The suggestions about intramolecular hydrogen bonding, which stem from the investigation of dissociation constants, have been confirmed, since X-ray crystal structure analysis showed this type of bond to be present in ammonium hydrogen *cis*-caronate and potassium hydrogen *cis*-caronate hydrate (Jessen & Küppers, 1991).

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Structure and Intramolecular Hydrogen Bonding of 1-Phenazinecarboxylic Acid

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Abstract. $C_{13}H_8N_2O_2$, $M_r = 224{\cdot}22$, monoclinic, $P2_1/n$, $a = 18{\cdot}149\,(2)$, $b = 14{\cdot}2768\,(9)$, $c = 3{\cdot}8191\,(3)$ Å, $\beta = 92{\cdot}029\,(6)^\circ$, $V = 988{\cdot}95$ Å^3, $Z = 4$, $D_x = 1{\cdot}51$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 7{\cdot}61$ cm^{-1}, $F(000) = 464$, $T = 163\,(1)$ K, $R = 0{\cdot}037$ for 1479 data with $I \geq 2\sigma(I)$. An intramolecular hydrogen bond is observed between the carboxyl hydrogen atom and the nearby nitrogen atom with the N···O distance being 2·67 Å.

Introduction. Previous spectroscopic studies of the fungal antibiotic produced by a fluorescent pseudomonad (*P. fluorescens* 2-79, NRRL B-15132) have shown evidences in favor of both a dimeric (Gurusiddaiah, Weller, Sarkar & Cook, 1986) and a monomeric (Brisbane, Janik, Tate & Warren, 1987) structure. The mass spectrum of our microbially produced material displayed a dimer peak in the gas phase, but vapor-pressure osmometry showed the material to be monomeric in solution (CH_2Cl_2). Melting-point determination, thin-layer chromatography, UV–visible spectroscopy and NMR spectroscopy (^{1}H, ^{13}C) all showed the microbially produced material to be identical to chemically synthesized 1-phenazinecarboxylic acid. The crystal structure of 1-phenazinecarboxylic acid at room temperature reported recently (Jones, Lewis, Tate, Snow & Tiekink, 1988) provided unequivocal evidence that the antibiotic has the monomeric structure. However, in the room-temperature structure, the carboxyl hydrogen was not located. The possible reason for this missing hydrogen atom was pointed out by the authors to be the 'disorder in the absence of hydrogen-bonding effects' (Jones *et al.*, 1988). In our low-temperature structure, the location of this hydrogen atom has been determined and it participates in an intramolecular hydrogen bond.

Experimental. A crystal of dimensions 0·05 × 0·06 × 0·30 mm was used for X-ray diffraction studies. The oscillation picture of this crystal showed that its needle axis was a very short crystallographic axis of

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3·8 Å. The X-ray diffraction data were collected at low temperature on an Enraf–Nonius CAD-4 diffractometer using Ni-filtered Cu $K\alpha$ radiation. 48 reflections ($44 > \theta > 25°$) and Cu $K\alpha_1$ wavelength (1·54051 Å) were used for lattice constants. Systematic absences were $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$). All data with $1·0 \leq 2\theta \leq 150·0°$ in $-22 \leq h \leq 22$, $0 \leq k \leq 17$ and $0 \leq l \leq 4$ were collected using ω–2θ scan techniques and a variable scan width calculated as $(0·85 + 0·20\tan\theta)°$. The maximum scan time for a single reflection was 90 s. The receiving aperture, located 173 mm from the data crystal, had a constant height at 6 mm and a variable width calculated as $(3·50 + 0·86\tan\theta)$ mm. Three intensity control monitors were measured every 7200 s of X-ray exposure time and they showed a maximum difference of 0·012 (3). The profiles of all the measured reflections were observed and stored.

The data set was processed using a profile analysis method (Blessing, 1987). Lorentz–polarization corrections were applied. No absorption correction was made. Among 2129 unique data, 1479 were observed [$I \geq 2\sigma(I)$]. The structure was solved by direct methods using *SHELX76* (Sheldrick, 1976). The 17 non-hydrogen atoms were refined anisotropically. The eight hydrogen atoms were located from successive difference Fourier syntheses and refined isotropically. A final R of 0·037 and wR of 0·040 were obtained by the full-matrix least-squares minimization of $\sum w(|F_o| - |kF_c|)^2$, where $w = 1/[\sigma^2(F) + 0·0001F^2]$. The maximum shift/e.s.d. = 0·016. The largest and the smallest peaks in the final difference Fourier map were +0·25 and $-0·18$ e Å^{-3}, located in the middle of the bonds of the conjugated ring system of the molecule. The e.o.f. = $[\sum w(F_o - F_c)^2/(N - NP)]^{1/2} = 2·1$, where N was the number of reflections used (1479) and NP was the number of parameters refined (186). There was no systematic change in $\overline{\Delta F}$ with either $\sin\theta/\lambda$ or F_o. Scattering factors were those imbedded in *SHELX76*.

Discussion. The final positional parameters and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 1.* Bond distances and bond angles are given in Fig. 1 which also shows the numbering scheme and the intramolecular hydrogen bond N(10)···H(13)—O(13). The N···O distance is 2·67 Å and the N···H distance is 1·72 Å. This hydrogen bond, however, was not found in the room-temperature structure previously reported

Table 1. *Final positional parameters and equivalent isotropic temperature factors for non-*H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$ (Å^2)
C(1)	0·22152 (9)	0·0868 (1)	0·6090 (4)	0·0249 (5)
C(2)	0·2124 (1)	−0·0063 (1)	0·6708 (5)	0·0291 (6)
C(3)	0·1489 (1)	−0·0560 (1)	0·5494 (5)	0·0291 (6)
C(4)	0·09356 (9)	−0·0109 (1)	0·3694 (5)	0·0262 (5)
C(4a)	0·09919 (8)	0·0864 (1)	0·3011 (4)	0·0220 (5)
N(5)	0·04337 (7)	0·12985 (9)	0·1254 (4)	0·0238 (4)
C(5a)	0·05098 (9)	0·2218 (1)	0·0615 (4)	0·0228 (5)
C(6)	−0·0070 (1)	0·2709 (1)	−0·1212 (5)	0·0282 (6)
C(7)	0·0007 (1)	0·3636 (1)	−0·1950 (5)	0·0303 (6)
C(8)	0·0662 (1)	0·4124 (1)	−0·0902 (5)	0·0304 (6)
C(9)	0·1220 (1)	0·3691 (1)	0·0904 (5)	0·0274 (5)
C(9a)	0·11629 (9)	0·2721 (1)	0·1709 (4)	0·0222 (5)
N(10)	0·17165 (7)	0·22834 (9)	0·3476 (4)	0·0232 (4)
C(10a)	0·16420 (8)	0·1365 (1)	0·4164 (4)	0·0217 (5)
C(11)	0·29097 (9)	0·1333 (1)	0·7468 (5)	0·0319 (6)
O(12)	0·33659 (7)	0·0912 (1)	0·9219 (4)	0·0440 (5)
O(13)	0·29997 (7)	0·2240 (1)	0·6729 (4)	0·0391 (5)

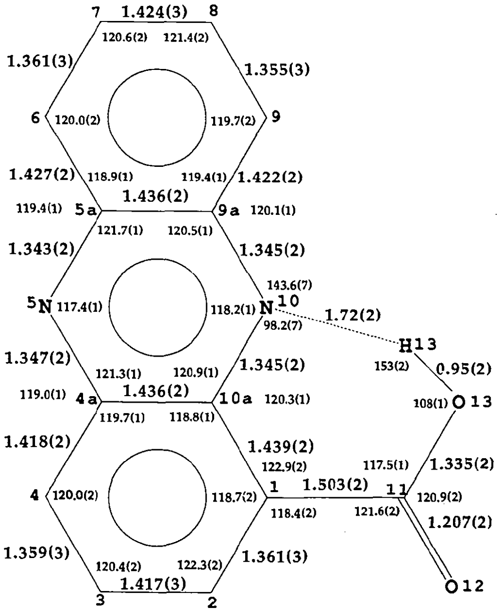

Fig. 1 Bond distances (Å) and bond angles (°) for 1-phenazinecarboxylic acid with e.s.d.'s in parentheses. Also shown is the intramolecular hydrogen bond N(10)···H(13)—O(13).

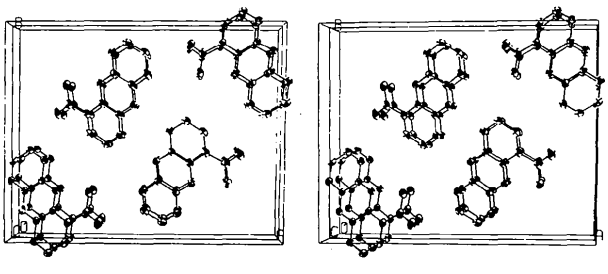

Fig. 2. Stereoview of the packing of 1-phenazinecarboxylic acid. The thermal ellipsoids are drawn at the 50% probability level (Johnson, 1965).

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* Tables of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54386 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Jones *et al.*, 1988). The bond distances and bond angles indicate that the molecule is a planar conjugated system. The r.m.s. of the least-squares plane C(1) through O(13) is 0·03 Å.

The crystal structure of phenazine has been determined (Herbstein & Schmidt, 1955) and further refined (Glazer, 1970). It has been shown that the phenazine molecule has D_{2h} symmetry within experimental error. This symmetry to a large extent remains in 1-phenazinecarboxylic acid with one important exception. The bond distance C(1)—C(10a) is significantly different from C(4)—C(4a), while C(9)—C(9a) and C(6)—C(5a) are equal. These structural features reflect the influence of the carboxylic group substitution at position 1, while the approximate symmetry observed in the present low-temperature structure was not apparent in the room-temperature structure (Jones *et al.*, 1988). In the crystal, the molecules of 1-phenazinecarboxylic acid are parallel to each other and packed along the *c* axis (Fig. 2). The distance between adjacent molecular planes is 3·34 Å.

The pK_a of the compound was found to be 5·2 in ethanol/water (50/50, 298 K, 0·1 *M* $NaClO_4$) and is consistent with the structurally determined location of the acidic proton and with known pK_a values (4·2 in water, 5·5 in 50/50 ethanol/water) of benzoic acid (Grunwald & Berkowitz, 1951).

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Structure du 2-Acétylamino-2′-(diacétylamino)biphényle

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Abstract. 2-Acetylamino-2′-(diacetylamino)biphenyl, $C_{18}H_{18}N_2O_3$, $M_r = 310{\cdot}34$, monoclinic, $P2_1/n$, $a = 9{\cdot}185\,(4)$, $b = 13{\cdot}657\,(5)$, $c = 13{\cdot}130\,(6)$ Å, $\beta = 105{\cdot}75\,(4)^\circ$, $V = 1587{\cdot}48\,(7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}31\,(2)$, $D_x = 1{\cdot}298$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 7·38 cm^{-1}, $F(000) = 656$, $T = 293$ K, $R = 0{\cdot}053$ for 1179 independent reflections. The torsion angle between the benzene rings is 72·2 (6)°.

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