Bis(pyridinium) Pamoate

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Abstract

Attempted crystallization of pamoic acid from its solution in pyridine instead produced the crystalline title compound, bis(pyridinium) 4,4'-methylenebis(3-hydroxy-2-naphthalenecarboxylate), $2C_5H_6N^+.C_{23}H_{14}O_6^{2-}$. In this structure, intramolecular hydrogen bonding involves hydroxy O atoms as donors and carboxylate O atoms as acceptors, while intermolecular hydrogen bonds involve N atoms as donors and carboxylate O atoms as acceptors. Each N atom and each O atom participates in a strong hydrogen bond. The H atoms involved in hydrogen bonding are ordered.

Comment

The structure of pamoic acid is of interest because of the potentially extensive hydrogen bonding: hydrogen bonding between hydroxy groups and carboxy groups *ortho* to them is well known [see, for example, the structural results for 3-hydroxy-2-naphthoic acid obtained by Gupta & Mahata (1975), and for γ-resorcylic acid by Gdaniec, Gilski & Denisov (1994)], and the carboxy groups may be expected to form hydrogen bonds between themselves as well, possibly in more than one manner. The present structural analysis of a crystal obtained from a solution of pamoic acid in pyridine establishes that an acid–base reaction had occurred to produce bis(pyridinium) pamoate, (I), which itself shows extensive hydrogen bonding. This structure has not been described previously. The pyridinium cations and the pamoate anion are shown in Fig. 1 with
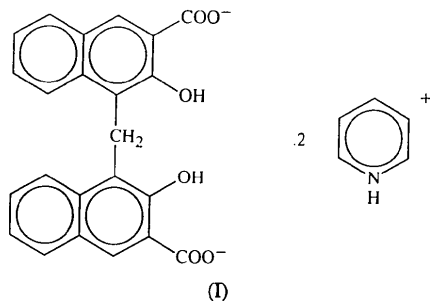
the numbering system. A view of the packing is given in Fig. 2.

As is apparent from Table 3, which gives geometric details of the hydrogen bonds, and from Fig. 2, two types of hydrogen bonding occur in this structure: intramolecular, involving the OH groups and O atoms from the carboxylate groups *ortho* to them, and intermolecular, between the pyridinium N atoms as donors and O atoms of the carboxylate groups as acceptors. As
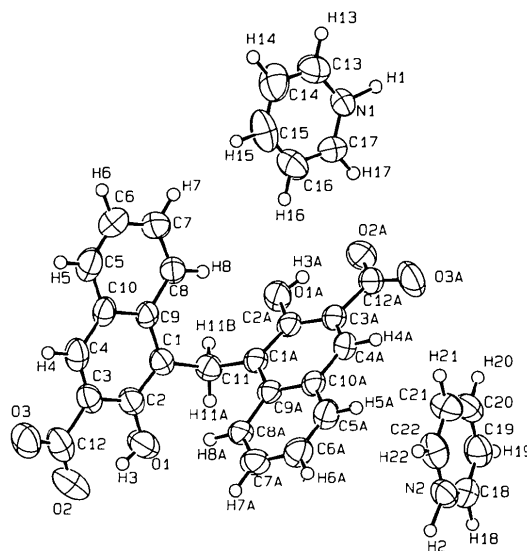

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of bis(pyridinium) pamoate showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H for which they have been set artificially small.
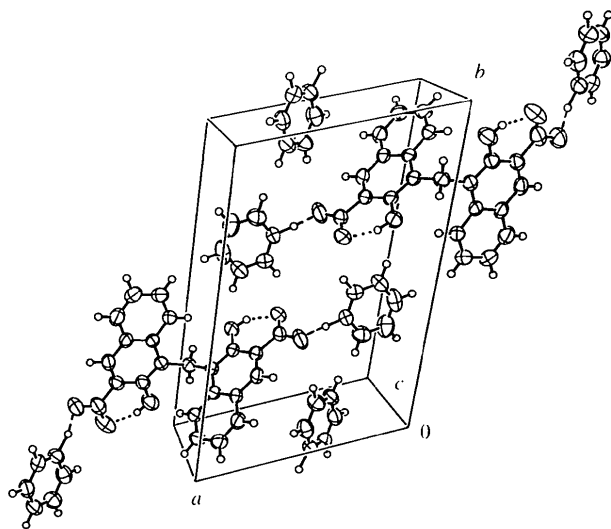

Fig. 2. A view of a portion of the title structure including a unit cell (*ORTEP*II; Johnson, 1976). Displacement ellipsoids are drawn at the 50% probability level for all atoms except H for which they have been set artificially small. Intramolecular hydrogen bonds are represented by dotted lines and intermolecular by dashed lines.

(I)

these data show, the two carboxylate H atoms have been transferred to the two pyridine N atoms, which leads to the N atoms being donor atoms and the carboxylate O atoms being acceptor atoms. They further show that the hydroxy O atoms are donors and carboxylate O atoms are acceptors in intramolecular hydrogen bonds. Finally, the data show that the H atoms involved in these bonds are ordered. It is also noteworthy that each O atom and each N atom in this structure is involved in a strong hydrogen bond.

The N1—H1 and N2—H2 distances found here, 1.13 (4) and 1.22 Å, are larger than the corresponding values in apparently similar cases: in the 1:1 complex pyridinium γ resorcylate (Gdaniec, Gilski & Denisov, 1994), the N—H distance was reported to be 0.97 (3) Å, and in the 1:1 complex pyridinium 1,1'-binaphthyl-8,8'-dicarboxylate (Csöregh, Czugler, Törnroos, Weber & Ahrendt, 1989) the distance was 0.96 Å. While the coordinates of H2 in the present study were fixed from a difference map and were not refinable, those of H1 were refined but also yielded a large value for the N—H distance. Whether the present results are simply fortuitous or indicate a real effect cannot be resolved without additional data.

It can be noted that although the largest positive residual peak in the final difference map is located ~1 Å from O3, it is not properly situated to be interpretable as an H atom involved in hydrogen bonding with N2 (the peak–N2 distance is ~3.2 Å, the O3–peak–N2 angle is ~45°) or any other potential acceptor.

The substituted rings of the two naphthalene cores of the pamoate anion deviate significantly more from planarity than the unsubstituted rings: the mean deviations of the corresponding atoms from the best-fit least-squares planes are 0.022 and 0.019 Å as compared with 0.009 and 0.008 Å, respectively. The dihedral angles between the carboxylate planes and the best-fit least-squares planes of the rings to which they are attached are 8.1 (2) and 5.3 (2)°.

Excluding approaches involving hydrogen-bonding atoms, the closest intermolecular approaches in this structure are between the pyridinium ring H atoms (H14, H18) and pamoate C atoms (C1A, C8A, C9A), and between C12 (pamoate ion) and C20 (pyridinium ion).

Experimental

Pamoic acid (Aldrich Chemical Co.) was dissolved in pyridine and the solution filtered. The filtrate was evaporated at room temperature and yielded clear colorless roughly equidimensional crystals. One of these was cut and mounted on a glass fiber with epoxy cement.

Crystal data

$2C_5H_6N^+.C_{23}H_{14}O_6^{2-}$
$M_r = 546.58$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Triclinic
$P\bar{1}$
$a = 11.276 (2)$ Å
$b = 16.599 (3)$ Å
$c = 7.516 (2)$ Å
$\alpha = 99.29 (2)°$
$\beta = 101.75 (2)°$
$\gamma = 98.76 (1)°$
$V = 1334.0 (5)$ Å^3
$Z = 2$
$D_x = 1.361$ Mg m^{-3}
D_m not measured

Cell parameters from 25
reflections
$\theta = 12.7–17.4°$
$\mu = 0.088$ mm^{-1}
$T = 296$ K
Cut chunk
$0.38 \times 0.38 \times 0.26$ mm
Colorless

Data collection

AFC-5S diffractometer
ω scans
Absorption correction:
none
6450 measured reflections
6136 independent reflections
2968 observed reflections
$[I > 3\sigma(I)]$
$R_{int} = 0.012$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 14$
$k = -21 \rightarrow 21$
$l = -9 \rightarrow 9$
6 standard reflections
monitored every 150
reflections
intensity variation: ±4.2%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.053$
$S = 1.80$
2968 reflections
392 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max} = 0.32$ e Å^{-3}
(next highest 0.16 e Å^{-3})
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction:
Zachariasen (1963, 1968)
Extinction coefficient:
$2.2 (2) \times 10^{-6}$
Atomic scattering factors
from Stewart, Davidson
& Simpson (1965) for H,
Cromer & Waber (1974)
for C, O and N

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

U_{iso} for H atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{eq}/U_{iso}
O1	0.1440 (2)	0.1287 (1)	0.8762 (3)	0.0786 (8)
O1A	−0.2077 (2)	0.3306 (1)	0.8103 (3)	0.0696 (7)
O2	0.3520 (2)	0.0901 (2)	0.8723 (3)	0.0942 (10)
O2A	−0.3991 (2)	0.3734 (1)	0.6336 (3)	0.0754 (7)
O3	0.5033 (2)	0.1814 (2)	0.8313 (3)	0.0962 (9)
O3A	−0.4652 (2)	0.3259 (1)	0.3296 (3)	0.0886 (8)
N1	−0.3260 (2)	0.6359 (2)	0.6675 (3)	0.0602 (8)
N2	−0.5832 (2)	−0.0452 (2)	0.2660 (3)	0.0704 (9)
C1	0.1147 (2)	0.2631 (2)	0.8396 (3)	0.0501 (8)
C1A	−0.1095 (2)	0.2369 (2)	0.6486 (3)	0.0472 (8)
C2	0.1920 (3)	0.2069 (2)	0.8579 (4)	0.0567 (9)
C2A	−0.2009 (2)	0.2845 (2)	0.6473 (4)	0.0516 (8)
C3	0.3176 (3)	0.2273 (2)	0.8536 (4)	0.0600 (9)
C3A	−0.2873 (2)	0.2852 (2)	0.4817 (4)	0.0539 (8)
C4	0.3656 (2)	0.3063 (2)	0.8438 (4)	0.0631 (9)
C4A	−0.2790 (2)	0.2395 (2)	0.3178 (4)	0.0562 (8)
C5	0.3441 (3)	0.4522 (2)	0.8442 (4)	0.074 (1)
C5A	−0.1872 (3)	0.1378 (2)	0.1430 (4)	0.0630 (9)
C6	0.2768 (3)	0.5129 (2)	0.8538 (4)	0.077 (1)
C6A	−0.1090 (3)	0.0837 (2)	0.1374 (4)	0.0667 (10)
C7	0.1515 (3)	0.4918 (2)	0.8562 (4)	0.070 (1)

C7A	−0.0299 (3)	0.0775 (2)	0.3021 (4)	0.0625 (9)
C8	0.0966 (2)	0.4115 (2)	0.8461 (4)	0.0562 (8)
C8A	−0.0278 (2)	0.1267 (2)	0.4679 (4)	0.0529 (8)
C9	0.1663 (2)	0.3470 (2)	0.8394 (3)	0.0487 (8)
C9A	−0.1083 (2)	0.1849 (1)	0.4782 (4)	0.0465 (7)
C10	0.2928 (2)	0.3687 (2)	0.8407 (3)	0.0545 (8)
C10A	−0.1904 (2)	0.1884 (2)	0.3115 (4)	0.0501 (8)
C11	−0.0219 (3)	0.2359 (2)	0.8296 (4)	0.0538 (9)
C12	0.3947 (3)	0.1604 (3)	0.8555 (4)	0.074 (1)
C12A	−0.3908 (3)	0.3322 (2)	0.4843 (5)	0.0614 (9)
C13	−0.2392 (3)	0.7016 (2)	0.6837 (4)	0.077 (1)
C14	−0.1225 (3)	0.6941 (2)	0.6763 (5)	0.088 (1)
C15	−0.0947 (3)	0.6174 (3)	0.6521 (5)	0.090 (1)
C16	−0.1819 (4)	0.5504 (2)	0.6424 (5)	0.093 (1)
C17	−0.2987 (3)	0.5611 (2)	0.6491 (5)	0.079 (1)
C18	−0.6713 (3)	−0.0551 (2)	0.3571 (5)	0.074 (1)
C19	−0.7202 (3)	0.0087 (2)	0.4263 (5)	0.075 (1)
C20	−0.6784 (3)	0.0859 (2)	0.4023 (4)	0.067 (1)
C21	−0.5873 (3)	0.0989 (2)	0.3107 (4)	0.073 (1)
C22	−0.5397 (3)	0.0313 (2)	0.2432 (4)	0.075 (1)
H11A	−0.038 (2)	0.178 (2)	0.853 (3)	0.056 (8)
H11B	−0.044 (2)	0.272 (1)	0.926 (3)	0.056 (8)
H1	−0.421 (3)	0.650 (2)	0.669 (4)	0.12 (1)
H2	−0.5324	−0.1005	0.2098	0.20 (2)
H3	0.204 (3)	0.105 (2)	0.869 (5)	0.10 (1)
H3A	−0.273 (3)	0.354 (2)	0.793 (4)	0.10 (1)

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

O1—C2	1.367 (3)	C6A—C7A	1.399 (4)
O1A—C2A	1.359 (3)	C7—C8	1.365 (4)
O2—C12	1.230 (4)	C7A—C8A	1.369 (3)
O2A—C12A	1.245 (3)	C8—C9	1.421 (3)
O3—C12	1.278 (4)	C8A—C9A	1.426 (3)
O3A—C12A	1.266 (3)	C9—C10	1.414 (3)
C1—C2	1.375 (3)	C9A—C10A	1.413 (3)
C1—C9	1.426 (3)	C11—H11A	1.00 (2)
C1—C11	1.520 (4)	C11—H11B	0.97 (2)
C1A—C2A	1.390 (3)	N1—C13	1.322 (4)
C1A—C9A	1.428 (3)	N1—C17	1.316 (3)
C1A—C11	1.514 (4)	C13—C14	1.352 (4)
C2—C3	1.414 (4)	C14—C15	1.350 (5)
C2A—C3A	1.419 (4)	C15—C16	1.349 (5)
C3—C4	1.359 (4)	C16—C17	1.365 (4)
C3A—C4A	1.366 (4)	N2—C18	1.321 (4)
C4—C10	1.418 (4)	N2—C22	1.340 (4)
C4A—C10A	1.410 (3)	C18—C19	1.347 (4)
C5—C6	1.352 (4)	C19—C20	1.350 (4)
C5A—C6A	1.352 (4)	C20—C21	1.359 (4)
C6—C7	1.408 (4)	C21—C22	1.385 (4)
C2—O1—H3	101 (2)	C1A—C9A—C8A	122.5 (2)
C2A—O1A—H3A	110 (2)	C1A—C9A—C10A	120.3 (2)
C2—C1—C9	118.7 (2)	C8A—C9A—C10A	117.2 (2)
C2—C1—C11	119.7 (3)	C4—C10—C5	121.7 (3)
C9—C1—C11	121.6 (2)	C4—C10—C9	118.9 (3)
C2A—C1A—C9A	117.9 (2)	C5—C10—C9	119.4 (2)
C2A—C1A—C11	120.0 (2)	C4A—C10A—C5A	120.8 (2)
C9A—C1A—C11	121.9 (2)	C4A—C10A—C9A	119.1 (2)
O1—C2—C1	118.4 (3)	C5A—C10A—C9A	120.0 (2)
O1—C2—C3	119.8 (2)	C1—C11—C1A	116.1 (2)
C1—C2—C3	121.8 (3)	C1—C11—H11A	110 (1)
O1A—C2A—C1A	118.6 (2)	C1—C11—H11B	109 (1)
O1A—C2A—C3A	119.6 (2)	C1A—C11—H11A	107 (1)
C1A—C2A—C3A	121.9 (2)	C1A—C11—H11B	107 (1)
C2—C3—C4	119.2 (3)	O2—C12—O3	123.4 (3)
C2—C3—C12	119.3 (3)	O2—C12—C3	121.0 (3)
C4—C3—C12	121.5 (3)	O3—C12—C3	115.5 (3)
C2A—C3A—C4A	119.3 (2)	O2A—C12A—O3A	124.5 (3)
C2A—C3A—C12A	121.3 (3)	O2A—C12A—C3A	119.6 (3)
C4A—C3A—C12A	119.4 (3)	O3A—C12A—C3A	115.9 (3)
C3—C4—C10	121.3 (3)	C13—N1—C17	119.9 (3)
C3A—C4A—C10A	121.3 (3)	N1—C13—C14	121.6 (3)
C6—C5—C10	121.7 (3)	C13—C14—C15	118.8 (3)
C6A—C5A—C10A	121.4 (3)	C14—C15—C16	119.7 (3)
C5—C6—C7	119.0 (3)	C15—C16—C17	119.2 (3)
C5A—C6A—C7A	119.2 (3)	C18—N2—C22	119.0 (3)
C6—C7—C8	121.3 (3)	N1—C17—C16	120.7 (3)

C6A—C7A—C8A	121.3 (2)	N2—C18—C19	122.4 (3)
C7—C8—C9	120.5 (3)	C18—C19—C20	119.3 (3)
C7A—C8A—C9A	120.8 (2)	C19—C20—C21	120.2 (3)
C1—C9—C8	122.4 (2)	C20—C21—C22	118.2 (3)
C1—C9—C10	119.6 (2)	N2—C22—C21	120.9 (3)
C8—C9—C10	117.9 (2)		

Table 3. *Hydrogen-bonding geometry ($\mathring{A}$, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H3···O2	0.84 (3)	1.72 (3)	2.529 (3)	161 (3)
O1A—H3A···O2A	0.88 (3)	1.77 (3)	2.556 (3)	148 (3)
N1—H1···O3A'	1.13 (4)	1.41 (4)	2.533 (3)	176 (3)
N2—H2···O3"	1.22	1.43	2.610 (3)	160*
N2—H2···O2"	1.22	2.23	3.143 (4)	129*

Symmetry codes: (i) $-1 - x, 1 - y, 1 - z$; (ii) $-x, -y, 1 - z$.

* E.s.d.'s not provided since H2 fixed.

Scan widths were $(1.30 + 0.35\tan\theta)°$ in ω, with a background/scan time ratio of 0.5. No correction was required for decay or absorption but the data were corrected for Lorentz and polarization effects. The average maximum relative intensity variation of the six standards was ±4.2%.

Intensity statistics indicated that the triclinic space group was centrosymmetric, so $P\bar{1}$ (No. 2) was given initial preference; since refinement proceeded well, it was adopted. The direct methods program *MITHRIL* (Gilmore, 1984) produced an E map from which the initial positions of the C, N and O atoms were identified. Fourier difference methods were used to locate the initial H-atom positions. Full-matrix least-squares refinement was performed. In later stages of the refinement, ring H atoms were assigned fixed geometry (C—H = 0.98 Å), each with an isotropic displacement parameter of magnitude 1.2 times that of the associated C atom. One of the two H atoms attached to the N atoms, the two hydroxy H atoms and the two H atoms bonded to C11 were refined isotropically; the other H atom attached to N was assigned fixed coordinates, but its isotropic displacement parameter was refined. Also in the late stages a secondary-extinction parameter (Zachariasen, 1963, 1968) was included; the maximum effect of extinction was 12.9% of F_o for 13$\bar{1}$. The maximum peak on the final difference map was located $\sim$1 Å from O3; the minimum peak occurred $\sim$1.3 Å from C1A and C2A.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *OR-TEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

$2C_5H_6N^+.C_{23}H_{14}O_6^{2-}$

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A Pyrazoline Derivative of Eunicin Acetate

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Abstract

The present crystal structure determination established spiro[{3a,4,5,6,7,8,11,12,13,14,15,15a-dodecahydro-6,10,14-trimethyl-2-oxo-5,15-epoxy-3*H*-cyclotetradeca-[*b*]furan}-3,3'-1'-pyrazoline]-6-yl acetate, $C_{23}H_{34}N_2O_5$, as a pyrazoline derivative of eunicin acetate. The spiro substitution of the pyrazoline ring causes elongation of the bonds within the lactone ring and also shortening of the carbonyl bond. The cembranolide skeleton is slightly more bent than that observed in the parent eunicin molecule.

Comment

During the extraction, isolation and structure determination of a novel cembranoid planaxool, (I), obtained from the mollusk *Planaxis sulcatus* (Alam *et al.*, 1993), one of the samples derived from an extract that had been stored in a polypropylene-lined drum was found to contain an additional chromatographic peak. Isolation of the compound responsible for this peak, using high-performance liquid chromatography (HPLC), gave a colorless compound, (II). The crystal structure was determined in order to properly identify the compound.

(I)   (II)
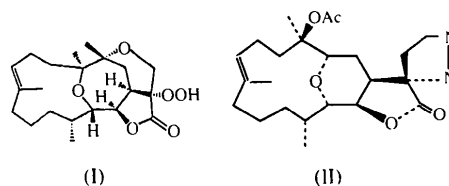
A perspective *ORTEP*II plot (Johnson, 1976) of the title molecule is shown in Fig. 1, which also shows the atom-numbering scheme. The X-ray structure established the compound as a pyrazoline derivative of eunicin acetate. The absolute configuration of the molecule was not determined but assigned according to that of eunicin (Hossain, Nicholas & van der Helm, 1968) and other cembranolides, the absolute configurations of which were determined by X-ray diffraction (van der Helm, Enwall, Weinheimer, Karns & Ciereszko, 1976; Ealick, van der Helm & Weinheimer, 1975; Chang, Ciereszko, Hossain & van der Helm, 1980). The bond distances and angles are in general agreement with those observed in eunicin iodoacetate (Weinheimer, Middlebrook, Bledsoe, Marsico & Karns, 1968; Hossain, Nicholas & van der Helm, 1968) and other cembranolides (van der Helm, Enwall, Weinheimer, Karns & Ciereszko, 1976; Ealick, van der Helm & Weinheimer, 1975; Chang, Ciereszko, Hossain & van der Helm,
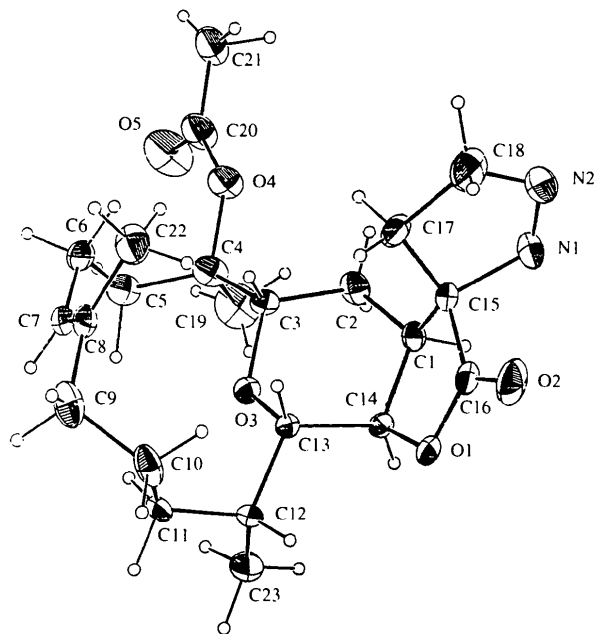

Fig. 1. The molecular structure of compound (II) showing 50% probability displacement ellipsoids.