

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{\max} = 0.125 \text{ e } \text{Å}^{-3}$
$wR(F^2) = 0.108$	$\Delta\rho_{\min} = -0.118 \text{ e } \text{Å}^{-3}$
$S = 1.032$	Extinction correction:
2335 reflections	<i>SHELXL97</i> (Sheldrick, 1997)
272 parameters	Extinction coefficient:
H-atom parameters	0.019 (2)
constrained	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.1300P]$	<i>International Tables for Crystallography</i> (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 5. Selected geometric parameters (Å , $^\circ$) for (V)

N1—C2	1.257 (4)	O21—C22	1.439 (4)
N1—C6	1.463 (4)	O51—C52	1.427 (4)
C2—O21	1.367 (3)	C4''—O41''	1.370 (4)
C3—N4	1.463 (4)	C5''—O51''	1.367 (4)
N4—C5	1.258 (4)	O41''—C42''	1.430 (5)
C5—O51	1.364 (3)	O51''—C52''	1.440 (5)
C2—N1—C6	118.5 (3)	O51—C5—C6	110.2 (3)
N1—C2—O21	120.0 (3)	N1—C6—C5	112.3 (2)
N1—C2—C3	129.4 (3)	N1—C6—C61	107.3 (2)
O21—C2—C3	110.6 (3)	N1—C6—C1''	107.0 (2)
N4—C3—C2	112.0 (3)	C2—O21—C22	115.4 (2)
N4—C3—C31	107.3 (3)	C5—O51—C52	116.9 (3)
N4—C3—C1'	107.4 (2)	O41''—C4''—C3''	124.9 (3)
C5—N4—C3	118.8 (2)	O41''—C4''—C5''	115.4 (3)
N4—C5—O51	120.9 (3)	O51''—C5''—C6''	125.0 (3)
N4—C5—C6	129.0 (3)	O51''—C5''—C4''	116.1 (3)

All H atoms were located by a difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ or $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model with C—H(aromatic) = 0.93, C—H(tertiary) = 0.98, C—H(secondary) = 0.97 or C—H(methyl) = 0.96 Å.

For all compounds, data collection: *D4* (Clegg, 1981); cell refinement: *D4*; data reduction: *REDU4* (Stoe & Cie, 1988); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1991).

We thank the late Professor Dr U. Schöllkopf (University of Göttingen) for providing the samples, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1255). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 973–975

Unexpectedly produced 2-*tert*-butyl-5-(*N,N*-dimethylcarbamoyl)pyridine† from 2-chloro-3-(*N,N*-dimethylcarbamoyl)-pyridine with a *tert*-butyl Grignard reagent

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(Received 29 May 1998; accepted 9 October 1998)

Abstract

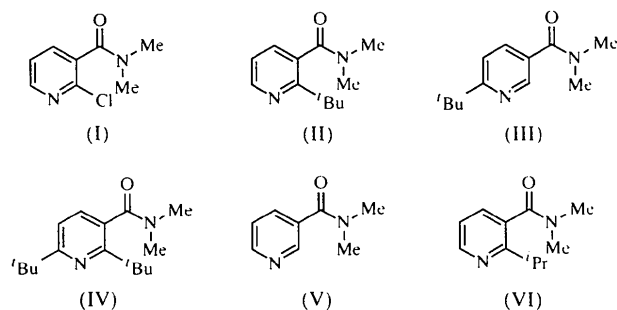
The title compound, $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}$, was obtained by the reaction of 2-chloro-3-(*N,N*-dimethylcarbamoyl)pyridine with *tert*-butylmagnesium chloride. The structure was confirmed by NMR spectroscopy and X-ray crystallography.

Comment

Much effort has been made to understand the *AB* face selectivity in nicotinamide (NAD) coenzyme based on the orientation of the carbamoyl dipole (Donkersloot & Buck, 1981; Okamura *et al.*, 1993; Ohno *et al.*, 1994; Mikata, 1997). The carbonyl-O atom might be considered to play an important role in determining the reactive face of the coenzyme. In this communication, a precursor of NAD model compounds was synthesized with bulky substituents at the 2 position in order to orientate the carbonyl-O atom perpendicular to the pyri-

† Alternative name: *N,N*-dimethyl-5-(2-*tert*-butyl)pyridinecarboxamide.

dine plane. The reaction of 2-chloro-3-(*N,N*-dimethylcarbamoyl)pyridine, (I), with *tert*-butylmagnesium chloride in the presence of an Ni catalyst gave 2-*tert*-butyl-3-(*N,N*-dimethylcarbamoyl)pyridine, (II), in 2.5% yield. During the synthesis of this compound, the unexpected product 2-*tert*-butyl-5-(*N,N*-dimethylcarbamoyl)pyridine, (III), was obtained in 11% yield. The structures of (II) and (III) were determined by coupling-constant analysis of ¹H NMR spectra and that of the latter compound was confirmed by X-ray crystallography. In the ¹H NMR spectra, the signals of the two methyl groups of compound (III) were broader and the difference in chemical shifts of these resonances was smaller than the difference in (II), indicating the exchange of two methyl groups.



The most stable conformation of (III) in the crystalline state is the out-of-plane conformation with respect to the carbonyl-O atom orientation as depicted in Fig. 1 [O1—C7—C2—C1 = -40.8 (2), O1—C7—C2—C3 = 133.7 (2)°]. However, the carbamoyl rotation was free even in the more hindered (II), which is confirmed by high-performance liquid chromatography analysis (Daicel CHIRALCEL OD, hexane/*i*-PrOH = 9:1). The absence of exchange of two methyl groups in (II) on the NMR time scale indicates the effect of

the 2-*tert*-butyl substituent to induce the out-of-plane conformation of the amide moiety, thus stabilizing the amide planarity. The other products in the reaction of (I) with ^tBuMgCl were trace amounts of 2,6-di-*tert*-butyl-3-(*N,N*-dimethylcarbamoyl)pyridine, (IV), and 3-(*N,N*-dimethylcarbamoyl)pyridine, (V). The corresponding 6-substituted product was not obtained from the reaction of (I) with isopropylmagnesium chloride in similar experimental conditions: 2-isopropyl-3-(*N,N*-dimethylcarbamoyl)pyridine (VI) was solely obtained in 52% yield. So, formation of (III) is considered to result from the steric hindrance of (II) and the stability of the *tert*-butyl radical.

Experimental

The condensation of 2-chloronicotiny chloride and dimethylamine gave (I) in 88% yield. This compound reacted with an excess amount of ^tBuMgCl or ⁱPrMgCl in the presence of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride to give the isolated compounds (II)–(VI) in 0.3–52% yield after silica gel chromatography. The crystal used for X-ray crystallographic analysis was obtained by recrystallization from ethyl acetate by slow evaporation of the solvent at room temperature.

Crystal data

C₁₂H₁₈N₂O
M_r = 206.29
 Monoclinic
*P*2₁/*n*
a = 7.712 (5) Å
b = 9.617 (5) Å
c = 16.155 (3) Å
 β = 101.88 (3)°
V = 1172.6 (9) Å³
Z = 4
D_x = 1.168 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 14.9–15.0°
 μ = 0.075 mm⁻¹
T = 173.2 K
 Prismatic
 0.70 × 0.60 × 0.30 mm
 Colourless

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
 Absorption correction:
 ψ scan (North *et al.*, 1968)
 T_{\min} = 0.950, T_{\max} = 0.978
 2365 measured reflections
 2055 independent reflections

1803 reflections with $I > 1.5\sigma(I)$
 R_{int} = 0.026
 θ_{max} = 24.94°
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 11$
 $l = -19 \rightarrow 18$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.24%

Refinement

Refinement on *F*
 R = 0.051
 wR = 0.085
 S = 1.420
 1803 reflections
 137 parameters
 H atoms not refined

$\Delta\rho_{\text{max}}$ = 0.25 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.28 e Å⁻³
 Extinction correction:
 Zachariasen (1967)
 type 2 Gaussian isotropic
 Extinction coefficient:
 0.031 (10)

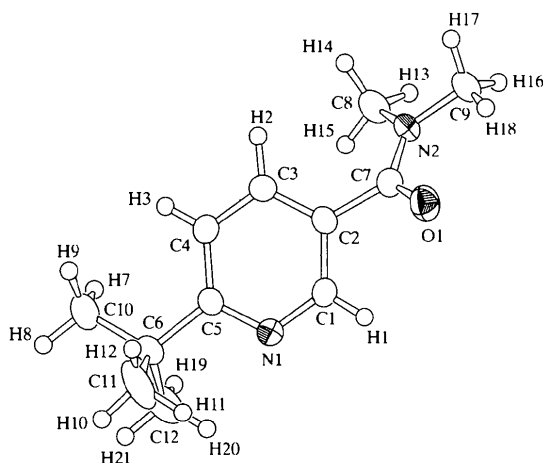


Fig. 1. ORTEP (Johnson, 1976) drawing of (III) showing displacement ellipsoids at the 50% probability level.

$$w = 1/[\sigma^2(F_o) + 0.00302|F_o|^2]$$

$$(\Delta/\sigma)_{\max} = 0.006$$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Acta Cryst. (1999). **C55**, 975–978

4-Methoxybenzaldehyde pentafluorophenyl-methylidenehydrazon†

Table 1. Selected geometric parameters (Å, °)

O1—C7	1.227 (2)	C2—C7	1.508 (2)
N1—C1	1.332 (2)	C3—C4	1.381 (2)
N1—C5	1.345 (2)	C4—C5	1.396 (2)
N2—C7	1.354 (2)	C5—C6	1.535 (2)
N2—C8	1.451 (2)	C6—C10	1.524 (3)
N2—C9	1.462 (2)	C6—C11	1.516 (3)
C1—C2	1.391 (2)	C6—C12	1.518 (3)
C2—C3	1.388 (2)		
C1—N1—C5	118.0 (1)	N1—C5—C6	115.2 (1)
C7—N2—C8	125.9 (1)	C4—C5—C6	123.5 (1)
C7—N2—C9	119.1 (1)	C5—C6—C10	111.6 (1)
C8—N2—C9	115.0 (1)	C5—C6—C11	108.3 (1)
N1—C1—C2	124.6 (1)	C5—C6—C12	109.1 (1)
C1—C2—C3	117.0 (1)	C10—C6—C11	108.0 (2)
C1—C2—C7	117.6 (1)	C10—C6—C12	109.1 (2)
C3—C2—C7	125.2 (1)	C11—C6—C12	110.8 (2)
C2—C3—C4	119.3 (1)	O1—C7—N2	122.6 (1)
C3—C4—C5	119.8 (1)	O1—C7—C2	118.6 (1)
N1—C5—C4	121.3 (1)	N2—C7—C2	118.8 (1)

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1072). Services for accessing these data are described at the back of the journal.

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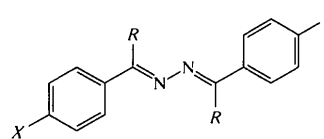
(Received 12 October 1998; accepted 9 February 1999)

Abstract

The crystal structure of the mixed azine C₁₅H₉F₅N₂O is described. The molecule has a high degree of planarity. The two phenyl rings deviate from perfect planarity by less than 2° and the dihedral angles between the *ipso*-C atoms and the azine bridge also show a minute deviation from planarity of less than 2°. The only dihedral angle that indicates any significant twisting is the dihedral angle about the azine bridge [C1—N1—N2—C8 174.8(6)°], and even this one is relatively small. Face-to-face arene–arene contacts are the dominant intermolecular interactions. There are double face-to-face contacts in which the two phenyl rings of one mixed azine interact with the two phenyl rings of another mixed azine. There are also single face-to-face contacts where one phenyl ring of one mixed azine interacts with a phenyl ring of another mixed azine. In the double face-to-face arene–arene contacts, the pentafluorinated phenyl ring of one mixed azine always interacts with the methoxy-substituted phenyl ring of another mixed azine. In the single face-to-face arene–arene contacts, the interactions are always between two pentafluorinated phenyl rings or two methoxy-substituted phenyl rings.

Comment

We have been investigating the stereochemistry (Glaser *et al.*, 1993, 1995; Chen *et al.*, 1995), electronics (Glaser *et al.*, 1993; Chen *et al.*, 1995; Glaser & Chen, 1998), and crystal packing (Glaser *et al.*, 1993; Chen *et al.*, 1995; Lewis *et al.*, 1998) of symmetric and unsymmetric azines. An azine is the condensation product between



† Part 10 in the series 'Stereochemistry and Stereoelectronics of Azines'. For part 9, see Hathaway *et al.* (1998).