Data collection: Siemens *P*4 software. Cell refinement: Siemens *P*4 software. Data reduction: Siemens *P*4 software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

This research was supported by NSERC, Canada, and the University of Toronto.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1133). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Bader, R. F. W., Gillespie, R. J. & MacDougall, P. J. (1988). *J. Am. Chem. Soc.* **110**, 7329–7336.
Berkow, R. & Fletcher, A. J. (1992). *The Merck Manual*, 16th ed., p. 1357. Rahway, NJ, USA: Merck & Co.
Cook, D. S. & White, R. F. M. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2212–2215.
Francis, M. D. & Centner, R. L. (1978). *J. Chem. Educ.* **55**, 760–766.
Maier, L. (1976). *Synth. React. Inorg. Met. Org. Chem.* **6**, 133–155.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Release 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Vepsalainen, J., Nupponen, H., Pohjala, E., Ahlgren, M. & Vainiotalo, P. (1992). *J. Chem. Soc. Perkin Trans.* 2, pp. 835–842.

Acta Cryst. (1996). C**52**, 654–656

The Zinc–Acetic Anhydride Reduction of Pyridines

Roy L. Beddoes, Nusrat Arshad and John A. Joule*

Department of Chemistry, University of Manchester,
Oxford Road, Manchester M13 9PL, England. E-mail:
j.a.joule@man.ac.uk

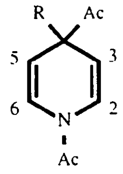
(*Received 18 July 1995; accepted 3 October 1995*)

Abstract

The crystal structure determination of 1,4-diacetyl-1,4-dihydro-4-phenylpyridine, $C_{15}H_{15}NO_2$, shows the six atoms of the heterocyclic ring and the atoms of the *N*-acetyl substituent to be essentially coplanar.

Comment

There have been only two papers discussing the products of the reduction of 4-substituted pyridines with a combination of zinc and acetic anhydride (Johnson & Anthony, 1972; Atlani, Biellmann & Moron, 1973). Both reports agreed that the products, formed in moderate-to-good yields, were 1,4-dihydropyridines carrying acetyl groups at the N atom and 4 position, *i.e.* (1). Johnson & Anthony (1972) described the ^{1}H NMR signals for the protons at the 2 and 6 positions of (1) (*R* = Me) as a 'double doublet', while Atlani, Biellmann & Moron (1973) used the phrase 'two doublets'. Neither group commented on the apparent anomaly that the molecule is symmetrical about a plane through the N atom and the C atom at the 4 position yet the protons at the 2 and 6 positions are magnetically non-equivalent.



(1)

Intrigued by the possibilities for synthetic exploitation inherent within such easily accessible structures, we have repeated some of the reductions and confirmed the earlier findings, but noted that when the 4-substituent is larger than a methyl group, not only are the protons at the 2 and 6 positions non-equivalent, but that the protons at the 3 and 5 positions also resonate at different chemical shifts. In order to shed further light on this, and to confirm the 1,4-dihydropyridine structure, we have examined crystals of 1,4-diacetyl-1,4-dihydro-4-phenylpyridine, (1) (*R* = Ph).

The crystal structure of (1) (*R* = Ph) shows the six atoms of the heterocyclic ring and the atoms of the *N*-acetyl unit to be essentially coplanar. We take this

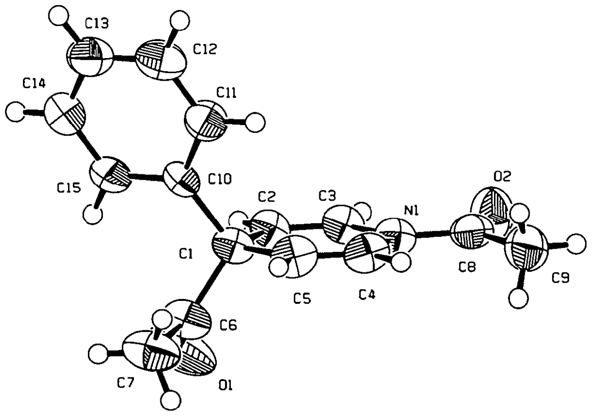


Fig. 1. *PLUTO* drawing (Motherwell & Clegg, 1978) of compound (1) (*R* = Ph), with ellipsoids plotted at the 50% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

to imply considerable resonance interaction involving the N-atom lone pair, both double bonds and the acetyl carbonyl group. This latter amide interaction must be the source of the non-equivalence of the protons at the 2 and 6 positions, there being restricted rotation about the N—acetyl bond. We suggest that the non-equivalence of the protons at the 3 and 5 positions can be accounted for by restricted rotation at the C—COMe bond, this time on steric grounds.

Experimental

4-Phenylpyridine was converted into (1) (R = Ph) as described previously by Atlani, Biellmann & Moron (1973) and crystallized from methanol.

Crystal data

$C_{15}H_{15}NO_2$
$M_r = 241.29$
Monoclinic
$P2_1/c$
$a = 6.1621\ (9)$ Å
$b = 15.731\ (4)$ Å
$c = 13.708\ (4)$ Å
$\beta = 102.07\ (2)°$
$V = 1299.5\ (5)$ Å^3
$Z = 4$
$D_x = 1.233$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 29.11–54.43°$
$\mu = 0.623$ mm^{-1}
$T = 294$ K
Prismatic
0.45 × 0.26 × 0.20 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1848 measured reflections
1683 independent reflections
1227 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.063$
$\theta_{\rm max} = 60.1°$
$h = -6 \rightarrow 6$
$k = -9 \rightarrow 15$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 150 reflections intensity decay: 3.66%

Refinement

Refinement on F
$R = 0.066$
$wR = 0.083$
$S = 2.320$
1227 reflections
164 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\rm max} = 0.0001$

$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 32.64
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	−0.2118 (5)	0.3379 (3)	0.1483 (2)	0.0985 (3)
O2	0.2374 (5)	0.5833 (2)	0.4711 (2)	0.0728 (3)
N1	0.2805 (4)	0.4812 (2)	0.3610 (2)	0.0468 (2)
C1	0.1361 (5)	0.3202 (2)	0.2607 (3)	0.0453 (2)
C2	0.0229 (6)	0.3657 (3)	0.3328 (3)	0.0457 (2)
C3	0.0932 (5)	0.4379 (3)	0.3778 (3)	0.0450 (2)
C4	0.3958 (6)	0.4446 (3)	0.2952 (3)	0.0521 (3)
C5	0.3363 (6)	0.3714 (3)	0.2494 (3)	0.0537 (3)
C6	−0.0253 (6)	0.3137 (3)	0.1579 (3)	0.0552 (3)
C7	0.0578 (8)	0.2784 (3)	0.0724 (3)	0.0778 (3)
C8	0.3410 (7)	0.5576 (3)	0.4114 (3)	0.0534 (3)
C9	0.5334 (7)	0.6048 (3)	0.3892 (3)	0.0723 (3)
C10	0.2007 (5)	0.2309 (2)	0.3021 (3)	0.0433 (3)
C11	0.4072 (6)	0.2146 (3)	0.3595 (3)	0.0602 (3)
C12	0.4614 (8)	0.1361 (3)	0.4002 (4)	0.0785 (3)
C13	0.3115 (9)	0.0717 (3)	0.3838 (3)	0.0776 (3)
C14	0.1024 (8)	0.0868 (3)	0.3277 (4)	0.0772 (3)
C15	0.0499 (7)	0.1662 (3)	0.2873 (3)	0.0607 (3)

Table 2. *Selected geometric parameters (Å, °)*

O1—C6	1.192 (4)	C4—C5	1.325 (5)
O2—C8	1.208 (5)	C6—C7	1.482 (5)
N1—C3	1.400 (4)	C8—C9	1.484 (5)
N1—C4	1.385 (5)	C10—C11	1.372 (5)
N1—C8	1.398 (5)	C10—C15	1.365 (5)
C1—C2	1.505 (5)	C11—C12	1.367 (6)
C1—C5	1.508 (5)	C12—C13	1.358 (6)
C1—C6	1.548 (5)	C13—C14	1.376 (6)
C1—C10	1.537 (5)	C14—C15	1.377 (6)
C2—C3	1.321 (5)		
C3—N1—C4	117.2 (3)	N1—C3—C2	122.9 (3)
C3—N1—C8	118.8 (3)	N1—C4—C5	122.7 (3)
C4—N1—C8	124.0 (3)	C1—C5—C4	124.5 (3)
C2—C1—C5	108.4 (3)	O1—C6—C1	120.0 (3)
C2—C1—C6	109.4 (3)	O1—C6—C7	121.1 (4)
C2—C1—C10	108.1 (3)	C1—C6—C7	118.8 (3)
C5—C1—C6	109.0 (3)	O2—C8—N1	119.9 (4)
C5—C1—C10	111.8 (3)	O2—C8—C9	122.0 (4)
C6—C1—C10	110.1 (3)	N1—C8—C9	118.1 (4)
C1—C2—C3	124.3 (3)		

MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1988) was used for data collection and cell refinement. The structure was determined by direct methods using *SHELXS*86 (Sheldrick, 1985). Each H atom was placed in an idealized position (C—H 0.95 Å) at the beginning of each least-squares cycle and assigned an isotropic displacement parameter 20% greater than the equivalent B value of the atom to which it is bonded. Neutral-atom scattering factors were taken from Cromer & Waber (1974), anomalous-dispersion effects were included in $F_{\rm calc}$ (Ibers & Hamilton, 1964) and values for f' and f'' were from Cromer (1974). All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985).

We thank the SERC, UK, for funds for the purchase of the Rigaku AFC-5*R* diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Atlani, P. M., Biellmann, J. F. & Moron, J. (1973). *Tetrahedron*, **29**, 391–398.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.
Johnson, S. L. & Anthony, S. A. (1972). *J. Org. Chem.* **37**, 2516–2517.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1996). C**52**, 656–658

1-Cyclohexyl-3-phenylthiourea

AKILAN RAMNATHAN,[a] KANDASAMY SIVAKUMAR,[a]† KULANDAIVELU SUBRAMANIAN,[a] NATARAJAN SRINIVASAN,[b] KRISHNAMOORTHY RAMADAS[b] AND HOONG-KUN FUN[c]*

[a]*Department of Physics, Anna University, Madras 600 025, India,* [b]*Centre for Agrochemical Research, SPIC Science Foundation, 110 Mount Road, Madras 600 032, India, and* [c]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

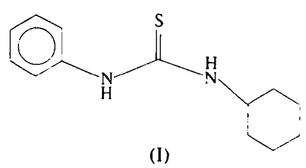
(*Received 7 July 1995; accepted 4 October 1995*)

Abstract

The cyclohexane ring in the title compound, $C_{13}H_{18}N_2S$, is in a chair conformation. The molecule adopts a *cis–trans* configuration with respect to the thiourea moiety. The molecules are linked by N—H···S intermolecular hydrogen bonds in the crystal lattice to form two-dimensional layers parallel to the *bc* plane.

Comment

Unsymmetrically substituted thioureas are found to exhibit agrochemical properties (Sarkis & Faisal, 1985). The title compound, (I), was synthesized in view of its agrochemical importance (Ramadas, Srinivasan & Janarthanan, 1993). The crystal structure determination of this compound forms part of our studies on a series of thiourea derivatives. We are interested in the solid-state conformation of these molecules and the nature of the N—H···S hydrogen bonds present in these compounds.



(I)

Fig. 1 shows the displacement ellipsoid plot of the molecule of (I) with the numbering scheme. The bond lengths and angles observed in this structure are normal and comparable to those of 1-cyclohexyl-3-(2-tolyl)-thiourea [(II); Ramnathan *et al.*, 1995*a*]. The dihedral angle between the planes of the thiourea moiety and the phenyl ring is 56.1 (1)°.

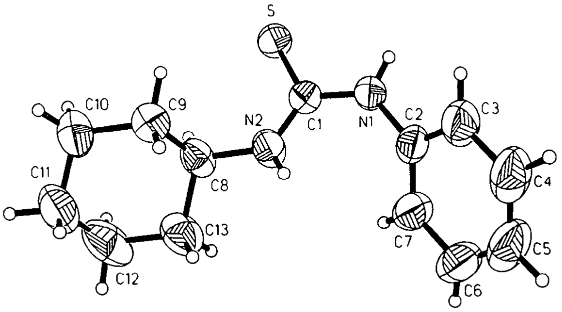


Fig. 1. A 50% probability displacement ellipsoid plot of molecule (I) with the atomic numbering scheme.

The two substituent groups (phenyl and cyclohexyl) are oriented in a *cis–trans* configuration with respect to the C=S bond. So far, the *cis–cis* configuration has been observed in both (II) and 1,3-diphenylthiourea (Ramnathan *et al.*, 1995*b*). Contrary to our expectation that molecule (II), with the methyl group in an *ortho* position (C7), would prefer the *cis–trans* configuration and molecule (I) the *cis–cis* configuration, the results turn out be the other way around. The phenyl groups of the two molecules are oriented in exactly opposite directions and the cyclohexane ring is rotated about the N2—C8 bond by nearly 10° for the two molecules; the torsion angles S—C1—N1—C2, C1—N2—C8—C9 and C1—N2—C8—C13 are −168.5 (2), −90.3 (2) and 146.6 (2)°, respectively, for (I), and −0.4 (2), −79.3 (2) and 157.3 (2)°, respectively, for (II). The *cis–trans* and *cis–cis* configurations show major differences in the N1—C1—N2 and S—C1—N1 angles, while the S—C1—N2 angle is unchanged; N1—C1—N2 is 117.3 (2) for (I) and 114.6 (1)° for (II), and S—C1—N1 is 119.1 (1) for (I) and 121.8 (1)° for (II). The molecules are more linear in the *cis–cis* configuration than in the *cis–trans* configuration. The packing of molecules of (I) in the crystal lattice is shown in Fig. 2.

The molecules of the title compound, (I), are connected by intermolecular N—H···S hydrogen bonds; one [N1···S^{i} 3.536 (2) Å, N1—H1···S^{i} 160 (2)°] forms dimers around the centre of inversion and the other

---

† Visiting Post Doctoral Research Fellow at the School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996