weight measurements indicate that HPTP is also highly associated in solutions. As in HMTP and HCTP (Mattes, Mühlsiepen & Rühl, 1983) the acid hydrogen atom is located in HPTP at the oxygen atom of the POS group. The O···S distance [3·138 (2) Å] is shorter than the sum of the van der Waals radii of oxygen and sulfur (~ 3·2 Å). This is not the case for the S—H···S hydrogen bonds in dithiophosphinic acids, with an S···S distance of 3·75–3·83 Å (Henkel, 1976; Krebs, 1983). Therefore, the O—H···S hydrogen bond has to be considered as a rather strong hydrogen bond. Its strength is mainly due to the high polarity of the O—H bond. The bond is linear within the experimental error. The P=S···H (or the more accurately determined P=S···O angle) is considerably smaller than 120°; this value can be expected if an acceptor atom is doubly bonded and this atom $sp^2$ hybridized. In thiophosphinic and dithiophosphinic acids the size of this angle varies between 90 and 110°. In the present work it is close to 97°, indicating a slightly higher s character of the P=S bond (and a higher p character of the acceptor orbital) compared to HMTP and HCTP. Here the values 103·3 (5) and 107 (1)° have been found. This might be the reason for the slight shortening of the P=S bond from 1·966 (1) and 1·973 (1) Å in the latter compounds to 1·956 (1) Å in HPTP. The overall hydrogen-bond pattern is also different in these three compounds, because HMTP and HCTP form dimers in the solid state and HPTP is polymeric. But the local structure of

the hydrogen bond is not affected. The question whether (di)thiophosphinic acids form dimers or polymers in the solid state is probably determined by crystal packing effects. The P—O bond length of 1·582 (2) Å is typical for a single bond. Whereas the distances $d$(PO) and $d$(PS) remain essentially unchanged after deprotonation and complex formation, $e.g.$ with Sb$^{III}$, the OPS angle slightly decreases in HPTP from 115·4 to approximately 111° for chelating ligands, but remains unchanged for bridging ligands (Mattes & Rühl, 1983). The remaining bond lengths of HPTP and distances are normal.

### References

FENSKE, D., MATTES, R., LÖNS, J. & TEBBE, K.-F. (1973). $Chem.$ $Ber.$ **106**, 1139–1143.
GIORDANO, F. & RIPAMONTI, A. (1967). $Acta$ $Cryst.$ **22**, 678–682.
HENKEL, G. (1976). S–H···S-$Wasserstoffbrückenbindungen$ $in$ $Thiosäuren$ $des$ $Phosphors$ $und$ $des$ $Kohlenstoffs.$ PhD Thesis, Univ. of Bielefeld.
KABACHNIK, M. I., MASTRUKOVA, T. A., SHIPOV, A. E. & MENTYEVA, T. A. (1960). $Tetrahedron,$ **9**, 10–28.
KREBS, B. (1983). $Angew.$ $Chem.$ **95**, 113–134.
MATTES, R., MÜHLSIEPEN, K.-M. & RÜHL, D. (1983). $Z.$ $Anorg.$ $Allg.$ $Chem.$ **499**, 67–74.
MATTES, R. & RÜHL, D. (1983). $Z.$ $Anorg.$ $Allg.$ $Chem.$ In the press.
SASSE, K. (1963). $Methoden$ $der$ $Organischen$ $Chemie$ ($Houben–Weyl$), edited by E. MÜLLER, Vol. 12/1, pp. 266–281. Stuttgart: Thieme.
SYNTEX (1976). $XTL/XTLE$ $Structure$ $Determination$ $System.$ Syntex Analytical Instruments, Cupertino, California.

# Structure of 5-Amino-4-phenyl-3,4-dihydro-2H-pyrrol-2-one, $C_{10}H_{10}N_2O$

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**Abstract.** $M_r = 174·19$, monoclinic, $P2_1/a$, $a = 12·770$ (2), $b = 5·761$ (1), $c = 12·001$ (2) Å, $\beta = 97·94$ (2)°, $V = 874·5$ (3) Å$^3$, $Z = 4$, $D_x = 1·323$ (1) Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·627$ mm$^{-1}$, $F(000) = 368$, $T = 293$ K. Final $R = 0·043$ for 1085 observed reflections. The C—N—C—N fragment of the molecule seems to reveal the diffused electron system, the exocyclic N atom being of amino character. Both amino H atoms form hydrogen bridges to the carbonyl O and hetero N atoms of neighbouring molecules, thus creating planar systems parallel to the $ab$ plane of the crystal.

**Introduction.** The title compound was synthesized according to Koberda & Lange (1976) in the course of studies carried out on new five-membered cyclic amidines related to the biologically active succinimides. Because the structural problems in those compounds (a possible amino–imino tautomerism) could not be unambiguously solved by means of other techniques, X-ray molecular and crystal structure research has been undertaken now. As no diffractometric data were available in the literature on any 5-amino (or 5-imino) derivatives of 2-pyrrolidinone, it was expected moreover that this research could bring some material for comparison with that reported for succinimide derivatives and 5-$X$-substituted 2-pyrrolidinones ($X$ is a C—C-linked substituent).

[structure diagram]

(I)      (II)
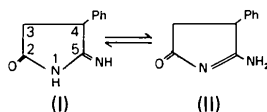
**Experimental.** Crystal (0·3 × 0·4 × 0·25 mm) obtained directly from reaction mixture. 25 reflections used for measuring lattice parameters. Siemens AED diffractometer, Cu $K\alpha$ radiation, $\omega/2\theta$ scan, $2\theta_{max} = 140°$ ($hkl_{max} = 15, 7, 14$). 1899 intensities collected, 1085 with $I > 2\sigma_I$; $R_{int} = 0\cdot031$ from 67 pairs of equivalent $hk0$ reflections. Stability controlled on two reflections. Space group $P2_1/a$ (from systematic absences). Lorentz and polarization but no absorption correction applied. Structure solved by direct methods ($SHELX76$, Sheldrick, 1976). Atomic parameters refined by full-matrix least-squares procedure ($SHELX$) with scattering factors implemented in program, minimizing $\Sigma(\Delta F)^2$ (unit weights) against 1085 observed reflections. Positions of all C-attached H atoms calculated geometrically, positions of two N-attached H atoms found from Fourier difference maps. Final refinement involved all positional and anisotropic thermal parameters (for non-H atoms); temperature factors for H atoms set as $B_{eq}$ of adjacent atom + 1 Å$^2$ and held invariant during refinement. Final $R = 0\cdot043$ (unit weights). $\Delta/\sigma < 0\cdot01$. Max. electron density on Fourier difference map $<0\cdot2$ e Å$^{-3}$.

**Discussion.** The refined atomic coordinates are presented in Table 1.* The relevant bond lengths and valence angles are given in Table 2. Fig. 1 shows a projection of the molecule with the crystallographic labelling of atoms.

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* Lists of structure factors, anisotropic thermal parameters, refined H-atom coordinates and phenyl-group bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38840 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The obtained data unequivocally indicate the amino-type tautomer (II) being predominant in crystals of the investigated compound. No traces of any H atom in the environment of N(9) were noted on the Fourier difference maps. It is, however, quite possible that in this case the position of the tautomeric equilibrium depends much on the lattice effects and on hydrogen bondings.

**Table 1.** *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors for the non-*H *atoms with e.s.d.'s in parentheses*

|        | $x$        | $y$       | $z$       | $B_{eq}$*(Å$^2$) |
|--------|-----------|-----------|-----------|-------------------|
| C(1)   | 2304 (2)  | 8650 (5)  | 2649 (2)  | 2·8 (1)           |
| C(2)   | 2182 (3)  | 6750 (6)  | 3318 (3)  | 3·8 (2)           |
| C(3)   | 2975 (3)  | 6107 (7)  | 4160 (3)  | 4·5 (2)           |
| C(4)   | 3897 (3)  | 7345 (8)  | 4339 (3)  | 4·5 (2)           |
| C(5)   | 4024 (3)  | 9232 (7)  | 3687 (3)  | 4·4 (2)           |
| C(6)   | 3237 (2)  | 9903 (6)  | 2842 (3)  | 3·6 (2)           |
| C(7)   | 1448 (2)  | 9383 (5)  | 1712 (2)  | 2·7 (1)           |
| C(8)   | 919 (2)   | 7405 (5)  | 1011 (2)  | 2·7 (1)           |
| N(9)   | −124 (2)  | 7560 (5)  | 784 (2)   | 2·9 (1)           |
| C(10)  | −443 (2)  | 9455 (6)  | 1346 (3)  | 2·9 (1)           |
| C(11)  | 478 (2)   | 10587 (6) | 2077 (3)  | 3·3 (2)           |
| O(12)  | −1353 (1) | 10148 (4) | 1262 (2)  | 3·6 (1)           |
| N(13)  | 1458 (2)  | 5738 (5)  | 628 (2)   | 3·1 (1)           |

* Calculated from anisotropic thermal parameters: $B_{eq} = 8\pi^2(U_1U_2U_3)^{1/3}$ where $U_i$ are eigenvalues of $U_{ij}$ matrix.

**Table 2.** *Bond lengths* (Å) *and valence angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(1)—C(2)   | 1·379 (5) | C(2)—C(3)   | 1·379 (5) |
| C(3)—C(4)   | 1·368 (6) | C(4)—C(5)   | 1·362 (6) |
| C(5)—C(6)   | 1·381 (5) | C(1)—C(6)   | 1·386 (4) |
| C(1)—C(7)   | 1·515 (4) | C(7)—C(8)   | 1·519 (4) |
| C(8)—N(9)   | 1·324 (3) | C(8)—N(13)  | 1·302 (4) |
| N(9)—C(10)  | 1·374 (4) | C(10)—C(11) | 1·514 (4) |
| C(7)—C(11)  | 1·536 (4) | C(10)—O(12) | 1·220 (3) |
| | | | |
| C(2)—C(1)—C(6)    | 118·7 (3) | C(1)—C(2)—C(3)     | 120·6 (3) |
| C(2)—C(3)—C(4)    | 120·3 (4) | C(3)—C(4)—C(5)     | 119·6 (3) |
| C(4)—C(5)—C(6)    | 120·9 (3) | C(1)—C(6)—C(5)     | 119·9 (3) |
| C(1)—C(7)—C(11)   | 116·2 (3) | C(2)—C(1)—C(7)     | 121·7 (3) |
| C(8)—C(7)—C(11)   | 100·5 (2) | C(6)—C(1)—C(7)     | 119·6 (3) |
| C(7)—C(8)—N(9)    | 114·9 (3) | C(7)—C(8)—N(13)    | 122·1 (2) |
| N(9)—C(8)—N(13)   | 122·9 (3) | C(8)—N(9)—C(10)    | 108·1 (2) |
| N(9)—C(10)—C(11)  | 111·5 (2) | N(9)—C(10)—O(12)   | 124·3 (3) |
| C(1)—C(7)—C(8)    | 115·0 (3) | C(11)—C(10)—O(12)  | 124·2 (3) |
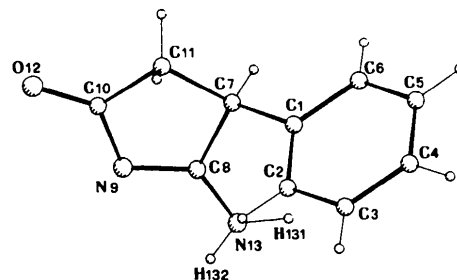


Fig. 1. Parallel projection of the molecule on the $ab$ plane with the labelling of atoms.

In the discussion of the bond lengths and, consequently, the bond character in the most interesting fragment of the molecule, *i.e.* in the O—C—N—C—N bond sequence, a comparison of present data with those available for other 5-substituted 2-pyrrolidinones seems to be most appropriate. Thus, in succinimides (Argay & Kálmán, 1973; Argay & Carstensen-Oeser, 1973; Argay, Simon & Kálmán, 1974; Lotter, Klein, Rüdiger & Scheer, 1977; Rosenfield & Dunitz, 1978; Mazhar-ul-Haque, 1980), both C—N bonds are significantly short (1·36–1·38 Å) and nearly equal in length. This was interpreted in terms of delocalization of the lone pair in the OC—N—CO fragment of the molecule (Argay & Kálmán, 1973). On the other hand, in 5-unsubstituted 2-pyrrolidinones as well as in those carrying a 5-$X$-substituent attached by means of a C—C bond (Molin-Case, Fleischer & Urry, 1970; Baert, Lobry & Warin, 1975; Kaas & Sørensen, 1977), the C—N bonds are of unequal length; the OC—N bond is roughly similar to that in succinimides, but the N—C$X$ bond, the length of which varies within the 1·45–1·47 Å range, seems to be a typical amino C—N bond.

In the present case, the OC—N bond length (Table 2) fits well the range reported for succinimides. The N—CN bond is, however, significantly shorter than any of the C—N bonds discussed previously. The same is true for the exocyclic C—N bond which is even still shorter. This indicates a strong delocalization of the nitrogen lone pairs [both at N(9) and N(13)], with all the C—N bonds in the system being to some extent multiple bonds.

A least-squares-plane calculation (*PLALIN*, Nardelli, Musatti, Domiano & Andreetti, 1965) revealed reasonable planarity of the OC—N—C—N moiety [out-of-plane deviations of the O(12), C(10), N(9), C(8) and N(13) atoms are within ±0·037 (3) Å]. By way of comparison, in succinimides the N atom deviates from the OC···CO least-squares plane by 0·07–0·17 Å.

Similarly, a calculation of the least-squares plane for the C(8)—N(13)—H$_2$ group showed its planarity [H atoms out of plane by 0·03 (2) Å].

The results discussed above indicate that 5-substitution of 2-pyrrolidinone with an amino (or imino) group produces a substantial change in the character of the OC—N—C bond sequence which becomes dissimilar to that observed in other related structures.

The conformation of the pyrrolidine ring in the compound under investigation may be defined as an almost pure twist ($T$) as shown by the asymmetry parameter $\Delta C_2^N = 0·8\,(4)°$ (Duax, Weeks & Rohrer, 1976).

The bond lengths and angles of the phenyl ring do not reveal any peculiarities. The dihedral angle formed by the least-squares planes for the phenyl ring and the OC—N—C—N bond sequence discussed above amounts to 73·0 (1)°.

The title molecule is involved in a system of intermolecular hydrogen bonds (Fig. 2). Both H atoms attached to N(13) form hydrogen bridges [bond, acceptor symmetry, donor···acceptor distance (Å), H···acceptor distance (Å), angle at H (°): N(13)—H1(N13)···O(12), $\frac{1}{2}+x$, $\frac{3}{2}-y$, $z$, 2·840 (3), 1·96 (3), 160 (2); N(13)—H2(N13)···N(9), $-x$, $1-y$, $-z$, 2·930 (4), 2·00 (2), 176 (2)]. The latter symmetry expression gives rise to a symmetrical hydrogen bond linking the same enantiomeric pair into a dimer. The dimers, in turn, are linked to each other by hydrogen bridges of the first mentioned type, thus forming layers parallel to the *ab* planes of the crystal.

It is legitimate to conclude, therefore, that the intermolecular hydrogen-bonding system may contribute to the stabilization of the amino tautomer.
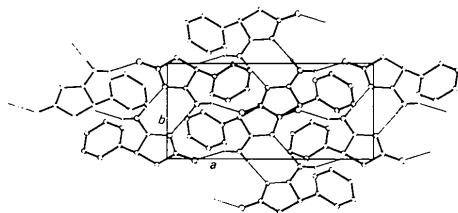


Fig. 2. Possible hydrogen bonds (light lines) in the crystal lattice. Parallel projection on the *ab* plane.

### References

ARGAY, GY. & CARSTENSEN-OESER, E. (1973). *Acta Cryst.* B29, 1186–1190.

ARGAY, GY. & KÁLMÁN, A. (1973). *Acta Cryst.* B29, 636–638.

ARGAY, GY., SIMON, K. & KÁLMÁN, A. (1974). *Acta Cryst.* B30, 805–809.

BAERT, F., LOBRY, M. & WARIN, V. (1975). *C. R. Acad. Sci. Sér. C*, 280, 743–745.

DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Top. Stereochem.* 9, 271–383.

KAAS, K. & SØRENSEN, H. (1977). *Acta Chem. Scand. Ser. A*, 31, 364–368.

KOBERDA, W. & LANGE, J. (1976). *Org. Prep. Proced. Int.* 8, 185–192.

LOTTER, H., KLEIN, G., RÜDIGER, W. & SCHEER, H. (1977). *Tetrahedron Lett.* pp. 2317–2320.

MAZHAR-UL-HAQUE (1980). *Acta Cryst.* B36, 2082–2086.

MOLIN-CASE, J. A., FLEISCHER, E. & URRY, D. W. (1970). *J. Am. Chem. Soc.* 92, 4728–4730.

NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. D. (1965). *PLALIN*. A program for the calculation of weighted least-squares planes and lines, of the angles formed by them, and of the e.s.d.'s. Univ. of Parma, Italy. *Ric. Sci.* 8A, 807–810.

ROSENFIELD, R. E. JR & DUNITZ, J. D. (1978). *Helv. Chim. Acta*, 61, 2176–2189.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.