

## A Comparison of Laue and Monochromatic X-ray Analyses: the Determination of the Hydrogen-Atom Positions of an Organic Small-Molecule Crystal

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### Abstract

As part of the development of the Laue method for quantitative structure analysis we report on a comparison of Mo  $K\alpha$  monochromatic and Laue X-ray analyses of 3-(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)-1,3-diphenylprop-2-en-1-one,  $C_{25}H_{20}N_2O_2$ . The crystal is of space group  $P2_12_12_1$  with  $a = 11.879$ ,  $b = 17.178$  and  $c = 9.711$  Å. We show that it is possible for the hydrogen-atom positions to be determined by successive difference Fourier analyses using both the Mo  $K\alpha$  and Laue data and this allows the correct tautomeric form to be determined. The final crystallographic  $R$  factors, with full anisotropic least-squares refinement *via* SHELX76 were 4.60 and 5.29% for the Mo  $K\alpha$  and Laue data, respectively.

### Introduction

The use of Laue data for quantitative structure analysis is being developed. In a previous paper (Gomez de Anderez *et al.*, 1989) we reported on a comparison of monochromatic (Mo  $K\alpha$  and Cu  $K\alpha$ ) and synchrotron Laue X-ray analyses of a single crystal of a small molecule of 14 atoms containing a weak anomalous scatterer (chlorine). In this paper we compare the efficacy of Mo  $K\alpha$  and Laue data to reveal the 20 hydrogen-atom positions in a larger structure of 29 non-hydrogen atoms ( $C_{25}N_2O_2$ ) using difference Fourier syntheses. Here, the anomalous-

scattering effect is negligible. This compound was selected for study because several tautomeric structures were possible and the correct formulation could only be established by X-ray analysis. The determination of the hydrogen-atom positions indicates the sensitivity of the method and the effectiveness of the Laue data recording and analysis.

### Details of the sample

Reaction of 3-methyl-1-phenyl- $\Delta^2$ -pyrazolin-5-one with 1,3-diphenylprop-2-yn-1-one in dry dimethylsulfoxide in the presence of sodium hydride afforded the dark-red 1:1 adduct, m.p. 394–395 K (Youssef, 1986). Recrystallization from toluene/dichloromethane yielded crystals suitable for X-ray crystallography.

Precession photography, on a conventional Mo  $K\alpha$  X-ray tube, showed the crystals to be orthorhombic, space group  $P2_12_12_1$ . The cell parameters were established using Mo  $K\alpha$  diffractometry to be  $a = 11.879$ ,  $b = 17.178$ ,  $c = 9.711$  Å. The molecular weight is 380.45. The linear absorption coefficient is  $0.46 \text{ cm}^{-1}$ . The density is  $1.25 \text{ g cm}^{-3}$  measured by flotation (and calculated as  $1.27 \text{ g cm}^{-3}$ ). The sample used in the Mo  $K\alpha$  diffractometry measured  $0.7 \times 0.5 \times 0.5 \text{ mm}^3$  and was cut from a larger crystal and mounted in a glass capillary tube. The sample used in the Laue case was irregular in shape and measured approximately  $(0.5 \text{ mm})^3$  and was cut from the same large red crystal. A collimator of diameter 0.2 mm determined the volume of crystal irradiated in the Laue case whereas the diffractometer crystal was fully bathed in the Mo  $K\alpha$  X-ray beam.

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## Data collection and processing

Mo  $K\alpha$  data

The Mo  $K\alpha$  data were collected on a specially upgraded Hilger & Watts four-circle diffractometer in the Physics Department of York University. Cell dimensions were obtained from 30 centred reflections. Reflection intensities were measured for  $2\theta \leq 54^\circ$  (resolution limit 0.79 Å) in  $\omega/2\theta$  scan mode with filtered Mo  $K\alpha$  radiation. The angular reflecting range (FWHM) was  $0.25^\circ$ . The measurement of four standard reflections every 200 reflections showed no signs of decay. Two equivalents were measured,  $hkl$  and  $\bar{h}\bar{k}l$ . An absorption correction was not necessary. LP corrections were applied in the usual way. The merging  $R$  factor on intensity was 1.8% for 5512 measurements which reduced to 2292 independent reflections.

## Laue data

The Daresbury Synchrotron Radiation Source station 9.7 was used to record Laue data on photographic film. A total of ten exposures were recorded at intervals of  $10^\circ$  from a preset crystal. The exposure time per film pack was 0.2 s with the SRS operating at 2 GeV, 216 mA and the wiggler at 5 T. Each film pack contained six films. The crystal-to-film distance was 61 mm.

The films were scanned at  $25 \mu\text{m}$  raster on a Scandig-3 microdensitometer. The data were processed using software developed at Daresbury following the procedures described by Gomez de Anderez *et al.* (1989) and Helliwell *et al.* (1989). The prediction involved  $\lambda_{\text{min}} = 0.2$ ,  $\lambda_{\text{max}} = 2.6$  Å and  $d_{\text{min}} = 0.9$  Å. Data beyond this resolution limit were not observed for the exposure conditions used. There were the expected percentage of energy overlaps (Cruickshank, Helliwell & Moffat, 1987), and no spatial overlaps. The wavelength normalization (program LAUENORM) used those singlet spots stimulated by wavelengths between 0.35 and 1.1 Å. The merging  $R$  factor on intensity was 7.4% involving 6403 measurements which reduced to 1125 independent reflections. The bulk of the data lay between 1.8 and 0.9 Å resolution (*i.e.*  $2d_{\text{min}}$  and  $d_{\text{min}}$ ), consistent with the distribution of Laue singlets (Cruickshank, Helliwell & Moffat, 1987).

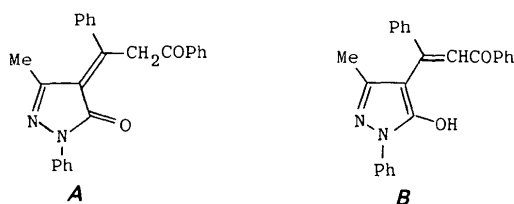


Fig. 1. The two possible tautomeric forms of the structure. Form B is identified as the correct one.

Table 1. Heights of the assigned hydrogen peaks in the difference Fourier maps.

	Peak height ( $\text{e} \text{ \AA}^{-3}$ )	
	Monochromatic	Laue
H2	0.15	0.20
H3	0.18	0.20
H4	0.64*	0.32
H5	0.17	0.20*
H6	0.21	0.40
H9	0.24 (0.69)†	0.35 (0.29)†
H12	0.29	0.21
H13	0.15	0.22
H14	0.31	0.20*
H15	0.18	0.21*
H16	0.27	0.35
H19	0.38* (0.37)†	0.18* (0.22)†
H231	0.18	0.20
H232	0.24	0.23
H233	0.45	0.18*
H25	0.25	0.33
H26	0.22	0.23
H27	0.22	0.20*
H28	0.30	0.25
H29	0.21	0.20*

\* These peaks occurred in the second difference map in either the monochromatic or Laue cases. For the first difference map the 29 non-hydrogen atoms had previously undergone anisotropic least-squares refinement. For the second difference map the hydrogen atoms determined in the first difference map had undergone isotropic refinement along with anisotropic refinement of the 29 non-hydrogen atoms.

† These peak heights were determined in difference Fourier maps for the monochromatic and Laue cases, respectively, where only these two hydrogens had been removed from the refinement. The electron density countours in the vicinity of H9 and H19 from this calculation are shown in Fig. 2. In each case the H9 peaks were the biggest in the respective maps. For the monochromatic case H19 was the next highest and then there was a noise peak with a value of  $0.29 \text{ e} \text{ \AA}^{-3}$ . In the Laue map there was a noise peak of  $0.22 \text{ e} \text{ \AA}^{-3}$ .

## Structure solution

The structure was solved completely for all non-hydrogen atoms using the Mo  $K\alpha$  data and the Sayre tangent formula (SAYTAN) for phase determination in MULTAN86 (Debaerdemaker, Tate & Woolfson, 1985). Phase set 7 had figure-of-merit values ABSFOM (1.020), PSIZERO (0.890), RESID (15.21) and CFOM (3.0). The MULTAN option did not yield the structure.

For the Laue data the structure was determined using starting phases generated by RANTAN and phase determination by SAYTAN. Phase set 110 yielded 24 atoms of the structure (out of 29) and had figure-of-merit values, ABSFOM (0.717), PSIZERO (1.236), RESID (26.93) and CFOM (2.767). A difference Fourier map phased on 24 atoms gave the remaining five non-hydrogen atoms.

## Structure refinement

SHELX (Sheldrick, 1976) was used to refine the structure by anisotropic least squares with the

Mo  $K\alpha$  and Laue data sets separately using the coordinates of the non-hydrogen atoms determined independently for each data set as described in the previous section. For the Mo  $K\alpha$  data the first difference Fourier map gave 17 of the hydrogen atoms as the highest peaks and within  $\sim 1$  Å of their bonded atoms. These 17 hydrogen atoms were then included in the refinement: they were refined isotropically and were not fixed in position. The subsequent difference Fourier map revealed the final three hydrogen atoms. The final  $R$  factor (on  $F$ ) was 4.60%, the weighted  $R$  factor was 4.72% using a weighting scheme of the form  $2.8961/[\sigma^2(F) + 0.0004449F^2]$  for 3487 reflections with  $I \geq 2\sigma(I)$  (Friedel opposites unmerged). For the Laue data the first difference Fourier map gave 13 hydrogen atoms under the same criteria and the subsequent map the remaining seven atoms. The final  $R$  factor (on  $F$ ) was 5.29%, the weighted  $R$  factor was 4.10% using a weighting scheme of the form  $9.9054/[\sigma^2(F) + 0.000081F^2]$  for 1914 reflections with  $I \geq 2\sigma(I)$  (Friedel opposites unmerged). The total number of parameters was 342 in each case.

In deciding between the two tautomeric forms (Fig. 1) it was important to see if a hydrogen atom was attached to O19 and if C9 had only one hydrogen atom attached (rather than two). Indeed H9 and H19 were determined in both the Laue and Mo  $K\alpha$  difference Fourier syntheses. In the Laue case H9 was the third highest peak in the first difference Fourier map, at a distance of 0.98 Å from C9. Table 1 compares the heights of the assigned hydrogen peaks in the monochromatic and Laue difference maps.

Because of the critical nature of H9 and H19 in deciding the tautomeric form we performed the following test. After the final refinements against the Mo  $K\alpha$  and Laue data the atoms H9 and H19 were deleted, the refinements repeated and difference Fourier maps calculated. In each case they were the biggest peaks in each map (H9 being the best in each – see Table 1). Fig. 2 shows the sections in  $y$  which contain H9 and H19 in these difference Fourier maps. Both clearly show H9 above background although the monochromatic map is better. For H19 there is a Laue peak but it is at the background level.

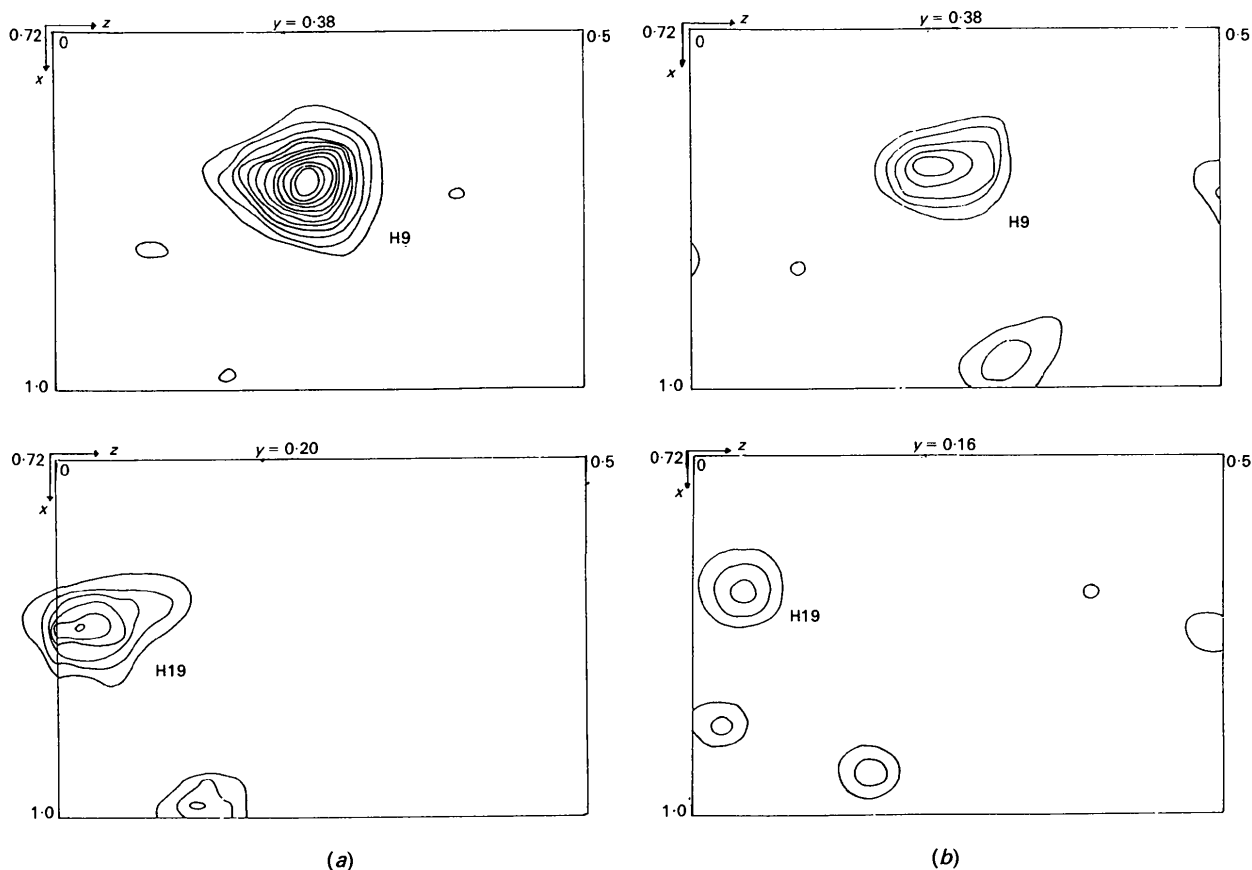


Fig. 2. Difference Fourier map sections containing H9 and H19 for (a) the Mo  $K\alpha$  and (b) the Laue analyses calculated after refinement of all the atoms except these two hydrogen atoms. The contour intervals are  $0.05 \text{ e \AA}^{-3}$  in each case starting at  $0.15 \text{ e}$  for (a) and  $0.10 \text{ e}$  for (b) (for clarity). Note that the maps show different equivalent positions to those in Table 2 for H9 and H19.

Table 2. Comparison of atomic parameters

(a) Coordinates and temperature factors for the atoms excluding the hydrogen atoms apart from H9 and H19 which were critical in defining the chemical structure and bonding. The e.s.d.'s are given in parentheses.

		Mo K $\alpha$	Laue
C1	x	0.1704 (2)	0.1695 (3)
	y	0.2158 (1)	0.2160 (2)
	z	0.6703 (2)	0.6696 (3)
	U	0.0430 (11)	0.0462 (19)
C2	x	0.0887 (2)	0.0888 (3)
	y	0.2742 (2)	0.2733 (3)
	z	0.6512 (3)	0.6519 (4)
	U	0.0568 (15)	0.0603 (23)
C3	x	-0.0038 (2)	-0.0031 (3)
	y	0.2614 (2)	0.2609 (3)
	z	0.5672 (3)	0.5677 (4)
	U	0.0660 (17)	0.0694 (29)
C4	x	-0.0169 (2)	-0.0155 (4)
	y	0.1912 (2)	0.1908 (3)
	z	0.5017 (3)	0.5015 (4)
	U	0.0626 (16)	0.0660 (27)
C5	x	0.0624 (3)	0.0628 (4)
	y	0.1333 (2)	0.1336 (3)
	z	0.5191 (3)	0.5180 (5)
	U	0.0635 (17)	0.0658 (26)
C6	x	0.1554 (2)	0.1553 (3)
	y	0.1457 (2)	0.1453 (2)
	z	0.6023 (3)	0.6025 (4)
	U	0.0553 (15)	0.0565 (22)
C7	x	0.2677 (2)	0.2685 (4)
	y	0.2335 (1)	0.2335 (4)
	z	0.7616 (2)	0.7609 (4)
	U	0.0438 (12)	0.0465 (23)
O8	x	0.2737 (1)	0.2736 (2)
	y	0.3000 (1)	0.3000 (1)
	z	0.8136 (2)	0.8139 (3)
	U	0.0593 (11)	0.0620 (17)
C9	x	0.3533 (2)	0.3530 (3)
	y	0.1748 (1)	0.1749 (2)
	z	0.7838 (2)	0.7840 (3)
	U	0.0437 (12)	0.0466 (20)
C10	x	0.4633 (2)	0.4634 (2)
	y	0.1835 (1)	0.1831 (2)
	z	0.8232 (2)	0.8232 (3)
	U	0.0390 (11)	0.0436 (17)
C11	x	0.5348 (2)	0.5343 (3)
	y	0.1114 (1)	0.1117 (2)
	z	0.8245 (2)	0.8244 (3)
	U	0.0403 (11)	0.0431 (17)
C12	x	0.6099 (2)	0.6098 (3)
	y	0.0989 (1)	0.0990 (2)
	z	0.9318 (3)	0.9317 (4)
	U	0.0483 (13)	0.0523 (21)
C13	x	0.6760 (2)	0.6756 (3)
	y	0.0325 (2)	0.0332 (3)
	z	0.9363 (3)	0.9354 (5)
	U	0.0583 (16)	0.0612 (24)
C14	x	0.6688 (2)	0.6685 (3)
	y	-0.0217 (2)	-0.0219 (2)
	z	0.8317 (3)	0.8322 (5)
	U	0.0615 (16)	0.0631 (24)
C15	x	0.5941 (2)	0.5950 (4)
	y	-0.0104 (2)	-0.0107 (3)
	z	0.7255 (3)	0.7250 (6)
	U	0.0636 (16)	0.0665 (26)
C16	x	0.5277 (2)	0.5274 (3)
	y	0.0559 (1)	0.0554 (2)
	z	0.7202 (3)	0.7201 (5)
	U	0.0542 (14)	0.0586 (22)
C17	x	0.5218 (2)	0.5216 (3)
	y	0.2543 (1)	0.2544 (2)
	z	0.8658 (2)	0.8654 (3)
	U	0.0392 (11)	0.0421 (17)
C18	x	0.4874 (2)	0.4879 (2)
	y	0.3097 (1)	0.3094 (2)
	z	0.9613 (2)	0.9610 (3)
	U	0.0409 (11)	0.0429 (18)
O19	x	0.3903 (2)	0.3906 (2)
	y	0.3162 (1)	0.3162 (2)
	z	1.0288 (2)	1.0282 (3)
	U	0.0607 (11)	0.0640 (17)
N20	x	0.5742 (2)	0.5732 (2)
	y	0.3599 (1)	0.3598 (2)
	z	0.9825 (2)	0.9822 (3)
	U	0.0414 (10)	0.0448 (16)

Table 2 (cont.)

		Mo K $\alpha$	Laue
N21	x	0.6657 (2)	0.6652 (2)
	y	0.3398 (1)	0.3398 (2)
	z	0.9013 (2)	0.9005 (3)
	U	0.0425 (10)	0.0451 (16)
C22	x	0.6348 (2)	0.6344 (3)
	y	0.2770 (1)	0.2774 (2)
	z	0.8333 (2)	0.8338 (3)
	U	0.0389 (11)	0.0440 (18)
C23	x	0.7143 (2)	0.7133 (5)
	y	0.2421 (2)	0.2431 (3)
	z	0.7309 (3)	0.7312 (6)
	U	0.0491 (14)	0.0505 (29)
C24	x	0.5814 (2)	0.5813 (3)
	y	0.4266 (1)	0.4267 (2)
	z	1.0699 (2)	1.0699 (3)
	U	0.0415 (11)	0.0446 (19)
C25	x	0.4916 (2)	0.4913 (4)
	y	0.4503 (1)	0.4510 (2)
	z	1.1506 (3)	1.1509 (4)
	U	0.0547 (14)	0.0570 (23)
C26	x	0.5038 (3)	0.5043 (5)
	y	0.5147 (2)	0.5147 (3)
	z	1.2364 (3)	1.2359 (5)
	U	0.0635 (16)	0.0661 (29)
C27	x	0.6034 (3)	0.6043 (4)
	y	0.5547 (1)	0.5549 (3)
	z	1.2439 (3)	1.2436 (5)
	U	0.0613 (16)	0.0648 (26)
C28	x	0.6929 (3)	0.6931 (4)
	y	0.5315 (1)	0.5314 (2)
	z	1.1617 (3)	1.1613 (4)
	U	0.0600 (16)	0.0639 (25)
C29	x	0.6823 (2)	0.6823 (4)
	y	0.4683 (1)	0.4682 (2)
	z	1.0737 (3)	1.0733 (5)
	U	0.0514 (13)	0.0524 (21)
H9	x	0.3292 (16)	0.3381 (25)
	y	0.1254 (13)	0.1257 (23)
	z	0.7641 (22)	0.7579 (29)
	U	0.0295 (50)	0.0337 (76)
H19	x	0.3348 (46)	0.3318 (57)
	y	0.3077 (33)	0.3131 (43)
	z	0.9552 (58)	0.9436 (83)
	U	0.1302 (220)	0.1147 (184)

(b) Bond lengths (Å)

	Mo K $\alpha$	Laue
C2—C1	1.407 (4)	1.385 (6)
C6—C1	1.385 (4)	1.389 (6)
C7—C1	1.488 (3)	1.503 (6)
C3—C2	1.386 (4)	1.381 (6)
C4—C3	1.373 (4)	1.374 (8)
C5—C4	1.380 (4)	1.362 (8)
C6—C5	1.386 (4)	1.386 (6)
O8—C7	1.250 (3)	1.255 (6)
C7—C9	1.449 (3)	1.439 (9)
C10—C9	1.370 (3)	1.372 (5)
H9—C9	0.916 (22)	0.899 (39)
C11—C10	1.502 (3)	1.488 (5)
C17—C10	1.461 (3)	1.465 (5)
C12—C11	1.388 (3)	1.392 (5)
C16—C11	1.394 (3)	1.403 (5)
C13—C12	1.385 (4)	1.375 (6)
C14—C13	1.381 (4)	1.380 (7)
C15—C14	1.374 (4)	1.373 (7)
C16—C15	1.386 (4)	1.392 (7)
C18—C17	1.391 (3)	1.384 (5)
C22—C17	1.433 (3)	1.430 (5)
O19—C18	1.331 (2)	1.333 (4)
N20—C18	1.359 (3)	1.348 (4)
H19—O19	0.984 (55)	1.079 (87)
N21—N20	1.386 (3)	1.393 (4)
C24—N20	1.430 (3)	1.433 (5)
C22—N21	1.317 (3)	1.305 (5)
C23—C22	1.497 (3)	1.489 (6)
C25—C24	1.385 (4)	1.392 (6)
C29—C24	1.397 (3)	1.396 (6)
C26—C25	1.392 (4)	1.379 (7)
C27—C26	1.371 (4)	1.375 (7)
C28—C27	1.388 (4)	1.384 (7)
C29—C28	1.389 (4)	1.388 (7)

(c) Bond angles (°)

	Mo K $\alpha$	Laue
C6—C1—C2	117.9 (2)	118.6 (2)
C7—C1—C2	118.0 (2)	118.2 (4)

Table 2 (cont.)

	Mo $K\alpha$	Laue
C7—C1—C6	124.1 (2)	123.2 (4)
C3—C2—C1	120.8 (3)	120.8 (4)
C4—C3—C2	120.1 (3)	119.8 (4)
C5—C4—C3	120.0 (3)	120.3 (4)
C6—C5—C4	120.3 (3)	120.4 (5)
C5—C6—C1	120.9 (3)	120.1 (4)
O8—C7—C1	118.1 (2)	117.5 (6)
C9—C7—C1	119.5 (2)	119.9 (4)
C9—C7—O8	122.4 (2)	122.7 (4)
C10—C9—C7	129.5 (2)	129.7 (4)
H9—C9—C7	113.2 (13)	118.4 (19)
H9—C9—C10	117.3 (13)	111.2 (19)
C11—C10—C9	116.9 (2)	117.4 (3)
C17—C10—C9	128.6 (2)	127.9 (3)
C17—C10—C11	114.5 (2)	114.7 (3)
C12—C11—C10	119.8 (2)	120.0 (3)
C16—C11—C10	121.5 (2)	121.9 (3)
C16—C11—C12	118.7 (2)	118.0 (3)
C13—C12—C11	121.0 (2)	121.0 (4)
C14—C13—C12	119.8 (3)	120.6 (4)
C15—C14—C13	119.8 (3)	119.6 (4)
C16—C15—C14	120.8 (3)	120.5 (5)
C15—C16—C11	120.0 (3)	120.3 (4)
C18—C17—C10	128.3 (2)	128.5 (3)
C22—C17—C10	127.6 (2)	127.8 (3)
C22—C17—C18	103.6 (2)	103.1 (3)
O19—C18—C17	129.8 (2)	129.7 (3)
N20—C18—C17	108.1 (2)	108.9 (2)
N20—C18—O19	122.0 (2)	121.3 (3)
H19—O19—C18	102.2 (33)	100.6 (33)
N21—N20—C18	110.6 (2)	110.1 (3)
C24—N20—C18	130.0 (2)	131.0 (3)
C24—N20—N21	119.4 (2)	118.9 (2)
C22—N21—N20	105.7 (2)	105.4 (2)
N21—C22—C17	112.0 (2)	112.5 (3)
C23—C22—C17	128.9 (2)	128.6 (4)
C23—C22—N21	119.0 (2)	118.8 (4)
C25—C24—N20	121.7 (2)	121.7 (3)
C29—C24—N20	118.5 (2)	118.7 (3)
C29—C24—C25	119.8 (2)	119.5 (3)
C26—C25—C24	119.4 (3)	119.4 (4)
C27—C26—C25	121.4 (3)	121.8 (6)
C28—C27—C26	119.2 (2)	118.8 (5)
C29—C28—C27	120.6 (3)	120.8 (4)
C28—C29—C24	119.6 (3)	119.6 (4)

In general the Mo  $K\alpha$  and Laue refined molecular coordinate sets agree very closely (Table 2).<sup>\*</sup> The root-mean-square displacement between the two sets of coordinates is 0.010 Å and the maximum displacement is 0.020 Å which is for the methyl carbon, C23. The temperature factors for the monochromatic and Laue refinements agree very closely (Fig. 3). This latter result should be contrasted with the comparison of values for the chlorine complex of Gomez de Anderez *et al.* (1989) where the temperature factors were somewhat less in the Laue case. In the study of an organometallic complex by Harding, Maginn, Campbell, Clifton & Machin (1988) the temperature factors were markedly less. This effect of structure refinement using Laue data is under investigation. The anomalous dispersion of metal atoms is not yet properly accounted for in structure refinement using Laue data and a different procedure needs to be used

<sup>\*</sup> Lists of structure factors, anisotropic thermal parameters and complete H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52214 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

for wavelength normalization. For an organic complex the anomalous-dispersion effect is insignificant.

### Description of the structures

5-Hydroxypyrazoles can exist in a variety of tautomeric forms, the preference for one or another of these being influenced by other ring substituents and by the medium (Katritzky & Maine, 1964; Newman & Pauwels, 1969, 1970).

<sup>1</sup>H and <sup>13</sup>C NMR spectra of the red compound in solution showed in each case two resonances for the CH<sub>3</sub> group, implying the presence of two tautomeric structures, or possibly two diastereoisomers. However, the X-ray results define not only the correct tautomeric structure in the crystal as a 5-hydroxy-

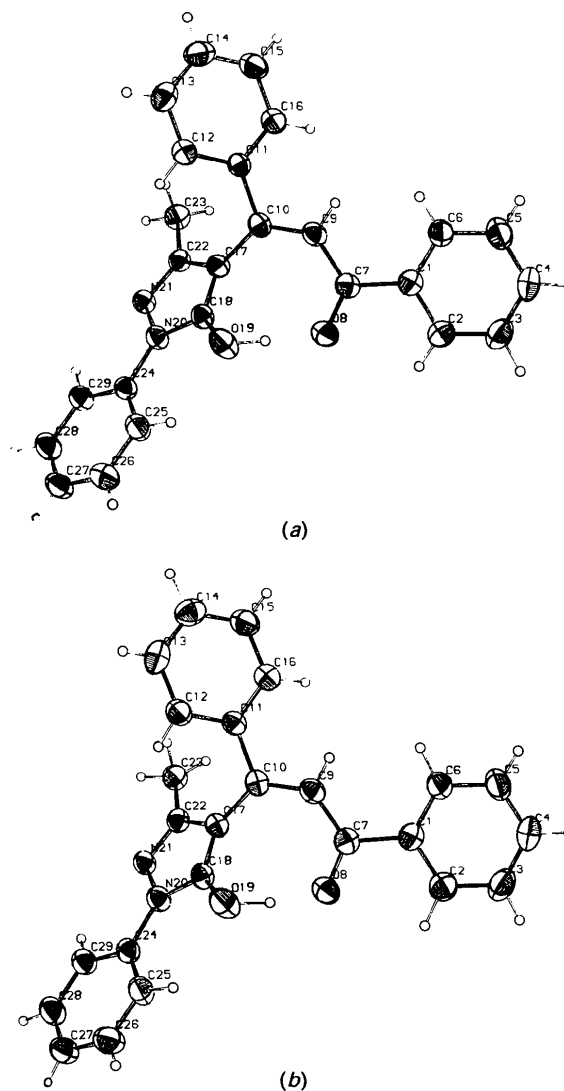


Fig. 3. ORTEP views of the molecule from (a) Mo  $K\alpha$  and (b) Laue data. Note the similarity of the temperature factors for each structure determination.

pyrazole derivative, but also the *Z* configuration of the side chain and the intramolecular hydrogen bond. The distance between O8 and O19 is 2.523 Å (2.518 Å), that between O19 and H19 is 0.984 Å (1.081 Å) and the O8-to-H19 non-bonding distance is 1.560 Å (1.452 Å); the figures in parentheses are the Laue-data-determined values. The extent of conjugation from O8 through C7, C9, C10, C17, C18 to O19 is apparent from the bond lengths listed in Table 2.

### Concluding remarks

In this study the X-ray crystal structure analyses by monochromatic or Laue methods identified the tautomeric form of an organic molecule. The 20 hydrogen atoms were identified in the respective difference Fourier syntheses after anisotropic refinement of the non-hydrogen atoms. Clearly the Laue data set was almost as sensitive to the hydrogen-atom scattering effects as the monochromatic data. This study gives confidence in the Laue method and the associated data-processing procedures being able to give data capable of discriminating between alternative, chemically possible, structures in the same way as the monochromatic method, at least, for a crystal with effectively absent anomalous-dispersion effects.

The total exposure time for the Laue data was 2 s *versus* at least 72 h for this diffractometer data. The analysis of the Laue data took approximately 1–2 weeks *versus* a few hours for the diffractometer data. Clearly, the main advantage of the synchrotron Laue

method lies in kinetic studies and utilization of small crystals or for the solution of other special crystallographic problems rather than routine structure solving.

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**3,17-Dioxo-19-norandrost-4-ene-7 $\beta$ -butyric Acid. Corrigendum.** By ROGER A. LALANCETTE,\* PAUL B. SLIFER and HUGH W. THOMPSON, *Carl A. Olsons Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ07102, USA*

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### Abstract

The crystalline (monoclinic, *P*<sub>2</sub>) cell parameters for the title compound, C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>, described [Precigoux, Busetta

& Hospital (1977). *Acta Cryst.* **B33**, 566–568] as *a* = 9.099 (5), *b* = 16.407 (8), *c* = 6.564 (4) Å,  $\beta$  = 98.59 (10)°, *Z* = 2 should be *a* = 9.099 (5), *b* = 6.564 (4), *c* = 16.407 (8) Å,  $\beta$  = 98.59 (10)°, *Z* = 2. A projection is presented which makes unambiguously clear the helical catemeric hydrogen-bonding pattern.

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