

All the H atoms were refined with a common isotropic displacement parameter ($U_{\text{iso}} = 0.071 \text{ \AA}^2$).

Data collection: local program. Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1995). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1208). Services for accessing these data are described at the back of the journal.

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Out-of-Plane Orientation of the Carbamoyl Group in an NAD Model Compound: Preferred 1,3-Diaxial Methyl Configuration

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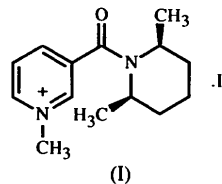
(Received 30 January 1997; accepted 7 May 1997)

Abstract

The carbamoyl group in 3-(*cis*-2,6-dimethylpiperidinyl-carbonyl)-1-methylpyridinium iodide, C₁₄H₂₁N₂O⁺.I⁻, has an out-of-plane orientation in the crystalline state. The planarity of the amide moiety is conserved and the two methyl groups in the piperidine ring are both in axial configurations.

Comment

There has been much argument by chemists and biologists over how the NAD-dependent enzymes discriminate the face of the coenzyme (Fisher, Conn, Vennesland & Westheimer, 1953; Nambiar, Stauffer, Kolodziej & Benner, 1983; You, 1985). There is a fascinating view on understanding this event based on the orientation of the carbamoyl dipole (Donkersloot & Buck, 1981; Okamura, Mikata, Yamazaki, Tsutsumi & Ohno, 1993; Ohno *et al.*, 1994). According to this argument, the carbonyl oxygen plays an important role in determining the reactive face of the coenzyme. A novel NAD model compound, (I), was synthesized having bulky substituents at the amide nitrogen in order to investigate the effect on the carbonyl group. Judging from the HPLC analysis (Daicel Chiralcel OD), the carbamoyl rotation of (I) oc-



curred freely in solution at room temperature, however, the most stable conformation in the crystalline state is an out-of-plane conformation with respect to the carbonyl oxygen orientation, as depicted in Fig. 1. The two methyl groups in the piperidine ring are in the diaxial direction in order to avoid steric repulsion between the pyridine ring and the equatorial methyl group. The planarity of the amide group in the NAD model compound is conserved in spite of the disadvantage of the

1,3-diaxial conformations of the methyl groups at the amide nitrogen. The result of this study is very important not only for the design of new NAD model compounds with atropisomerism, but generally to control the carbonyl dipole in the aromatic carboxylate system.

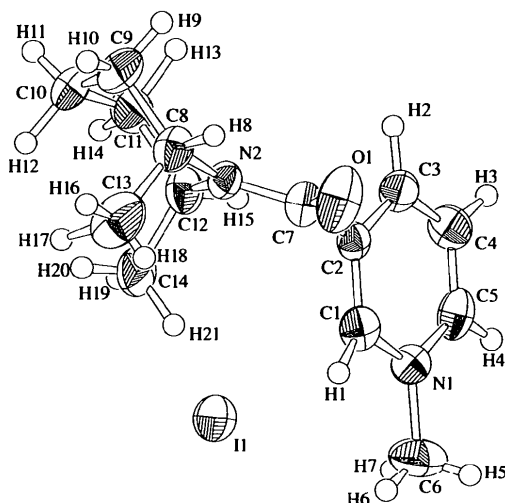


Fig. 1. ORTEP (Johnson, 1976) drawing of (I) showing displacement ellipsoids at the 50% probability level.

Experimental

The condensation of nicotinyl chloride and *cis*-2,6-dimethylpiperidine followed by methylation with methyl iodide gave (I) in 78% yield. The crystal used for X-ray crystallographic analysis was obtained by recrystallization from dichloromethane-ethanol solution in a refrigerator.

Crystal data

$C_{14}H_{21}N_2O^+ \cdot I^-$

$M_r = 360.24$

Orthorhombic

Pbca

$a = 14.531(4) \text{ \AA}$

$b = 15.867(5) \text{ \AA}$

$c = 13.481(4) \text{ \AA}$

$V = 3108(1) \text{ \AA}^3$

$Z = 8$

$D_x = 1.539 \text{ Mg m}^{-3}$

$D_m = 1.59 \text{ Mg m}^{-3}$

D_m measured by flotation in C_6H_{14}/CCl_4

Data collection

Rigaku AFC-7R diffractometer

ω -2 θ scans

Absorption correction:

ψ scans (North, Phillips & Mathews, 1968)

$T_{\min} = 0.642$, $T_{\max} = 0.814$

4009 measured reflections

4009 independent reflections

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10.0$ – 13.3°

$\mu = 2.054 \text{ mm}^{-1}$

$T = 293.2 \text{ K}$

Needle

$0.4 \times 0.1 \times 0.1 \text{ mm}$

Colorless

2024 reflections with

$I > \sigma(I)$

$\theta_{\max} = 27.51^\circ$

$h = 0 \rightarrow 18$

$k = 0 \rightarrow 20$

$l = 0 \rightarrow 17$

3 standard reflections

every 150 reflections

intensity decay: -1.9%

Refinement

Refinement on F

$R = 0.051$

$wR = 0.071$

$S = 1.000$

2024 reflections

247 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o) + 0.0025|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.014$

$\Delta\rho_{\max} = 0.86 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.71 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray*

Crystallography (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O(1)—C(7)	1.212 (9)	C(2)—C(7)	1.514 (10)
N(1)—C(1)	1.352 (10)	C(3)—C(4)	1.37 (1)
N(1)—C(5)	1.37 (1)	C(4)—C(5)	1.36 (1)
N(1)—C(6)	1.48 (1)	C(8)—C(9)	1.54 (1)
N(2)—C(7)	1.329 (9)	C(8)—C(13)	1.55 (1)
N(2)—C(8)	1.475 (9)	C(9)—C(10)	1.51 (2)
N(2)—C(12)	1.487 (10)	C(10)—C(11)	1.51 (1)
C(1)—C(2)	1.37 (1)	C(11)—C(12)	1.54 (1)
C(2)—C(3)	1.383 (10)	C(12)—C(14)	1.49 (1)
C(1)—N(1)—C(5)	120.6 (7)	O(1)—C(7)—N(2)	125.4 (7)
C(1)—N(1)—C(6)	120.8 (8)	O(1)—C(7)—C(2)	116.8 (7)
C(5)—N(1)—C(6)	118.6 (8)	N(2)—C(7)—C(2)	117.8 (6)
C(7)—N(2)—C(8)	118.3 (6)	N(2)—C(8)—C(9)	111.4 (7)
C(7)—N(2)—C(12)	122.0 (6)	N(2)—C(8)—C(13)	112.2 (7)
C(8)—N(2)—C(12)	119.5 (6)	C(9)—C(8)—C(13)	112.0 (8)
N(1)—C(1)—C(2)	120.5 (7)	C(8)—C(9)—C(10)	110.8 (8)
C(1)—C(2)—C(3)	119.1 (7)	C(9)—C(10)—C(11)	109.6 (8)
C(1)—C(2)—C(7)	118.6 (6)	C(10)—C(11)—C(12)	112.1 (7)
C(3)—C(2)—C(7)	122.2 (7)	N(2)—C(12)—C(11)	108.8 (7)
C(2)—C(3)—C(4)	120.0 (8)	N(2)—C(12)—C(14)	111.8 (7)
C(3)—C(4)—C(5)	120.2 (8)	C(11)—C(12)—C(14)	114.6 (7)
N(1)—C(5)—C(4)	119.6 (7)		

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: *SHELXS86* (Sheldrick, 1990). 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: OA1026). Services for accessing these data are described at the back of the journal.

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A Nitroxide Tetradical Exhibiting Ferromagnetic Coupling

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Abstract

The crystal structure of a nitroxide radical exhibiting ferromagnetic exchange interactions is described. The closest NO· · · NO contact in 4,4',4''4'''-[1,2,4,5-benzene-tetrayltetrakis(carbonyloxy)]tetrakis(2,2,6,6-tetramethyl-1-piperidinyloxy), C₄₆H₇₀N₄O₁₂, involves an orthogonal arrangement of two nitroxide groups, leading to a ferromagnetic exchange interaction.

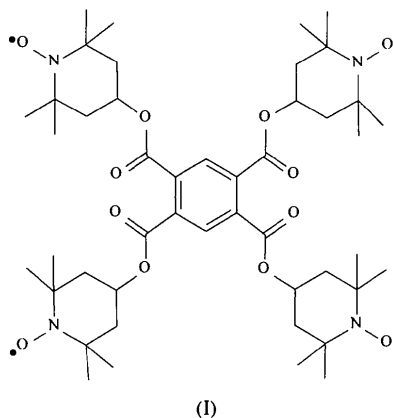
Comment

The synthesis and characterization of new organic compounds showing cooperative magnetic phenomena is currently an area of increasing interest. However, a well characterized chemically stable organic ferromagnet which has an ordering temperature about room temperature is not yet available. A necessary condition for the existence of such a 'molecular ferromagnet' consisting of molecular units is the occurrence of an inter- or intramolecular ferromagnetic exchange interaction.

Very few metal-free organic radicals have been reported to exhibit magnetic ordering. The series of nitroxides provides probably the most efficient source of organic compounds exhibiting extended magnetic interactions (Rassat, 1990). Many of them form linear chains, with some showing three-dimensional magnetic ordering at very low temperatures. However, only a limited number of these nitroxide radicals possess positive Weiss constants and the mechanism which may provide such ferromagnetic exchange interactions is not

yet completely explained. For compounds containing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical groups, the occurrence of a positive Weiss constant was explained in terms of the assumption of dipolar interactions between the adjacent spin centres (see for example Miller & Epstein, 1994). However, the structural arrangement which may provide this spin pairing is still under discussion.

This has prompted us to resynthesize a nitroxide tetradical and investigate the magnetic properties on the basis of X-ray structure investigations. The synthesis and some EPR data of this compound, (I), have been reported previously by Sholle, Prokop'ev, Sortova, Sarymsakov & Rozantev (1981). The effective magnetic moment increases gradually with decreasing temperature. This clearly indicates the existence of a ferromagnetic exchange interaction which can be described by a Curie–Weiss law with a positive Weiss constant of +0.7 (1) K.



The crystal structure of (I) has two centrosymmetric molecules in the unit cell, the asymmetric unit being half a molecule (Fig. 1). The intramolecular bond distances and angles within the TEMPO rings have expected values, such as those observed by Seff (1972). Of particular importance with respect to the dipolar interaction between the spin centres is the distance between the nitroxide NO groups and their relative orientation. The closest contacts between nitroxide O atoms are 4.184 (3) [O1· · · O1(2 - x, y - 1/2, 3/2 - z), intermolecular] and 4.974 (3) Å [O6· · · O1(1 - x, y - 1/2, 3/2 - z), intermolecular]. The O1· · · N1(2 - x, y + 1/2, 3/2 - z) distance is 3.545 (3) Å. The N· · · O bonds corresponding to the closest O(nitroxide) contacts are approximately perpendicularly oriented [angles O1· · · N1ⁱ—O1ⁱ 111.4(1) and N1—O1· · · N1ⁱ 168.8(1)°; symmetry code: (i) 2 - x, y + 1/2, 3/2 - z]. The near orthogonality is not a consequence of symmetry. This arrangement, leading to orthogonal magnetic orbitals, is most probably the origin of the ferromagnetic interactions in the title compound.