Crystal data

$C_9H_9N_3O_2S_2$
$M_r = 255.31$
Monoclinic
$P2_1/n$
$a = 10.399\,(2)$ Å
$b = 15.132\,(3)$ Å
$c = 14.280\,(3)$ Å
$\beta = 91.21\,(3)°$
$V = 2246.6\,(8)$ Å^3
$Z = 8$
$D_x = 1.51$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 2749 reflections
$\theta = 3.05–25.00°$
$\mu = 0.462$ mm^{-1}
$T = 150\,(2)$ K
Block
$0.15 \times 0.10 \times 0.08$ mm
Colourless

Data collection

Nonius KappaCCD area-detector diffractometer
$\varphi + \omega$ scans to fill the Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.868$, $T_{max} = 0.990$
28 369 measured reflections

3936 independent reflections
2749 reflections with $I > 2\sigma(I)$
$R_{int} = 0.098$
$\theta_{max} = 25°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.079$
$S = 0.858$
3936 reflections
319 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.038$
$\Delta\rho_{max} = 0.256$ e Å^{-3}
$\Delta\rho_{min} = -0.373$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H10···N12^i	0.90 (2)	2.14 (2)	3.016 (4)	165 (3)
N11—H10···O11^i	0.90 (2)	2.54 (3)	3.211 (4)	132 (3)
N11—H11···O22^{ii}	0.93 (2)	2.10 (2)	3.010 (4)	167 (5)
N13—H17···O21^{iii}	0.86	2.04	2.865 (4)	161
N21—H20···O12^{iv}	0.90 (2)	2.24 (2)	3.061 (4)	152 (3)
N21—H21···O21^{v}	0.90 (2)	2.37 (3)	3.116 (4)	141 (3)
N21—H21···N22^{v}	0.90 (2)	2.44 (2)	3.267 (4)	154 (3)
N23—H27···O11^{vi}	0.86	1.94	2.794 (4)	173

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

The H atoms on N11 and N21 were refined isotropically using *DFIX* restraints (Sheldrick, 1997); all other H atoms were treated as riding atoms.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998). Cell refinement: *DENZO* and *COLLECT*. Data reduction: *DENZO* and *COLLECT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *CAMERON* (Chemical Crystallography Laboratory, 1993). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1566). Services for accessing these data are described at the back of the journal.

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N-(4-Chlorophenyl)-*N*-methylcyanamide

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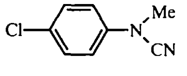
Abstract

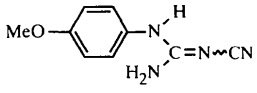
An X-ray structural analysis of the title compound, $C_8H_7ClN_2$, shows an essentially planar molecule, but with an unusually long aryl-C to planar-N bond.

Comment

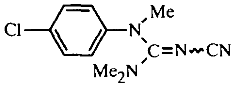
In the course of on-going investigations of *N*-arylcyanoguanidines, the title compound, (1), was prepared and isolated. In simple *N*-arylcyanoguanidines such as *N*-cyano-*N*′-(4-methoxyphenyl)guanidine, (2), the aryl-bearing amino lone pair conjugates predominantly with the cyanoguanidine part allowing the aryl group to tilt out of plane (Cunningham *et al.*, 1997). However, when N-methylation makes a planar system untenable due to steric hindrance, the aryl-bearing amino lone pair conjugates with the aryl group and the arylamino unit is tilted out of plane as in *N*-(4-chlorophenyl)-*N*′-cyano-*N*,*N*″,*N*″-trimethylguanidine, (3) (Cunningham, Coles *et al.*, 1999). The title compound is a rather more simple case of a molecule with the potential for such conjugative dichotomy and we undertook an X-ray crystallographic structure determination of (1).



(1)



(2)



(3)

The structure (Fig. 1, arbitrary numbering) shows an essentially planar system, as indicated by the torsional angles C3—C4—N1—C7 and C5—C4—N1—C8 in Table 1. This might be expected to reflect the usual conjugation between an amino lone pair and an aromatic ring. However, the C4—N1 bond length of 1.412 (3) Å seems too long for a standard C_{aryl}—N—$(Csp^3)_2$ substructure (typically 1.371 Å) (Allen *et al.*, 1987). This suggests that the planarity of the molecule is due more to the requirement for a regular packing pattern than to a conjugative effect. Estimation of the bond order between N1 and C8 is difficult in the absence of comparable data. However, the evidence of the 'typical' bond length [1.139 (3) Å] for the C≡N (Allen *et al.*, 1987) suggests that resonance delocalization of the lone pair towards CN is small. This reinforces the concept of cyano as an electron-withdrawing group by induction rather than resonance. If so, and given the lack of Ar—N conjugation, it suggests a planar tri-substituted N atom bearing only inductive substituents.

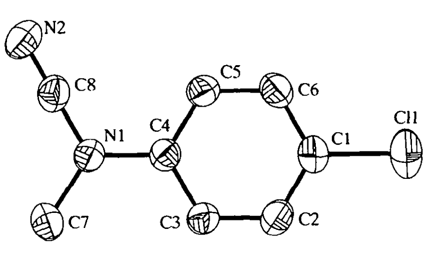


Fig. 1. The molecular structure of (1) showing displacement ellipsoids at 30% probability.

Experimental

The compound (1) was isolated by column chromatography on silica gel following treatment of *N*-(4-chlorophenyl)-*N*′-cyanoguanidine with butyllithium and methyl iodide in tetrahydrofuran (Cunningham, Cox *et al.*, 1999).

Crystal data

$C_8H_7ClN_2$
$M_r = 166.61$
Monoclinic
*C*2/*c*
$a = 17.3562\,(19)$ Å
$b = 6.0765\,(6)$ Å
$c = 15.8695\,(17)$ Å
$\beta = 98.732\,(4)^\circ$
$V = 1654.3\,(3)$ Å^3
$Z = 8$
$D_x = 1.338$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 11 814 reflections
$\theta = 3.24$–25.03°
$\mu = 0.393$ mm^{-1}
$T = 293\,(2)$ K
Block
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
ϕ and ω scans to fill Ewald sphere
Absorption correction: empirical (*SORTAV*; Blessing, 1997)
$T_{min} = 0.926$, $T_{max} = 0.962$
11 814 measured reflections
1449 independent reflections

798 reflections with $I > 2\sigma(I)$
$R_{int} = 0.088$
$\theta_{max} = 25.03^\circ$
$h = -20 \rightarrow 20$
$k = -7 \rightarrow 7$
$l = -18 \rightarrow 18$
Intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.049$
$wR(F^2) = 0.141$
$S = 0.993$
1449 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0753P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.11$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C8	1.331 (4)	C8—N2	1.139 (3)
N1—C4	1.412 (3)		
C8—N1—C4	119.4 (2)	C4—N1—C7	122.6 (2)
C8—N1—C7	118.0 (2)	N2—C8—N1	179.5 (3)
C7—N1—C4—C3	−4.5 (4)	C8—N1—C4—C5	−2.5 (4)

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998). Cell refinement: *DENZO* and *COLLECT*. Data reduction: *DENZO*, *COLLECT* and *MAXUS* (Mackay *et al.*, 1998). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *WinGX* (Farrugia, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1331). Services for accessing these data are described at the back of the journal.

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Filic-3-ene, a pentacyclic triterpene from *Davallia canariensis*

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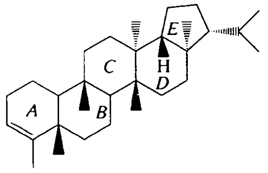
Abstract

The triterpene filic-3-ene, 3-isopropyl-3a,5a,7a,8,11b,13a-hexamethyl-2,3,3a,4,5,5a,5b,6,7,7a,10,11,11a,11b,12,-13,13a,13b-octadecahydro-1*H*-cyclopenta[α]chrysene, $C_{30}H_{50}$, was isolated from *Davallia canariensis*, a fern from Tenerife (Canary Islands), and its structure was elucidated. It was confirmed to be a pentacyclic molecule, with four six-membered rings and one five-membered ring. The two independent molecules in the asymmetric unit do not differ significantly.

Comment

This paper, part of a systematic study of bioactive metabolites from Canary Island ferns, presents the results of a structural study of filic-3-ene, (I), a triterpene hydrocarbon isolated from *Davallia canariensis* as a minor component (Bermejo, 1998). This fern is called 'batatilla' locally and features in traditional medicine as having emollient, aperient, restorative and expectorant properties (Pérez de Paz & Medina, 1988). Xanthones are known to occur frequently in the *Davallia* genus (Soeder, 1985).



(I)

Filic-3-ene (or 3-filicene) was isolated from *Adiantum monochlamys* (Ageta *et al.*, 1964) and from *Adiantum pedatum* (Ageta & Iwata, 1966). The structural model was established by these authors by means of chemical and spectroscopic investigations and is now confirmed by our X-ray analysis. We were not able to determine the absolute stereochemistry by X-ray methods and the configuration shown here was chosen to be in accord with that reported in previous chemical studies (Ageta *et al.*, 1964; Ageta & Iwata, 1966).

After extraction followed by chromatography on silica gel to afford filic-3-ene as a colourless oil, crystals were grown from a benzene/acetone mixture; there are two molecules, *A* and *B*, in the asymmetric unit with remarkably similar conformations overall, including the substituents. A quantitative measure of the similarity of the two molecules (*A* and *B*) was obtained using a least-squares fit. The weighted r.m.s. deviation was 0.0663 Å with 0.202 Å for maximum deviation in 30 C atoms. All bond lengths and angles are in the expected ranges and need no further discussion.

In the molecules (see Fig. 1) which involve the pentacyclic ring system *A*–*E*, one endocyclic double bond C3═C4 was identified, indicated by the bond length of 1.307 (8) in molecule *A* and 1.323 (7) Å in molecule *B*.

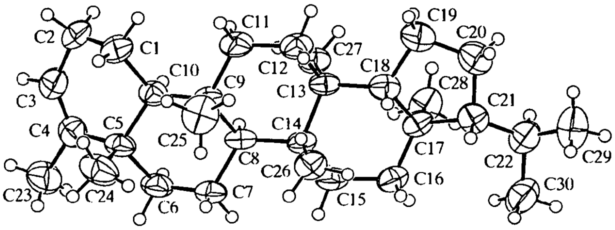


Fig. 1. A perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.