molecule 1 shows more parallelism between substituents than molecule 2 (see Table 3) and the latter is more puckered. All atoms which deviate significantly from the ring plane are involved in the shortest intramolecular O—O and C—O contacts between atoms of different substituents, the minimum values corresponding to O(112)—O(122) (2·90), C(161)—O(152) (2·73), C(121)—O(112) (2·77), C(121)—O(132) (2·77), O(252)—O(262) (2·90), C(211)—O(222) (2·71) and (C251)—O(242) (2·74 Å).

References

BOOTH, B. L., HASZELDINI, R. N. & PERKINS, I. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2593–2595.

GALEŠIĆ, N., MATIJAŠIĆ, I. & BRUVO, M. (1984). *Acta Cryst.* C40, 308–311.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

KÖLLE, V. & FUSS, B. (1986). *Chem. Ber.* 119, 116–128.

LEE, C. L., HUNT, C. T. & BALCH, A. L. (1981). *Inorg. Chem.* 20, 2498–2504.

MAIN, P., FISKE, S J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MAITLIS, P. M. (1973). *Pure Appl. Chem.* 33, 489–512.

ROMERO, A., SANTOS, A. & VEGAS, A. (1987). Unpublished results.

STAAL, L. H., VAN KOTEN, G., VRIEZE, K., VAN SANTEN, B. & STAN, S. (1981). *Inorg. Chem.* 20, 3598–3606.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1980). The *XRAY80* system. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

VILA, E. & VEGAS, A. (1987). *GRACOS. A Program for Graphical Representation of Crystal Structures in P.C.* CSIC, Madrid, Spain.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

WARD, D. L. & LUEHRS, D. C. (1983). *Acta Cryst.* C39, 1370–1372.

Structure of Ethyl [4-Methyl-2(3H)-oxo-1,5-diphenylpyrrol-3-yl]acetate

BY I. FONSECA, C. FOCES, S. MARTÍNEZ-CARRERA AND S. GARCÍA-BLANCO

Instituto de Química-Física 'Rocasolano', Dpto de Rayos X, Serrano 119, 28006 Madrid, Spain

Abstract. $C_{21}H_{21}NO_3$, $M_r = 335\cdot4$, triclinic, $P\bar{1}$, $a = 14\cdot743$ (5), $b = 12\cdot941$ (7), $c = 10\cdot548$ (3) Å, $\alpha = 76\cdot65$ (3), $\beta = 90\cdot92$ (4), $\gamma = 68\cdot46$ (4)°, $V = 1810$ (1) Å^3, $Z = 4$, $D_m = 1\cdot222$, $D_x = 1\cdot23$ Mg m^{-3}, $\lambda(Cu\,K\alpha) = 1\cdot54178$ Å, $\mu = 0\cdot62$ mm^{-1}, $F(000) = 712$, room temperature, $R = 0\cdot065$ ($wR = 0\cdot074$) for 5314 observed reflections. The N-phenyl ring is almost coplanar with the pyrroline ring while the 5-phenyl is nearly perpendicular to it. The most significant difference between the two molecules lies in the different orientation of the ethoxycarbonyl chain.

Introduction. This compound has been synthetized in the Departamento de Química Orgánica de la Universidad de Oviedo. This work has been undertaken in order to ascertain whether the central group of the final product of this synthesis was a pyridine or a pyrroline.

Experimental. Colourless prismatic crystals (0·3 × 0·3 × 0·2 mm); Philips PW1100 diffractometer, Cu $K\alpha$ radiation with graphite monochromator, $\omega/2\theta$ scan technique, room temperature. D_m by flotation. Refined unit-cell parameters obtained from setting angles of 32 reflections $(2 < 2\theta < 25°)$. 6170 unique reflections

measured $[(\sin\theta)/\lambda]_{max} = 0\cdot58$ Å^{-1}, 5314 $[I > 2\sigma(I)]$ considered observed, index range: $h\ -17/17$, $k\ -14/14$, $l\ 0/12$; two check reflections measured every 90 reflections, net count constant; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods, *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Positional and anisotropic thermal parameters for all non-hydrogen atoms refined (on F) by block-diagonal least squares; positions of H atoms from a difference synthesis excepting H8, H9 and H10 that were calculated geometrically; H atoms assigned the same isotropic temperature factors as the atoms to which they are bonded and included in the refinement with positional and thermal parameters fixed (451 parameters); an empirical weighting scheme was used to give similar values of $w\Delta F^2$ over ranges of $(\sin\theta)/\lambda$ and F_o. Final $R = 0\cdot065$; $wR = 0\cdot074$, $S = 6\cdot3$. $(\Delta/\sigma)_{max} = 0\cdot38$; residual electron density in difference map 0·57 e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computations carried out on UNIVAC 1100 computer using the *XRAY* system (Stewart, Kundell & Baldwin, 1970), *PESOS* (Martínez-Ripoll & Cano, 1975) and *PARST* (Nardelli, 1983).

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Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å²×10⁴)

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

	x	y	z	U_{eq}
N1A	4192 (1)	6162 (1)	3614 (1)	466 (6)
C2A	4203 (1)	6747 (2)	4550 (2)	479 (7)
C3A	4857 (1)	7365 (2)	4167 (2)	507 (7)
C4A	5261 (1)	7104 (2)	3106 (2)	515 (7)
C5A	4835 (1)	6357 (1)	2616 (2)	471 (6)
C11A	3687 (1)	5426 (1)	3596 (2)	451 (6)
C12A	3012 (2)	5325 (2)	4477 (2)	572 (8)
C13A	2534 (2)	4588 (2)	4416 (2)	660 (9)
C14A	2705 (2)	3957 (2)	3498 (2)	661 (9)
C15A	3385 (2)	4044 (2)	2640 (2)	613 (8)
C16A	3875 (2)	4770 (2)	2682 (2)	538 (7)
O1A	3766 (1)	6740 (1)	5528 (1)	651 (7)
C6A	4976 (2)	8158 (2)	4927 (2)	626 (9)
C7A	4276 (2)	9390 (2)	4401 (2)	576 (8)
O2A	3855 (2)	10001 (2)	5066 (2)	868 (9)
O3A	4214 (2)	9721 (1)	3116 (2)	779 (8)
C8A	3597 (2)	10904 (2)	2487 (3)	869 (12)
C9A	3716 (4)	11116 (3)	1102 (4)	1232 (20)
C10A	5995 (2)	7472 (2)	2389 (3)	747 (11)
C51A	4294 (1)	6971 (1)	1252 (2)	458 (6)
C52A	4647 (2)	6587 (2)	163 (2)	605 (8)
C53A	4170 (2)	7190 (2)	−1081 (2)	722 (11)
C54A	3353 (2)	8171 (2)	−1258 (2)	704 (10)
C55A	2990 (2)	8570 (2)	−180 (2)	654 (9)
C56A	3457 (2)	7966 (2)	1064 (2)	554 (7)
N1B	748 (1)	3756 (1)	−712 (2)	520 (6)
C2B	741 (1)	3146 (2)	550 (2)	552 (7)
C3B	92 (1)	2532 (2)	458 (2)	579 (8)
C4B	−288 (2)	2782 (2)	−772 (2)	614 (9)
C5B	130 (1)	3553 (2)	−1644 (2)	532 (7)
C11B	1254 (1)	4490 (2)	−1109 (2)	497 (7)
C12B	1908 (2)	4610 (2)	−237 (2)	637 (9)
C13B	2404 (2)	5323 (2)	−681 (3)	718 (10)
C14B	2274 (2)	5925 (2)	−1979 (3)	690 (10)
C15B	1615 (2)	5821 (2)	−2830 (2)	636 (9)
C16B	1108 (2)	5116 (2)	−2411 (2)	585 (8)
O1B	1179 (1)	3132 (2)	1551 (1)	720 (7)
C6B	−52 (2)	1764 (2)	1668 (2)	685 (9)
C7B	844 (2)	678 (2)	2157 (2)	623 (9)
O2B	1500 (2)	289 (2)	1545 (2)	988 (9)
O3B	837 (2)	221 (2)	3395 (2)	886 (8)
C8B	1665 (2)	−823 (3)	4027 (3)	909 (12)
C9B	1509 (3)	−1161 (4)	5374 (4)	1256 (19)
C10B	−1004 (2)	2409 (3)	−1352 (3)	922 (15)
C51B	693 (1)	2964 (2)	−2646 (2)	502 (7)
C52B	1577 (2)	2031 (2)	−2247 (2)	616 (8)
C53B	2075 (2)	1476 (2)	−3155 (3)	703 (10)
C54B	1698 (2)	1848 (2)	−4461 (3)	713 (11)
C55B	828 (2)	2775 (2)	−4864 (2)	748 (11)
C56B	329 (2)	3331 (2)	−3957 (2)	644 (9)

Table 2. *Bond lengths* (Å) *and angles* (°)

|	Molecule A	Molecule B		Molecule A	Molecule B
N1—C2	1·380 (3)	1·385 (2)	C14—C15	1·379 (4)	1·375 (4)
N1—C5	1·467 (3)	1·460 (3)	C15—C16	1·386 (4)	1·383 (4)
N1—C11	1·411 (3)	1·408 (3)	C6—C7	1·509 (3)	1·506 (3)
C2—C3	1·470 (3)	1·467 (4)	C7—O2	1·190 (3)	1·191 (3)
C2—O1	1·225 (2)	1·221 (3)	C7—O3	1·314 (3)	1·305 (3)
C3—C4	1·331 (3)	1·323 (3)	O3—C8	1·449 (3)	1·452 (3)
C3—C6	1·495 (3)	1·496 (3)	C8—C9	1·449 (5)	1·435 (5)
C4—C5	1·504 (3)	1·506 (3)	C51—C52	1·390 (3)	1·388 (3)
C4—C10	1·485 (4)	1·486 (5)	C51—C56	1·388 (2)	1·382 (3)
C5—C51	1·519 (2)	1·524 (3)	C52—C53	1·386 (3)	1·388 (4)
C11—C12	1·393 (3)	1·395 (4)	C53—C54	1·364 (3)	1·382 (4)
C11—C16	1·393 (3)	1·391 (3)	C54—C55	1·391 (4)	1·373 (4)
C12—C13	1·390 (4)	1·384 (4)	C55—C56	1·382 (3)	1·388 (4)
C13—C14	1·375 (4)	1·381 (4)			
C5—N1—C11	122·3 (2)	122·2 (2)	C12—C13—C14	121·6 (3)	121·6 (3)
C2—N1—C11	127·1 (2)	127·3 (2)	C13—C14—C15	118·7 (3)	118·3 (3)
C2—N1—C5	110·5 (2)	110·5 (2)	C14—C15—C16	120·9 (2)	121·2 (2)
N1—C2—O1	126·7 (3)	127·0 (3)	C11—C16—C15	120·3 (2)	120·6 (2)
N1—C2—C3	106·9 (2)	106·6 (2)	C3—C6—C7	113·5 (2)	112·0 (2)
C3—C2—O1	126·4 (2)	126·4 (2)	C6—C7—O3	111·8 (2)	110·5 (3)
C2—C3—C6	120·7 (2)	119·7 (2)	C6—C7—O2	124·3 (2)	126·4 (3)
C2—C3—C4	109·7 (2)	110·1 (3)	O2—C7—O3	123·8 (3)	123·0 (3)
C4—C3—C6	129·7 (3)	130·2 (3)	C7—O3—C8	117·5 (2)	117·4 (3)
C3—C4—C10	129·7 (3)	130·4 (3)	O3—C8—C9	108·2 (3)	107·9 (3)
C3—C4—C5	109·9 (2)	109·8 (2)	C5—C51—C56	120·2 (2)	121·0 (3)
C5—C4—C10	120·4 (2)	119·8 (2)	C5—C51—C52	121·1 (2)	120·1 (2)
N1—C5—C4	102·8 (2)	102·8 (2)	C52—C51—C56	118·6 (2)	118·9 (3)
C4—C5—C51	110·0 (2)	110·3 (2)	C51—C52—C53	120·3 (3)	120·0 (3)
N1—C5—C51	113·6 (2)	113·6 (2)	C52—C53—C54	120·7 (2)	120·4 (3)
N1—C11—C16	119·5 (2)	119·5 (3)	C53—C54—C55	119·8 (3)	119·8 (3)
N1—C11—C12	121·9 (2)	122·1 (2)	C54—C55—C56	119·8 (3)	119·8 (3)
C12—C11—C16	118·8 (3)	118·4 (3)	C51—C56—C55	120·8 (2)	121·0 (3)
C11—C12—C13	119·6 (2)	119·9 (2)			
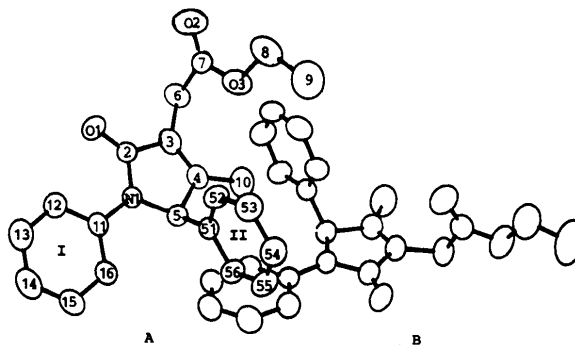
Fig. 1. Molecular structure with the numbering of the atoms.

Discussion. Table 1* lists the fractional atomic coordinates and equivalent isotropic values (U_{eq}) of the anisotropic temperature coefficients of the non-hydrogen atoms. Table 2 shows the bond lengths and angles. The structure is illustrated in Fig. 1 which includes the atomic numbering scheme.

The solution of the structure showed that the title compound has as central ring a five-membered pyrroline. There are two independent molecules (*A* and *B*) in the asymmetric unit; they are very similar in bond lengths and angles, but the conformation of the ethoxycarbonyl chain differs in the two molecules as

can be seen from the values of the torsion angles C2—C3—C6—C7 [for molecule *A* −92·1 (3), for molecule *B* −71·9 (4)°] and C3—C6—C7—O3 [−44·2 (4), molecule *A*, 158·8 (3)°, molecule *B*]. In the pyrroline ring the torsion angles indicate near planarity with a maximum deviation from the mean plane of 0·028 (3) Å for molecule *A* and 0·022 (3) Å for molecule *B* corresponding to C4 in both molecules. The plane of ring I makes angles of 7·3 (1)° for molecule *A* and 5·0 (1)° for molecule *B* with the pyrroline plane, and the plane of ring II forms angles of 89·6 (1)° (molecule *A*) and 94·1 (1)° (molecule *B*); thus the two phenyl rings have only a slightly different orientation with respect to the pyrroline ring, the *N*-substituted phenyl being coplanar with and the 5-substituted phenyl perpendicular to the pyrroline ring. The coplanarity

Table 3. *Details of the weak intramolecular bond forcing coplanarity of the pyrroline and N-phenyl rings*

	Molecule A	Molecule B
O1···C12	2·866 (4) Å	2·878 (4) Å
O1···H12	2·22	2·11
C12–H12	1·03	1·04
O1–H12–C12	119°	129°
C11–C12–H12	122	115

between pyrroline and the phenyl ring I is caused by the weak interaction between O1 and C12 through H12 (Table 3); also, some π conjugation along the C—N—C—O system can contribute to this effect. The sum of the bond angles around the heteroatom N1 is 359·9° for molecule A, 360·0° for molecule B, supporting an sp^2 hybridization for this atom; the distances in the pyrroline ring and the planarity of the sequence C11—N1—C2—O1 [torsion angles −0·9 (5)°, molecule A; −0·3 (5)°, molecule B] indicate a delocalization of the lone pair of the N atom (Argay & Kálmán, 1973). The ethoxycarbonyl group shows planarity at the C6—C7—O2—O3 level; in molecule B, C8 is also in this

plane; this planarity is in agreement with what is observed in this type of ester (Théobald, Birouk & Robert, 1982). Packing is regulated by normal van der Waals contacts.

References

ARGAY, GY. & KÁLMÁN, A. (1973). *Acta Cryst.* B29, 636–638.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS.* Computer program for the automatic treatment of weighting schemes. Instituto 'Rocasolano', Madrid, Spain.
NARDELLI, M. (1983). *Comput. Chem.* 7, 95–97.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY* system. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
THÉOBALD, F., BIROUK, M. & ROBERT, J.-F. (1982). *Acta Cryst.* B38, 1764–1768.

A Neutron Diffraction Study of 2,6-Diaminopyridine* at 20 K

BY CARL H. SCHWALBE†

Drug Development Research Group, Pharmaceutical Sciences Institute, Department of Pharmaceutical Sciences, Aston University, Aston Triangle, Birmingham B4 7ET, England

AND GRAHEME J. B. WILLIAMS‡ AND THOMAS F. KOETZLE

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, USA

Abstract. $C_5H_7N_3$, $M_r = 109·14$, orthorhombic, $P2_12_12_1$, $a = 5·397$ (2), $b = 7·337$ (3), $c = 13·597$ (7) Å, $U = 538·4$ (4) Å^3, $Z = 4$, $D_n = 1·35$ Mg m^{-3}, $\lambda = 1·1604$ Å, $\mu = 2·325$ cm^{-1}, $T = 20$ (1) K, final $R(F^2) = 0·093$ for 815 independent reflections. The ring N atom and the two amino N atoms each accept one H bond from a neighboring molecule. Two H atoms of one NH_2 group and one H atom of the other are donors in this three-dimensional network, which differs from the pattern of hydrogen-bonded centrosymmetric dimers commonly occurring in aminopyridine and aminopyrimidine crystals. The exocyclic C—N distances in the title compound are relatively long [1·377 (4) and 1·396 (4) Å], and the amino groups are substantially pyramidalized. Geometry optimization based on *ab initio* molecular-orbital calculations indicates that pyramidalization persists even in the absence of intermolecular interactions.

Introduction. Aminopyrimidine and diaminopyrimidine moieties occur in many biologically important molecules such as cytosine derivatives, folates, and antifolate drugs. Characteristically they associate to form dimers *via* paired N—H···N hydrogen bonds about a center or pseudo-center of inversion, the amino group acting as proton donor and the ring N atom as acceptor (Schwalbe & Cody, 1983). Where the number of amino groups, *m*, exceeds the number of ring N