

Fig. 2. Projection of the crystal structure along the *c* axis.

of these rings (*A*–*B* 9.4, *B*–*C* 16.4, *C*–*D* 13.4, *D*–*E* 13.5°). The ring junctions *A/B*, *B/C*, *C/D* and *D/E* are, respectively, *cis*, *trans*, *trans*, *gauche*. The *D* and *E* rings are considerably distorted to relieve the repulsive interaction between the C(25) and C(24) substituents which occupy the axial positions of the *D* and *E* rings (Nakai & Shiro, 1987). The non-bonded distances between C atoms of diaxial methyl groups C(24)···C(25) and C(25)···C(26) are 3.212 (8) and

3.141 (8) Å, and are larger than the values expected for non-distorted rings. A projection of the crystal structure is shown in Fig. 2. The shortest intermolecular distance |O(29)–H(29)···O(32) ( $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ) = 2.860 (6) Å| implies possible hydrogen bonding but the angle around H is only 88 (4)°. Other than this, the crystal structure is stabilized by van der Waals forces.

One of the authors (SS) thanks the UGC, New Delhi, India, for the award of a Research Fellowship.

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*Acta Cryst.* (1989). **C45**, 923–926

## Ethyl (*Z*)-3-(2-Dimethylamino-4-methyl-6-oxo-6*H*-1,3-oxazin-5-yl)but-2-enoate (1) and Ethyl (*E*)-3-(2-Dimethylamino-6-oxo-4-phenyl-6*H*-1,3-oxazin-5-yl)but-2-enoate (2)

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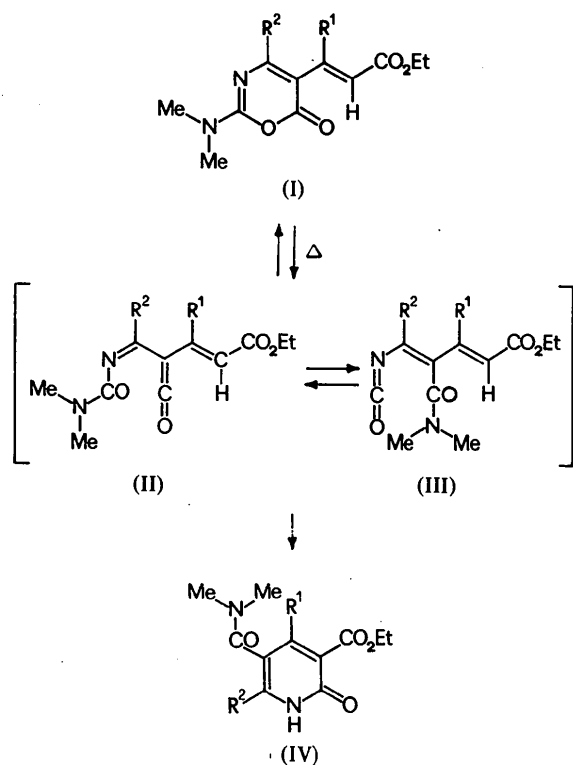
(Received 20 October 1988; accepted 1 December 1988)

**Abstract.** (1):  $C_{13}H_{18}N_2O_4$ ,  $M_r = 266.3$ , monoclinic,  $P2_1/n$ ,  $a = 6.595$  (1),  $b = 11.708$  (1),  $c = 18.307$  (2) Å,  $\beta = 97.17$  (1)°,  $V = 1402.5$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.261$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.88$  cm<sup>-1</sup>,  $F(000) = 568$ , room temperature, final  $R = 0.047$  for 1844 observed reflections. (2):  $C_{18}H_{20}N_2O_4$ ,  $M_r = 328.4$ , monoclinic,  $P2_1/n$ ,  $a = 10.535$  (1),  $b = 9.454$  (1),  $c = 17.201$  (2) Å,  $\beta = 91.27$  (1)°,  $V = 1712.8$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.273$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.85$  cm<sup>-1</sup>,  $F(000) = 696$ , room temperature, final  $R = 0.046$  for 2225 observed reflections. The 2-amino-6*H*-1,3-oxazin-6-one nuclei of the two molecules are very similar; this probably means that the different reactivity of the *Z* and *E* isomers is only due to steric reasons. Distances and angles along

the butenoic chain are quite different in (1) and (2) because of the *Z* and *E* configuration.

**Introduction.** Becalli & Marchesini (1987) have studied the synthesis and reactivity of 2-dimethylamino-6*H*-1,3-oxazin-6-ones. Pilati (1988) (hereinafter P88) has shown that the reactivity of these compounds mainly depends on electronic reasons, as evidenced by significant variations in the 1,3-oxazin-6-one geometry. Becalli & Marchesini (1988) have recently extended their work on 5-vinyl substituted molecules; in particular they found that the *Z* and *E* isomers of  $-CR^1=CH-CO_2Et$  derivatives have very different reactivity. For example, *E* compounds react very quickly by pyrolysis, according to the following

scheme, while Z isomers, under the same conditions, are very stable.



We undertook the X-ray study of (1) and (2) to define unambiguously their configuration and to discover if their different reactivity is due to electronic or steric reasons. The two compounds give good crystals, and for this reason were chosen as examples of the two configurations.

**Experimental.** Colourless crystals of both compounds were obtained from ethyl ether and light ether; crystal sizes (mm): (1) 0.30 × 0.28 × 0.20, (2) 0.40 × 0.38 × 0.160. Nonius CAD-4 diffractometer with graphite monochromator; lattice parameters measured with 25 reflections in the  $\theta$  range 16–20°;  $\theta$ - $2\theta$  data collection;  $\theta$  range 0–25°;  $hkl$  range: (1) 0→7, 0→13,  $\pm 21$ , (2) 0→12, 0→11,  $\pm 20$ ; three standard reflections, no significant variation of the intensities. Data were corrected for Lorentz and polarization factors but not for absorption. Number of data collected and, in parentheses, number of observed data [criterion  $I > \sigma(I)$ ]: (1) 2456 (1844), (2) 3025 (2225). Both structures were solved by direct methods using the program MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 4I_o / [\sigma^2(I_o) + 0.0004I_o^2]$  and  $I_o$  is the intensity on an absolute scale. A secondary-extinction parameter  $g$  [Larson (1967), eqn 3] was refined for both structures

Table 1. Fractional coordinates and  $U_{eq}$  for (1)

$$U_{eq} = (\sum_i \sum_j \beta_{ij} a_i \cdot a_j) / 6\pi^2.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O(1)	0.1701 (2)	0.1095 (1)	0.44535 (8)	0.0561 (5)
O(7)	0.2399 (3)	0.2810 (1)	0.4920 (1)	0.0762 (7)
O(15)	0.1739 (3)	0.3677 (1)	0.3172 (1)	0.0865 (8)
O(16)	0.1957 (3)	0.5556 (1)	0.33133 (9)	0.0757 (7)
N(3)	-0.1419 (3)	0.0640 (1)	0.3749 (1)	0.0545 (7)
N(8)	0.1150 (3)	-0.0683 (1)	0.4039 (1)	0.0639 (8)
C(2)	0.0388 (3)	0.0367 (2)	0.4066 (1)	0.0507 (8)
C(4)	-0.1975 (3)	0.1762 (2)	0.3798 (1)	0.0511 (8)
C(5)	-0.0780 (3)	0.2582 (2)	0.4159 (1)	0.0482 (8)
C(6)	0.1157 (3)	0.2251 (2)	0.4536 (1)	0.0531 (8)
C(9)	0.3238 (6)	-0.0952 (3)	0.4340 (3)	0.074 (1)
C(10)	-0.0074 (7)	-0.1553 (3)	0.3613 (2)	0.088 (2)
C(11)	-0.3007 (6)	-0.4054 (3)	0.4699 (3)	0.066 (1)
C(12)	-0.1399 (3)	0.3800 (2)	0.4216 (1)	0.0558 (8)
C(13)	-0.0502 (3)	0.4655 (2)	0.3893 (1)	0.0615 (9)
C(14)	0.1131 (3)	0.4545 (2)	0.3424 (1)	0.0588 (9)
C(17)	0.3693 (5)	0.5562 (2)	0.2891 (2)	0.093 (1)
C(18)	0.4931 (5)	0.6553 (3)	0.3079 (2)	0.108 (2)
C(19)	-0.4040 (4)	0.2022 (3)	0.3388 (2)	0.074 (1)

Table 2. Fractional coordinates and  $U_{eq}$  for (2)

$$U_{eq} = (\sum_i \sum_j \beta_{ij} a_i \cdot a_j) / 6\pi^2.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O(1)	0.1269 (1)	0.5484 (2)	0.39994 (8)	0.0545 (6)
O(7)	0.3206 (1)	0.4679 (2)	0.3825 (1)	0.0703 (7)
O(15)	0.4155 (2)	-0.0550 (2)	0.3272 (1)	0.0915 (8)
O(16)	0.3511 (2)	-0.1091 (2)	0.4460 (1)	0.0744 (7)
N(3)	-0.0558 (2)	0.4101 (2)	0.3794 (1)	0.0492 (7)
N(8)	-0.0638 (2)	0.6431 (2)	0.4199 (1)	0.0565 (7)
C(2)	-0.0005 (2)	0.5279 (2)	0.3988 (1)	0.0477 (8)
C(4)	0.0204 (2)	0.3002 (2)	0.3568 (1)	0.0457 (7)
C(5)	0.1504 (2)	0.3074 (2)	0.3581 (1)	0.0455 (8)
C(6)	0.2091 (2)	0.4387 (2)	0.3793 (1)	0.0521 (8)
C(9)	-0.0004 (3)	0.7783 (3)	0.4338 (2)	0.068 (1)
C(10)	-0.2017 (3)	0.6411 (4)	0.4181 (2)	0.070 (1)
C(11)	0.3207 (3)	0.2158 (4)	0.2686 (2)	0.074 (1)
C(12)	0.2420 (2)	0.1923 (2)	0.3398 (1)	0.0493 (8)
C(13)	0.2541 (2)	0.0830 (3)	0.3873 (2)	0.0524 (9)
C(14)	0.3478 (2)	-0.0320 (3)	0.3810 (2)	0.0600 (9)
C(17)	0.4497 (3)	-0.2189 (4)	0.4497 (2)	0.092 (2)
C(18)	0.4431 (3)	-0.2874 (4)	0.5243 (3)	0.110 (2)
C(19)	-0.0535 (2)	0.1750 (2)	0.3289 (1)	0.0482 (8)
C(20)	-0.1682 (2)	0.1419 (3)	0.3632 (2)	0.0612 (9)
C(21)	-0.2418 (3)	0.0321 (3)	0.3346 (2)	0.076 (1)
C(22)	-0.2040 (3)	-0.0444 (3)	0.2713 (2)	0.075 (1)
C(23)	-0.0913 (3)	-0.0128 (3)	0.2373 (2)	0.072 (1)
C(24)	-0.0162 (2)	0.0961 (3)	0.2654 (1)	0.0597 (9)

[ $g(\times 10^6)$ : (1) 21(2), (2) 15(2)]. Four H atoms of (1) and one of (2) were introduced into structure-factor calculations but not refined, all other H atoms located in difference Fourier maps and refined isotropically. Non-H atoms refined anisotropically. Final  $R$ : (1) 0.047, (2) 0.046;  $wR$ : (1) 0.041, (2) 0.045;  $S$ : (1) 2.43, (2) 2.94;  $(\Delta/\sigma)_{\max}$ : (1) 0.03, (2) 0.05;  $\Delta\rho$  (1)  $\pm 0.03$ , (2)  $\pm 0.02$  e  $\text{\AA}^{-3}$ . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Programs used include Enraf-Nonius SDP (Frenz, 1983), ORTEPII (Johnson, 1976), PARST (Nardelli, 1983) and various in-house programs for refinement and geometrical analysis running on a Gould 32/97 computer.

**Discussion.** Tables 1 and 2 list final refined coordinates and  $U_{eq}$  values for the non-H atoms.\* Fig. 1 shows the two molecules; the numbering scheme of heavy atoms is the same for corresponding atoms. Table 3 gives bond distances and bond angles together with some mean values for similar molecules taken from P88. The 2-amino-6*H*-1,3-oxazin-6-one moiety of the two molecules is similar; the greatest differences are due to the influence of the substituents at C(4): in fact, as found in P88, a phenyl group at C(4) increases the C(4)=C(5) bond length and the C(2)–N(3)–C(4) bond angle, while it reduces the O(1)–C(6) bond and the N(3)–C(4)–C(5) angle. On the other hand these variations (about 0.01 Å and 1°, see Table 3) are about one half of those found in P88 for compounds with an electron-withdrawing group directly bonded to C(5). The greater separation between the amino group and

\* Lists of anisotropic thermal parameters, structure factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51662 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

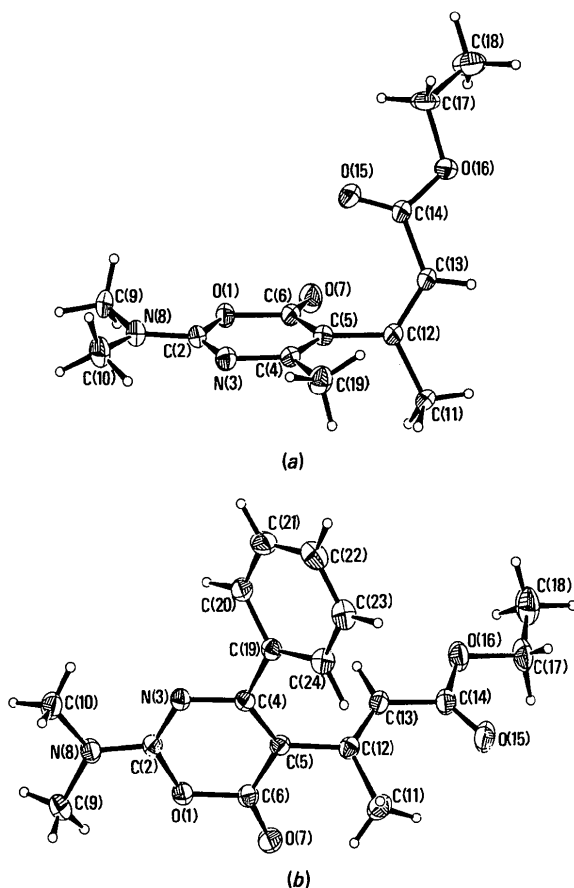


Fig. 1. ORTEP plot of the two molecules with numbering scheme: (a) molecule (1), (b) molecule (2); thermal ellipsoids at 20% probability, H atoms are not to scale.

Table 3. Bond distances (Å) and angles (°) for (1) and (2)

	(1)	(2)	Mean*
O(1)–C(2)	1.351 (2)	1.356 (2)	1.350 (5)
O(1)–C(6)	1.413 (3)	1.402 (2)	1.413 (5)
O(7)–C(6)	1.204 (3)	1.207 (2)	1.201 (8)
O(15)–C(14)	1.205 (3)	1.201 (4)	
O(16)–C(14)	1.329 (3)	1.335 (4)	
O(16)–C(17)	1.459 (4)	1.469 (4)	
N(3)–C(2)	1.299 (3)	1.297 (3)	1.313 (7)
N(3)–C(4)	1.370 (3)	1.374 (3)	1.357 (7)
N(8)–C(2)	1.331 (3)	1.332 (3)	1.325 (6)
N(8)–C(9)	1.453 (4)	1.459 (4)	
N(8)–C(10)	1.463 (4)	1.453 (4)	
C(4)–C(5)	1.360 (3)	1.371 (3)	1.373 (11)
C(4)–C(19)	1.502 (3)	1.490 (3)	
C(5)–C(6)	1.428 (3)	1.431 (3)	1.426 (7)
C(5)–C(12)	1.491 (3)	1.493 (3)	
C(11)–C(12)	1.493 (5)	1.511 (4)	
C(12)–C(13)	1.338 (3)	1.322 (4)	
C(13)–C(14)	1.464 (3)	1.474 (4)	
C(17)–C(18)	1.436 (4)	1.440 (6)	
C(19)–C(20)		1.392 (3)	
C(19)–C(24)		1.387 (3)	
C(20)–C(21)		1.380 (4)	
C(21)–C(22)		1.374 (5)	
C(22)–C(23)		1.368 (5)	
C(23)–C(24)		1.379 (4)	
C(2)–O(1)–C(6)	120.4 (2)	120.5 (1)	121.3 (9)
C(14)–O(16)–C(17)	116.7 (2)	115.3 (2)	
C(2)–N(3)–C(4)	116.4 (2)	117.4 (2)	116.2 (10)
C(9)–N(8)–C(10)	119.0 (2)	118.0 (2)	
C(2)–N(8)–C(10)	118.5 (2)	119.4 (2)	
C(2)–N(8)–C(9)	122.0 (2)	122.1 (2)	
N(3)–C(2)–N(8)	122.7 (2)	123.2 (2)	122.2 (3)
O(1)–C(2)–N(8)	112.4 (2)	112.4 (2)	113.5 (6)
O(1)–C(2)–N(3)	124.9 (2)	124.4 (2)	124.3 (5)
N(3)–C(4)–C(5)	113.3 (2)	112.8 (2)	
N(3)–C(4)–C(19)	124.4 (2)	123.2 (2)	124.6 (21)
C(5)–C(4)–C(19)	122.3 (2)	124.0 (2)	
C(4)–C(5)–C(6)	124.2 (2)	127.6 (2)	
C(4)–C(5)–C(12)	118.2 (2)	118.3 (2)	118.5 (10)
C(6)–C(5)–C(12)	117.5 (2)	114.1 (2)	
O(7)–C(6)–C(5)	129.6 (2)	128.7 (2)	130.2 (14)
O(1)–C(6)–C(5)	115.6 (2)	116.1 (2)	114.8 (8)
O(1)–C(6)–O(7)	114.8 (2)	115.2 (2)	115.1 (7)
C(5)–C(12)–C(11)	116.9 (2)	115.7 (2)	
C(11)–C(12)–C(13)	119.9 (2)	124.7 (2)	
C(5)–C(12)–C(13)	123.0 (2)	119.6 (2)	
C(12)–C(13)–C(14)	126.3 (2)	125.9 (3)	
O(16)–C(14)–C(13)	110.9 (2)	110.3 (3)	
O(15)–C(14)–C(13)	127.1 (2)	126.9 (3)	
O(15)–C(14)–O(16)	122.0 (2)	122.8 (2)	
O(16)–C(17)–C(18)	109.7 (3)	108.0 (3)	
C(4)–C(19)–C(24)		121.7 (2)	
C(4)–C(19)–C(20)		119.6 (2)	
C(20)–C(19)–C(24)		118.5 (2)	
C(19)–C(20)–C(21)		120.3 (2)	
C(20)–C(21)–C(22)		120.6 (3)	
C(21)–C(22)–C(23)		119.6 (3)	
C(22)–C(23)–C(24)		120.6 (3)	
C(19)–C(24)–C(23)		120.5 (2)	

\* Mean values from P88 for seven 2-dialkylamino-6*H*-1,3-oxazin-6-ones.

the electron-withdrawing group in (1) and (2) with respect to the compounds in P88 is probably the reason why the N(8)–C(2), C(2)–N(3) and N(3)–C(4) bonds are slightly but significantly more alternating in the first than in the second compound. Distances and angles along the butenoic chain are quite different in (1)

and (2) because of the *Z* and *E* configuration: in particular, the strong interaction between the C(14)=O(15) group and the heterocycle in (1) enlarges the C(5)–C(12)–C(13) angle; in contrast, in (2), the carbonyl group interacts with C(11), increasing the C(11)–C(12)–C(13) angle. The  $\pi$  systems of the butenoic chain and the oxazine group interact poorly with each other in both structures; in fact the torsion angle C(4)–C(5)–C(12)–C(13) is  $-112.8$  (3) and  $-68.9$  (3) $^\circ$  in (1) and (2) respectively. The ring O(1), C(2), N(3), C(4), C(5), C(6) is not completely planar in both molecules: in (1) it has an approximate <sup>1</sup>*E* conformation, with total puckering amplitude (Cremer & Pople, 1975)  $Q_t = 0.036$  (2)  $\text{\AA}^2$ , while its conformation in (2) is approximately <sup>3</sup>*S*<sub>2</sub>, with  $Q_t = 0.028$  (2)  $\text{\AA}^2$ . In contrast, the phenyl ring of (2) is strictly planar; the dihedral angle between this and the heterocycle mean plane is  $37.67$  (6) $^\circ$ . The cyclization of (I) to give (IV) (see scheme) requires a change of configuration around the C(4)=C(5) double bond in the case of *E* compounds and also, for *Z* isomers, around the C(12)=C(13) double bond. The similarity of the heterocycle in (1) and (2) indicates that the equilibrium (I) $\leftrightarrow$ (II) [and probably (II) $\leftrightarrow$ (III)] is not affected by the *E* or *Z* conformation of the C(12)=C(13) double bond; clearly this bond is thermally much more stable than C(4)=C(5), and does not permit the cyclization (I) $\leftrightarrow$ (IV) of *Z* compounds.

The molecular packing is essentially due to van der Waals forces in both compounds, although some very weak hydrogen bonds are present.

I wish to thank Professor M. Marchesini for the suggestion of the work and the gift of crystals.

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*Acta Cryst.* (1989). **C45**, 926–928

### Structure of Methyl $\alpha$ -Benzamido- $\beta$ -mercaptophenyl- $\beta$ -phenylpropionate\*

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(Received 17 August 1988; accepted 6 December 1988)

**Abstract.** C<sub>23</sub>H<sub>21</sub>NO<sub>3</sub>S,  $M_r = 391.5$ , triclinic,  $P\bar{1}$ ,  $a = 9.277$  (1),  $b = 9.572$  (1),  $c = 11.970$  (1)  $\text{\AA}$ ,  $\alpha = 103.09$  (1),  $\beta = 92.42$  (1),  $\gamma = 102.68$  (1) $^\circ$ ,  $V = 1005.3$  (2)  $\text{\AA}^3$ ,  $Z = 2$ ,  $D_m$  (floatation in KI solution) = 1.31,  $D_x = 1.29$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$   $\text{\AA}$ ,  $\mu = 0.186$  mm<sup>-1</sup>,  $F(000) = 412$ ,  $T = 293$  K,  $R = 0.031$  for 1910 observed reflections. There is a short intramolecular N–H...S contact [3.040 (2)  $\text{\AA}$ ] and an intermolecular N–H...O hydrogen bond [3.109 (3)  $\text{\AA}$ ] which stabilize the crystal and molecular structure. The propionate group is *gauche* with respect to the  $\beta$ -phenyl ring.

**Introduction.** Phenylalanine is a molecule of importance as an essential amino acid and also as a requisite for the artificial sweetener 'aspartame'. The title compound resulted in an effort to prepare enantioselective  $\alpha$ -phenylalanine as a precursor for such a synthesis (Keniya, Natu & Gogate, 1986). This article reports the stereochemical details as determined by X-ray crystallography.

**Experimental.** Crystal approx.  $0.17 \times 0.35 \times 0.45$  mm, Nonius CAD-4F-11M diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\omega/2\theta$  scan mode, scan speed  $1^\circ \text{ min}^{-1}$ ,  $\theta < 23.5^\circ$ ,  $h$  0 to 10,  $k$  -10 to 10,  $l$  -13 to 13, 3189 reflections collected, 1910 judged significant ( $|F_o| > 3\sigma|F_o|$ ), lattice param-

\* NCL Communication No. 4527.

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