	C(1)—C(6)—C(61)	122.4 (2)
C(1)—C(2)—C(21)	124.7 (2)	C(5)—C(6)—C(61)	117.6 (2)
C(3)—C(2)—C(21)	117.1 (2)	O(1)—C(41)—O(2)	123.2 (2)
C(2)—C(3)—C(4)	119.8 (2)	O(1)—C(41)—C(4)	123.7 (2)
C(2)—C(3)—C(31)	122.0 (2)	O(2)—C(41)—C(4)	113.1 (2)
C(4)—C(3)—C(31)	117.8 (2)	O(3)—C(51)—O(4)	122.8 (2)
C(3)—C(4)—C(5)	120.2 (2)	O(3)—C(51)—C(5)	126.4 (2)
C(3)—C(4)—C(41)	122.0 (2)	O(4)—C(51)—C(5)	110.8 (2)
C(6)—C(1)—C(2)—C(3)	27.6 (2)	C(11)—C(1)—C(2)—C(21)	50.3 (2)
C(1)—C(2)—C(3)—C(4)	19.5 (2)	C(21)—C(2)—C(3)—C(31)	38.0 (2)
C(2)—C(3)—C(4)—C(5)	−0.1 (2)	C(31)—C(3)—C(4)—C(41)	−4.8 (3)
C(3)—C(4)—C(5)—C(6)	11.2 (3)	C(41)—C(4)—C(5)—C(51)	−9.6 (2)
C(4)—C(5)—C(6)—C(1)	2.5 (3)	C(51)—C(5)—C(6)—C(61)	−7.2 (3)
C(2)—C(1)—C(6)—C(5)	17.0 (2)	C(11)—C(1)—C(6)—C(61)	33.1 (2)

molecular dimensions obtained by IPD-WAS are comparable with those of 4-C, in spite of the small number of reflections of IPD-WAS. Close examination of the temperature factors showed that the general features of anisotropic temperature parameters U_{ij} of each atom obtained by the two measurements were similar, but B_{eq} values of each atom obtained by IPD-WAS were larger than those of 4-C by *ca* 0.5–1.0 Å^2. This systematic error in the overall temperature factor is probably caused during the data processing of IPD-WAS, in which the readout system of IP uses two sets of photomultiplier according to the intensity range (Kamiya & Iwasaki, 1995).

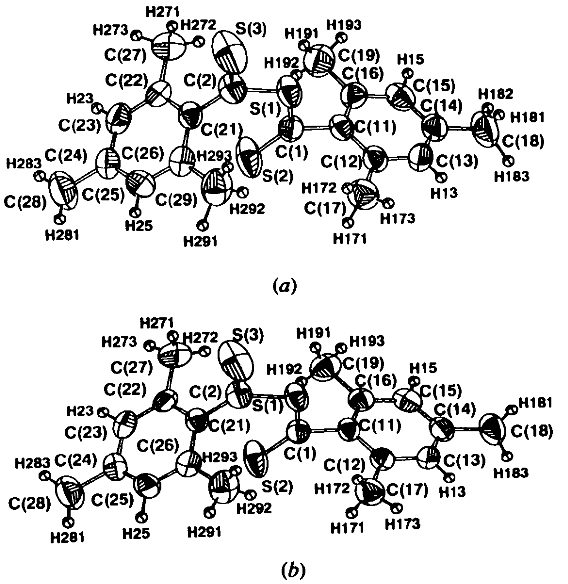

Fig. 1. *ORTEP* drawings (Johnson, 1976) of (I) with atom numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å. (*a*) IPD-WAS and (*b*) 4-C.

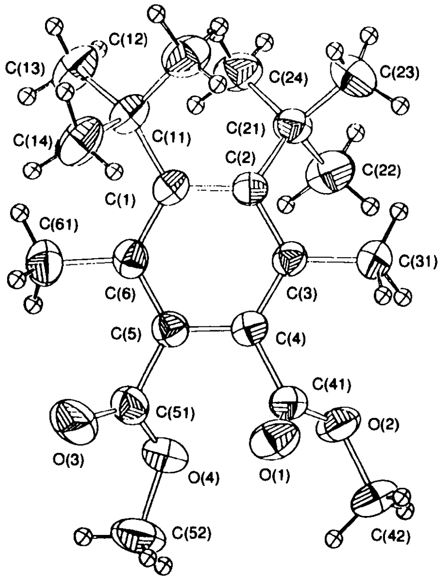

Fig. 2. *ORTEP* drawing (Johnson, 1976) of (II) obtained by IPD-WAS with atom numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

Table 7. *R values of IPD-WAS and 4-C for some sections of 2θ ranges*

R values for common reflections observed in both IPD-WAS and 4-C and R_{merge} defined by $(\sum ||F_{o,\text{IP}}| - |F_{o,4\text{C}}||)/\sum |F_{o,\text{mean}}|$ are also listed.

	IPD-WAS		4-C			IPD-WAS	4-C	
2θ range	Reflections	*R*	Reflections	*R*	Common reflections	*R*	*R*	R_{merge}
(I)								
0–22.3	307	0.037	309	0.035	291	0.036	0.035	0.030
22.3–28.2	294	0.044	295	0.038	273	0.041	0.036	0.034
28.2–32.4	274	0.046	282	0.044	252	0.041	0.041	0.040
32.4–35.8	276	0.053	289	0.050	243	0.045	0.044	0.045
35.8–38.7	216	0.077	223	0.063	176	0.057	0.052	0.050
38.7–41.2	194	0.087	231	0.074	158	0.066	0.053	0.059
41.2–43.5	182	0.101	198	0.089	142	0.084	0.071	0.067
43.5–45.6	144	0.114	184	0.081	103	0.078	0.062	0.066
45.6–47.5	70	0.163	160	0.104	48	0.127	0.092	0.083
47.5–55.0	38	0.170	562	0.126	22	0.098	0.098	0.072
All	1995	0.055	2733	0.058	1708	0.046	0.043	0.040
(II)								
0–22.3	303	0.039	304	0.040	297	0.038	0.040	0.028
22.3–28.2	311	0.042	302	0.054	296	0.040	0.055	0.030
28.2–32.4	298	0.045	290	0.044	277	0.040	0.043	0.033
32.4–35.8	291	0.041	294	0.046	270	0.037	0.045	0.035
35.8–38.7	276	0.050	268	0.048	247	0.043	0.047	0.040
38.7–41.2	247	0.060	241	0.053	212	0.051	0.050	0.042
41.2–43.5	242	0.087	260	0.065	208	0.071	0.062	0.048
43.5–45.6	203	0.098	227	0.062	165	0.078	0.062	0.051
45.6–47.5	107	0.107	221	0.072	86	0.088	0.065	0.056
47.5–55.0	82	0.167	817	0.097	58	0.117	0.077	0.085
All	2360	0.050	3224	0.055	2116	0.049	0.048	0.035

An *ORTEP* drawing of the molecular structures of (II) obtained from IPD-WAS is shown in Fig. 2, with atom numbering. Molecular dimensions obtained by IPD-WAS are listed in Table 6. The coincidence of the atomic parameters, and bond lengths and angles obtained from two data sets are again quite satisfactory, as shown in Table 5, although the temperature factors from IPD-WAS are larger than those from 4-C.

3.2. *Comparison between data sets of IPD-WAS and* 4-C

To examine the quality of intensity data, a comparison between distributions of *R* values for the data sets of IPD-WAS and 4-C was made. Table 7 shows the variation in *R* values against 2θ values. For IPD-WAS most the reflections in the range $2\theta > 45°$ are recorded on the corners or edges of the imaging plates. Higher *R* values for these higher angle reflections observed in IPD-WAS are ascribed to the difficulties of profile fitting to the integration of spots, because of the broadenings of these spots and crowding of the neighboring spots. Table 8 shows the variation in *R* values against $|F_o|$ values. In both cases, IPD-WAS and 4-C, an *R* value increases rapidly as $|F_o|$ becomes smaller. A significant difference between IPD-WAS and 4-C cannot be observed in the region $|F_o| > 7$. In the range $2 < |F_o| < 7$, *R* values of IPD-WAS are lower than those of 4-C for (I) and *vice versa* for (II). It is very notable that very weak reflections were observed in the case of IPD-WAS, although as a total the number of reflections of 4-C are larger than those of IPD-WAS, because of the limitation of $2\theta_{\max}$ of IPD-WAS. R_{merge} defined by $(\Sigma||F_{o,\text{IP}}| - |F_{o,4\text{C}}||)/\Sigma|F_{o,\text{mean}}|$ for several sections of 2θ and $|F_o|$ ranges are also listed in Tables 7 and 8, respectively.

4. Results

4.1. *Structure of* (I)

The molecule of (I) has an *anti* conformation, *i.e.* S(2) is *cis* and C(11) is *trans* to C(2) across the C(1)—S(1) bond, while S(3) is *trans* and C(21) is *cis* to C(1) across the C(2)—S(1) bond. These torsion angles are listed in Table 4. Five atoms, S(2)═C(1)—S(1)—C(2)═S(3), of the dithioacylsulfide are coplanar within the maximum deviation of 0.070 (4) Å of C(2) [0.060 (4) Å for 4-C]. The two phenyl planes are almost perpendicular to this framework. The dihedral angles between the dithioacylsulfide plane and the phenyl planes, C(11)–C(16) and C(21)–C(26), are 85.6 (1) and 93.5 (1)°, respectively. For 4-C the corresponding angles are 85.5 (1) and 93.4 (1)°, respectively. The dimensions of the two halves of the thioacyl groups are not equivalent. The S(1)—C(1) bond is longer than S(1)—C(2) by 0.01 Å, while S(2)—C(1) is shorter than S(3)—C(2). C(1)—C(11) is significantly longer than C(2)—C(21). The S(1)—C(1)—S(2) angle is larger than S(1)—C(2)—S(3), and S(1)—C(1)—C(11) is smaller than S(1)—C(2)—C(21). These differences in angles are related to the *syn* conformation of S(2)—C(1)—S(1)—C(2)—C(21). The differences in bond lengths may correspond to those in the angles with a contribution from the limiting structure of $S(3)^-$—C(2)═$S(1)^+$—C(1)═S(1). There are no special contacts between molecules, except van der Waals contacts.

4.2. *Structure of* (II)

The benzene ring is distorted from a normal hexagon, because of the crowded bulky substituents. The max-

Table 8. *R values of IPD-WAS and 4-C for some sections of $|F_o|$ ranges*

R_{merge}* defined by $(\sum ||F_{o,\mathrm{IP}}| - |F_{o,4\mathrm{C}}||)/\sum |F_{o,\mathrm{mean}}|$ are also listed.

	IPD-WAS		4-C				
$\lvert F_o\rvert$ range	Reflections	R	Reflections	R	$\langle\lvert F_{o,4\mathrm{C}}\rvert\rangle$	Common reflections	R_{merge}
(I)							
0–2.65	199	0.418	4	0.350	2.47	4	0.159
2.65–3.82	203	0.298	155	0.353	3.40	62	0.120
3.82–5.2	200	0.170	464	0.228	4.52	167	0.107
5.2–7.0	201	0.103	451	0.113	6.07	222	0.080
7.0–8.9	197	0.080	332	0.076	7.99	183	0.057
8.9–11.6	203	0.062	330	0.064	10.27	224	0.050
11.6–15.1	199	0.048	280	0.045	13.32	206	0.040
15.1–19.8	198	0.035	247	0.037	17.40	206	0.039
19.8–30.0	198	0.028	230	0.026	23.92	209	0.035
30.0–	197	0.023	240	0.022	47.04	225	0.029
(II)							
0–2.1	246	0.426	33	0.291	1.91	25	0.095
2.1–3.1	241	0.232	431	0.251	2.64	185	0.094
3.1–4.1	231	0.152	426	0.127	3.59	197	0.070
4.1–5.3	238	0.105	475	0.088	4.72	246	0.058
5.3–7.0	244	0.067	432	0.060	6.11	245	0.042
7.0–9.0	241	0.050	350	0.052	8.01	226	0.037
9.0–11.8	240	0.038	318	0.044	10.31	260	0.034
11.8–16.0	249	0.029	277	0.040	13.87	259	0.033
16.0–25.0	226	0.021	252	0.033	19.84	246	0.029
25.0–	204	0.029	230	0.032	41.12	227	0.028

* R_{merge} was calculated between the reflections of 4-C within the $|F_o|$ range in the table and the reflections of IPD-WAS having the same indices as those of 4-C. Therefore, the reflections of IPD-WAS were not necessarily within the same $|F_o|$ range and the number of common reflections in some ranges were larger than those of IPD-WAS.

imum endocyclic torsion angle of the benzene ring is −27.6 (2)° of C(6)—C(1)—C(2)—C(3) [−27.8 (2)° for 4-C]. Very large torsion angles are observed for C(11)—C(1)—C(2)—C(21), C(21)—C(2)—C(3)—C(31) and C(11)—C(1)—C(6)—C(61), which are exocyclic torsions about the bulky *tert*-butyl groups. C(1)—C(2), C(1)—C(6) and C(2)—C(3) bonds, which are related to the *tert*-butyl groups, are longer than the normal C—C length of the benzene rings. $\mathrm{C—C}_{t\text{-butyl}}$ bonds, C(1)—C(11) and C(2)—C(21), are significantly longer than $\mathrm{C—C}_{\mathrm{methyl}}$ bonds, C(3)—C(31) and C(6)—C(61). Large C(2)—C(1)—C(11) and C(1)—C(2)—C(21) angles are attributed to a steric interaction of the *ortho* substituents of bulky *tert*-butyl groups. The dimensions of the methoxycarbonyl groups are normal values. The planes of these groups are not in one plane with that of the benzene ring; the dihedral angles are 56.98 (8) and 41.16 (8)° [57.20 (7) and 41.39 (7)° for 4-C] for C(4)—C(41)O(1)—O(2)—C(42) and C(5)—C(51)O(3)—O(4)—C(52), respectively.

4.3. *Structure of the unstable crystal* (III)

An *ORTEP* drawing of the molecular structure of (III) obtained from IPD-WAS is shown in Fig. 3, with atom numberings. Atomic parameters and molecular dimensions are listed in Tables 9 and 10, respectively. The structure of (III) is a trigonal bipyramid, which is typical with the penta-coordinated Bi compounds. Three tolyl groups occupy equatorial positions and two electronegative Cl atoms occupy the apical positions. The lengths Bi—Cl, 2.599 (5) and 2.592 (6) Å, and Bi—C, 2.20–2.22 (2) Å, are similar to those of triphenyl bismuth dichloride (Hawley & Ferguson, 1968). The angle of Cl—Bi—Cl is 175.9 (2)° and those of Cl—Bi—C and C—Bi—C are 87.7–92.8 (4) and 119.0–121.9 (7)°, respectively. The deviation of the Bi atom from the plane defined by the three atoms C(1), C(11) and C(21) is 0.010 (10) Å. The dihedral angles between this plane and the three phenyl planes are 54.6 (6), 72.7 (7) and 40.6 (6)°. Reasonable values are also obtained for the dimensions of the tolyl groups.

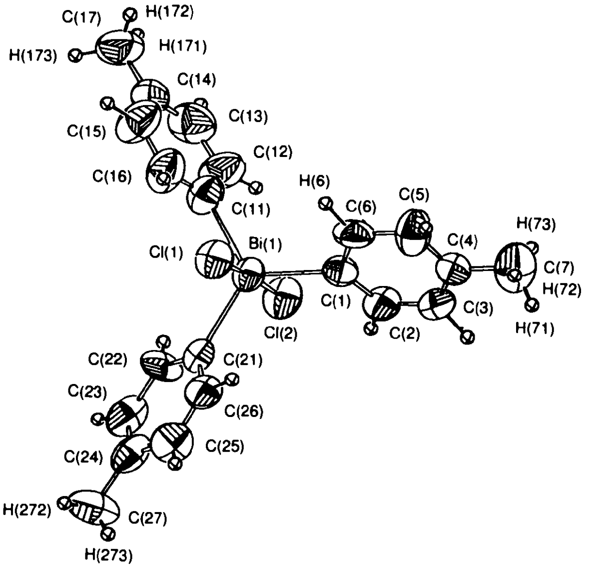

Fig. 3. *ORTEP* drawing (Johnson, 1976) of (III) with atom numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

Table 9. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (III)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Bi(1)	0.02450 (4)	0.19288 (3)	0.04389 (4)	4.84 (3)
Cl(1)	−0.0616 (3)	0.0994 (2)	0.0951 (3)	6.03 (16)
Cl(2)	0.1108 (3)	0.2801 (2)	−0.0162 (3)	6.72 (18)
C(1)	0.1678 (10)	0.1554 (7)	0.1552 (10)	4.9 (5)
C(2)	0.2475 (11)	0.1559 (8)	0.1394 (10)	5.4 (6)
C(3)	0.3322 (11)	0.1292 (8)	0.2041 (11)	5.8 (6)
C(4)	0.3432 (11)	0.1042 (8)	0.2911 (11)	6.0 (6)
C(5)	0.2666 (12)	0.1062 (9)	0.3137 (14)	7.4 (8)
C(6)	0.1732 (12)	0.1322 (9)	0.2418 (11)	6.0 (7)
C(7)	0.4385 (15)	0.0729 (9)	0.3680 (17)	8.9 (9)
C(11)	−0.0508 (12)	0.2730 (8)	0.0849 (13)	6.4 (7)
C(12)	−0.0129 (15)	0.3380 (9)	0.0990 (16)	8.3 (9)
C(13)	−0.0644 (16)	0.3896 (10)	0.1179 (15)	8.7 (10)
C(14)	−0.1451 (13)	0.3776 (9)	0.1303 (13)	7.5 (7)
C(15)	−0.1745 (15)	0.3123 (10)	0.1194 (19)	8.7 (10)
C(16)	−0.1281 (13)	0.2600 (9)	0.0960 (15)	8.0 (8)
C(17)	−0.1964 (16)	0.4338 (11)	0.1474 (16)	9.3 (10)
C(21)	−0.0465 (9)	0.1521 (7)	−0.1056 (10)	4.6 (5)
C(22)	−0.0950 (13)	0.1945 (7)	−0.1817 (10)	5.7 (6)
C(23)	−0.1446 (13)	0.1670 (9)	−0.2761 (12)	7.1 (8)
C(24)	−0.1447 (12)	0.0988 (8)	−0.2920 (13)	6.0 (7)
C(25)	−0.0901 (13)	0.0565 (7)	−0.2114 (13)	6.7 (7)
C(26)	−0.0453 (11)	0.0837 (9)	−0.1182 (10)	5.8 (6)
C(27)	−0.1985 (17)	0.0712 (10)	−0.3957 (13)	8.8 (9)

Table 10. *Selected bond lengths* (Å) *and angles* (°) *of non*-H *atoms of* (III)

Bi(1)—Cl(1)	2.599 (5)	Bi(1)—C(11)	2.219 (20)
Bi(1)—Cl(2)	2.592 (6)	Bi(1)—C(21)	2.200 (14)
Bi(1)—C(1)	2.210 (12)		
Cl(1)—Bi(1)—Cl(2)	175.9 (2)	C(1)—Bi(1)—C(21)	121.9 (6)
Cl(1)—Bi(1)—C(1)	89.6 (4)	C(11)—Bi(1)—C(21)	119.1 (7)
Cl(1)—Bi(1)—C(11)	90.7 (5)	Bi(1)—C(1)—C(2)	121.5 (12)
Cl(1)—Bi(1)—C(21)	88.9 (4)	Bi(1)—C(1)—C(6)	117.3 (12)
Cl(2)—Bi(1)—C(1)	90.4 (4)	Bi(1)—C(11)—C(12)	117.9 (15)
Cl(2)—Bi(1)—C(11)	92.8 (5)	Bi(1)—C(11)—C(16)	121.8 (16)
Cl(2)—Bi(1)—C(21)	87.7 (4)	Bi(1)—C(21)—C(22)	119.5 (13)
C(1)—Bi(1)—C(11)	119.0 (7)	Bi(1)—C(21)—C(26)	118.6 (12)

5. Concluding remarks

The structures of the stable compounds (I) and (II) were solved successfully by conventional direct methods using the intensity data obtained by a newly developed diffractometer with imaging plates. The total time for data collection was *ca* 2–3 h for each compound, in contrast to *ca* 3–4 d using the four-circle diffractometer. Agreement between the two sets of structural geometry and e.s.d.'s obtained from both the IPD-WAS and four-circle diffractometers was quite satisfactory.

The structure of the unstable crystal (III) was solved by the Patterson and heavy-atom method, and could be refined successfully. Compound (III) is unstable when exposed to X-rays and its accurate intensities had not been obtained with a four-circle diffractometer. These results strongly indicate that the accuracy of the intensity data taken with our new rapid X-ray measurement system are reliable and the system can work quite satisfactorily as a tool of ordinary crystallography and is very useful for unstable crystals.

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