C25	0.1804 (2)	1.04731 (15)	0.6204 (2)	0.0416 (6)
C26	0.1482 (2)	1.02818 (13)	0.4750 (2)	0.0339 (5)
C31	0.2198 (2)	1.07360 (12)	0.1381 (2)	0.0249 (4)
C32	0.2996 (2)	1.13061 (13)	0.2166 (2)	0.0299 (5)
C33	0.3152 (2)	1.20978 (14)	0.1616 (2)	0.0377 (5)
C34	0.2521 (2)	1.23238 (14)	0.0263 (3)	0.0405 (6)
C35	0.1743 (2)	1.17634 (14)	−0.0540 (2)	0.0395 (6)
C36	0.1574 (2)	1.09760 (14)	0.0019 (2)	0.0331 (5)

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

P1—C21	1.828 (2)	C11—C16	1.396 (3)
P1—C11	1.846 (2)	C11—C12	1.422 (3)
P1—C31	1.851 (2)	C12—C13	1.400 (3)
O1—C3	1.211 (2)	C13—C14	1.381 (3)
C1—C2	1.511 (3)	C14—C15	1.377 (3)
C2—C3	1.516 (3)	C15—C16	1.387 (3)
C3—C12	1.492 (3)		
C21—P1—C11	104.37 (9)	C13—C12—C3	120.2 (2)
C21—P1—C31	99.69 (9)	C11—C12—C3	120.2 (2)
C11—P1—C31	102.24 (9)	C14—C13—C12	121.3 (2)
C1—C2—C3	113.0 (2)	C15—C14—C13	119.7 (2)
O1—C3—C12	120.0 (2)	C14—C15—C16	120.0 (2)
O1—C3—C2	121.3 (2)	C15—C16—C11	122.1 (2)
C12—C3—C2	118.8 (2)	C22—C21—P1	125.4 (2)
C16—C11—C12	117.4 (2)	C26—C21—P1	116.4 (2)
C16—C11—P1	121.43 (15)	C36—C31—P1	115.8 (2)
C12—C11—P1	120.70 (14)	C32—C31—P1	125.6 (2)
C13—C12—C11	119.5 (2)		
O1—C3—C12—C11	−11.2 (2)	C1—C2—C3—O1	0.3 (2)

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1987). Software used to prepare material for publication: *SHELXL93*.

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2,6-Diphenyl-3-vinylpyridine

William Clegg,* Cheryl T. Hewkin and Richard F. W. Jackson

Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

Abstract

In the structure of $C_{19}H_{15}N$, steric interactions force all three substituents (one vinyl and two phenyl groups) out of coplanarity with the central pyridine ring. Individual torsion angles around the relevant bonds are in the ranges 33.2 (3)–36.1 (3), 38.9 (3)–41.8 (3) and 29.6 (3)–31.1 (3)°.

Comment

In connection with an investigation of the chemistry of 5,6-dihydro-4*H*-1,2-oxazines (Ellames, Hewkin, Jackson, Smith & Standen, 1989), we treated 3-phenyl-5,6-dihydro-4*H*-1,2-oxazine, (1), with potassium *t*-amyloxide (6 equivalents) in *t*-amyl alcohol at reflux for 4 h. Flash chromatography allowed the isolation of the title compound (2) (13% yield) and the structure was determined by X-ray crystallography. This structure is consistent with the spectroscopic data obtained.

(1)   (2)   (3)
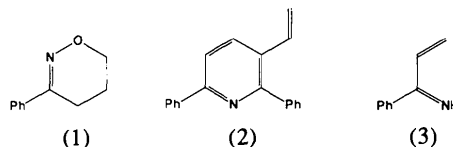
We believe that the title compound arises as a result of a Diels–Alder cycloaddition reaction between the imine (3) [which we have already postulated as an intermediate in the base-induced reactions of oxazine (1)] and 1-phenylbuta-1,3-diene, also derived from oxazine (1) by base-induced double-bond migration and a retro-Diels–Alder reaction. A final air oxidation would then lead to the aromatic title compound (2).

Although a number of copper and nickel complexes of 2-vinylpyridine have been structurally characterized (Engelhardt, Healy, Kildea & White, 1989; Hoberg, Guhl & Betz, 1990; Munakata, Kitagawa, Simono, Emori & Masuda, 1987), this appears to be the first report of the crystal structure of a 3-vinylpyridine, or indeed of any vinylpyridine not complexed to a metal. The three aromatic rings are essentially planar (r.m.s. deviations of 0.004, 0.003 and 0.004 Å), but the two phenyl and one vinyl substituent are twisted markedly

out of the plane of the central pyridine ring by 40.4, 30.4 and 34.6°, respectively. This entails a loss of conjugation, but is necessitated by the steric interactions of the H atoms, as is commonly observed for connected aromatic rings.
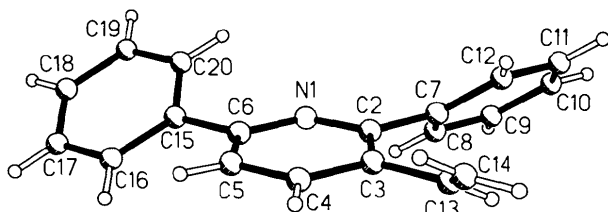

Fig. 1. Molecular structure of the title compound with atom labels.

Experimental

A suitable crystal was obtained by evaporation of the appropriate fractions following chromatography.

Crystal data

$C_{19}H_{15}N$	Cu $K\alpha$ radiation
$M_r = 257.32$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 32
$P2_1/c$	reflections
$a = 11.8386 (9)$ Å	$\theta = 15.0{-}20.0°$
$b = 15.3158 (12)$ Å	$\mu = 0.538$ mm^{-1}
$c = 7.7899 (6)$ Å	$T = 295 (2)$ K
$\beta = 95.970 (8)°$	Block
$V = 1404.8 (2)$ Å^3	$0.50 \times 0.40 \times 0.40$ mm
$Z = 4$	Colourless
$D_x = 1.217$ Mg m^{-3}	

Data collection

Stoe Siemens diffractometer	$R_{int} = 0.0617$
ω/θ scans with on-line	$\theta_{max} = 65.02°$
profile fitting (Clegg,	$h = -13 \rightarrow 13$
1981)	$k = -17 \rightarrow 18$
Absorption correction:	$l = -9 \rightarrow 9$
none	3 standard reflections
2277 measured reflections	frequency: 60 min
2264 independent reflections	intensity decay: 1%
2014 observed reflections	
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.26$ e Å^{-3}
$R(F) = 0.0588$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$wR(F^2) = 0.1739$	Extinction correction:
$S = 1.059$	SHELXL93 (Sheldrick,
2260 reflections	1993)
182 parameters	Extinction coefficient:
H atoms riding with U(H) $=$	0.0073 (12)
$1.2U_{eq}(C)$	Atomic scattering factors
$w = 1/[\sigma^2(F_o^2) + (0.1134P)^2$	from *International Tables*
$+ 0.2574P]$	*for Crystallography* (1992,
where $P = (F_o^2 + 2F_c^2)/3$	Vol. C, Tables 4.2.6.8 and
$(\Delta/\sigma)_{max} < 0.001$	6.1.1.4)

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

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

	x	y	z	U_{eq}
N1	0.55484 (12)	0.35169 (9)	0.2542 (2)	0.0444 (4)
C2	0.65647 (14)	0.32838 (11)	0.2074 (2)	0.0417 (4)
C3	0.6905 (2)	0.24060 (11)	0.1973 (2)	0.0442 (5)
C4	0.6124 (2)	0.17766 (12)	0.2367 (2)	0.0507 (5)
C5	0.5090 (2)	0.20144 (12)	0.2863 (2)	0.0510 (5)
C6	0.48146 (15)	0.28963 (11)	0.2928 (2)	0.0443 (5)
C7	0.72857 (15)	0.40341 (11)	0.1641 (2)	0.0430 (5)
C8	0.6770 (2)	0.47393 (12)	0.0740 (2)	0.0517 (5)
C9	0.7410 (2)	0.54497 (13)	0.0319 (3)	0.0598 (6)
C10	0.8552 (2)	0.54777 (13)	0.0804 (3)	0.0628 (6)
C11	0.9076 (2)	0.47892 (14)	0.1716 (3)	0.0590 (6)
C12	0.8444 (2)	0.40763 (12)	0.2128 (2)	0.0500 (5)
C13	0.8002 (2)	0.21386 (12)	0.1406 (2)	0.0519 (5)
C14	0.8588 (2)	0.14516 (15)	0.1994 (3)	0.0695 (7)
C15	0.37090 (15)	0.32083 (12)	0.3429 (2)	0.0460 (5)
C16	0.2723 (2)	0.27216 (14)	0.3082 (3)	0.0575 (5)
C17	0.1699 (2)	0.3031 (2)	0.3533 (3)	0.0699 (7)
C18	0.1646 (2)	0.3823 (2)	0.4353 (3)	0.0712 (7)
C19	0.2611 (2)	0.4313 (2)	0.4708 (3)	0.0661 (6)
C20	0.3637 (2)	0.40137 (13)	0.4238 (3)	0.0551 (5)

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

N1—C2	1.341 (2)	C8—C9	1.385 (3)
N1—C6	1.343 (2)	C9—C10	1.366 (3)
C2—C3	1.408 (2)	C10—C11	1.382 (3)
C2—C7	1.491 (2)	C11—C12	1.381 (3)
C3—C4	1.392 (3)	C13—C14	1.316 (3)
C3—C13	1.472 (3)	C15—C16	1.388 (3)
C4—C5	1.371 (3)	C15—C20	1.392 (3)
C5—C6	1.392 (3)	C16—C17	1.381 (3)
C6—C15	1.483 (2)	C17—C18	1.376 (3)
C7—C12	1.386 (3)	C18—C19	1.371 (3)
C7—C8	1.394 (3)	C19—C20	1.383 (3)
C2—N1—C6	119.48 (15)	N1—C6—C15	116.1 (2)
N1—C2—C3	122.6 (2)	C5—C6—C15	122.6 (2)
N1—C2—C7	114.03 (14)	C12—C7—C8	118.1 (2)
C3—C2—C7	123.3 (2)	C12—C7—C2	123.2 (2)
C4—C3—C2	116.6 (2)	C8—C7—C2	118.7 (2)
C4—C3—C13	120.0 (2)	C14—C13—C3	124.6 (2)
C2—C3—C13	123.3 (2)	C16—C15—C20	118.3 (2)
C5—C4—C3	120.8 (2)	C16—C15—C6	121.5 (2)
C4—C5—C6	119.2 (2)	C20—C15—C6	120.1 (2)
N1—C6—C5	121.3 (2)		
Phenyl C—C—C	119.8 (2)–121.2 (2)		
C14—C13—C3—C4	−36.1 (3)	C3—C2—C7—C12	−41.8 (3)
C14—C13—C3—C2	146.8 (3)	N1—C6—C15—C16	149.1 (3)
N1—C2—C7—C8	−38.9 (3)	N1—C6—C15—C20	−29.6 (3)
N1—C2—C7—C12	139.4 (3)	C5—C6—C15—C16	−31.1 (3)
C3—C2—C7—C8	139.9 (3)	C5—C6—C15—C20	150.1 (3)

The data set before averaging consisted of a complete unique set of reflections ($k,l \geq 0$), together with a few Friedel opposites, which are responsible for the index limits given.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: MU1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(1) R = Me   (3)
(2) R = H

2,2-Dimethyl-5-(2-methyl-4-phenyl-3,4-diaza-2-butenylidene)-1,3-dioxane-4,6-dione

ALEXANDER J. BLAKE AND HAMISH MCNAB

*Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland*

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Abstract

The molecular conformation of the title compound, $C_{15}H_{16}N_2O_4$, is described in terms of three planar sections which are mutually twisted. The main intermolecular contacts are N—H⋯O hydrogen bonds where the O⋯N separation is 3.063 (3) Å.

Comment

The study of the structure of the title compound, (1), was undertaken to determine whether there were conformational reasons for its ready cyclization to give a 3-oxopyridazinecarboxylic acid upon thermolysis in solution, while the corresponding unsubstituted compound (2) is recovered unchanged under similar conditions (McNab & Stobie, 1982). The structure of (1) is also related to that of the propenylidene Meldrum's acid derivative (3), which we have described recently (Blake, McNab & Monahan, 1991).
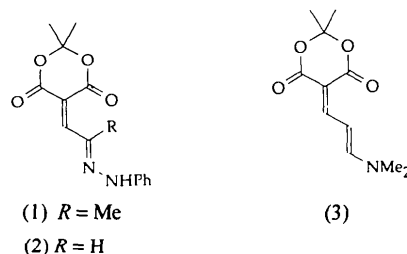
The conjugated system from C5 to N10 in (1) is exclusively *trans*, as found for (3), and so the cyclization reaction cannot be explained by a ground-state proximity of N10 and C4.

A feature of the structure of (3) is that electron delocalization occurs along the propenyl chain such that the lengths of all the C—C and C=C bonds are comparable [1.385 (8)–1.409 (8) Å]. In the case of (1), the system is much more localized [C=C 1.355 (3), C—C 1.439 (3) Å], partly due to poorer electron donation from the hydrazone N atom N10 compared with the terminal amino group in (3), and also partly due to the non-planarity of the system (see below). This reduced electron donation is also reflected in the lengths of the C4—C5 and C5—C6 bonds [both 1.469 (3) Å], which are substantially longer than the corresponding values for (3) [1.449 (8), 1.417 (8) Å].

The presence of the C8*M* methyl substituent in (1) has a dramatic effect on the angles subtended at C8 and C5. Non-bonded contacts between the C8*M* methyl group and O4 lead to widening of the C7—C8—C8*M* and C8*M*—C8—N9 angles to 125.7 (2) and 123.7 (2)°, respectively, with a concomitant reduction in the C7—C8—N9 angle to 110.5 (2)°. The C4—C5—C7 angle is widened to 126.0 (2)°, compared with an angle of 120.9 (5)° in (3). This distortion is almost entirely at the expense of the endocyclic C4—C5—C6 angle [116.5 (2)°, compared with 121.7 (5)° in (3)]. A similar trend at C5 has been noted for the corresponding angles in the dimethylaminomethylene Meldrum's acid, which has analogous steric constraints (Blake, McNab & Monahan, 1991). In (1), the two exocyclic N—C—C angles involving the phenyl group differ significantly, possibly because of repulsion between the *ortho* H6*P* atom and the lone pair on N9.

The molecular conformation of (1) can be described in terms of three planar sections: the phenyl ring, the five-atom chain C5—C7—C8—N9—N10 with its C8*M* substituent, and four atoms (O1, O3, C4 and C6) of the Meldrum's acid ring. The angle between the normals to the phenyl ring and the chain is 10.2 (2)° and the angle between the normals to the chain and the plane of the Meldrum's acid ring is 20.5 (2)°. In contrast, there is a much greater degree of coplanarity between the chain and the Meldrum's acid ring in (3). The mean deviation from the plane of the chain is 0.058 Å, while the four atoms defining the Meldrum's acid plane