Crystal Structure of Acenaphthene-1'-one-spiro[2'.3]-[4-ethoxycarbonyl]-N-methyl-pyrrolidine-spiro[2.2'']-acenaphthene-1''-one

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In the title compound, $C_{30}H_{23}NO_4$, the molecule includes two spiro junctions connecting acenaphthene rings and the pyrrolidine moiety. The acenaphthene ring atoms (C2, C7–C17) and (C3, C18–C28) make dihedral angles of 87.0(1) and 81.3(1)°, respectively, with the pyrrolidine ring system. The pyrrolidine ring exhibits an envelope conformation. In the crystal, packing is stabilized by C–H... π and π – π interactions.

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Spiro pyrrolidine derivatives are often used in the synthesis of biologically active compounds. The spiro ring system is also very interesting from a biogenetic point of view. Synthetic pyrrolidine derivatives have activity against the aldose reductase enzyme, which controls influenza.¹ Acenaphthene of a known concentration added to soil samples helps one to investigate the anaerobic degradation potential of polycyclic aromatic hydrocarbons.² Polycyclic azaarenes (PAA) are relatively rigid planar hosts for metal ions and organic molecules.³ In view of its varied importance, crystal and molecular structure determinations of the title compound were carried out by X-ray diffraction (Fig. 1).

The crystal data were collected on a CCD Area Detector diffractometer (Table 1) with graphite-monochromated Mo K_α radiation. The structure was solved by direct methods and refined by a full-matrix least-squares procedure. The non-hydrogen atoms were refined anisotropically. The H atoms were positioned geometrically and were treated as riding on their parent C atoms and refined isotropically. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2.

The selected bond lengths and bond angles are given in Table 3. The C–C distances and C–C–C angles of the pyrrolidine

moiety shows variations, which can be considered to be the characteristic feature of compounds containing spiro junctions. The endocyclic torsion angles show the five-membered ring in an envelope conformation with the N1 atom out of the plane of the four others, which are planar within 0.002 Å. The displacement of the N1 atom from the plane is –0.611(2) Å. The sum of the angles around the N1 atom is 338.1(1)°, showing sp^3 hybridization.

The bond lengths and angles of the acenaphthene rings of atoms C2, C7–C17 and C3, C18–C28 are in the same range, and closely resemble the values of the related structures reported so far.⁴ The acenaphthene rings are almost planar with the associated ketone atoms O1 and O2 displaced by –0.207(2) and –0.301(1) Å, respectively.

Fig. 1 Chemical diagram.

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Table 1 Crystal and experimental data

CCDC No.	270968
Empirical formula	$C_{30}H_{23}NO_4$
Formula weight	461.49
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.3442(8)\text{Å}$ $\alpha = 79.538(2)^\circ$ $b = 10.3875(9)\text{Å}$ $\beta = 1.8570(10)^\circ$ $c = 12.1667(10)\text{Å}$ $\gamma = 87.1640(10)^\circ$
Volume	$1149.25(17)\text{Å}^3$
Z	2
Density (calculated)	1.334 Mg/m^3
θ_{max}	28°
No. of reflections used	4574
R	0.0570
$(\Delta/\sigma)_{\text{max}}$	<0.001
$(\Delta\rho)_{\text{max}}$	0.278 eÅ^{-3}
$(\Delta\rho)_{\text{min}}$	-0.203 eÅ^{-3}
Measurement	CCD Area Detector diffractometer
Program system	SAINT
Structure determination	SHELXS97
Refinement method	Full-matrix least-squares

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the non-hydrogen atoms

Atom	x	y	z	$*U_{\text{eq}}$
O1	853(2)	9131(1)	6488(2)	66(1)
O2	-511(2)	6108(2)	9874(1)	56(1)
O3	-1704(2)	11010(2)	8014(2)	108(1)
O4	-3738(2)	9943(2)	8597(2)	84(1)
N1	557(2)	7525(1)	8833(1)	44(1)
C2	-62(2)	7207(2)	7882(2)	38(1)
C3	-1697(2)	7657(2)	8140(2)	38(1)
C4	-1607(2)	8738(2)	8874(2)	47(1)
C5	-17(2)	8819(2)	8985(2)	53(1)
C6	2113(2)	7355(2)	8797(2)	62(1)
C7	642(2)	7965(2)	6704(2)	44(1)
C8	1074(2)	7005(2)	5954(2)	42(1)
C9	1660(2)	7122(2)	4849(2)	55(1)
C10	2011(2)	5979(3)	4402(2)	64(1)
C11	1800(2)	4765(3)	5047(2)	59(1)
C12	1213(2)	4604(2)	6193(2)	46(1)
C13	828(2)	5759(2)	6616(2)	38(1)
C14	206(2)	5787(2)	7730(2)	36(1)
C15	7(2)	4627(2)	8458(2)	44(1)
C16	384(2)	3450(2)	8044(2)	54(1)
C17	953(2)	3420(2)	6961(2)	54(1)
C18	-2581(2)	6493(2)	8887(2)	39(1)
C19	-3577(2)	6065(2)	8196(2)	40(1)
C20	-4526(2)	5052(2)	8405(2)	49(1)
C21	-5412(2)	4969(2)	7585(2)	59(1)
C22	-5377(2)	5874(2)	6615(2)	59(1)
C23	-4435(2)	6946(2)	6387(2)	49(1)
C24	-3526(2)	6984(2)	7204(2)	40(1)
C25	-2482(2)	7957(2)	7106(2)	40(1)
C26	-2366(2)	8904(2)	6166(2)	53(1)
C27	-3285(3)	8895(2)	5344(2)	63(1)
C28	-4293(2)	7961(2)	5444(2)	62(1)
C29	-2311(2)	10030(2)	8445(2)	61(1)
C30	-4576(4)	11113(3)	8207(4)	123(2)
C31	-5947(5)	10792(4)	8041(4)	139(2)

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

Table 3 Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]

O1	853(2)	9131(1)	6488(2)	66(1)
O2	-511(2)	6108(2)	9874(1)	56(1)
O3	-1704(2)	11010(2)	8014(2)	108(1)
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C25	-2482(2)	7957(2)	7106(2)	40(1)
C26	-2366(2)	8904(2)	6166(2)	53(1)
C27	-3285(3)	8895(2)	5344(2)	63(1)
C28	-4293(2)	7961(2)	5444(2)	62(1)
C29	-2311(2)	10030(2)	8445(2)	61(1)
C30	-4576(4)	11113(3)	8207(4)	123(2)
C31	-5947(5)	10792(4)	8041(4)	139(2)

Table 4 Non-bonded interactions [$\text{\AA}$ and $^\circ$]

D-H...A	D-H	H...A	D...A	<(DHA)
C4-H4...O2	0.98	2.40	2.896(2)	111
C5-H5A...O1	0.97	2.41	2.995(3)	118
C5-H5A...O3	0.97	2.54	2.874(3)	100
C26-H26...O1	0.93	2.50	3.113(3)	124

Fig. 2 Molecular structure of the title compound, showing 30% probability displacement ellipsoids.

An ORTEP diagram of the molecule, together with the atomic labelling scheme is shown in Fig. 2. Ethoxycarbonyl group atoms show large anisotropic thermal motion. The molecule is stabilized by a number of C-H...O type intramolecular interactions. The C-H... π interaction between C11 and the ring (A) of atoms (C23-C28) at $-x, 1-y, 1-z$ [$\text{C11}\cdots\text{CgA} = 3.642(3)\text{\AA}$; $\angle\text{C11-H11}\cdots\text{CgA} = 167.2^\circ$; CgA is the centroid of ring A] and the π - π interaction between ring (B) of atoms (C8-C13) at x, y, z and $-x, 1-y, 1-z$ with centroid-centroid distance of $3.770(1)\text{\AA}$ are observed in the crystal. These interactions stabilize the crystal packing in addition to van der Waals interactions.

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