Three closely related dibenzazepine carboxylic acids: hydrogen-bonded aggregation in one, two and three dimensions

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In the structure of (6*R**,11*R**)-5-acetyl-11-ethyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acid, C₁₉H₁₉NO₃, (I), the molecules are linked into sheets by a combination of O—H...O and C—H...O hydrogen bonds; in the structure of the monomethyl analogue (6*RS*,11*SR*)-5-acetyl-11-ethyl-2-methyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acid, C₂₀H₂₁NO₃, (II), the molecules are linked into simple *C*(7) chains by O—H...O hydrogen bonds; and in the structure of the dimethyl analogue (6*RS*,11*SR*)-5-acetyl-11-ethyl-1,3-dimethyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acid, C₂₁H₂₃NO₃, (III), a combination of O—H...O, C—H...O and C—H... π (arene) hydrogen bonds links the molecules into a three-dimensional framework structure. None of these structures exhibits the *R*₂²(8) dimer motif characteristic of simple carboxylic acids.

Keywords: crystal structure; dibenzo[*b,e*]azepine-6-carboxylic acid; hydrogen bonding; hydrogen-bonded supramolecular aggregation.

1. Introduction

The dibenzo[*b,e*]azepine ring is an important pharmacophore in drug discovery and many of its derivatives exhibit a broad spectrum of biological activities (Van der Burg *et al.*, 1970; Brogden *et al.*, 1978; Nickolson & Wieringa, 1981; Berger *et al.*, 1989; De Boer *et al.*, 1996; Roeder *et al.*, 1998; Andrés *et al.*, 2002; Wikström *et al.*, 2002). Consequently, a significant number of synthetic methods have been developed for the synthesis of new derivatives of this heterocyclic system (Moriconi & Maniscalco, 1972; Sasakura & Sugawara, 1981; Stappers *et al.*, 2002). In this context, we have recently developed a simple and practical synthetic route for obtaining a novel series of 6,11-dihydrodibenzo[*b,e*]azepines from

readily available 2-allyl-*N*-benzyl-substituted anilines (Palma *et al.*, 2004, 2010). To broaden the scope of this route, and in continuation of our research programme on the preparation of new potentially bioactive molecules containing the dihydrodibenzo[*b,e*]azepine nucleus, we have achieved a simple synthesis of three previously unknown 5-acetyl-11-ethyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acids. Here we report the molecular structures and supramolecular assembly of three closely related compounds, namely (6*R**,11*R**)-5-acetyl-11-ethyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acid, (I) (Fig. 1), (6*RS*,11*SR*)-5-acetyl-11-ethyl-2-methyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acid, (II) (Fig. 2), and (6*RS*,11*SR*)-5-acetyl-11-ethyl-1,3-dimethyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acid, (III) (Fig. 3), the constitutions of which differ only in the presence of one methyl substituent in (II) and two in (III), while there are none in (I). The synthesis of compounds (I)–(III) was achieved by intramolecular Friedel–Crafts alkylation of the corresponding methyl 2-[*N*-(2-allylaryl)acetamido]-2-phenylacetates using concentrated sulfuric acid at 373 K (see Scheme).

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of each of (I)–(III), a suspension of the appropriately substituted racemic methyl 2-[*N*-(2-allylaryl)acetamido]-2-phenylacetate (see Scheme) (1.0 g) in concen-

Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	C ₁₉ H ₁₉ NO ₃	C ₂₀ H ₂₁ NO ₃	C ₂₁ H ₂₃ NO ₃
<i>M_r</i>	309.35	323.38	337.40
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Temperature (K)	120	120	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8053 (3), 10.9821 (4), 9.0080 (6)	15.2894 (16), 10.760 (2), 10.538 (2)	9.2283 (11), 16.691 (2), 11.9824 (18)
β (°)	118.510 (3)	100.990 (11)	103.820 (11)
<i>V</i> (Å ³)	765.45 (6)	1701.9 (5)	1792.2 (4)
<i>Z</i>	2	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.09	0.09	0.08
Crystal size (mm)	0.26 × 0.14 × 0.10	0.41 × 0.30 × 0.24	0.23 × 0.20 × 0.20
Data collection			
Diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T</i> _{min} , <i>T</i> _{max}	0.977, 0.991	0.966, 0.980	0.981, 0.984
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13276, 1851, 1638	28096, 3903, 2589	27558, 3316, 2090
<i>R</i> _{int}	0.049	0.092	0.139
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650	0.650	0.606
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.081, 1.15	0.059, 0.155, 1.05	0.058, 0.120, 1.08
No. of reflections	1851	3903	3316
No. of parameters	210	220	230
No. of restraints	1	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.21, -0.24	0.68, -0.29	0.25, -0.29

Computer programs: *COLLECT* (Nonius, 1998), *DIRAX/LSQ* (Duisenberg *et al.*, 2000), *EVALCCD* (Duisenberg *et al.*, 2003), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *SIR2004* (Burla *et al.*, 2005) and *PLATON* (Spek, 2009).

trated sulfuric acid (3 ml) was stirred at 373 K for 7 min. The reaction mixture was cooled to ambient temperature by the addition of ice and then extracted with ethyl acetate (3 × 50 ml). The combined organic extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The resulting crude products were subjected to column chromatographic purification over silica gel using heptane–ethyl acetate–acetic acid (1:2:0.04 *v/v/v*). Crystallization from ethyl acetate–ethanol (30:1 *v/v*) at ambient temperature and in the presence of air gave colourless crystals of (I)–(III) suitable for single-crystal X-ray diffraction. Compound (I): yield 35%, m.p. 449–450 K, HRMS *m/z* [*M*]⁺ found 309.1366, C₁₉H₁₉NO₃ requires 309.1365. Compound (II): yield 20%, m.p. 460–462 K, HRMS *m/z* [*M*]⁺ found 323.1525, C₂₀H₂₁NO₃ requires 323.1521. Compound (III): yield 41%, m.p. 497–499 K, HRMS *m/z* [*M*]⁺ found 337.1653, C₂₁H₂₁NO₃ requires 337.1678.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and subsequently treated as riding atoms. C-bound H atoms were permitted to ride in geometrically idealized positions, with C–H = 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic C–H), and with *U*_{iso}(H) = *kU*_{eq}(C), where *k* = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other

C-bound H atoms. H atoms bound to O atoms were permitted to ride at the positions located in difference maps, with *U*_{iso}(H) = 1.5*U*_{eq}(O), giving the O–H distances shown in Table 3. Several low-angle reflections, which had been wholly or partially attenuated by the beam stop, were omitted from

Figure 1
The molecular structure of the (6*R*,11*R*) enantiomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Figure 2

The molecular structure of the (6*R*,11*S*) enantiomer of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

the final refinements. The value of the Flack *x* parameter (Flack, 1983) for (I) was indeterminate (Flack & Bernardinelli, 2000); accordingly, Friedel-equivalent reflections were merged prior to the final refinement. Examination of the refined structures using *PLATON* (Spek, 2009) showed the presence of two small cavities in the structure of (II), centred at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and each of volume $24 \text{ \AA}^3$; these cavities are far too small to contain any plausible solvent molecule but, nonetheless, the largest peak in the difference map, *viz.* $0.68 \text{ e \AA}^{-3}$ at $(0.523, 0.482, 0.064)$, was very close to one of the cavities. However, application of the SQUEEZE procedure in *PLATON* revealed only one excess electron per cavity. Accordingly, we regard both the difference peak and the excess electron count as minor artefacts of the data.

3. Results and discussion

The molecules of (I)–(III) all contain two stereogenic centres at atoms C6 and C11 (Figs. 1–3). In (I), the exocyclic substituents at atoms C6 and C11 have a *cis* arrangement relative to the azepine ring, while those in (II) and (III) have a *trans* arrangement. For each compound, the reference molecule was selected as one having the *R* configuration at atom C6. On this basis, the reference molecule of (I) has the *R* configuration at atom C11, while those of (II) and (III) have the *S* configuration at atom C11. Compounds (II) and (III) crystallize as racemic mixtures, as shown by the centrosymmetric space group, but (I) crystallizes in the Sohnke space group $P2_1$. Hence, in the absence of twinning, for which no evidence was found, each crystal of (I) contains only one enantiomorph. It was not possible to determine the absolute configuration of the molecules in the crystal of (I) which was selected for data collection, and hence the configuration of the reference molecule was set to have the *R* configuration at atom C6, just as for (II) and (III).

Since the methyl 2-[*N*-(2-allylaryl)acetamido]-2-phenylacetates used as the precursors to (I)–(III) (see Scheme) are

Figure 3

The molecular structure of the (6*R*,11*S*) enantiomer of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

all racemic, the crystallization of (II) and (III) as racemic mixtures is unsurprising, and the method of synthesis makes it probable that (I) is formed in solution as a racemic mixture, which then crystallizes as a conglomerate rather than as a racemate. More problematic is the difference in relative configurations at atoms C6 and C11 between (I) on the one hand, where the configuration is (6*R**,11*R**), and (II) and (III) on the other, where the configuration is (6*RS*,11*SR*). Since the yields of the purified crystallized products are all significantly less than 50% (see *Experimental*), it is at least possible that the compounds may be formed as diastereoisomeric mixtures, and that the stereoisomers reported here are simply those which crystallized preferentially. However, it must be emphasized that there is no direct evidence on this point, and so this suggestion must be regarded as speculative.

Within the amide unit, the N5–C51 and C51–O51 distances (Table 2) are typical of those found in *N,N*-disubstituted amides (Allen *et al.*, 1987), while the C–O distances in the carboxylic acid units are fully consistent with the locations of the carboxylic H atoms as found in difference maps. The remaining bond distances present no unusual values. In each of (I)–(III), the azepine ring adopts a conformation intermediate between the boat and twist-boat forms (Evans & Boeyens, 1989; Entrena *et al.*, 1997). For (II) and (III), the ring-puckering parameters (Cremer & Pople, 1975) are very similar (Table 2), but the extent of the ring puckering, as shown by the overall puckering amplitude *Q*, is somewhat larger in (I) than in (II) and (III). This may be associated with the *cis* stereochemistry at atoms C6 and C11 in (I), compared with the *trans* arrangement in (II) and (III). The orientation of the amide unit relative to the azepine ring is very similar in all three compounds, as shown by the values of the torsion angles C6–N5–C51–O51 and C6–N5–C51–C52 (Table 2, and Figs. 1–3). By contrast, the orientation of the carboxylic acid unit varies widely, and this variation may be a consequence of the different hydrogen-bonding arrangements in the three structures. The conformations adopted by the ethyl group also

Table 2

Selected geometric parameters (Å, °) for (I)–(III).

Ring-puckering parameters are calculated for the atom sequence N5–C4a–C11a–C11–C10a–C6a–C6.

Bond lengths and angles			
Parameter	(I)	(II)	(III)
N5–C51	1.354 (3)	1.356 (3)	1.358 (3)
C51–O51	1.249 (3)	1.241 (3)	1.246 (3)
C61–O61	1.328 (3)	1.325 (3)	1.319 (3)
C61–O62	1.207 (3)	1.204 (3)	1.207 (3)
N5–C6–C61–O61	−155.01 (18)	−49.6 (2)	159.0 (2)
N5–C6–C61–O62	24.4 (3)	131.7 (2)	−24.6 (3)
C6–N5–C51–O51	0.7 (3)	6.0 (3)	3.1 (4)
C6–N5–C51–C52	179.1 (2)	−175.6 (2)	−179.2 (2)
C10–C10a–C11–C111	−18.3 (3)	−96.7 (2)	−89.4 (3)
C10a–C11–C111–C112	−168.0 (2)	71.1 (2)	169.2 (2)
Puckering parameters for seven-membered rings			
Q	1.079 (3)	0.842 (2)	0.800 (3)
φ_2	44.93 (14)	23.01 (13)	17.2 (2)
φ_3	274.6 (8)	311.3 (4)	313.2 (5)

vary widely, and since this substituent plays no part in the supramolecular assembly it seems likely that these conformations are determined by the methyl groups, based on atom C112 finding accommodation in whatever suitable spaces are available within the hydrogen-bonded structure.

Accordingly, despite their very similar constitutions, (I)–(III) differ not only in the relative configurations at their two stereogenic centres, but also in their crystallization characteristics, *i.e.* as a conglomerate for (I) and as a racemate for each of (II) and (III), with Z values of 2, 4 and 4, respectively, as well as in their molecular conformations. They also differ in their modes of supramolecular assembly, with the formation of a simple hydrogen-bonded chain in (II), a hydrogen-bonded sheet in (I) and a three-dimensional framework structure in (III). It is convenient to discuss the supramolecular assembly in the structures of (I)–(III) in the order of increasing complexity.

The O–H...O hydrogen bond in compound (II) (Table 3) links molecules related by a 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ into a $C(7)$ (Bernstein *et al.*, 1995) chain running parallel to the [010] direction. (Fig. 4). The two shortest intermolecular C–H...O contacts (Table 3) have H...O distances not significantly less than the sum of the van der Waals radii for H and O (2.61 Å; Bondi, 1964; Rowland & Taylor, 1996). In any event, both contacts have fairly small C–H...O angles (*cf.* Wood *et al.*, 2009), so that neither can be regarded as structurally significant. Two chains of this type, related to one another by inversion, pass through each unit cell but there are no direction-specific interactions between adjacent chains.

The supramolecular assembly in (I) and (III) can most readily be analysed in terms of a series of one-dimensional substructures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000). In (I), molecules related by a 2_1 screw axis are similarly linked by an O–H...O hydrogen bond to form a $C(7)$ chain running parallel to the [010] direction but, in contrast with (II), chains in (I) which are related by translation along the [101] direction

Figure 4

Part of the crystal structure of (II), showing the formation of a hydrogen-bonded (dashed lines) chain parallel to [010]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(-x + 1, y + \frac{1}{2}, -z + \frac{1}{2})$, $(-x + 1, y - \frac{1}{2}, -z + \frac{1}{2})$, $(x, y + 1, z)$ and $(x, y - 1, z)$, respectively.

are linked by a C–H...O hydrogen bond to form a sheet of $R_4^3(26)$ rings parallel to $(10\bar{1})$ (Fig. 5). The only other short intermolecular contact involves a low-acidity C–H bond from a methyl group and is thus unlikely to be structurally significant.

The molecules of (III) are linked into a three-dimensional framework structure by a combination of O–H...O, C–H...O and C–H... π (arene) hydrogen bonds (Table 3). The O–H...O hydrogen bond links molecules related by an n -glide plane at $y = \frac{3}{4}$ to form a $C(7)$ chain running parallel to the [101] direction (Fig. 6), and the C–H...O hydrogen bond links molecules related by a 2_1 screw axis along $(\frac{3}{4}, y, \frac{1}{4})$ to form a $C(8)$ chain running parallel to the [010] direction (Fig. 6). The combination of these two chains generates a sheet lying parallel to $(10\bar{1})$ and built from a single type of centrosymmetric $R_4^4(30)$ ring (Fig. 6). Sheets of this type are linked to form a continuous three-dimensional framework structure by the C–H... π (arene) hydrogen bond, which links molecules related by translation along the [100] direction (Fig. 7). The combination of chains along [100], [010] and [101] is sufficient to form a three-dimensional structure.

It is thus striking that none of (I)–(III) exhibits the $R_2^2(8)$ dimer motif so characteristic of simple carboxylic acids. Instead, all utilize atom O51 of the *N*-acetyl group as acceptor

Figure 5

A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded (dashed lines) sheet parallel to (101). For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

in an O—H...O hydrogen bond, and it is of interest briefly to compare the substructures which can be identified in the supramolecular assemblies of (I)–(III). In each of the structures, a *C*(7) chain motif can be identified built from O—H...O hydrogen bonds. However, as discussed above, these chains differ in that those in (I) and (II) contain molecules related by a 2_1 screw axis, whereas that in (III) contains molecules related by an *n*-glide plane. Similarly, sheets built from a combination of O—H...O and C—H...O hydrogen bonds can be identified in the structures of (I) and (III) (Figs. 5 and 6). Both sheets exhibit (4,4) topology (Batten & Robson, 1998). The ring sizes in the sheets in (I) and (III) differ, as do the numbers of hydrogen-bond acceptors within these rings, since in (I) amide atom O51 acts as a double acceptor of hydrogen bonds, unlike that in (III). However, within the sheet in (III) the constituent rings are centrosymmetric, while those in (I) are not centrosymmetric. Chain formation by

Figure 6

A stereoview of part of the crystal structure of (III), showing the formation of a hydrogen-bonded (dashed lines) sheet of $R_4^4(30)$ rings parallel to (101) and built from a combination of O—H...O and C—H...O hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

Figure 7

A stereoview of part of the crystal structure of (III), showing the formation of a chain parallel to [100] built from C—H... π (arene) hydrogen bonds (dashed lines). For the sake of clarity, H atoms not involved in the motif shown have been omitted.

Table 3

Hydrogen bonds and short intermolecular contacts ($\text{\AA}$, $^\circ$) for (I)–(III).

Cg1 represents the centroid of the C1–C4/C4a/C11a ring.

Compound	<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
(I)	O61—H61...O51 ⁱ	0.86	1.83	2.672 (2)	167
	C2—H2...O51 ⁱⁱ	0.95	2.49	3.309 (3)	144
	C112—H12A...O62 ⁱⁱⁱ	0.98	2.46	3.418 (4)	165
(II)	O61—H61...O51 ^{iv}	0.92	1.67	2.572 (2)	167
	C4—H4...O62 ^v	0.95	2.58	3.220 (3)	125
	C8—H8...O62 ^{vi}	0.95	2.58	3.405 (3)	145
(III)	O61—H61...O51 ^{vii}	0.86	1.76	2.575 (3)	156
	C9—H9...O62 ^{viii}	0.95	2.50	3.329 (3)	145
	C8—H8...Cg1 ^{ix}	0.95	2.75	3.569 (3)	144

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z$; (ii) $x + 1, y, z + 1$; (iii) $-x + 1, y + \frac{1}{2}, -z + 1$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (vii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (viii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x + 1, y, z$.

means of O—H...O hydrogen bonds has been extensively studied in keto acids, where the chain motif follows directly from the mutual disposition of the carboxyl and keto groups. Thus, γ -keto acids form *C*(7) chains (e.g. Thompson *et al.*, 2004; Malak *et al.*, 2006), δ -keto acids form *C*(8) chains (e.g. Davison, Kikolski *et al.*, 2004) and ε -keto acids form *C*(9) chains (e.g. Davison, Thompson *et al.*, 2004), while longer chain motifs are generated in steroidal keto acids (e.g. Kikolski *et al.*, 2006).

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supplementary materials

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Three closely related dibenzazepine carboxylic acids: hydrogen-bonded aggregation in one, two and three dimensions

Carlos M. Sanabría, Alirio Palma, Justo Cobo and Christopher Glidewell

Computing details

For all compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003). Program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005) for (I), (II); *SHELXS97* (Sheldrick, 2008) for (III). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(I) (6*R**,11*R**)-5-Acetyl-11-ethyl-6,11-dihydro-5*H*-dibenzo[*b,e*]azepine-6-carboxylic acid

Crystal data

C ₁₉ H ₁₉ NO ₃	$F(000) = 328$
$M_r = 309.35$	$D_x = 1.342 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: P 2yb	Cell parameters from 1853 reflections
$a = 8.8053 (3) \text{ \AA}$	$\theta = 3.2\text{--}27.5^\circ$
$b = 10.9821 (4) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 9.0080 (6) \text{ \AA}$	$T = 120 \text{ K}$
$\beta = 118.510 (3)^\circ$	Rod, colourless
$V = 765.45 (6) \text{ \AA}^3$	$0.26 \times 0.14 \times 0.10 \text{ mm}$
$Z = 2$	

Data collection

Bruker Nonius KappaCCD area-detector diffractometer	$T_{\min} = 0.977, T_{\max} = 0.991$
Radiation source: Bruker Nonius FR591 rotating anode	13276 measured reflections
Graphite monochromator	1851 independent reflections
Detector resolution: $9.091 \text{ pixels mm}^{-1}$	1638 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.049$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	$\theta_{\max} = 27.5^\circ, \theta_{\min} = 3.7^\circ$
	$h = -11 \rightarrow 11$
	$k = -14 \rightarrow 14$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.036$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.081$	Hydrogen site location: inferred from neighbouring sites
$S = 1.15$	
1851 reflections	
210 parameters	

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.1657P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6424 (3)	0.5942 (2)	0.7939 (3)	0.0186 (5)
H1	0.6599	0.6154	0.9031	0.022*
C2	0.7828 (3)	0.5595 (2)	0.7731 (3)	0.0211 (5)
H2	0.8953	0.5589	0.8678	0.025*
C3	0.7604 (3)	0.5255 (2)	0.6149 (3)	0.0202 (5)
H3	0.8563	0.4993	0.6019	0.024*
C4	0.5955 (3)	0.5306 (2)	0.4757 (3)	0.0166 (5)
H4	0.5780	0.5079	0.3669	0.020*
C4a	0.4576 (3)	0.5687 (2)	0.4973 (3)	0.0142 (5)
N5	0.2883 (2)	0.58197 (17)	0.3533 (2)	0.0132 (4)
C6	0.1469 (3)	0.4966 (2)	0.3244 (3)	0.0128 (4)
H6	0.0389	0.5461	0.2831	0.015*
C6a	0.1714 (3)	0.4295 (2)	0.4842 (3)	0.0145 (5)
C7	0.1243 (3)	0.3077 (2)	0.4737 (3)	0.0174 (5)
H7	0.0884	0.2652	0.3704	0.021*
C8	0.1286 (3)	0.2465 (2)	0.6107 (3)	0.0189 (5)
H8	0.0977	0.1628	0.6008	0.023*
C9	0.1780 (3)	0.3073 (2)	0.7616 (3)	0.0188 (5)
H9	0.1759	0.2670	0.8540	0.023*
C10	0.2305 (3)	0.4277 (2)	0.7762 (3)	0.0185 (5)
H10	0.2674	0.4685	0.8808	0.022*
C10a	0.2307 (3)	0.4909 (2)	0.6412 (3)	0.0151 (5)
C11	0.3097 (3)	0.6185 (2)	0.6677 (3)	0.0150 (5)
H11	0.2307	0.6694	0.5686	0.018*
C11a	0.4763 (3)	0.5982 (2)	0.6566 (3)	0.0145 (5)
C51	0.2534 (3)	0.6720 (2)	0.2388 (3)	0.0142 (5)
O51	0.10670 (19)	0.68043 (16)	0.11339 (19)	0.0180 (4)
C52	0.3950 (3)	0.7609 (2)	0.2675 (3)	0.0189 (5)
H52A	0.4784	0.7219	0.2397	0.028*
H52B	0.4537	0.7862	0.3862	0.028*
H52C	0.3452	0.8324	0.1952	0.028*
C61	0.1208 (3)	0.4093 (2)	0.1806 (3)	0.0145 (5)
O61	-0.0387 (2)	0.36474 (17)	0.10291 (19)	0.0186 (4)
H61	-0.0487	0.3107	0.0297	0.028*
O62	0.2327 (2)	0.38608 (17)	0.1438 (2)	0.0224 (4)
C111	0.3325 (3)	0.6837 (2)	0.8280 (3)	0.0202 (5)
H11A	0.2247	0.6761	0.8362	0.024*
H11B	0.4266	0.6440	0.9284	0.024*
C112	0.3752 (3)	0.8181 (2)	0.8272 (3)	0.0229 (5)
H12A	0.4821	0.8260	0.8195	0.034*
H12B	0.3905	0.8565	0.9317	0.034*
H12C	0.2804	0.8583	0.7300	0.034*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0214 (12)	0.0168 (12)	0.0133 (11)	−0.0021 (10)	0.0048 (10)	−0.0003 (10)
C2	0.0163 (12)	0.0170 (13)	0.0222 (13)	−0.0025 (9)	0.0027 (10)	0.0035 (10)
C3	0.0158 (11)	0.0198 (13)	0.0252 (13)	0.0018 (10)	0.0101 (11)	0.0052 (10)
C4	0.0191 (11)	0.0145 (12)	0.0168 (11)	−0.0002 (9)	0.0091 (10)	0.0012 (9)
C4a	0.0138 (11)	0.0128 (12)	0.0136 (11)	−0.0010 (8)	0.0045 (10)	0.0021 (9)
N5	0.0120 (9)	0.0137 (10)	0.0117 (9)	−0.0010 (7)	0.0038 (8)	0.0010 (8)
C6	0.0117 (10)	0.0148 (11)	0.0113 (10)	−0.0006 (8)	0.0049 (9)	−0.0002 (9)
C6a	0.0133 (11)	0.0176 (12)	0.0136 (11)	0.0010 (9)	0.0071 (9)	0.0004 (9)
C7	0.0156 (11)	0.0201 (12)	0.0151 (11)	−0.0004 (9)	0.0061 (9)	−0.0019 (9)
C8	0.0177 (12)	0.0162 (12)	0.0217 (12)	−0.0028 (10)	0.0085 (10)	0.0009 (10)
C9	0.0173 (12)	0.0222 (13)	0.0183 (12)	0.0008 (10)	0.0097 (10)	0.0054 (10)
C10	0.0172 (12)	0.0242 (13)	0.0135 (11)	0.0020 (10)	0.0069 (10)	−0.0006 (10)
C10a	0.0125 (10)	0.0167 (11)	0.0162 (11)	0.0006 (9)	0.0068 (9)	0.0002 (9)
C11	0.0152 (11)	0.0167 (12)	0.0135 (11)	−0.0009 (9)	0.0073 (9)	−0.0015 (9)
C11a	0.0184 (12)	0.0098 (10)	0.0156 (11)	−0.0010 (9)	0.0083 (10)	0.0006 (9)
C51	0.0168 (11)	0.0142 (11)	0.0121 (11)	0.0004 (9)	0.0074 (9)	−0.0020 (9)
O51	0.0161 (8)	0.0186 (9)	0.0150 (8)	0.0005 (7)	0.0040 (7)	0.0025 (7)
C52	0.0207 (12)	0.0162 (12)	0.0194 (12)	−0.0010 (10)	0.0092 (10)	0.0029 (10)
C61	0.0176 (11)	0.0127 (11)	0.0117 (10)	0.0001 (9)	0.0058 (9)	0.0022 (9)
O61	0.0176 (8)	0.0213 (9)	0.0150 (8)	−0.0045 (7)	0.0062 (7)	−0.0065 (7)
O62	0.0221 (9)	0.0252 (10)	0.0241 (9)	−0.0024 (7)	0.0144 (8)	−0.0062 (8)
C111	0.0243 (12)	0.0195 (13)	0.0176 (12)	−0.0018 (11)	0.0106 (10)	−0.0036 (11)
C112	0.0265 (13)	0.0208 (13)	0.0248 (13)	−0.0031 (10)	0.0151 (11)	−0.0065 (10)

Geometric parameters ($\text{\AA}$, $^\circ$)

C1—C2	1.388 (4)	C9—C10	1.386 (3)
C1—C11a	1.395 (3)	C9—H9	0.9500
C1—H1	0.9500	C10—C10a	1.401 (3)
C2—C3	1.393 (4)	C10—H10	0.9500
C2—H2	0.9500	C10a—C11	1.532 (3)
C3—C4	1.395 (3)	C11—C11a	1.533 (3)
C3—H3	0.9500	C11—C111	1.536 (3)
C4—C4a	1.383 (3)	C11—H11	1.0000
C4—H4	0.9500	C51—O51	1.249 (3)
C4a—C11a	1.402 (3)	C51—C52	1.506 (3)
C4a—N5	1.442 (3)	C52—H52A	0.9800
N5—C51	1.354 (3)	C52—H52B	0.9800
N5—C6	1.479 (3)	C52—H52C	0.9800
C6—C6a	1.538 (3)	C61—O62	1.207 (3)
C6—C61	1.538 (3)	C61—O61	1.328 (3)
C6—H6	1.0000	O61—H61	0.8602
C6a—C7	1.390 (3)	C111—C112	1.523 (4)
C6a—C10a	1.423 (3)	C111—H11A	0.9900
C7—C8	1.390 (3)	C111—H11B	0.9900
C7—H7	0.9500	C112—H12A	0.9800
C8—C9	1.386 (3)	C112—H12B	0.9800

C8—H8	0.9500	C112—H12C	0.9800
C2—C1—C11a	120.9 (2)	C10a—C10—H10	119.0
C2—C1—H1	119.5	C10—C10a—C6a	118.4 (2)
C11a—C1—H1	119.5	C10—C10a—C11	120.5 (2)
C1—C2—C3	120.7 (2)	C6a—C10a—C11	120.8 (2)
C1—C2—H2	119.6	C10a—C11—C11a	103.51 (18)
C3—C2—H2	119.6	C10a—C11—C111	114.78 (19)
C2—C3—C4	119.1 (2)	C11a—C11—C111	115.41 (19)
C2—C3—H3	120.4	C10a—C11—H11	107.6
C4—C3—H3	120.4	C11a—C11—H11	107.6
C4a—C4—C3	119.6 (2)	C111—C11—H11	107.6
C4a—C4—H4	120.2	C1—C11a—C4a	117.4 (2)
C3—C4—H4	120.2	C1—C11a—C11	125.3 (2)
C4—C4a—C11a	122.1 (2)	C4a—C11a—C11	116.87 (19)
C4—C4a—N5	120.27 (19)	O51—C51—N5	120.3 (2)
C11a—C4a—N5	117.61 (19)	O51—C51—C52	121.4 (2)
C51—N5—C4a	121.36 (18)	N5—C51—C52	118.30 (19)
C51—N5—C6	117.57 (18)	C51—C52—H52A	109.5
C4a—N5—C6	121.06 (17)	C51—C52—H52B	109.5
N5—C6—C6a	114.16 (18)	H52A—C52—H52B	109.5
N5—C6—C61	108.54 (17)	C51—C52—H52C	109.5
C6a—C6—C61	112.80 (19)	H52A—C52—H52C	109.5
N5—C6—H6	107.0	H52B—C52—H52C	109.5
C6a—C6—H6	107.0	O62—C61—O61	125.0 (2)
C61—C6—H6	107.0	O62—C61—C6	123.3 (2)
C7—C6a—C10a	118.7 (2)	O61—C61—C6	111.64 (18)
C7—C6a—C6	119.6 (2)	C61—O61—H61	110.7
C10a—C6a—C6	121.6 (2)	C112—C111—C11	111.7 (2)
C8—C7—C6a	121.6 (2)	C112—C111—H11A	109.3
C8—C7—H7	119.2	C11—C111—H11A	109.3
C6a—C7—H7	119.2	C112—C111—H11B	109.3
C9—C8—C7	120.0 (2)	C11—C111—H11B	109.3
C9—C8—H8	120.0	H11A—C111—H11B	108.0
C7—C8—H8	120.0	C111—C112—H12A	109.5
C8—C9—C10	119.2 (2)	C111—C112—H12B	109.5
C8—C9—H9	120.4	H12A—C112—H12B	109.5
C10—C9—H9	120.4	C111—C112—H12C	109.5
C9—C10—C10a	122.0 (2)	H12A—C112—H12C	109.5
C9—C10—H10	119.0	H12B—C112—H12C	109.5
C11a—C1—C2—C3	−1.3 (4)	C7—C6a—C10a—C11	170.7 (2)
C1—C2—C3—C4	2.1 (4)	C6—C6a—C10a—C11	−13.4 (3)
C2—C3—C4—C4a	−0.1 (4)	C10—C10a—C11—C11a	108.4 (2)
C3—C4—C4a—C11a	−2.7 (4)	C6a—C10a—C11—C11a	−65.6 (3)
C3—C4—C4a—N5	176.0 (2)	C10—C10a—C11—C111	−18.3 (3)
C4—C4a—N5—C51	−70.0 (3)	C6a—C10a—C11—C111	167.7 (2)
C11a—C4a—N5—C51	108.7 (2)	C2—C1—C11a—C4a	−1.4 (3)
C4—C4a—N5—C6	109.3 (2)	C2—C1—C11a—C11	171.5 (2)

C11a—C4a—N5—C6	−72.0 (3)	C4—C4a—C11a—C1	3.4 (3)
C51—N5—C6—C6a	−158.55 (19)	N5—C4a—C11a—C1	−175.3 (2)
C4a—N5—C6—C6a	22.1 (3)	C4—C4a—C11a—C11	−170.1 (2)
C51—N5—C6—C61	74.7 (2)	N5—C4a—C11a—C11	11.2 (3)
C4a—N5—C6—C61	−104.7 (2)	C10a—C11—C11a—C1	−103.1 (3)
N5—C6—C6a—C7	−141.2 (2)	C111—C11—C11a—C1	23.1 (4)
C61—C6—C6a—C7	−16.7 (3)	C10a—C11—C11a—C4a	69.8 (2)
N5—C6—C6a—C10a	42.9 (3)	C111—C11—C11a—C4a	−163.9 (2)
C61—C6—C6a—C10a	167.43 (19)	C4a—N5—C51—O51	178.7 (2)
C10a—C6a—C7—C8	2.2 (3)	C6—N5—C51—O51	−0.7 (3)
C6—C6a—C7—C8	−173.8 (2)	C4a—N5—C51—C52	−1.5 (3)
C6a—C7—C8—C9	1.0 (4)	C6—N5—C51—C52	179.1 (2)
C7—C8—C9—C10	−3.0 (3)	N5—C6—C61—O62	24.4 (3)
C8—C9—C10—C10a	1.8 (3)	C6a—C6—C61—O62	−103.1 (3)
C9—C10—C10a—C6a	1.4 (3)	N5—C6—C61—O61	−155.01 (18)
C9—C10—C10a—C11	−172.7 (2)	C6a—C6—C61—O61	77.5 (2)
C7—C6a—C10a—C10	−3.4 (3)	C10a—C11—C111—C112	−168.0 (2)
C6—C6a—C10a—C10	172.6 (2)	C11a—C11—C111—C112	71.7 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O61—H61 $\cdots$ O51 ⁱ	0.86	1.83	2.672 (2)	167
C2—H2 $\cdots$ O51 ⁱⁱ	0.95	2.49	3.309 (3)	144
C112—H12A $\cdots$ O62 ⁱⁱⁱ	0.98	2.46	3.418 (4)	165

Symmetry codes: (i) $-x, y-1/2, -z$; (ii) $x+1, y, z+1$; (iii) $-x+1, y+1/2, -z+1$.

(II) (6*RS*,11*SR*)-5-Acetyl-11-ethyl-2-methyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine-6-carboxylic acid

Crystal data

C₂₀H₂₁NO₃

M_r = 323.38

Monoclinic, *P*2₁/*c*

Hall symbol: $-P\ 2_1/c$

a = 15.2894 (16) Å

b = 10.760 (2) Å

c = 10.538 (2) Å

β = 100.990 (11)°

V = 1701.9 (5) Å³

Z = 4

F(000) = 688

D_x = 1.262 Mg m^{−3}

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3906 reflections

θ = 2.7–27.5°

μ = 0.09 mm^{−1}

T = 120 K

Block, colourless

0.41 × 0.30 × 0.24 mm

Data collection

Bruker Nonius KappaCCD area-detector
diffractometer

Radiation source: Bruker Nonius FR591
rotating anode

Graphite monochromator

Detector resolution: 9.091 pixels mm^{−1}

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2003)

T_{min} = 0.966, *T_{max}* = 0.980

28096 measured reflections

3903 independent reflections

2589 reflections with *I* > 2σ(*I*)

R_{int} = 0.092

$\theta_{\max}$ = 27.5°, $\theta_{\min}$ = 3.3°

h = −19→19

k = −13→13

l = −13→13

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.155$
 $S = 1.05$

3903 reflections

220 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 1.5377P]$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.11423 (15)	0.5736 (2)	0.1081 (2)	0.0183 (5)
H1	0.0551	0.5673	0.1234	0.022*
C2	0.13034 (15)	0.6464 (2)	0.0050 (2)	0.0200 (5)
C3	0.21783 (16)	0.6576 (2)	−0.0142 (2)	0.0203 (5)
H3	0.2303	0.7089	−0.0819	0.024*
C4	0.28655 (15)	0.5946 (2)	0.0642 (2)	0.0189 (5)
H4	0.3459	0.6025	0.0502	0.023*
C4a	0.26855 (14)	0.5197 (2)	0.1637 (2)	0.0160 (5)
N5	0.33846 (12)	0.45422 (17)	0.24821 (17)	0.0153 (4)
C6	0.36955 (15)	0.5095 (2)	0.3762 (2)	0.0164 (5)
H6	0.4184	0.4543	0.4213	0.020*
C6a	0.30137 (15)	0.5169 (2)	0.4643 (2)	0.0166 (5)
C7	0.33741 (16)	0.5563 (2)	0.5908 (2)	0.0216 (5)
H7	0.3989	0.5765	0.6123	0.026*
C8	0.28551 (17)	0.5662 (2)	0.6846 (2)	0.0257 (5)
H8	0.3111	0.5930	0.7694	0.031*
C9	0.19597 (18)	0.5366 (2)	0.6534 (2)	0.0267 (6)
H9	0.1594	0.5439	0.7165	0.032*
C10	0.15979 (16)	0.4962 (2)	0.5295 (2)	0.0220 (5)
H10	0.0983	0.4754	0.5094	0.026*
C10a	0.21130 (15)	0.4849 (2)	0.4325 (2)	0.0176 (5)
C11	0.16359 (14)	0.4346 (2)	0.3022 (2)	0.0180 (5)
H11	0.0985	0.4447	0.3014	0.022*
C11a	0.18239 (15)	0.5102 (2)	0.1891 (2)	0.0166 (5)
C21	0.05529 (16)	0.7126 (2)	−0.0825 (2)	0.0279 (6)
H21A	0.0756	0.7409	−0.1604	0.042*
H21B	0.0366	0.7844	−0.0371	0.042*
H21C	0.0049	0.6556	−0.1069	0.042*
C51	0.38517 (14)	0.3587 (2)	0.2100 (2)	0.0182 (5)
O51	0.44856 (11)	0.31255 (16)	0.28673 (15)	0.0231 (4)
C52	0.35754 (17)	0.3077 (2)	0.0754 (2)	0.0265 (6)
H52A	0.4064	0.3181	0.0282	0.040*
H52B	0.3049	0.3526	0.0305	0.040*
H52C	0.3433	0.2192	0.0800	0.040*
C61	0.41375 (15)	0.6350 (2)	0.3559 (2)	0.0188 (5)

O61	0.47155 (11)	0.61912 (15)	0.27831 (17)	0.0259 (4)
H61	0.4981	0.6936	0.2657	0.039*
O62	0.39924 (12)	0.73197 (15)	0.40492 (16)	0.0270 (4)
C111	0.17878 (16)	0.2930 (2)	0.2890 (2)	0.0204 (5)
H11A	0.1583	0.2681	0.1977	0.024*
H11B	0.2434	0.2751	0.3125	0.024*
C112	0.12941 (17)	0.2163 (2)	0.3747 (2)	0.0254 (5)
H12A	0.1478	0.2429	0.4648	0.038*
H12B	0.1437	0.1281	0.3673	0.038*
H12C	0.0651	0.2286	0.3472	0.038*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0180 (11)	0.0202 (11)	0.0166 (11)	0.0000 (9)	0.0034 (9)	−0.0008 (9)
C2	0.0249 (12)	0.0211 (12)	0.0128 (11)	0.0011 (9)	0.0008 (9)	−0.0013 (9)
C3	0.0278 (12)	0.0210 (11)	0.0117 (10)	−0.0006 (10)	0.0026 (9)	0.0011 (9)
C4	0.0209 (11)	0.0231 (12)	0.0137 (10)	−0.0016 (9)	0.0063 (9)	−0.0007 (9)
C4a	0.0189 (11)	0.0173 (11)	0.0117 (10)	0.0005 (9)	0.0026 (9)	−0.0007 (9)
N5	0.0161 (9)	0.0180 (9)	0.0118 (9)	0.0001 (7)	0.0026 (7)	0.0007 (7)
C6	0.0189 (11)	0.0188 (11)	0.0110 (10)	0.0003 (9)	0.0012 (8)	−0.0014 (9)
C6a	0.0236 (11)	0.0138 (10)	0.0134 (10)	0.0017 (9)	0.0057 (9)	0.0013 (8)
C7	0.0279 (12)	0.0214 (12)	0.0150 (11)	−0.0016 (10)	0.0028 (9)	−0.0002 (9)
C8	0.0385 (14)	0.0260 (13)	0.0129 (11)	−0.0029 (11)	0.0055 (10)	−0.0007 (10)
C9	0.0374 (14)	0.0294 (13)	0.0170 (12)	−0.0032 (11)	0.0144 (11)	−0.0013 (10)
C10	0.0256 (12)	0.0234 (12)	0.0190 (12)	−0.0039 (10)	0.0092 (10)	−0.0008 (10)
C10a	0.0230 (11)	0.0164 (11)	0.0139 (10)	0.0005 (9)	0.0049 (9)	0.0004 (9)
C11	0.0168 (11)	0.0241 (12)	0.0128 (10)	0.0001 (9)	0.0026 (9)	0.0025 (9)
C11a	0.0198 (11)	0.0185 (11)	0.0117 (10)	−0.0024 (9)	0.0032 (9)	−0.0015 (9)
C21	0.0264 (13)	0.0319 (14)	0.0240 (13)	0.0011 (11)	0.0008 (10)	0.0079 (11)
C51	0.0175 (11)	0.0200 (11)	0.0181 (11)	−0.0007 (9)	0.0055 (9)	0.0001 (9)
O51	0.0236 (9)	0.0262 (9)	0.0190 (8)	0.0066 (7)	0.0026 (7)	−0.0024 (7)
C52	0.0298 (13)	0.0286 (13)	0.0216 (12)	0.0045 (11)	0.0058 (10)	−0.0070 (11)
C61	0.0197 (11)	0.0220 (12)	0.0141 (10)	0.0007 (9)	0.0018 (9)	0.0018 (9)
O61	0.0279 (9)	0.0218 (9)	0.0323 (10)	−0.0053 (7)	0.0166 (8)	−0.0036 (7)
O62	0.0377 (10)	0.0196 (9)	0.0256 (9)	−0.0007 (7)	0.0111 (8)	−0.0024 (7)
C111	0.0246 (12)	0.0239 (12)	0.0132 (11)	−0.0057 (10)	0.0048 (9)	−0.0011 (9)
C112	0.0310 (13)	0.0257 (13)	0.0197 (12)	−0.0060 (10)	0.0054 (10)	0.0040 (10)

Geometric parameters ($\text{\AA}$, $^\circ$)

C1—C11a	1.393 (3)	C10—C10a	1.409 (3)
C1—C2	1.398 (3)	C10—H10	0.9500
C1—H1	0.9500	C10a—C11	1.527 (3)
C2—C3	1.396 (3)	C11—C11a	1.515 (3)
C2—C21	1.507 (3)	C11—C111	1.551 (3)
C3—C4	1.384 (3)	C11—H11	1.0000
C3—H3	0.9500	C21—H21A	0.9800
C4—C4a	1.390 (3)	C21—H21B	0.9800
C4—H4	0.9500	C21—H21C	0.9800

C4a—C11a	1.397 (3)	C51—O51	1.241 (3)
C4a—N5	1.439 (3)	C51—C52	1.504 (3)
N5—C51	1.356 (3)	C52—H52A	0.9800
N5—C6	1.468 (3)	C52—H52B	0.9800
C6—C6a	1.524 (3)	C52—H52C	0.9800
C6—C61	1.543 (3)	C61—O62	1.204 (3)
C6—H6	1.0000	C61—O61	1.325 (3)
C6a—C10a	1.397 (3)	O61—H61	0.9200
C6a—C7	1.407 (3)	C111—C112	1.526 (3)
C7—C8	1.385 (3)	C111—H11A	0.9900
C7—H7	0.9500	C111—H11B	0.9900
C8—C9	1.383 (4)	C112—H12A	0.9800
C8—H8	0.9500	C112—H12B	0.9800
C9—C10	1.387 (3)	C112—H12C	0.9800
C9—H9	0.9500		
C11a—C1—C2	121.9 (2)	C10—C10a—C11	116.5 (2)
C11a—C1—H1	119.1	C11a—C11—C10a	112.81 (19)
C2—C1—H1	119.1	C11a—C11—C111	113.73 (18)
C3—C2—C1	118.5 (2)	C10a—C11—C111	112.05 (18)
C3—C2—C21	120.6 (2)	C11a—C11—H11	105.8
C1—C2—C21	120.9 (2)	C10a—C11—H11	105.8
C4—C3—C2	120.7 (2)	C111—C11—H11	105.8
C4—C3—H3	119.7	C1—C11a—C4a	118.0 (2)
C2—C3—H3	119.7	C1—C11a—C11	120.9 (2)
C3—C4—C4a	119.8 (2)	C4a—C11a—C11	121.1 (2)
C3—C4—H4	120.1	C2—C21—H21A	109.5
C4a—C4—H4	120.1	C2—C21—H21B	109.5
C4—C4a—C11a	121.1 (2)	H21A—C21—H21B	109.5
C4—C4a—N5	121.3 (2)	C2—C21—H21C	109.5
C11a—C4a—N5	117.50 (19)	H21A—C21—H21C	109.5
C51—N5—C4a	123.97 (18)	H21B—C21—H21C	109.5
C51—N5—C6	118.90 (18)	O51—C51—N5	120.0 (2)
C4a—N5—C6	116.29 (17)	O51—C51—C52	120.8 (2)
N5—C6—C6a	116.21 (18)	N5—C51—C52	119.2 (2)
N5—C6—C61	107.51 (17)	C51—C52—H52A	109.5
C6a—C6—C61	113.99 (18)	C51—C52—H52B	109.5
N5—C6—H6	106.1	H52A—C52—H52B	109.5
C6a—C6—H6	106.1	C51—C52—H52C	109.5
C61—C6—H6	106.1	H52A—C52—H52C	109.5
C10a—C6a—C7	119.4 (2)	H52B—C52—H52C	109.5
C10a—C6a—C6	126.77 (19)	O62—C61—O61	125.2 (2)
C7—C6a—C6	113.8 (2)	O62—C61—C6	125.3 (2)
C8—C7—C6a	121.7 (2)	O61—C61—C6	109.52 (18)
C8—C7—H7	119.2	C61—O61—H61	110.0
C6a—C7—H7	119.2	C112—C111—C11	112.24 (19)
C9—C8—C7	119.2 (2)	C112—C111—H11A	109.2
C9—C8—H8	120.4	C11—C111—H11A	109.2
C7—C8—H8	120.4	C112—C111—H11B	109.2

C8—C9—C10	119.7 (2)	C11—C111—H11B	109.2
C8—C9—H9	120.2	H11A—C111—H11B	107.9
C10—C9—H9	120.2	C111—C112—H12A	109.5
C9—C10—C10a	122.1 (2)	C111—C112—H12B	109.5
C9—C10—H10	118.9	H12A—C112—H12B	109.5
C10a—C10—H10	118.9	C111—C112—H12C	109.5
C6a—C10a—C10	117.8 (2)	H12A—C112—H12C	109.5
C6a—C10a—C11	125.67 (19)	H12B—C112—H12C	109.5
C11a—C1—C2—C3	−1.7 (3)	C6—C6a—C10a—C11	0.6 (4)
C11a—C1—C2—C21	179.1 (2)	C9—C10—C10a—C6a	−0.5 (3)
C1—C2—C3—C4	2.2 (3)	C9—C10—C10a—C11	177.7 (2)
C21—C2—C3—C4	−178.5 (2)	C6a—C10a—C11—C11a	−48.5 (3)
C2—C3—C4—C4a	−0.3 (3)	C10—C10a—C11—C11a	133.4 (2)
C3—C4—C4a—C11a	−2.3 (3)	C6a—C10a—C11—C111	81.4 (3)
C3—C4—C4a—N5	−179.1 (2)	C10—C10a—C11—C111	−96.7 (2)
C4—C4a—N5—C51	−67.9 (3)	C2—C1—C11a—C4a	−0.8 (3)
C11a—C4a—N5—C51	115.2 (2)	C2—C1—C11a—C11	178.4 (2)
C4—C4a—N5—C6	101.4 (2)	C4—C4a—C11a—C1	2.8 (3)
C11a—C4a—N5—C6	−75.5 (2)	N5—C4a—C11a—C1	179.75 (19)
C51—N5—C6—C6a	−126.5 (2)	C4—C4a—C11a—C11	−176.4 (2)
C4a—N5—C6—C6a	63.6 (2)	N5—C4a—C11a—C11	0.5 (3)
C51—N5—C6—C61	104.4 (2)	C10a—C11—C11a—C1	−116.4 (2)
C4a—N5—C6—C61	−65.5 (2)	C111—C11—C11a—C1	114.6 (2)
N5—C6—C6a—C10a	−4.9 (3)	C10a—C11—C11a—C4a	62.8 (3)
C61—C6—C6a—C10a	121.0 (2)	C111—C11—C11a—C4a	−66.2 (3)
N5—C6—C6a—C7	172.59 (19)	C4a—N5—C51—O51	175.1 (2)
C61—C6—C6a—C7	−61.5 (3)	C6—N5—C51—O51	6.0 (3)
C10a—C6a—C7—C8	−1.1 (3)	C4a—N5—C51—C52	−6.6 (3)
C6—C6a—C7—C8	−178.8 (2)	C6—N5—C51—C52	−175.6 (2)
C6a—C7—C8—C9	0.0 (4)	N5—C6—C61—O62	131.7 (2)
C7—C8—C9—C10	0.8 (4)	C6a—C6—C61—O62	1.4 (3)
C8—C9—C10—C10a	−0.6 (4)	N5—C6—C61—O61	−49.6 (2)
C7—C6a—C10a—C10	1.3 (3)	C6a—C6—C61—O61	−179.92 (18)
C6—C6a—C10a—C10	178.6 (2)	C11a—C11—C111—C112	−159.48 (19)
C7—C6a—C10a—C11	−176.7 (2)	C10a—C11—C111—C112	71.1 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O61—H61...O51 ⁱ	0.92	1.67	2.572 (2)	167
C4—H4...O62 ⁱⁱ	0.95	2.58	3.220 (3)	125
C8—H8...O62 ⁱⁱⁱ	0.95	2.58	3.405 (3)	145

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $x, -y+3/2, z-1/2$; (iii) $x, -y+3/2, z+1/2$.

(III) (6*RS*,11*SR*)-5-Acetyl-11-ethyl-1,3-dimethyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine-6-carboxylic acid

Crystal data

$C_{21}H_{23}NO_3$	$F(000) = 720$
$M_r = 337.40$	$D_x = 1.250 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P 2_1 n$	Cell parameters from 3320 reflections
$a = 9.2283 (11) \text{ \AA}$	$\theta = 2.8\text{--}25.5^\circ$
$b = 16.691 (2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 11.9824 (18) \text{ \AA}$	$T = 120 \text{ K}$
$\beta = 103.820 (11)^\circ$	Block, colourless
$V = 1792.2 (4) \text{ \AA}^3$	$0.23 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Bruker Nonius KappaCCD area-detector diffractometer	$T_{\min} = 0.981, T_{\max} = 0.984$
Radiation source: Bruker Nonius FR591 rotating anode	27558 measured reflections
Graphite monochromator	3316 independent reflections
Detector resolution: $9.091 \text{ pixels mm}^{-1}$	2090 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.139$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	$\theta_{\max} = 25.5^\circ, \theta_{\min} = 3.9^\circ$
	$h = -11 \rightarrow 11$
	$k = -20 \rightarrow 19$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.120$	$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 1.5359P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
3316 reflections	$(\Delta/\sigma)_{\max} = 0.001$
230 parameters	$\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3227 (3)	0.48561 (16)	0.3898 (2)	0.0174 (6)
C2	0.2439 (3)	0.53647 (17)	0.4458 (2)	0.0197 (6)
H2	0.2072	0.5158	0.5076	0.024*
C3	0.2165 (3)	0.61670 (17)	0.4150 (2)	0.0205 (6)
C4	0.2709 (3)	0.64561 (17)	0.3246 (2)	0.0174 (6)
H4	0.2549	0.7001	0.3020	0.021*
C4a	0.3486 (3)	0.59547 (15)	0.2670 (2)	0.0141 (6)
N5	0.4052 (2)	0.62796 (12)	0.17360 (17)	0.0132 (5)
C6	0.5661 (3)	0.64307 (15)	0.1962 (2)	0.0146 (6)
H6	0.5817	0.6680	0.1241	0.018*
C6a	0.6650 (3)	0.56840 (16)	0.2147 (2)	0.0155 (6)
C7	0.8137 (3)	0.58138 (16)	0.2103 (2)	0.0172 (6)
H7	0.8446	0.6342	0.1972	0.021*

C8	0.9167 (3)	0.51994 (17)	0.2243 (2)	0.0206 (6)
H8	1.0173	0.5308	0.2228	0.025*
C9	0.8724 (3)	0.44232 (17)	0.2404 (2)	0.0225 (7)
H9	0.9418	0.3993	0.2503	0.027*
C10	0.7248 (3)	0.42871 (16)	0.2419 (2)	0.0194 (6)
H10	0.6940	0.3753	0.2510	0.023*
C10a	0.6187 (3)	0.49019 (16)	0.2306 (2)	0.0149 (6)
C11	0.4610 (3)	0.46222 (16)	0.2309 (2)	0.0161 (6)
H11	0.4741	0.4097	0.2723	0.019*
C11a	0.3770 (3)	0.51523 (16)	0.2974 (2)	0.0148 (6)
C12	0.3465 (3)	0.39932 (17)	0.4299 (2)	0.0256 (7)
H12A	0.2968	0.3901	0.4925	0.038*
H12B	0.4536	0.3889	0.4575	0.038*
H12C	0.3045	0.3633	0.3658	0.038*
C31	0.1284 (4)	0.67011 (19)	0.4762 (3)	0.0313 (8)
H31A	0.0923	0.7169	0.4282	0.047*
H31B	0.1925	0.6878	0.5495	0.047*
H31C	0.0432	0.6403	0.4905	0.047*
C51	0.3141 (3)	0.65751 (16)	0.0762 (2)	0.0163 (6)
O51	0.3684 (2)	0.69395 (11)	0.00503 (15)	0.0212 (5)
C52	0.1502 (3)	0.64286 (18)	0.0543 (2)	0.0231 (7)
H52A	0.1063	0.6805	0.0997	0.035*
H52B	0.1325	0.5879	0.0764	0.035*
H52C	0.1042	0.6506	−0.0275	0.035*
C61	0.6070 (3)	0.70912 (16)	0.2882 (2)	0.0160 (6)
O61	0.7497 (2)	0.70908 (11)	0.34155 (16)	0.0223 (5)
H61	0.7652	0.7474	0.3911	0.034*
O62	0.5169 (2)	0.75766 (11)	0.30369 (18)	0.0268 (5)
C111	0.3721 (3)	0.44278 (17)	0.1067 (2)	0.0190 (6)
H11A	0.3513	0.4933	0.0626	0.023*
H11B	0.4343	0.4087	0.0691	0.023*
C112	0.2253 (3)	0.40005 (18)	0.1024 (3)	0.0273 (7)
H11C	0.2449	0.3498	0.1457	0.041*
H11D	0.1752	0.3885	0.0223	0.041*
H11E	0.1612	0.4344	0.1365	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0145 (15)	0.0211 (15)	0.0154 (13)	−0.0016 (12)	0.0008 (11)	0.0038 (12)
C2	0.0160 (16)	0.0306 (17)	0.0129 (13)	−0.0002 (12)	0.0044 (11)	0.0035 (12)
C3	0.0161 (16)	0.0286 (17)	0.0157 (14)	0.0010 (12)	0.0016 (12)	−0.0018 (12)
C4	0.0174 (16)	0.0171 (15)	0.0165 (13)	0.0010 (12)	0.0017 (11)	−0.0019 (11)
C4a	0.0119 (14)	0.0192 (14)	0.0095 (13)	−0.0024 (11)	−0.0011 (11)	0.0001 (11)
N5	0.0127 (12)	0.0133 (11)	0.0129 (11)	−0.0004 (9)	0.0014 (9)	0.0021 (9)
C6	0.0131 (15)	0.0160 (14)	0.0142 (13)	−0.0015 (11)	0.0022 (11)	0.0026 (11)
C6a	0.0185 (15)	0.0173 (14)	0.0103 (13)	0.0000 (12)	0.0026 (11)	−0.0020 (11)
C7	0.0188 (16)	0.0189 (15)	0.0151 (14)	−0.0031 (12)	0.0063 (12)	−0.0019 (11)
C8	0.0163 (16)	0.0257 (16)	0.0199 (14)	−0.0034 (13)	0.0048 (12)	−0.0067 (12)
C9	0.0192 (16)	0.0247 (16)	0.0232 (15)	0.0058 (12)	0.0040 (12)	−0.0013 (13)

C10	0.0230 (17)	0.0159 (15)	0.0199 (14)	−0.0009 (12)	0.0063 (12)	−0.0012 (12)
C10a	0.0176 (15)	0.0166 (14)	0.0102 (12)	−0.0011 (11)	0.0026 (11)	0.0008 (11)
C11	0.0177 (16)	0.0137 (14)	0.0165 (14)	−0.0002 (11)	0.0032 (11)	0.0002 (11)
C11a	0.0123 (15)	0.0176 (14)	0.0134 (13)	−0.0004 (11)	0.0011 (11)	−0.0003 (11)
C12	0.0296 (18)	0.0251 (16)	0.0242 (16)	−0.0015 (14)	0.0101 (14)	0.0099 (13)
C31	0.035 (2)	0.0386 (19)	0.0241 (16)	0.0080 (15)	0.0154 (14)	−0.0010 (14)
C51	0.0174 (16)	0.0154 (14)	0.0162 (14)	−0.0002 (11)	0.0040 (12)	−0.0008 (11)
O51	0.0179 (11)	0.0247 (11)	0.0200 (10)	0.0004 (9)	0.0027 (8)	0.0088 (9)
C52	0.0161 (16)	0.0306 (17)	0.0209 (15)	−0.0009 (13)	0.0012 (12)	0.0046 (13)
C61	0.0154 (16)	0.0144 (14)	0.0167 (14)	−0.0036 (12)	0.0011 (11)	0.0019 (11)
O61	0.0175 (11)	0.0236 (11)	0.0233 (10)	0.0012 (8)	−0.0005 (8)	−0.0111 (9)
O62	0.0214 (12)	0.0189 (11)	0.0375 (12)	0.0027 (9)	0.0020 (9)	−0.0101 (9)
C111	0.0190 (16)	0.0210 (15)	0.0175 (14)	−0.0034 (12)	0.0051 (12)	−0.0051 (12)
C112	0.0257 (18)	0.0274 (17)	0.0284 (17)	−0.0079 (14)	0.0057 (14)	−0.0074 (13)

Geometric parameters (Å, °)

C1—C2	1.390 (4)	C10—H10	0.9500
C1—C11a	1.408 (4)	C10a—C11	1.529 (4)
C1—C12	1.518 (4)	C11—C11a	1.522 (4)
C2—C3	1.396 (4)	C11—C111	1.552 (4)
C2—H2	0.9500	C11—H11	1.0000
C3—C4	1.384 (4)	C12—H12A	0.9800
C3—C31	1.509 (4)	C12—H12B	0.9800
C4—C4a	1.389 (4)	C12—H12C	0.9800
C4—H4	0.9500	C31—H31A	0.9800
C4a—C11a	1.396 (4)	C31—H31B	0.9800
C4a—N5	1.448 (3)	C31—H31C	0.9800
N5—C51	1.358 (3)	C51—O51	1.246 (3)
N5—C6	1.466 (3)	C51—C52	1.492 (4)
C6—C6a	1.529 (4)	C52—H52A	0.9800
C6—C61	1.541 (4)	C52—H52B	0.9800
C6—H6	1.0000	C52—H52C	0.9800
C6a—C10a	1.400 (4)	C61—O62	1.207 (3)
C6a—C7	1.403 (4)	C61—O61	1.319 (3)
C7—C8	1.381 (4)	O61—H61	0.8604
C7—H7	0.9500	C111—C112	1.521 (4)
C8—C9	1.386 (4)	C111—H11A	0.9900
C8—H8	0.9500	C111—H11B	0.9900
C9—C10	1.385 (4)	C112—H11C	0.9800
C9—H9	0.9500	C112—H11D	0.9800
C10—C10a	1.402 (4)	C112—H11E	0.9800
C2—C1—C11a	119.3 (2)	C10a—C11—C111	110.3 (2)
C2—C1—C12	118.6 (2)	C11a—C11—H11	105.4
C11a—C1—C12	122.1 (2)	C10a—C11—H11	105.4
C1—C2—C3	122.8 (3)	C111—C11—H11	105.4
C1—C2—H2	118.6	C4a—C11a—C1	117.6 (2)
C3—C2—H2	118.6	C4a—C11a—C11	120.5 (2)
C4—C3—C2	117.7 (3)	C1—C11a—C11	121.9 (2)

C4—C3—C31	120.8 (3)	C1—C12—H12A	109.5
C2—C3—C31	121.5 (3)	C1—C12—H12B	109.5
C3—C4—C4a	120.4 (3)	H12A—C12—H12B	109.5
C3—C4—H4	119.8	C1—C12—H12C	109.5
C4a—C4—H4	119.8	H12A—C12—H12C	109.5
C4—C4a—C11a	122.3 (2)	H12B—C12—H12C	109.5
C4—C4a—N5	118.9 (2)	C3—C31—H31A	109.5
C11a—C4a—N5	118.8 (2)	C3—C31—H31B	109.5
C51—N5—C4a	122.4 (2)	H31A—C31—H31B	109.5
C51—N5—C6	119.2 (2)	C3—C31—H31C	109.5
C4a—N5—C6	117.2 (2)	H31A—C31—H31C	109.5
N5—C6—C6a	115.4 (2)	H31B—C31—H31C	109.5
N5—C6—C61	108.6 (2)	O51—C51—N5	119.8 (2)
C6a—C6—C61	116.3 (2)	O51—C51—C52	121.1 (2)
N5—C6—H6	105.1	N5—C51—C52	119.0 (2)
C6a—C6—H6	105.1	C51—C52—H52A	109.5
C61—C6—H6	105.1	C51—C52—H52B	109.5
C10a—C6a—C7	118.8 (2)	H52A—C52—H52B	109.5
C10a—C6a—C6	126.1 (2)	C51—C52—H52C	109.5
C7—C6a—C6	115.1 (2)	H52A—C52—H52C	109.5
C8—C7—C6a	122.1 (3)	H52B—C52—H52C	109.5
C8—C7—H7	118.9	O62—C61—O61	124.8 (2)
C6a—C7—H7	118.9	O62—C61—C6	122.0 (2)
C7—C8—C9	119.6 (3)	O61—C61—C6	113.1 (2)
C7—C8—H8	120.2	C61—O61—H61	108.4
C9—C8—H8	120.2	C112—C111—C11	113.2 (2)
C10—C9—C8	118.6 (3)	C112—C111—H11A	108.9
C10—C9—H9	120.7	C11—C111—H11A	108.9
C8—C9—H9	120.7	C112—C111—H11B	108.9
C9—C10—C10a	123.0 (3)	C11—C111—H11B	108.9
C9—C10—H10	118.5	H11A—C111—H11B	107.8
C10a—C10—H10	118.5	C111—C112—H11C	109.5
C6a—C10a—C10	117.8 (2)	C111—C112—H11D	109.5
C6a—C10a—C11	127.3 (2)	H11C—C112—H11D	109.5
C10—C10a—C11	114.8 (2)	C111—C112—H11E	109.5
C11a—C11—C10a	115.4 (2)	H11C—C112—H11E	109.5
C11a—C11—C111	113.9 (2)	H11D—C112—H11E	109.5
C11a—C1—C2—C3	−0.5 (4)	C9—C10—C10a—C6a	1.4 (4)
C12—C1—C2—C3	180.0 (3)	C9—C10—C10a—C11	178.3 (2)
C1—C2—C3—C4	0.0 (4)	C6a—C10a—C11—C11a	−43.6 (4)
C1—C2—C3—C31	179.0 (3)	C10—C10a—C11—C11a	139.8 (2)
C2—C3—C4—C4a	0.6 (4)	C6a—C10a—C11—C111	87.1 (3)
C31—C3—C4—C4a	−178.4 (3)	C10—C10a—C11—C111	−89.4 (3)
C3—C4—C4a—C11a	−0.8 (4)	C4—C4a—C11a—C1	0.4 (4)
C3—C4—C4a—N5	−179.4 (2)	N5—C4a—C11a—C1	179.0 (2)
C4—C4a—N5—C51	−62.8 (3)	C4—C4a—C11a—C11	179.3 (2)
C11a—C4a—N5—C51	118.6 (3)	N5—C4a—C11a—C11	−2.1 (4)
C4—C4a—N5—C6	105.2 (3)	C2—C1—C11a—C4a	0.2 (4)

C11a—C4a—N5—C6	−73.5 (3)	C12—C1—C11a—C4a	179.8 (2)
C51—N5—C6—C6a	−123.6 (2)	C2—C1—C11a—C11	−178.6 (2)
C4a—N5—C6—C6a	68.0 (3)	C12—C1—C11a—C11	0.9 (4)
C51—N5—C6—C61	103.6 (3)	C10a—C11—C11a—C4a	59.8 (3)
C4a—N5—C6—C61	−64.8 (3)	C111—C11—C11a—C4a	−69.3 (3)
N5—C6—C6a—C10a	−11.2 (4)	C10a—C11—C11a—C1	−121.4 (3)
C61—C6—C6a—C10a	117.9 (3)	C111—C11—C11a—C1	109.5 (3)
N5—C6—C6a—C7	166.2 (2)	C4a—N5—C51—O51	170.9 (2)
C61—C6—C6a—C7	−64.7 (3)	C6—N5—C51—O51	3.1 (4)
C10a—C6a—C7—C8	−1.8 (4)	C4a—N5—C51—C52	−11.5 (4)
C6—C6a—C7—C8	−179.4 (2)	C6—N5—C51—C52	−179.2 (2)
C6a—C7—C8—C9	1.6 (4)	N5—C6—C61—O62	−24.6 (3)
C7—C8—C9—C10	0.1 (4)	C6a—C6—C61—O62	−156.9 (2)
C8—C9—C10—C10a	−1.6 (4)	N5—C6—C61—O61	159.0 (2)
C7—C6a—C10a—C10	0.4 (4)	C6a—C6—C61—O61	26.7 (3)
C6—C6a—C10a—C10	177.6 (2)	C11a—C11—C111—C112	−59.2 (3)
C7—C6a—C10a—C11	−176.1 (2)	C10a—C11—C111—C112	169.2 (2)
C6—C6a—C10a—C11	1.1 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O61—H61 $\cdots$ O51 ⁱ	0.86	1.76	2.575 (3)	156
C9—H9 $\cdots$ O62 ⁱⁱ	0.95	2.50	3.329 (3)	145
C8—H8 $\cdots$ Cg1 ⁱⁱⁱ	0.95	2.75	3.569 (3)	144

Symmetry codes: (i) $x+1/2, -y+3/2, z+1/2$; (ii) $-x+3/2, y-1/2, -z+1/2$; (iii) $x+1, y, z$.

Selected geometric parameters (Å, °) for (I)–(III)

Bond lengths and angles

Parameter	(I)	(II)	(III)
N5—C51	1.354 (3)	1.356 (3)	1.358 (3)
C51—O51	1.249 (3)	1.241 (3)	1.246 (3)
C61—O61	1.328 (3)	1.325 (3)	1.319 (3)
C61—O62	1.207(3)	1.204 (3)	1.207 (3)
N5—C6—C61—O61	−155.01 (18)	−49.6 (2)	159.0 (2)
N5—C6—C61—O62	24.4 (3)	131.7 (2)	−24.6 (3)
C6—N5—C51—O51	0.7 (3)	6.0 (3)	3.1 (4)
C6—N5—C51—C52	179.1 (2)	−175.6 (2)	−179.2 (2)
C10—C10a—C11—C111	−18.3 (3)	−96.7 (2)	−89.4 (3)
C10a—C11—C111—C112	−168.0 (2)	71.1 (2)	169.2 (2)

Puckering parameters for seven-membered rings

<i>Q</i>	1.079 (3)	0.842 (2)	0.800 (3)
φ_2	44.93 (14)	23.01 (13)	17.2 (2)
φ_3	274.6 (8)	311.3 (4)	313.2 (5)

Ring-puckering parameters are calculated for the atom sequence N5—C4a—C11a—C11—C10a—C6a—C6

Hydrogen bonds and short intermolecular contacts ($\text{\AA}$, $^\circ$) for (I)–(III)

Compound	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(I)	O61—H61 $\cdots$ O51 ⁱ	0.86	1.83	2.672 (2)	167
	C2—H2 $\cdots$ O51 ⁱⁱ	0.95	2.49	3.309 (3)	144
	C112—				
	H12A $\cdots$ O62 ⁱⁱⁱ	0.98	2.46	3.418 (4)	165
(II)	O61—H61 $\cdots$ O51 ^{iv}	0.92	1.67	2.572 (2)	167
	C4—H4 $\cdots$ O62 ^v	0.95	2.58	3.220 (3)	125
	C8—H8 $\cdots$ O62 ^{vi}	0.95	2.58	3.405 (3)	145
(III)	O61—H61 $\cdots$ O51 ^{vii}	0.86	1.76	2.575 (3)	156
	C9—H9 $\cdots$ O62 ^{viii}	0.95	2.50	3.329 (3)	145
	C8—H8 $\cdots$ Cg1 ^{ix}	0.95	2.75	3.569 (3)	144

Cg1 represents the centroid of the ring C1–C4/C4a/C11a. Symmetry codes: (i) $-x, y - 1/2, -z$; (ii) $x + 1, y, z + 1$; (iii) $-x + 1, y + 1/2, -z + 1$; (iv) $-x + 1, y + 1/2, -z + 1/2$; (v) $x, -y + 3/2, z - 1/2$; (vi) $x, -y + 3/2, z + 1/2$; (vii) $x + 1/2, -y + 3/2, z + 1/2$; (viii) $-x + 3/2, y - 1/2, -z + 1/2$; (ix) $x + 1, y, z$.