

C3—C3a	1.515 (6)	C8—C8a	1.415 (6)
C3a—C11	1.507 (5)	C8a—C9	1.496 (6)
C3a—C4	1.520 (6)	C9—O9	1.222 (6)
C3a—C10a	1.526 (5)	C9—C10	1.506 (6)
C4—C4a	1.508 (6)	C10—C10a	1.514 (6)
C4a—C5	1.401 (6)	C10a—C11	1.510 (6)
C4a—C8a	1.412 (6)	C11—Br11'	1.929 (4)
C5—C6	1.392 (6)	C11—Br11	1.933 (4)
C6—O6	1.354 (5)		
C2—C1—C10a	106.9 (4)	C4a—C8a—C8	118.2 (4)
C1—C2—C3	107.9 (4)	C4a—C8a—C9	126.9 (4)
C2—C3—C3a	107.1 (4)	C8—C8a—C9	114.9 (4)
C3—C3a—C4	117.9 (4)	C8a—C9—O9	120.2 (4)
C3—C3a—C10a	108.7 (3)	C8a—C9—C10	121.3 (4)
C3—C3a—C11	117.4 (3)	O9—C9—C10	118.5 (4)
C4—C3a—C10a	117.8 (3)	C9—C10—C10a	111.3 (3)
C4—C3a—C11	120.7 (4)	C1—C10a—C3a	108.4 (3)
C10a—C3a—C11	59.7 (3)	C1—C10a—C10	118.4 (4)
C3a—C4—C4a	112.7 (3)	C1—C10a—C11	117.3 (4)
C4—C4a—C5	115.8 (4)	C3a—C10a—C10	118.4 (3)
C4—C4a—C8a	125.2 (4)	C3a—C10a—C11	59.5 (3)
C5—C4a—C8a	119.0 (4)	C10—C10a—C11	120.0 (4)
C4a—C5—C6	122.0 (4)	C3a—C11—C10a	60.8 (3)
C5—C6—O6	124.9 (4)	C3a—C11—Br11	120.9 (3)
C5—C6—C7	118.7 (4)	C3a—C11—Br11'	120.4 (3)
O6—C6—C7	116.4 (4)	C10a—C11—Br11	120.6 (3)
C6—O6—C6'	118.6 (4)	C10a—C11—Br11'	120.7 (3)
C6—C7—C8	120.3 (4)	Br11—C11—Br11'	107.5 (2)
C7—C8—C8a	121.8 (4)		
C1—C2—C3—C3a	9.6 (5)	C10—C10a—C3a—C4	-1.1 (6)
C2—C3—C3a—C10a	-6.0 (5)	C10a—C3a—C4—C4a	-66.6 (5)
C3—C3a—C10a—C1	0.1 (4)	C3—C3a—C11—Br11	13.6 (5)
C3a—C10a—C1—C2	5.9 (5)	C10—C10a—C11—Br11'	2.7 (5)
C10a—C1—C2—C3	-9.6 (5)	C4—C4a—C5—C6	-177.9 (4)
C3a—C4—C4a—C8a	53.0 (5)	C4a—C5—C6—O6	178.5 (4)
C4—C4a—C8a—C9	1.6 (6)	C5—C6—O6—C6'	-0.5 (7)
C4a—C8a—C9—C10	1.7 (6)	C10—C9—C8a—C8	-176.4 (4)
C8a—C9—C10—C10a	-59.0 (5)	C10a—C10—C9—O9	122.7 (5)
C9—C10—C10a—C3a	71.3 (5)		

Data collection: *AFSCIMSC* (Rigaku Corporation, 1988). Cell refinement: *AFSCIMSC*. Data reduction: *AFSCIMSC*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1166). Services for accessing these data are described at the back of the journal.

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4,4'-Azinodimethyldipyridinium Dip perchlorate, $C_{12}H_{12}N_4^{2+} \cdot 2ClO_4^-$

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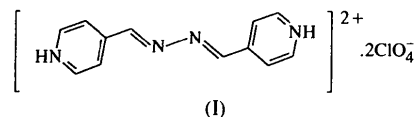
(Received 3 February 1997; accepted 18 April 1997)

Abstract

The centrosymmetric 4,4'-azinodimethyldipyridinium cations, $C_{12}H_{12}N_4^{2+}$, are planar and lie in planes parallel to the *c* axis. There is a strong intermolecular hydrogen bond, $N1—H \cdots O4^i$ [2.896 (3) Å; symmetry code: (i) $-x, 1-y, -z$], and a number of weaker hydrogen bonds between the C atoms of the pyridine rings and the O atoms of the perchlorate anions [3.234–3.246 (4) Å].

Comment

The cation of the title compound, (I), is well known as a precursor of atactic poly-4-vinylpyridine which has been used to coordinate transition metal ions such as Fe^{2+} , Co^{2+} and Ni^{2+} (Biedermann, Obwandner & Wichmann, 1972). In addition, the Schiff base ligand derived from hydrazine has applications in coordination chemistry owing to its polydentate chelating ability (Tarafder & Khan, 1991). Although the synthesis and characterization of the 4,4'-azinodimethyldipyridinium cation have been discussed previously (Biedermann & Schmid, 1973; El-Rayyes & Katrib, 1983), its crystal structure, to the best of our knowledge, has not been reported; it is of interest to us owing to the cation's ability to act as a potential bridging ligand. In this paper, we report the crystal structure of 4,4'-azinodimethyldipyridinium dip perchlorate, (I).



An *ORTEPII* (Johnson, 1976) plot of the title compound is shown in Fig. 1. The $N2=C6$ double-bond distance [1.260 (4) Å] is slightly shorter than that of another Schiff base compound derived from hydrazine, namely, 2,2'-azinodimethyldiphenol [$C=N$ 1.285 (7) Å; Xu, You & Sun, 1994], while the $N2—N2^i$ single-bond distance [1.400 (4) Å; symmetry code: (i) $-2-x,$

2 - y, 1 - z] is slightly longer than that in 2,2'-azinodimethyldiphenol [1.386 (9) Å]. The bond angles C6—N2—N2ⁱ [112.3 (3)°] and N2—C6—C3 [119.4 (3)°] are slightly smaller than those of 2,2'-azinodimethyldiphenol [113.4 (6) and 121.3 (5)°, respectively]. Other bond distances and angles are as expected.

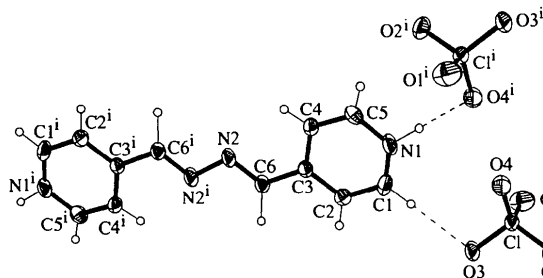


Fig. 1. ORTEP (Johnson, 1976) plot drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.

A number of weak hydrogen bonds were found: C1—H1...O3 3.244 (4), C6—H6...O3ⁱⁱ 3.234 (4) and C5—H5...O2ⁱⁱⁱ 3.246 (4) Å [symmetry codes: (ii) -1 - x, 1 - y, 1 - z; (iii) -x, 1 - y, -z]. A similar trend was observed in the Schiff base-copper(II) complex [Cu(appn)](ClO₄)₂·H₂O [where appn is propylenebis(2-acetylpyridineiminato)] (Liu, Xiong, You, Fun & Sivakumar, 1997), but the hydrogen bonds (C_{pyridine}—H...O_{perchlorate} average 3.266 Å) were slightly weaker compared with those in the title compound. The distance between the cationic planes is about 3.3 Å [C3...C6^{iv} 3.367 (4) Å; symmetry code: (iv) -1 - x, 2 - y, 1 - z].

Experimental

The title complex was prepared by stirring [Cd(ClO₄)₂].6H₂O, NH₂NH₂·2HCl and 4-pyridylcarboxaldehyde under flowing N₂ in anhydrous EtOH solution at 273 K for 8 h. The resulting solution was evaporated at room temperature for a few weeks, affording orange block-shaped crystals.

Crystal data

C₁₂H₁₂N₄²⁺·2ClO₄⁻
M_r = 205.58
 Triclinic
*P*1̄
a = 5.2894 (5) Å
b = 8.6106 (8) Å
c = 9.1884 (9) Å
 α = 101.801 (7)°
 β = 97.055 (9)°
 γ = 96.293 (8)°
V = 402.61 (7) Å³
Z = 2
D_x = 1.696 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 5–10°
 μ = 0.457 mm⁻¹
T = 300 (2) K
 Block
 0.3 × 0.2 × 0.2 mm
 Orange

Data collection

CAD-4 diffractometer
 ω scans
 Absorption correction:
 ψ scan (North, Phillips & Mathews, 1968)
 T_{\min} = 0.799, T_{\max} = 0.913
 1590 measured reflections
 1421 independent reflections
 1075 reflections with $I > 2\sigma(I)$

R_{int} = 0.010
 θ_{max} = 24.99°
 h = -6 → 6
 k = -10 → 10
 l = 0 → 10
 3 standard reflections
 frequency: 60 min
 intensity decay: 0.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.041
 $wR(F^2)$ = 0.110
 S = 1.019
 1421 reflections
 118 parameters
 H-atom coordinates fixed
 $w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.1394P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.265 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.365 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N2—C6	1.260 (4)	C3—C6	1.470 (4)
N2—N2 ⁱ	1.400 (4)		
C6—N2—N2 ⁱ	112.3 (3)	C4—C3—C6	122.3 (3)
C2—C3—C6	119.0 (2)	N2—C6—C3	119.4 (3)

Symmetry code: (i) -2 - x, 2 - y, 1 - z.

Data collection: CAD-4 VAX/PC (Enraf-Nonius, 1988). Cell refinement: CAD-4 VAX/PC. Data reduction: NRCVAX (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTI/PC (Sheldrick, 1990b). 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: KH1150). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1501–1502

(1 α ,2 β ,3 α ,6 α ,7 β ,8 α ,9 β ,13 β)-9,13-Di-bromo-11-methyl-14,15-dioxa-11-azapenta-cyclo[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]pentadec-4-ene-10,12-dione

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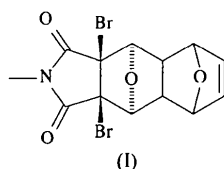
(Received 18 February 1997; accepted 30 April 1997)

Abstract

The crystal structure of the minor 2:1 isomer (C₁₃H₁₁Br₂NO₄) formed by the reaction of furan with *N*-methyl-3,4-dibromomaleimide is reported.

Comment

The reaction of furan with *N*-methyl-3,4-dibromomaleimide produces a single 1:1 adduct when conducted in neat furan (sealed vessel) at 443 K for 17 h in 40% yield together with unreacted maleimide (50%). Increasing the reaction time (3 days) leads to the formation of the 1:1 adduct plus two isomeric 2:1 adducts (ratio 3:1) (Warrener, Maksimovic & Butler, 1994) which have different stereochemistry of the terminal 7-oxanorbornane ring. It was not possible to obtain single crystals of the 1:1 adduct nor to determine its stereochemistry by spectroscopic means. The title 2:1 adduct [(I); minor



isomer, m.p. 516–521 K] not only provides interesting data in its own right, but also defines the stereochemistry of the succinimide ring. The stereochemical information obtained herein is critical to a theoretical study of the specificity of cycloaddition reactions of furan and cyclopentadiene with halo-substituted dienophiles (Warrener & Margetic, 1996).

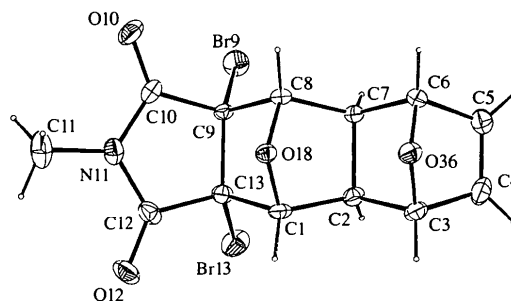


Fig. 1. Plot of the title compound with displacement ellipsoids plotted at the 20% probability level.

Experimental

The reaction of furan with *N*-methyl-3,4-dibromomaleimide yields a 1:1 adduct which on further heating produces two 2:1 adducts.

Crystal data

C₁₃H₁₁Br₂NO₄
M_r = 405.05
 Monoclinic
*P*2₁/*a*
a = 7.377 (1) Å
b = 18.664 (3) Å
c = 9.897 (2) Å
 β = 95.314 (8)°
V = 1356.8 (4) Å³
Z = 4
D_x = 1.983 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 23 reflections
 θ = 6–14°
 μ = 5.986 mm⁻¹
T = 298 (2) K
 Needle
 0.23 × 0.15 × 0.11 mm
 Colourless

Data collection

CAD-4 MicroVAX-controlled diffractometer
 2 θ / ω scans
 Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.21, *T_{max}* = 0.52
 3412 measured reflections
 3412 independent reflections

1913 reflections with *I* > 2 σ (*I*)
 θ_{\max} = 29.9°
h = 0 → 8
k = 0 → 26
l = -13 → 13
 3 standard reflections every 250 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.047
 wR (*F*²) = 0.110

$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 1.0814P]$
 where $P = (F_o^2 + 2F_c^2)/3$