

Acridine form IX

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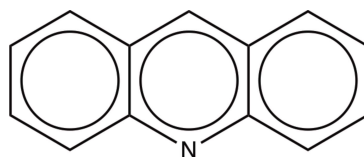
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We report a new polymorph of acridine, C₁₃H₉N, denoted form IX, obtained as thin needles by slow evaporation of a toluene solution. The structure was solved and refined from powder X-ray data. The structures of five unsolvated forms were previously known, but this is only the second with one molecule in the asymmetric unit. The melting point [differential scanning calorimetry (DSC) onset] and heat of fusion are 108.8 (3) °C and 19.2 (4) kJ mol⁻¹, respectively.

1. Chemical context

With the crystal structures of five forms already reported, acridine is already one of the more prolifically polymorphic molecules known [see Phillips (1956), Phillips *et al.* (1960), Mei & Wolf (2004), Braga *et al.* (2010), Kupka *et al.* (2012), and Lusi *et al.* (2015)]; two additional forms have been described, but structures were not reported, by Herbstein & Schmidt (1955) and Braga *et al.* (2010). This large number of observed forms seems particularly noteworthy in view of the fact that the molecule has zero degrees of flexibility, although perhaps counterintuitively, some 40 rigid molecules are observed to be polymorphic (Cruz-Cabeza & Bernstein, 2013).



2. Structural commentary

The form described here was previously predicted by Price & Price (unpublished) using *CrystalPredictor* (Karamertzanis & Pantilides, 2005) to generate a crystal energy landscape, limited to one independent molecule in the asymmetric unit cell in the most common space groups. These were relaxed to mechanically stable structures with *DMACRYS* (Price *et al.*, 2010). This new form corresponded to one of two structures with the lowest computed lattice energy. Further details are available in Schur *et al.* (2019). Geometry details for form IX are given in Table 1.

3. Supramolecular features

The four molecules in the unit cell are connected by a cycle of C··H (2.81 Å) and N··H (2.73 Å) contacts that are shorter than the sum of the van der Waals radii. There is also an H··H interaction of 2.29 Å.

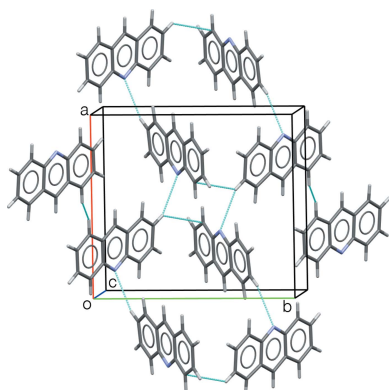


Table 1
 Selected geometric parameters (Å, °).

N1–C10	1.315 (18)	C5–C12	1.388 (6)
N1–C13	1.317 (18)	C6–C7	1.366 (17)
C1–C2	1.37 (3)	C6–C12	1.436 (12)
C1–C10	1.44 (3)	C7–C8	1.41 (3)
C2–C3	1.41 (2)	C8–C9	1.36 (4)
C3–C4	1.367 (16)	C9–C13	1.44 (4)
C4–C11	1.435 (9)	C10–C11	1.444 (7)
C5–C11	1.389 (5)	C12–C13	1.443 (11)
C10–N1–C13	116.9 (7)	N1–C10–C11	124.5 (8)
C2–C1–C10	121.3 (12)	C1–C10–C11	116.6 (11)
C1–C2–C3	121.7 (17)	C4–C11–C5	122.5 (5)
C2–C3–C4	119.7 (13)	C4–C11–C10	120.0 (7)
C3–C4–C11	120.8 (10)	C5–C11–C10	117.6 (5)
C11–C5–C12	118.9 (4)	C5–C12–C6	122.4 (8)
C7–C6–C12	120.9 (14)	C5–C12–C13	117.7 (6)
C6–C7–C8	119.4 (15)	C6–C12–C13	119.8 (8)
C7–C8–C9	122 (2)	N1–C13–C9	119.0 (13)
C8–C9–C13	121.3 (18)	N1–C13–C12	124.5 (9)
N1–C10–C1	118.9 (10)	C9–C13–C12	116.5 (13)

4. Synthesis and crystallization

Crystals were grown by slow evaporation from a toluene solution. Thin needles of form IX samples were taken from the walls of crystallization vials. The material was gently crushed and loaded into a glass capillary for powder diffraction measurements. Further details are available in Schur (2013).

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. Data were collected at the high resolution powder diffractometer at the National Synchrotron Light Source beamline X16C, operated in step scanning mode. X-rays of wavelength 0.69979 Å were selected by a Si(111) channel cut monochromator. Diffracted X-rays were selected by a Ge(111) analyzer before an NaI(Tl) scintillation detector. The sample of form IX was obtained concomitantly with forms III (1.4%) and VII (1.1%), which were included in the Rietveld fit, with atomic positions fixed at literature values.

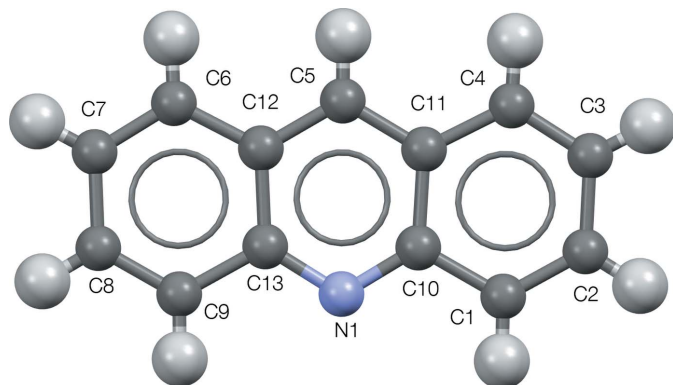


Figure 1
 The acridine molecule in form IX, with atom labels and 50% probability displacement spheres.

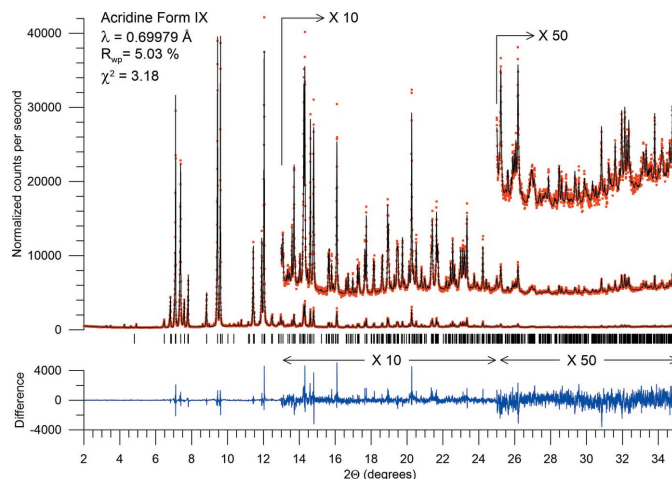


Figure 2
 Rietveld plot of acridine form IX. Red dots are measured intensities, black line is the fit, and the blue trace at the bottom is the difference plot, measured minus fit. Note the two vertical scale changes. Vertical tick lines show allowed peak positions of form IX peaks. Fit includes two impurity phases: 1.4% form III and 1.1% form VII. Tick marks were omitted for clarity.

The molecule was defined by a *z*-matrix for refinement. Mirror symmetry was imposed on bond distances and angles; 7 distances, 6 angles, and 11 torsions were refined. There is a single isotropic displacement parameter for all C and N atoms; that of H atoms is 1.5 times greater. All H atoms are tethered.

Standard uncertainties were calculated by a bootstrap method, described in Coelho (2016). As such, they reflect the propagation of statistical errors from the raw data and do not

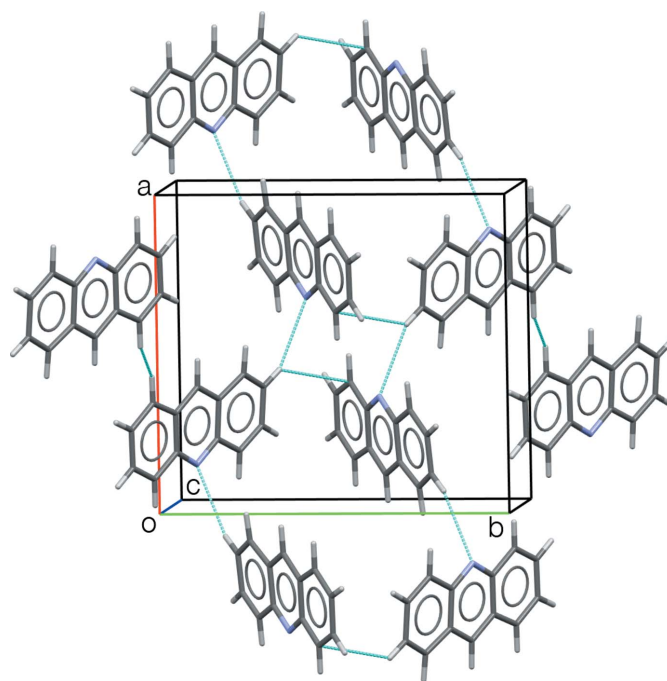


Figure 3
 Packing diagram of acridine form IX. Close intermolecular interactions (less than the sum of van der Waals radii) are marked in turquoise dashed lines.

take account of systematic errors. Realistic estimates of the precision of measurements are somewhat larger.

The Rietveld refinement plot is shown in Fig. 1. Fig. 2 illustrates the atom-labeling scheme, and Fig. 3 shows the three-dimensional structure, with short intermolecular interactions shown as broken lines.

The refinement model included preferred orientation parameter 1.08 in the (100) direction (March, 1932; Dollase, 1986), and anisotropic microstrain broadening (Stephens, 1999).

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₉ N
<i>M_r</i>	179.21
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.28453 (11), 12.38182 (12), 6.67905 (9)
β (°)	92.0618 (6)
<i>V</i> (Å ³)	932.61 (2)
<i>Z</i>	4
Radiation type	Synchrotron, $\lambda = 0.699789$ Å
μ (mm ⁻¹)	0.08
Specimen shape, size (mm)	Cylinder, 8 × 1
Data collection	
Diffractometer	Huber 401 diffractometer, Ge(111) analyzer crystal
Specimen mounting	1 mm glass capillary, spun during data collection
Data collection mode	Transmission
Scan method	Step
2θ values (°)	$2\theta_{\min} = 2$, $2\theta_{\max} = 35$, $2\theta_{\text{step}} = 0.005$
Refinement	
<i>R</i> factors and goodness of fit	$R_p = 0.041$, $R_{\text{wp}} = 0.050$, $R_{\text{exp}} = 0.028$, $R_{\text{Bragg}} = 0.011$, $\chi^2 = 3.183$
No. of parameters	81
No. of restraints	12
H-atom treatment	H-atom parameters not refined

Computer programs: *TOPAS-Academic* (Coelho, 2016) and *Mercury* (Macrae *et al.*, 2008).

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Computing details

Data collection: spec; cell refinement: TOPAS-Academic (Coelho, 2016); data reduction: TOPAS-Academic (Coelho, 2016); program(s) used to solve structure: TOPAS-Academic (Coelho, 2016); program(s) used to refine structure: TOPAS-Academic (Coelho, 2016); molecular graphics: *Mercury* (Macrae *et al.*, 2008).

Acridine

Crystal data

$C_{13}H_9N$

$M_r = 179.21$

Monoclinic, $P2_1/n$

$a = 11.28453$ (11) Å

$b = 12.38182$ (12) Å

$c = 6.67905$ (9) Å

$\beta = 92.0618$ (6)°

$V = 932.61$ (2) Å³

$Z = 4$

$D_x = 1.276$ Mg m⁻³

Synchrotron radiation, $\lambda = 0.699789$ Å

$\mu = 0.08$ mm⁻¹

$T = 295$ K

Particle morphology: thin needles

yellow-white

cylinder, 8 × 1 mm

Data collection

Huber 401

diffractometer, Ge(111) analyzer crystal

Radiation source: National Synchrotron Light

Source

Channel cut Si(111) monochromator

Specimen mounting: 1 mm glass capillary, spun during data collection

Data collection mode: transmission

Scan method: step

$2\theta_{\min} = 2^\circ$, $2\theta_{\max} = 35^\circ$, $2\theta_{\text{step}} = 0.005^\circ$

Refinement

Least-squares matrix: full

$R_p = 0.041$

$R_{\text{wp}} = 0.050$

$R_{\text{exp}} = 0.028$

$R_{\text{Bragg}} = 0.011$

6601 data points

Profile function: Convolution of Gaussian and Lorentzian, with anisotropic strain broadening per Stephens (1999).

81 parameters

12 restraints

22 constraints

H-atom parameters not refined

Weighting scheme based on measured s.u.'s

$(\Delta/\sigma)_{\max} = 0.02$

Background function: 9th order Chebyshev plus broad pseudo-Voigt

Preferred orientation correction: March parameter 1.084 in (1 0 0) direction

Special details

Refinement. Mirror symmetry imposed on bond distances and angles.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.1540 (5)	0.1053 (19)	0.045 (2)	0.0474 (5)*
C1	0.1213 (11)	0.003 (3)	-0.252 (4)	0.0474 (5)*
C2	0.1640 (14)	-0.048 (2)	-0.417 (3)	0.0474 (5)*
C3	0.2853 (15)	-0.0476 (11)	-0.4573 (15)	0.0474 (5)*
C4	0.3633 (9)	0.0068 (7)	-0.3327 (10)	0.0474 (5)*
C5	0.4001 (2)	0.1154 (2)	-0.0256 (3)	0.0474 (5)*
C6	0.4263 (13)	0.2290 (7)	0.2776 (12)	0.0474 (5)*
C7	0.379 (2)	0.2748 (11)	0.4427 (15)	0.0474 (5)*
C8	0.256 (2)	0.266 (2)	0.471 (3)	0.0474 (5)*
C9	0.1830 (18)	0.210 (4)	0.341 (6)	0.0474 (5)*
C10	0.1992 (5)	0.0588 (10)	-0.1120 (15)	0.0474 (5)*
C11	0.3234 (4)	0.0603 (4)	-0.1568 (6)	0.0474 (5)*
C12	0.3543 (7)	0.1655 (3)	0.1406 (7)	0.0474 (5)*
C13	0.2282 (7)	0.1578 (9)	0.1666 (17)	0.0474 (5)*
H1	0.0388 (12)	0.002 (4)	-0.229 (6)	0.0711 (8)*
H2	0.1103 (18)	-0.086 (2)	-0.504 (4)	0.0711 (8)*
H3	0.313 (2)	-0.0838 (17)	-0.572 (2)	0.0711 (8)*
H4	0.4453 (10)	0.0071 (13)	-0.3603 (18)	0.0711 (8)*
H5	0.4825 (3)	0.1185 (6)	-0.0491 (8)	0.0711 (8)*
H6	0.5086 (12)	0.2370 (14)	0.256 (2)	0.0711 (8)*
H7	0.428 (3)	0.315 (2)	0.535 (3)	0.0711 (8)*
H8	0.224 (3)	0.299 (3)	0.586 (4)	0.0711 (8)*
H9	0.1006 (19)	0.205 (6)	0.364 (7)	0.0711 (8)*

Geometric parameters (\AA , $^\circ$)

N1—C10	1.315 (18)	C9—C13	1.44 (4)
N1—C13	1.317 (18)	C10—C11	1.444 (7)
C1—C2	1.37 (3)	C12—C13	1.443 (11)
C1—C10	1.44 (3)	C1—H1	0.95
C2—C3	1.41 (2)	C2—H2	0.95
C3—C4	1.367 (16)	C3—H3	0.95
C4—C11	1.435 (9)	C4—H4	0.95
C5—C11	1.389 (5)	C5—H5	0.95
C5—C12	1.388 (6)	C6—H6	0.95
C6—C7	1.366 (17)	C7—H7	0.95
C6—C12	1.436 (12)	C8—H8	0.95
C7—C8	1.41 (3)	C9—H9	0.95
C8—C9	1.36 (4)		
C10—N1—C13	116.9 (7)	N1—C13—C12	124.5 (9)
C2—C1—C10	121.3 (12)	C9—C13—C12	116.5 (13)
C1—C2—C3	121.7 (17)	C2—C1—H1	120 (4)
C2—C3—C4	119.7 (13)	C10—C1—H1	119 (4)
C3—C4—C11	120.8 (10)	C1—C2—H2	119 (2)

C11—C5—C12	118.9 (4)	C3—C2—H2	119 (2)
C7—C6—C12	120.9 (14)	C2—C3—H3	120 (2)
C6—C7—C8	119.4 (15)	C4—C3—H3	120 (2)
C7—C8—C9	122 (2)	C3—C4—H4	119.6 (12)
C8—C9—C13	121.3 (18)	C11—C4—H4	119.6 (11)
N1—C10—C1	118.9 (10)	C11—C5—H5	120.5 (4)
N1—C10—C11	124.5 (8)	C12—C5—H5	120.6 (5)
C1—C10—C11	116.6 (11)	C7—C6—H6	119.5 (15)
C4—C11—C5	122.5 (5)	C12—C6—H6	119.6 (12)
C4—C11—C10	120.0 (7)	C6—C7—H7	120 (3)
C5—C11—C10	117.6 (5)	C8—C7—H7	120 (2)
C5—C12—C6	122.4 (8)	C7—C8—H8	119 (3)
C5—C12—C13	117.7 (6)	C9—C8—H8	120 (3)
C6—C12—C13	119.8 (8)	C8—C9—H9	120 (5)
N1—C13—C9	119.0 (13)	C13—C9—H9	119 (5)
