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N-Acetylminodiacetate Dimethyl Ester

PAULA PRAYZNER,^a EMMANUEL C. A. OJADI,^a JAMES A. GOLEN^a AND PAUL G. WILLIARD^b

^aDepartment of Chemistry, University of Massachusetts Dartmouth, North Dartmouth, MA 02747, USA, and

^bDepartment of Chemistry, Brown University, Providence, RI 02912, USA

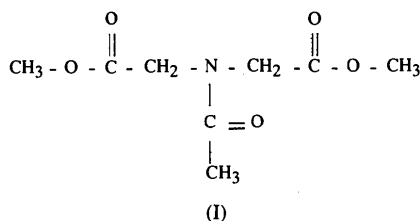
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Abstract

N-Acetylminodiacetate dimethyl ester, C₈H₁₃NO₅, was prepared for the synthesis of 3,4-diphenylpyrrole in a multi-step synthetic route to a model porphyrin. The technique used in this preparation yielded colorless crystals of high purity. Site geometry around the central N atom is nearly trigonal planar.

Comment

In the search for synthetic routes for porphyrins, the title compound, (I) (Fig. 1), was synthesized. The crystal structure determination was undertaken to verify the synthetic procedure and to ascertain the geometry around the N atom.



A unique feature of the title structure is the trigonal planar site geometry around the central N atom. The sum of the three angles around N(1) is 360° and the mean deviation of the plane formed by atoms N(1), C(1), C(4) and C(7) is 0.0080 Å [deviations with respect to the other atoms are N(1) –0.0160, C(1) 0.0050, C(4) 0.0050, C(7) 0.0060 Å]. Bond lengths N(1)—C(1) and N(1)—C(4) of the diester portions of the struc-

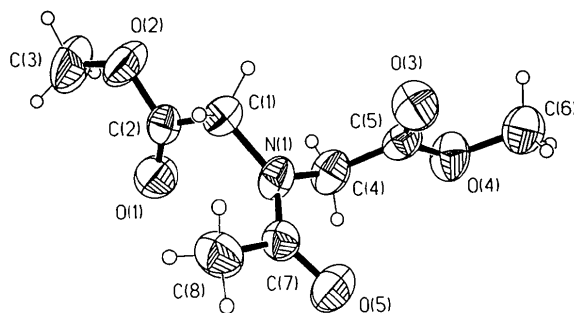


Fig. 1. View of C₈H₁₃NO₅ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

ture are comparable to those found in dithiocarbamates, 1.460 (5), 1.467 (6) and 1.475 (8), 1.477 (8) Å, respectively (Heinemann, Dölling & Hartung, 1992), and in *N*-methylnitritolotriacetamide, 1.448 (4), 1.466 (3) and 1.477 (4) Å (Skrzypczak-Jankun & Smith, 1994). The N—C bond of the amide linkage, N(1)—C(7), is shorter by 0.1 Å and is similar to values found in linuron, 1.361 (6) and 1.395 (7) Å (Cadiergue, Pèpe, Astier, Boistelle & Fiard, 1993), and in *N*-methylnitritolotriacetamide, 1.307 (3), 1.318 (4) and 1.321 (4) Å (Skrzypczak-Jankun & Smith, 1994). This shorter N(1)—C(7) bond length indicates some double-bond character which is characteristic of zwitterion formation in N(1)—C(7)—O(5).

Experimental

Iminodiacetate dimethyl ester hydrochloride was isolated from a refluxing solution of iminodiacetic acid (Jongkees, 1907) which had been saturated with hydrogen chloride gas. Conversion to the *N*-acetylminodiacetate dimethyl ester was achieved by neutralizing 10 g of the ester hydrochloride with 15 ml of 3 M ammonium carbonate followed by the addition of 8 ml of acetic anhydride and extraction with chloroform. The solution was evaporated to give a white solid. The resulting material was washed with hexane and recrystallized from acetone to give clear colorless crystals of the title compound, yield 60.0% (Prayzner, 1994).

Crystal data

C₈H₁₃NO₅
M_r = 203.2
 Monoclinic
*P*2₁/*c*
a = 9.411 (2) Å
b = 14.457 (3) Å
c = 7.853 (2) Å
 β = 105.95 (3)°
V = 1027.2 (4) Å³
Z = 4
D_x = 1.314 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 12.0–12.5°
 μ = 0.110 mm⁻¹
T = 297 K
 Wedge
 0.40 × 0.35 × 0.20 mm
 Colorless

Data collection

Siemens *R3m/V* diffractometer

*R*_{int} = 0.022
 θ_{max} = 23.5°

ω scans	$h = -10 \rightarrow 10$
Absorption correction:	$k = -1 \rightarrow 16$
none	$l = -1 \rightarrow 8$
2061 measured reflections	3 standard reflections
1519 independent reflections	monitored every 97
925 observed reflections	reflections
$[F > 4\sigma(F)]$	intensity decay: 2.0%

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0005F^2]$
$R = 0.0536$	$(\Delta/\sigma)_{\max} < 0.001$
$wR = 0.0603$	$\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
$S = 1.51$	$\Delta\rho_{\min} = -0.22 \text{ e } \text{Å}^{-3}$
925 reflections	Extinction correction: none
127 parameters	Atomic scattering factors
H atoms were refined as a	from <i>International Tables</i>
riding model with fixed	for <i>X-ray Crystallography</i>
isotropic U	(1974, Vol. IV)

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

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
O(1)	0.4549 (3)	0.2094 (2)	0.1065 (4)	0.077 (1)
O(2)	0.2602 (3)	0.2718 (2)	-0.0838 (4)	0.077 (1)
O(3)	0.7418 (3)	0.4752 (2)	-0.1287 (4)	0.070 (1)
O(4)	0.9021 (3)	0.3648 (2)	-0.1442 (4)	0.068 (1)
O(5)	0.8259 (3)	0.4024 (2)	0.3067 (4)	0.074 (1)
N(1)	0.6253 (3)	0.3650 (2)	0.0926 (4)	0.052 (1)
C(1)	0.4676 (4)	0.3647 (3)	0.0059 (5)	0.051 (2)
C(2)	0.3963 (4)	0.2733 (3)	0.0190 (6)	0.049 (2)
C(3)	0.1762 (5)	0.1878 (3)	-0.0882 (8)	0.098 (3)
C(4)	0.7216 (4)	0.3255 (3)	-0.0066 (6)	0.059 (2)
C(5)	0.7871 (4)	0.3984 (3)	-0.0987 (5)	0.050 (2)
C(6)	0.9768 (4)	0.4271 (4)	-0.2367 (6)	0.078 (2)
C(7)	0.6906 (4)	0.4020 (3)	0.2524 (5)	0.050 (2)
C(8)	0.5968 (4)	0.4405 (3)	0.3607 (6)	0.066 (2)

Table 2. Selected geometric parameters (Å , $^\circ$)

O(1)—C(2)	1.193 (5)	O(2)—C(2)	1.313 (4)
O(2)—C(3)	1.444 (6)	O(3)—C(5)	1.190 (6)
O(4)—C(5)	1.322 (5)	O(4)—C(6)	1.453 (6)
O(5)—C(7)	1.227 (4)	N(1)—C(1)	1.453 (4)
N(1)—C(4)	1.463 (6)	N(1)—C(7)	1.347 (5)
C(1)—C(2)	1.499 (6)	C(4)—C(5)	1.502 (7)
C(7)—C(8)	1.492 (7)		
C(2)—O(2)—C(3)	117.6 (3)	C(5)—O(4)—C(6)	116.9 (3)
C(1)—N(1)—C(4)	116.9 (3)	C(1)—N(1)—C(7)	125.7 (4)
C(4)—N(1)—C(7)	117.4 (3)	N(1)—C(1)—C(2)	112.9 (3)
O(1)—C(2)—O(2)	124.1 (4)	O(1)—C(2)—C(1)	125.3 (3)
O(2)—C(2)—C(1)	110.6 (3)	N(1)—C(4)—C(5)	112.3 (3)
O(3)—C(5)—O(4)	124.4 (4)	O(3)—C(5)—C(4)	125.3 (4)
O(4)—C(5)—C(4)	110.3 (4)	O(5)—C(7)—N(1)	119.3 (4)
O(5)—C(7)—C(8)	121.3 (4)	N(1)—C(7)—C(8)	119.4 (3)

The crystal was mounted on the tip of a glass fiber with epoxy. Data collection was carried out on an upgraded Nicolet/Siemens R3m/V four-circle diffractometer using XSCANS (Siemens, 1994). The structure was solved by direct methods, and refinement and molecular graphics were obtained using standard SHELXTL-Plus programs (Sheldrick, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Molecular, Crystal Structure and Fluorescence Emission Properties of Diprotonated 7,10,19,22-Tetraoxa-4,13-diaza[16.8^{4,13}](9,10)anthracenophane ($A_{33}\cdot 2\text{H}^+$)

NACER LAHRAHAR,^a PIERRE MARSAU,^a HENRI BOUAS-LAURENT,^b JEAN-PIERRE DESVERGNE^b AND FRÉDÉRIC FAGES^b

^aLaboratoire de Cristallographie et Physique Cristalline, CNRS ERS 133, Université Bordeaux I, 351 Cours de la Libération, 33405 Talence CEDEX, France, and

^bLaboratoire de Photophysique et Photochimie Moléculaire, CNRS URA 348, Université Bordeaux I, 351 Cours de la Libération, 33405 Talence CEDEX, France

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Abstract

7,10,19,22-Tetraoxa-4,13-diaza[16.8^{4,13}](9,10)anthracenophane. $2\text{HClO}_4\cdot\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_{32}\text{H}_{44}\text{N}_2\text{O}_4\cdot 2\text{HClO}_4\cdot\text{C}_7\text{H}_8$, is a diprotonated form of a molecular receptor described previously and the homologue of $A_{22}\cdot 2\text{H}^+$ is also described. The present $A_{33}\cdot 2\text{H}^+$ compound crystallizes with one molecule of solvent (toluene) and the $\text{N}^+—\text{H}$ bonds are oriented outside the empty cavity towards