

1,4a-Dimethyl-6-methylene-5-(5,5,6,6-tetracyano-2-methylcyclohex-2-enylmethyl)decahydronaphthalene-1-carboxylic acid: a *trans*-commenic acid derivative

Nezha Rejouani,^a Aziz Auhmani,^a My Youssef Ait Itto,^a Ahmed Benharref^a and Jean-Claude Daran^{b*}

^aLaboratoire de Chimie Biomoléculaire, Substances Naturelles et Réactivité, Equipe de Chimie des Substances Naturelles, Département de Chimie, Faculté des Sciences Semlalia, BP 2390 Marrakech, Morocco, and ^bLaboratoire de Chimie de Coordination, UPR CNRS 8241, 205 route de Narbonne, 31077 Toulouse Cedex, France
Correspondence e-mail: daran@lcc-toulouse.fr

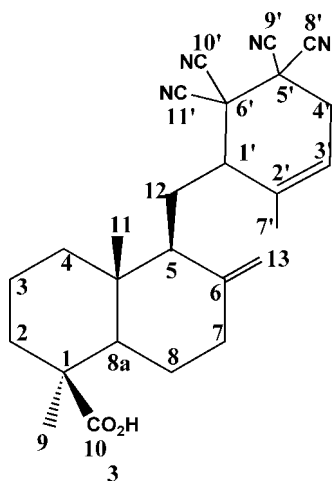
Received 18 September 2007; accepted 10 January 2008

Key indicators: single-crystal X-ray study; $T = 180$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.038; wR factor = 0.086; data-to-parameter ratio = 8.9.

In the search for cancer chemopreventive agents, we have studied the Diels–Alder reaction of *trans*-commenic acid with tetracyanoethylene in the presence of SiO_2 as catalyst. The title cycloadduct, $\text{C}_{26}\text{H}_{30}\text{N}_4\text{O}_2$, was obtained in 75% yield. The molecules are arranged in pairs through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, forming an $R_2^2(8)$ ring motif. Both the fused cyclohexyl rings adopt a chair conformation, whereas the nonfused ring adopts a half-chair conformation.

Related literature

For literature on anti-tumour activity, see: Bouhal *et al.* (1988); Iwamoto *et al.* (2001). For structural analyses, see: Etter *et al.* (1990); Bernstein *et al.* (1995); Cremer & Pople (1975). For the treatment of disordered solvent, see: Spek (2003).



Experimental

Crystal data

$\text{C}_{26}\text{H}_{30}\text{N}_4\text{O}_2$
 $M_r = 430.54$
Monoclinic, $C2$
 $a = 30.664$ (4) Å
 $b = 11.8233$ (19) Å
 $c = 7.1857$ (10) Å
 $\beta = 93.260$ (12)°

$V = 2600.9$ (6) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 180$ (2) K
 $0.52 \times 0.08 \times 0.07$ mm

Data collection

Oxford Diffraction Xcalibur
Sapphire-I diffractometer
Absorption correction: none
5114 measured reflections

2615 independent reflections
1302 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.085$
 $S = 0.82$
2615 reflections
293 parameters

1 restraint
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.13$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.12$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O9}-\text{H9}\cdots\text{O9}^{\text{i}}$	0.84	1.79	2.631 (3)	178

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2042).

References

- Altomare, A., Burla, M. C., Camalli, M., Casciarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bouhal, K., Meynadier, J. M., Peyron, J. L., Peyron, L., Marion, J. P., Bonetti, G. & Meynadier, J. (1988). *Le Cade en Dermatologie, Parfums, Cosmétiques et Aromes*, **83**, 73–82.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Iwamoto, M., Ohtsu, H., Tokuda, H., Nishino, H., Matasunaga, S. & Tanaka, R. (2001). *Bioorg. Med. Chem.* **9**, 1911–1921.
- Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.31.5. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2008). E64, o475 [doi:10.1107/S1600536808001086]

1,4a-Dimethyl-6-methylene-5-(5,5,6,6-tetracyano-2-methylcyclohex-2-enylmethyl)decahydronaphthalene-1-carboxylic acid: a *trans*-communic acid derivative

N. Rejouani, A. Auhmani, M. Y. Ait Itto, A. Benharref and J.-C. Daran

Comment

Juniperus oxycedrus has been used in traditional folk medicine for the treatment of chronic eczema and other several skin diseases (Bouhal *et al.*, 1988). *Trans* communic acid **1** is one of the compounds which were isolated from *Juniperusoxycedrus* and known by its moderate anti-tumor activity (Iwamoto *et al.*, 2001). In the search for cancer chemo preventive agents with strong activity, we have studied the Diels-Alder reaction of *trans* communic acid **1** with tetracyanoethylene **2** in the presence of SiO₂ as catalyst (Fig.1). One cycloadduct **3** was obtained in 75% yield.

Its structure was identified as 1,4a-Dimethyl-6-methylene-5-(5,5,6,6-tetracyano-2-methylcyclohex-2-enylmethyl)-decahydronaphthalene-1-carboxylic acid using spectral methods including ¹H and ¹³C NMR and confirmed by an X-ray crystallographic analysis. The ¹H NMR spectrum of **3** exhibits three methyl singlets at 1.96, 1.29 and 0.69 p.p.m., a triplet (J=3 Hz, at 5.57ppm) due to proton H-3' and two singlets (at 4.50 and 5.08 p.p.m.) assigned to methylenic protons at 13 position. The ¹³C NMR spectra reveals twenty six signals including specially a carbonyl group at 183.36 p.p.m. and four cyano group signals at 109.19; 110.07; 110.94 and 111.54ppm.

The molecule is build up by two fused six cyclohexyl rings linked linked through a CH₂ spacer to a tetracyano-2-methylcyclohexyl ring (Fig. 2). The fused cyclohexyl rings, C1 to C8a and C4A to C8A, adopt a chair conformation as indicated by the puckering parameters [Q= 0.533 (6)°, 0.576 (6)° and θ= 0. 0(6)°, 0.4 (6)°, Cremer & Pople, (1975)]. The non fused cyclohexyl ring adopt a half-chair conformation[Q= 0.510 (6)° and θ= 50.7 (5)°]. The occurrence of O—H···O hydrogen bonds form pairs of molecules through a R²₂(8) ring motif (Etter *et al.*, 1990; Bernstein *et al.*, 1995) (Fig. 3).

Experimental

To a solution of Compound **1**(1 g, 2.5 mmol) in 20 ml of dichloromethane, was added tetracyanoethylene (TCNE)(0.32 g, 2.5 mmol). The mixture was refluxed for 72 h. After cooling, the solvent was removed by evaporation under reduced pressure. The obtained residue was purified by chromatography on silica gel column (eluent: hexane/ethyl acetate 90/10), then the isolated product was recrystallized from ethyl acetate to give compound **3**(750 mg, 75%).

Colourless crystal, mp=208–210°C (ethyl acetate). ¹H NMR (300 MHz, CDCl₃)δ (p.p.m.): 5.57 (t, 1H, J=4.45 Hz); 5.08 (s, 1H); 4.50 (s, 1H); 3.28 (br d, 1H, J=11.5 Hz); 3.00 (m, 2H); 2.48 (br d, 1H, J=11.5 Hz); 2.29–1.96 (m, 5H); 1.92 (s, 3H); 1.81 (m, 3H); 1.62 (m, 1H); 1.45 (dd, 1H, J=12.21 and 2.60); 1.29 (s, 3H); 1.26 (m, 2H); 1.15 (m, 1H); 0.69 (s, 3H). ¹³C NMR δ (p.p.m.) CDCl₃: 12.64 C11, 19.85 C3, 21.78 C7, 25.59 C8, 26.13 C4, 29.01 C9, 31.75 C12, 37.70 C2, 38.07 C4', 38.58 C7, 39.56 C4a, 41.37 C6', 41.74 C1', 43.41 C5', 44.29 C1, 51.63 C5, 56.47 C8a, 107.59 C13, 109.19 C8', 110.07 C9', 110.94 C10', 111.54 C11', 116.37 C3', 135.27 C6, 147.14 C2', 183.36 C10

Refinement

All H atoms attached to C atoms and O atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic), 0.99 Å (methylene), 0.98 Å (methyl), 1.0 Å (methine) and O—H = 0.84 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic, methine, methylene})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl \& hydroxyl})$. In the absence of significant anomalous scattering, the absolute configuration could not be reliably determined and then the Friedel pairs were merged and any references to the Flack parameter were removed. Some residual electron density were difficult to modelize and therefore, the SQUEEZE function of *PLATON* (Spek, 2003) was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. There are two cavities of 158 Å³ per unit cell. *PLATON* estimated that each cavity contains about 11 electrons. Owing to the solvent used for crystallization, one may estimate that the voids contain 0.25 ethyl acetate molecule.

Figures

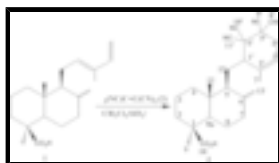


Fig. 1. Scheme showing the synthetic pathway for the title compound.

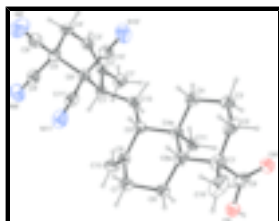


Fig. 2. Molecular view of compound 3 with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.



Fig. 3. Partial packing view showing pair of molecules connected by O—H...O hydrogen bonds and forming a $R_2^2(8)$ ring motif. Hydrogen bonds are shown as dashed lines. Hydrogen not involved in hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $1 - x, y, 1 - z$].

1,4a-Dimethyl-6-methylene-5-(5,5,6,6-tetracyano-2-methylcyclohex-2-enylmethyl)decahydronaphthalene-1-carboxylic acid ?

Crystal data

$\text{C}_{26}\text{H}_{30}\text{N}_4\text{O}_2$

$M_r = 430.54$

Monoclinic, $C2$

Hall symbol: C 2y

$a = 30.664 (4) \text{ \AA}$

$b = 11.8233 (19) \text{ \AA}$

$c = 7.1857 (10) \text{ \AA}$

$\beta = 93.260 (12)^\circ$

$F_{000} = 920$

$D_x = 1.099 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 907 reflections

$\theta = 3.1\text{--}26.4^\circ$

$\mu = 0.07 \text{ mm}^{-1}$

$T = 180 (2) \text{ K}$

Needle, colorless

$V = 2600.9 (6) \text{ \AA}^3$
 $Z = 4$

$0.52 \times 0.08 \times 0.07 \text{ mm}$

Data collection

Oxford-Diffraction Xcalibur Sapphire-I diffractometer	2615 independent reflections
Radiation source: fine-focus sealed tube	1302 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.037$
Detector resolution: $8.2632 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 26.4^\circ$
$T = 180(2) \text{ K}$	$\theta_{\text{min}} = 3.1^\circ$
ω and ϕ scans	$h = -23 \rightarrow 38$
Absorption correction: none	$k = -11 \rightarrow 14$
5114 measured reflections	$l = -7 \rightarrow 8$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.085$	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2]$
$S = 0.82$	where $P = (F_o^2 + 2F_c^2)/3$
2615 reflections	$(\Delta/\sigma)_{\text{max}} = 0.003$
293 parameters	$\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.59538 (10)	0.4362 (3)	0.2817 (5)	0.0536 (10)
C1'	0.64958 (9)	-0.0975 (3)	0.2534 (4)	0.0364 (9)
H1'	0.6284	-0.1263	0.1537	0.044*

supplementary materials

C2'	0.65560 (10)	-0.1895 (3)	0.3989 (4)	0.0398 (9)
C2	0.63385 (10)	0.4539 (3)	0.4201 (6)	0.0623 (11)
H2A	0.6608	0.4605	0.3509	0.075*
H2B	0.6298	0.5262	0.4864	0.075*
C3'	0.69097 (10)	-0.2504 (3)	0.4250 (4)	0.0507 (10)
H3'	0.6914	-0.3052	0.5217	0.061*
C3	0.63991 (10)	0.3605 (3)	0.5617 (5)	0.0592 (11)
H3A	0.6147	0.3597	0.6416	0.071*
H3B	0.6665	0.3757	0.6424	0.071*
C4	0.64403 (10)	0.2457 (3)	0.4706 (5)	0.0495 (10)
H4A	0.6458	0.1869	0.5689	0.059*
H4B	0.6716	0.2433	0.4055	0.059*
C4'	0.73066 (10)	-0.2407 (3)	0.3154 (5)	0.0529 (10)
H4'A	0.7427	-0.3170	0.2938	0.063*
H4'B	0.7532	-0.1960	0.3865	0.063*
C4A	0.60575 (9)	0.2174 (3)	0.3301 (4)	0.0361 (9)
C5	0.61843 (9)	0.1098 (3)	0.2159 (4)	0.0351 (8)
H5	0.6457	0.1294	0.1529	0.042*
C5'	0.71920 (10)	-0.1833 (3)	0.1284 (5)	0.0481 (10)
C6	0.58379 (11)	0.0870 (4)	0.0639 (5)	0.0494 (10)
C6'	0.69273 (9)	-0.0707 (3)	0.1609 (5)	0.0417 (9)
C7'	0.61661 (10)	-0.2127 (3)	0.5115 (5)	0.0564 (11)
H7'A	0.6219	-0.2811	0.5866	0.085*
H7'B	0.5907	-0.2239	0.4272	0.085*
H7'C	0.6118	-0.1484	0.5939	0.085*
C7	0.57720 (12)	0.1836 (4)	-0.0693 (5)	0.0692 (13)
H7A	0.5535	0.1652	-0.1636	0.083*
H7B	0.6043	0.1966	-0.1350	0.083*
C8'	0.69222 (12)	-0.2582 (4)	0.0066 (6)	0.0508 (10)
C8	0.56546 (11)	0.2901 (3)	0.0358 (5)	0.0593 (12)
H8A	0.5366	0.2797	0.0887	0.071*
H8B	0.5631	0.3545	-0.0523	0.071*
C8A	0.59952 (10)	0.3178 (3)	0.1931 (5)	0.0472 (10)
H8	0.6277	0.3213	0.1297	0.057*
C9	0.55363 (10)	0.4563 (3)	0.3803 (6)	0.0470 (10)
C9'	0.75865 (11)	-0.1575 (4)	0.0316 (5)	0.0602 (11)
C10'	0.72097 (11)	0.0021 (3)	0.2844 (6)	0.0548 (11)
C10	0.59748 (14)	0.5294 (3)	0.1310 (6)	0.0858 (16)
H10A	0.5710	0.5266	0.0482	0.129*
H10B	0.6231	0.5170	0.0581	0.129*
H10C	0.5997	0.6037	0.1913	0.129*
C11	0.56460 (9)	0.1932 (3)	0.4331 (4)	0.0438 (9)
H11A	0.5700	0.1298	0.5190	0.066*
H11B	0.5406	0.1739	0.3428	0.066*
H11C	0.5567	0.2605	0.5035	0.066*
C11'	0.68511 (11)	-0.0140 (3)	-0.0200 (6)	0.0486 (10)
C12	0.62924 (10)	0.0071 (3)	0.3388 (4)	0.0403 (9)
H12A	0.6019	-0.0172	0.3937	0.048*
H12B	0.6493	0.0326	0.4431	0.048*

C13	0.55899 (11)	-0.0039 (4)	0.0508 (5)	0.0696 (13)
H13A	0.5364	-0.0090	-0.0448	0.084*
H13B	0.5637	-0.0642	0.1368	0.084*
N8'	0.67137 (11)	-0.3154 (3)	-0.0892 (5)	0.0749 (11)
N9'	0.78989 (10)	-0.1379 (4)	-0.0408 (5)	0.0974 (14)
N10'	0.74280 (11)	0.0563 (3)	0.3805 (5)	0.0864 (13)
N11'	0.68067 (11)	0.0254 (3)	-0.1637 (5)	0.0767 (11)
O9	0.51784 (7)	0.4467 (2)	0.2691 (3)	0.0616 (8)
H9	0.4958	0.4589	0.3303	0.092*
O9'	0.55236 (7)	0.4807 (2)	0.5443 (4)	0.0569 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.042 (2)	0.056 (3)	0.065 (3)	0.0049 (18)	0.023 (2)	0.014 (2)
C1'	0.0289 (17)	0.047 (2)	0.034 (2)	-0.0031 (15)	0.0035 (16)	-0.0048 (18)
C2'	0.043 (2)	0.044 (2)	0.032 (2)	-0.0001 (17)	0.0037 (15)	-0.0009 (19)
C2	0.0362 (19)	0.046 (3)	0.106 (3)	-0.0033 (18)	0.020 (2)	-0.002 (3)
C3'	0.057 (2)	0.060 (3)	0.035 (2)	0.008 (2)	0.0042 (18)	0.008 (2)
C3	0.041 (2)	0.056 (3)	0.079 (3)	-0.0013 (19)	-0.0142 (19)	-0.016 (3)
C4	0.0387 (19)	0.058 (3)	0.051 (2)	0.0003 (18)	-0.0047 (16)	-0.001 (2)
C4'	0.047 (2)	0.071 (3)	0.041 (2)	0.0157 (19)	-0.0008 (17)	0.009 (2)
C4A	0.0301 (17)	0.046 (2)	0.033 (2)	0.0065 (15)	0.0034 (15)	0.0118 (18)
C5	0.0336 (18)	0.045 (2)	0.027 (2)	0.0009 (15)	0.0025 (15)	0.0057 (19)
C5'	0.0338 (19)	0.065 (3)	0.046 (2)	0.0010 (19)	0.0073 (17)	0.000 (2)
C6	0.042 (2)	0.071 (3)	0.035 (2)	0.011 (2)	0.0020 (18)	-0.005 (2)
C6'	0.0365 (18)	0.049 (2)	0.040 (2)	-0.0049 (17)	0.0040 (16)	0.002 (2)
C7'	0.053 (2)	0.071 (3)	0.046 (2)	0.0026 (18)	0.0139 (17)	0.016 (2)
C7	0.074 (3)	0.105 (4)	0.029 (2)	0.036 (2)	0.0067 (18)	0.007 (3)
C8'	0.053 (3)	0.057 (3)	0.043 (3)	0.005 (2)	0.013 (2)	0.009 (2)
C8	0.064 (2)	0.086 (3)	0.028 (2)	0.033 (2)	0.0061 (18)	0.014 (2)
C8A	0.0355 (18)	0.065 (3)	0.043 (2)	0.0142 (17)	0.0170 (16)	0.009 (2)
C9	0.039 (2)	0.043 (2)	0.059 (3)	0.0040 (16)	0.006 (2)	0.020 (2)
C9'	0.049 (2)	0.082 (3)	0.050 (3)	0.006 (2)	0.0087 (19)	-0.001 (2)
C10'	0.039 (2)	0.060 (3)	0.067 (3)	-0.0105 (19)	0.013 (2)	-0.007 (2)
C10	0.100 (3)	0.060 (3)	0.104 (4)	0.018 (2)	0.059 (3)	0.047 (3)
C11	0.042 (2)	0.060 (3)	0.030 (2)	-0.0030 (17)	0.0069 (16)	-0.001 (2)
C11'	0.052 (2)	0.046 (3)	0.049 (3)	0.0067 (18)	0.017 (2)	0.010 (2)
C12	0.0415 (18)	0.048 (2)	0.031 (2)	-0.0010 (16)	0.0030 (15)	0.0012 (18)
C13	0.046 (2)	0.099 (4)	0.062 (3)	0.011 (3)	-0.015 (2)	-0.004 (3)
N8'	0.089 (3)	0.084 (3)	0.053 (2)	-0.013 (2)	0.016 (2)	-0.005 (2)
N9'	0.057 (2)	0.143 (4)	0.095 (3)	0.001 (2)	0.032 (2)	0.004 (3)
N10'	0.063 (2)	0.101 (3)	0.095 (3)	-0.031 (2)	0.008 (2)	-0.042 (3)
N11'	0.094 (3)	0.088 (3)	0.051 (2)	0.023 (2)	0.028 (2)	0.019 (2)
O9	0.0462 (14)	0.092 (2)	0.0471 (15)	0.0210 (14)	0.0064 (12)	0.0007 (16)
O9'	0.0444 (13)	0.075 (2)	0.0519 (16)	-0.0021 (12)	0.0105 (13)	-0.0057 (16)

supplementary materials

Geometric parameters (Å, °)

C1—C2	1.513 (5)	C5'—C6'	1.584 (5)
C1—C9	1.517 (5)	C6—C13	1.316 (5)
C1—C8A	1.546 (5)	C6—C7	1.497 (5)
C1—C10	1.549 (5)	C6'—C11'	1.470 (5)
C1'—C2'	1.513 (4)	C6'—C10'	1.480 (5)
C1'—C12	1.529 (4)	C7'—H7'A	0.9800
C1'—C6'	1.547 (4)	C7'—H7'B	0.9800
C1'—H1'	1.0000	C7'—H7'C	0.9800
C2'—C3'	1.306 (4)	C7—C8	1.521 (5)
C2'—C7'	1.506 (4)	C7—H7A	0.9900
C2—C3	1.506 (5)	C7—H7B	0.9900
C2—H2A	0.9900	C8'—N8'	1.136 (5)
C2—H2B	0.9900	C8—C8A	1.530 (5)
C3'—C4'	1.491 (4)	C8—H8A	0.9900
C3'—H3'	0.9500	C8—H8B	0.9900
C3—C4	1.516 (5)	C8A—H8	1.0000
C3—H3A	0.9900	C9—O9'	1.216 (4)
C3—H3B	0.9900	C9—O9	1.325 (4)
C4—C4A	1.541 (4)	C9'—N9'	1.139 (4)
C4—H4A	0.9900	C10'—N10'	1.133 (4)
C4—H4B	0.9900	C10—H10A	0.9800
C4'—C5'	1.528 (5)	C10—H10B	0.9800
C4'—H4'A	0.9900	C10—H10C	0.9800
C4'—H4'B	0.9900	C11—H11A	0.9800
C4A—C11	1.526 (4)	C11—H11B	0.9800
C4A—C8A	1.547 (4)	C11—H11C	0.9800
C4A—C5	1.574 (4)	C11'—N11'	1.134 (4)
C5—C6	1.504 (4)	C12—H12A	0.9900
C5—C12	1.527 (4)	C12—H12B	0.9900
C5—H5	1.0000	C13—H13A	0.9500
C5'—C9'	1.462 (5)	C13—H13B	0.9500
C5'—C8'	1.466 (5)	O9—H9	0.8400
C2—C1—C9	108.6 (3)	C13—C6—C5	125.4 (4)
C2—C1—C8A	108.5 (3)	C7—C6—C5	113.1 (3)
C9—C1—C8A	115.2 (3)	C11'—C6'—C10'	108.8 (3)
C2—C1—C10	107.4 (3)	C11'—C6'—C1'	112.1 (3)
C9—C1—C10	106.5 (3)	C10'—C6'—C1'	110.3 (3)
C8A—C1—C10	110.4 (3)	C11'—C6'—C5'	108.0 (3)
C2'—C1'—C12	109.9 (2)	C10'—C6'—C5'	106.9 (3)
C2'—C1'—C6'	111.7 (2)	C1'—C6'—C5'	110.5 (3)
C12—C1'—C6'	112.7 (3)	C2'—C7'—H7'A	109.5
C2'—C1'—H1'	107.4	C2'—C7'—H7'B	109.5
C12—C1'—H1'	107.4	H7'A—C7'—H7'B	109.5
C6'—C1'—H1'	107.4	C2'—C7'—H7'C	109.5
C3'—C2'—C7'	120.0 (3)	H7'A—C7'—H7'C	109.5
C3'—C2'—C1'	124.3 (3)	H7'B—C7'—H7'C	109.5

C7'—C2'—C1'	115.7 (3)	C6—C7—C8	110.0 (3)
C3—C2—C1	113.8 (3)	C6—C7—H7A	109.7
C3—C2—H2A	108.8	C8—C7—H7A	109.7
C1—C2—H2A	108.8	C6—C7—H7B	109.7
C3—C2—H2B	108.8	C8—C7—H7B	109.7
C1—C2—H2B	108.8	H7A—C7—H7B	108.2
H2A—C2—H2B	107.7	N8'—C8'—C5'	179.3 (4)
C2'—C3'—C4'	125.3 (3)	C7—C8—C8A	111.9 (3)
C2'—C3'—H3'	117.3	C7—C8—H8A	109.2
C4'—C3'—H3'	117.3	C8A—C8—H8A	109.2
C2—C3—C4	112.0 (3)	C7—C8—H8B	109.2
C2—C3—H3A	109.2	C8A—C8—H8B	109.2
C4—C3—H3A	109.2	H8A—C8—H8B	107.9
C2—C3—H3B	109.2	C8—C8A—C4A	111.1 (3)
C4—C3—H3B	109.2	C8—C8A—C1	115.4 (3)
H3A—C3—H3B	107.9	C4A—C8A—C1	116.3 (3)
C3—C4—C4A	113.5 (3)	C8—C8A—H8	104.1
C3—C4—H4A	108.9	C4A—C8A—H8	104.1
C4A—C4—H4A	108.9	C1—C8A—H8	104.1
C3—C4—H4B	108.9	O9'—C9—O9	122.3 (3)
C4A—C4—H4B	108.9	O9'—C9—C1	124.4 (3)
H4A—C4—H4B	107.7	O9—C9—C1	113.4 (3)
C3'—C4'—C5'	110.2 (3)	N9'—C9'—C5'	178.7 (4)
C3'—C4'—H4'A	109.6	N10'—C10'—C6'	178.9 (5)
C5'—C4'—H4'A	109.6	C1—C10—H10A	109.5
C3'—C4'—H4'B	109.6	C1—C10—H10B	109.5
C5'—C4'—H4'B	109.6	H10A—C10—H10B	109.5
H4'A—C4'—H4'B	108.1	C1—C10—H10C	109.5
C11—C4A—C4	110.1 (3)	H10A—C10—H10C	109.5
C11—C4A—C8A	112.1 (2)	H10B—C10—H10C	109.5
C4—C4A—C8A	108.2 (3)	C4A—C11—H11A	109.5
C11—C4A—C5	109.7 (3)	C4A—C11—H11B	109.5
C4—C4A—C5	108.4 (2)	H11A—C11—H11B	109.5
C8A—C4A—C5	108.3 (2)	C4A—C11—H11C	109.5
C6—C5—C12	113.5 (3)	H11A—C11—H11C	109.5
C6—C5—C4A	109.8 (3)	H11B—C11—H11C	109.5
C12—C5—C4A	113.2 (2)	N11'—C11'—C6'	176.2 (4)
C6—C5—H5	106.6	C5—C12—C1'	119.4 (2)
C12—C5—H5	106.6	C5—C12—H12A	107.5
C4A—C5—H5	106.6	C1'—C12—H12A	107.5
C9'—C5'—C8'	107.2 (3)	C5—C12—H12B	107.5
C9'—C5'—C4'	110.8 (3)	C1'—C12—H12B	107.5
C8'—C5'—C4'	110.5 (3)	H12A—C12—H12B	107.0
C9'—C5'—C6'	109.9 (3)	C6—C13—H13A	120.0
C8'—C5'—C6'	108.6 (3)	C6—C13—H13B	120.0
C4'—C5'—C6'	109.7 (3)	H13A—C13—H13B	120.0
C13—C6—C7	121.4 (4)	C9—O9—H9	109.5

supplementary materials

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O9-H9\cdots O9^i$	0.84	1.79	2.631 (3)	178

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

Fig. 1

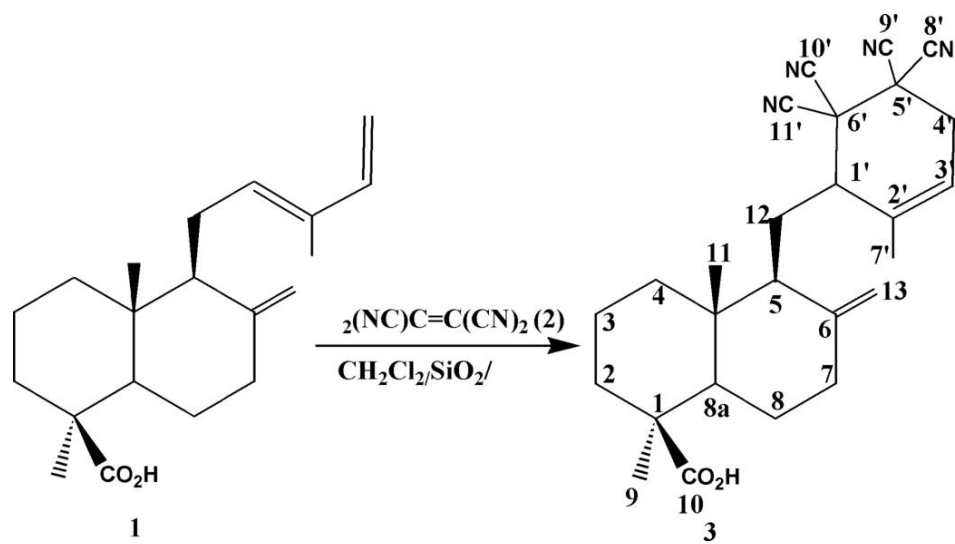


Fig. 2

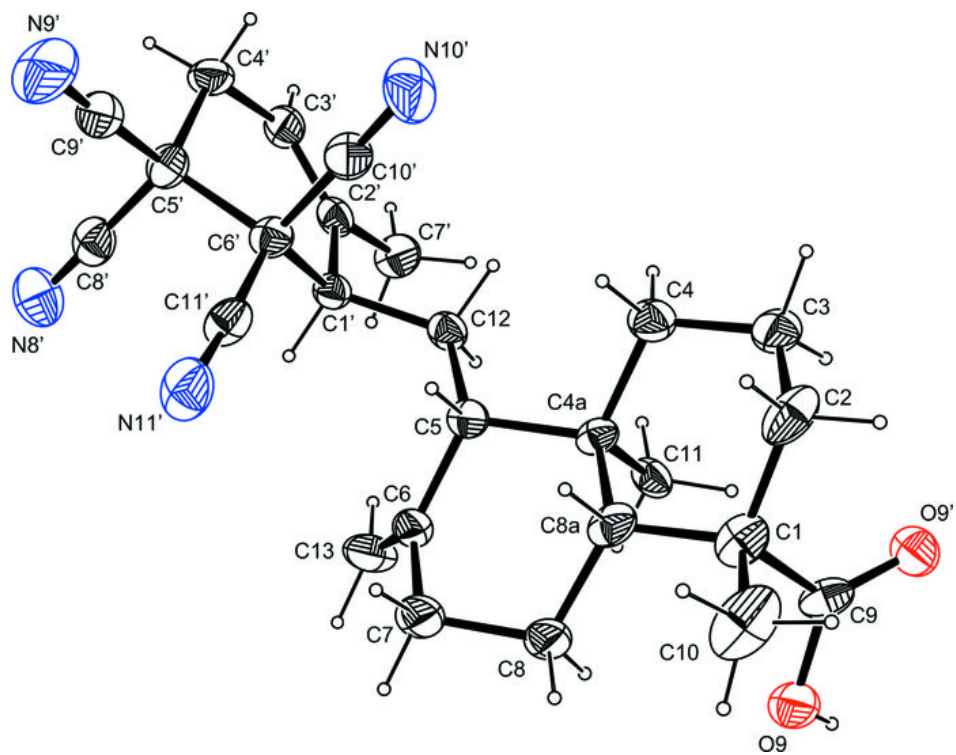


Fig. 3

