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# 9-(Trichloroacetylimino)acridine monohydrate

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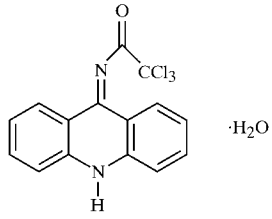
The title compound, alternatively called *N*-acridin-9(10*H*)-ylidene-2,2,2-trichloroacetamide monohydrate, $C_{15}H_9Cl_3N_2O\cdot H_2O$, crystallizes in space group $P2_1/c$ with $Z = 4$. The acridine moieties are arranged in layers, tilted at an angle of 15.20 (4)° relative to the *ac* plane, while adjacent molecules pack in a head-to-tail manner. Acridine and water molecules form columns along the *b* axis held in place by a network of hydrogen bonds, which is the major factor stabilizing the lattice. The acridine molecule exhibits structural features of both the amino and imino forms, which could be due to the presence of the strong electronegative trichloroacetyl substituent at the exocyclic N atom.

## Comment

Numerous experimental investigations and theoretical studies indicate that 9-aminoacridine can occur in two tautomeric forms, *viz*. amino or imino, in the gaseous and liquid phases (Rak *et al.*, 1997), while only the amino tautomer is present in the crystalline phase (Chaudhuri, 1983). Theory also predicts the co-existence of tautomeric forms in 9-aminoacridines monosubstituted at the exocyclic N atom (Rak *et al.*, 1998). The structures of only two such derivatives have been determined, namely 9-(*tert*-butylamino)acridine (Meszko *et al.*, 2002) and 9-(phenylamino)acridine (Leardini *et al.*, 1998). It was found that crystals of these compounds are composed of molecules of the amino tautomer. The question thus arises as to which substituents at the exocyclic N atom could force the occurrence of 9-iminoacridines, particularly in the crystalline phase. The possibility of finding an $N_{exo}$-substituted 9-aminoacridine whose imino form is more stable than its amino form was indicated by Gurevich & Sheinker (1962), and is reinforced by the fact that we synthesized and determined the structure of 10-methyl-9-(methylimino)acridine, *i.e.* a blocked derivative of 9-iminoacridine (Rak *et al.*, 1998). 9-Aminoacridines, with a well recognized biological relevance, are able to interact specifically with molecules in their immediate environment. The properties of these compounds are undoubtedly dependent on the form in which they occur (Barbe *et al.*, 1996; Rak *et al.*, 1997), and this was the reason for undertaking the present study.




(I)

Crystals of the title compound, (I), contain molecules of the imino form (Fig. 1) and four of these occupy the unit cell (Fig. 2). The acridine moiety in (I) is nearly planar in the crystalline phase (Table 1), with atoms C9, N10 and H10 arranged almost linearly, and the C9—N16 bond deflected from the mean plane of the acridine nucleus by an angle of 7.8 (5)°. The dihedral angle between the mean plane of the acridine nucleus and the plane formed by atoms C9, N15 and C16, which can be regarded as a measure of the arrangement of the exocyclic imino substituent relative to the acridine moiety, is 61.5 (5)°. The N10—H10 bond is relatively short, which may be an attribute of 9-iminoacridines. The properties of the crystalline phase of (I) result from a network of hydrogen bonds (Fig. 2 and Table 2). Thus, the H atom attached to the endocyclic N atom is involved in a hydrogen bond with the O atom of a neighbouring water molecule, *viz*. N10—H10···O22. Furthermore, one of the H atoms of the water molecule participates in a hydrogen bond with the O atom of the trichloroacetyl group of an adjacent 9-iminoacridine molecule, *i.e.* O22—H22*A*···O17$^{i}$ [symmetry code: (i)

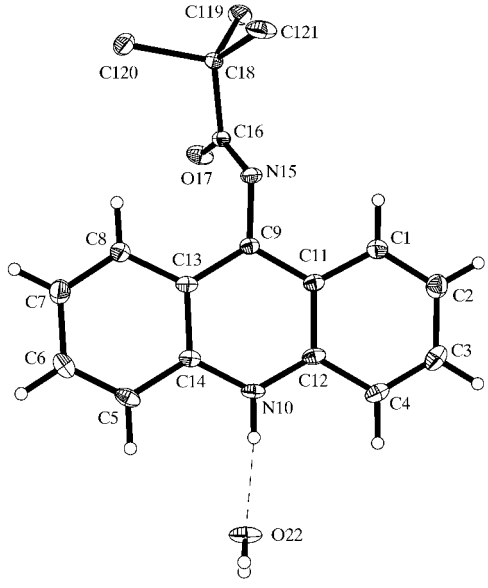



**Figure 1**
The molecular structure of (I), showing the atom-labeling scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. The N10—H10···O22 hydrogen bond is represented by a dashed line.

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$2 - x, 1 - y, 1 - z$], and the second H atom interacts with one of the three Cl atoms of another neighbouring 9-iminoacridine molecule, *viz*. O22—H22*B*···Cl21$^{ii}$ [symmetry code: (ii) $2 - x$, $-y$, $1 - z$].

The acridine moieties are arranged in layers tilted at an angle of 15.20 (4)° relative to the (010) plane, while neighbouring molecules pack in a head-to-tail manner. It can also be seen (Fig. 3) that the above-mentioned acridine fragments and water molecules form columns along the [010] direction, held in place by the network of multidirectional hydrogen bonds that is the principal factor stabilizing the lattice.

The title compound is the first known derivative of 9-aminoacridine substituted at the exocyclic N atom that contains molecules of the imino tautomeric form in the crystalline phase. It is thus interesting to compare its structural properties with those of other 9-amino- or 9-iminoacridines. Table 3 shows selected structural parameters for (I) and five other compounds, the structures of which were determined by X-ray analysis. The lengths of the C9—C11 and C9—N15 bonds in (I) are between those of four 9-aminoacridines and 10-methyl-9-(methylimino)acridine. The angle N10···C9—N15 in (I) is typical of imino tautomers, *i.e.* it is similar to that in 10-methyl-9-(methylimino)acridine. Finally, the acridine nucleus in (I) is almost planar, which is typical of amino but atypical of imino tautomers, *e.g.* in 10-methyl-9-(methylimino)acridine, the central ring is substantially folded along the N10···C9 axis. The above analysis indicates that (I) exhibits structural features of both the amino and imino tautomers, and that this may be caused by the presence of the strong electronegative trichloroacetyl substituent at the exocyclic N atom.

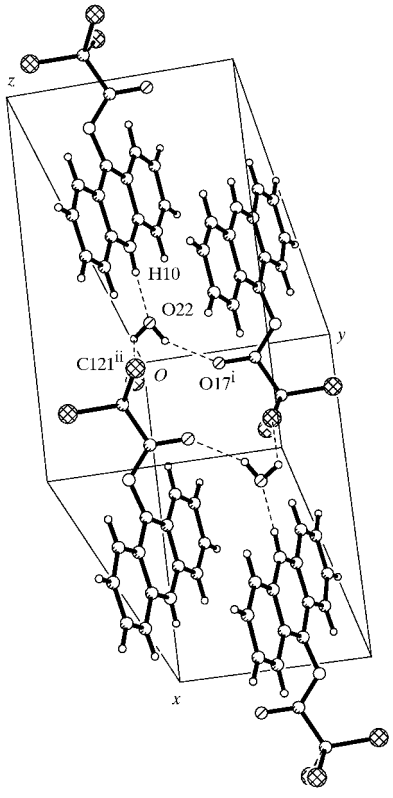


**Figure 2**
The arrangement of molecules of (I) in the unit cell, viewed along the *c* axis. Hydrogen bonds are represented by dashed lines. Symmetry codes are as in Table 2.

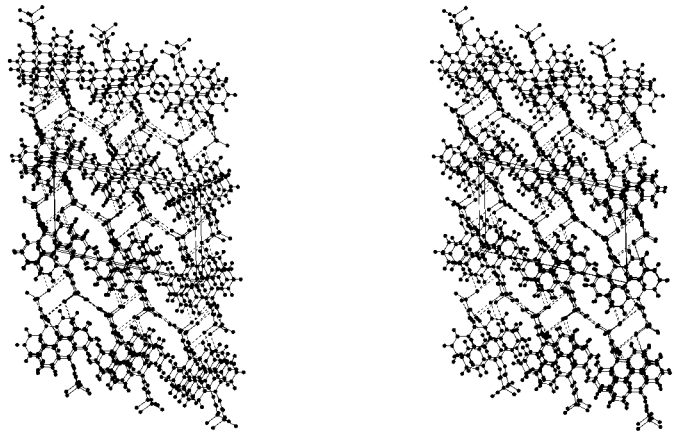

**Figure 3**
A stereoview of the packing diagram of (I), viewed along the *b* axis, with the *a* axis vertical and the *c* axis horizontal. Hydrogen bonds (Table 2) are represented by dashed lines.

## Experimental

9-(Trichloroacetylimino)acridine, (I), was synthesized by adding an equimolar mixture of 9-aminoacridine and trimethylamine in dimethylformamide dropwise to a mixture of trichloroacetic acid in the same solvent (Gurevich & Sheinker, 1962). The product was purified chromatographically and yellow crystals of the monohydrate suitable for X-ray investigations were grown from ethanol.

*Crystal data*

$C_{15}H_9Cl_3N_2O\cdot H_2O$
$M_r = 357.61$
Monoclinic, $P2_1/c$
$a = 11.780$ (2) Å
$b = 6.906$ (1) Å
$c = 18.823$ (4) Å
$\beta = 103.88$ (3)°
$V = 1486.6$ (5) Å$^3$
$Z = 4$
$D_x = 1.598$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 1.5$–30°
$\mu = 0.62$ mm$^{-1}$
$T = 293$ (2) K
Prism, yellow
0.5 × 0.3 × 0.2 mm

*Data collection*

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
4500 measured reflections
4369 independent reflections
1671 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 30.1°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -26 \rightarrow 0$
3 standard reflections
every 200 reflections
intensity decay: 3.9%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.194$
$S = 1.03$
4369 reflections
210 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0854P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{min} = -0.51$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| C9—C11 | 1.427 (5) | N10—C12 | 1.352 (6) |
| C9—C13 | 1.419 (6) | N10—C14 | 1.357 (5) |
| C9—N15 | 1.354 (5) | | |
| | | | |
| C9—N15—C16 | 124.6 (4) | C12—N10—H10 | 119 (4) |
| C11—C9—C13 | 118.7 (3) | C12—N10—C14 | 123.0 (3) |
| C11—C9—N15 | 118.4 (4) | | |
| | | | |
| C9—N15—C16—O17 | −16.1 (8) | C11—C12—N10—H10 | 178 (5) |
| C11—C9—C13—C14 | 2.1 (6) | C12—N10—C14—C13 | −1.1 (6) |
| C11—C9—N15—C16 | 123.0 (5) | | |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N10—H10···O22 | 0.74 (6) | 1.99 (5) | 2.717 (5) | 170 (7) |
| O22—H22*A*···O17$^{i}$ | 0.82 (6) | 1.87 (6) | 2.694 (5) | 170.8 (6) |
| O22—H22*B*···Cl21$^{ii}$ | 0.82 (5) | 2.84 (5) | 3.420 (4) | 128.4 (7) |

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

The H10 atom (bonded to N10) and the H atoms belonging to the water molecule were refined isotropically. All H atoms attached to C atoms were placed geometrically and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ and with C—H distances fixed at 0.96 Å.

Data collection: *KM*-4 *Software* (Kuma, 1989); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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**Table 3**
Selected structural data (Å, °) for 9-acridinamine derivatives.

| | (I) | (II) | (III) | (IV) | (V) | (VI) |
|---|---|---|---|---|---|---|
| Space group | $P2_1/c$ | $I4_1/acd$ | *Pbca* | $P2_1/a$ | $P2_1/c$ | $P2_1/c$ |
| *Z* | 4 | 32 | 8 | 4 | 4 | 4 |
| Bond lengths | | | | | | |
| C9—C11 | 1.429 (5) | 1.415 | 1.410 (3) | 1.408 | 1.419 (4) | 1.284 (2) |
| C9—N15 | 1.353 (5) | 1.357 | 1.412 (2) | 1.393 | 1.384 (3) | 1.284 (2) |
| Angles | | | | | | |
| N10···C9—N15 | 171.9 (4) | 180 | 175.9 (2) | 178.9 | 177.7 (6) | 158.1 (2) |
| C11—C9—C13—C14 | 2.0 (6) | −0.3 | −8.7 (3) | 5.4 | 2.4 (4) | −25.4 (2) |
| C12—N10—C14—C13 | −1.1 (6) | −0.3 | 1.7 (3) | −4.0 | 1.0 (3) | 22.3 (2) |

Notes: (I) 9-(trichloroacetylimino)acridine monohydrate (this work); (II) 9-acridinamine hemihydrate (Chaudhuri, 1983); (III) 9-(*tert*-butylamino)acridine (Meszko *et al.*, 2002); (IV) 9-(phenylamino)acridine (Leardini *et al.*, 1998); (V) 9-(dimethylamino)acridine (Rak *et al.*, 1998); (VI) 10-methyl-9-(methylimino)acridine (Rak *et al.*, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1205). Services for accessing these data are described at the back of the journal.

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