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1-Ethynylcyclohexylammonium acetate

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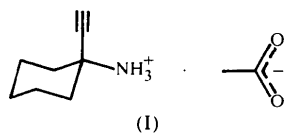
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Abstract

The title compound, C₈H₁₄N⁺·CH₃CO₂⁻, contains a short C≡C—H···O hydrogen bond to the acetate ion with a C···O distance of 3.139 (2) Å and a normalized H···O distance of 2.11 Å. N—H···O and C≡C—H···O hydrogen bonds are linked together to form a ribbon motif.

Comment

Terminal alkynes, R—C≡C—H, are an interesting model system to study C—H···X hydrogen bonds (Steiner, 1998*a*). This is because the acetylenic C—H group is relatively acidic, and therefore one of the best hydrogen-bond donors of all C—H groups (Desiraju & Steiner, 1999). The title compound, (I), was prepared and its crystal structure was determined in expectation of finding a short hydrogen bond C≡C—H···O⁻, which is one of the less well investigated kinds of C—H···O interaction.



In the crystal structure of (I), the cyclohexane ring adopts a chair conformation with the ammonium group

in an equatorial and the ethynyl group in an axial position. The chair is almost undistorted with the ethynyl group close to perpendicular to the ring [angles C3···C1—C7 = 95.6 (1), C5···C1—C7 = 95.7 (1)°]. The geometry of the ethynyl group is normal with C7≡C8 = 1.188 (2) Å and C1—C7≡C8 = 179.2 (1)°.

As expected, the primary ammonium group forms three N⁺—H···O⁻ hydrogen bonds to the acetate ion, with geometries as given in Table 1. The ethynyl group donates a hydrogen bond to the acetate ion too, Fig. 1, with a C···O distance of 3.139 (2) Å. If the C—H bond is normalized to 1.08 Å, an H···O distance of 2.11 Å and a C—H···O angle of 159° are obtained. Even for an acetylenic donor, this is a short C—H···O contact. For comparison, the mean distance in 145 C≡C—H···O bonds in organic and organometallic structures has been found as H···O = 2.40 (2) Å, and C···O = 3.35 (1) Å (Steiner, 1998*b*). However, much shorter (C)H···O distances also occur in crystal structures of terminal alkynes. Examples are the adduct triphenylsilylacetylene–triphenylphosphin oxide, H···O = 1.99 Å with a P=O acceptor (for normalized C—H; Steiner *et al.*, 1997), 1:2:4 1,4-diethynylbenzene–water–triphenylphosphin oxide, H···O = 1.96 Å with an H₂O acceptor (for normalized C—H; Kariuki *et al.*, 1997), and 2-ethynyladamantan-2-ol, H···O = 2.07 Å with a C—O—H acceptor [neutron diffraction study by Allen *et al.* (1996)]. It is interesting that these three examples are all in uncharged compounds.

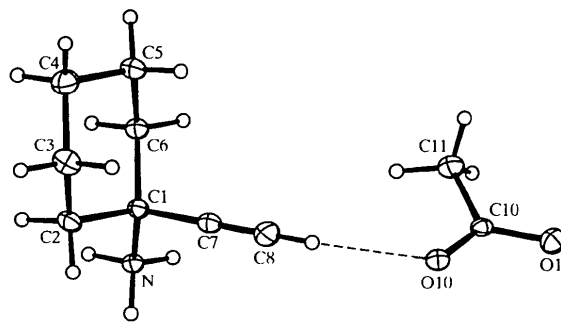


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

The hydrogen-bond interactions of the acetate ion are shown in detail in Fig. 2. All four hydrogen bonds are directed at the oxygen lone-pair regions. It is obvious that the C≡C—H···O bond acts as a full member in hydrogen-bond coordination of the ion, not just as a bystander. The covalent bond O11—C10 of the acetate ion [1.276 (2) Å] is slightly but significantly longer than O10—C10 [1.249 (2) Å]. Because in X—H···O=C bonds, O=C is lengthened, this would indicate that the sum of the hydrogen bonds accepted by O11 (two N⁺—H···O⁻ bonds) is significantly stronger than the sum of the bonds accepted by O10 (one N⁺—H···O⁻ and one

C≡C—H···O⁻ bond). This is as to be expected. In the crystal lattice, symmetry-related hydrogen-bond motifs as shown in Fig. 1 are linked together to form a ribbon running in the direction of the *b* axis (vertical in Fig. 1).

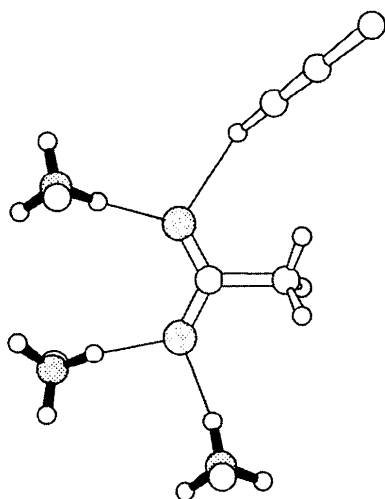


Fig. 2. Hydrogen-bond interactions of the acetate ion drawn in projection onto the molecular plane.

Experimental

Crystals were obtained by slow evaporation of a solution of 1-ethynylcyclohexylamine (Aldrich) in dilute acetic acid.

Crystal data

C ₈ H ₁₄ N ⁺ ·C ₂ H ₃ O ₂ ⁻	Mo K α radiation
<i>M_r</i> = 183.25	λ = 0.71073 Å
Monoclinic	Cell parameters from 42 reflections
C2/c	θ = 3.3–17.9°
<i>a</i> = 24.573 (3) Å	μ = 0.078 mm ⁻¹
<i>b</i> = 6.477 (1) Å	<i>T</i> = 125 K
<i>c</i> = 17.435 (3) Å	Block
β = 128.72 (1)°	0.45 × 0.25 × 0.25 mm
<i>V</i> = 2165.0 (6) Å ³	Colourless
<i>Z</i> = 8	
<i>D_x</i> = 1.124 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Nonius KappaCCD diffractometer	2098 reflections with <i>I</i> > 2σ(<i>I</i>)
φ (κ = 0) and ω (κ = 147.78) scans	<i>R</i> _{int} = 0.079
Absorption correction: none	θ_{\max} = 27.50°
10 253 measured reflections	<i>h</i> = -31 → 31
2487 independent reflections	<i>k</i> = -8 → 5
	<i>l</i> = -18 → 22

Refinement

Refinement on <i>F</i> ²	(Δ/σ) _{max} < 0.001
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.049	$\Delta\rho_{\max}$ = 0.40 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.124	$\Delta\rho_{\min}$ = -0.24 e Å ⁻³

<i>S</i> = 1.095	Extinction correction:
2487 reflections	<i>SHELXL97</i> (Sheldrick, 1997)
147 parameters	Extinction coefficient:
H atoms treated by a mixture of independent and constrained refinement	0.0039 (13)
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 2.445P]$	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Hydrogen-bonding 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>
N1—H1N···O11 ⁱ	0.94 (2)	1.83 (2)	2.756 (2)	169 (2)
N1—H2N···O10	0.96 (2)	1.80 (2)	2.758 (2)	176 (2)
N1—H3N···O11 ⁱⁱ	0.93 (2)	1.84 (2)	2.758 (2)	169 (2)
C8—H8···O10 ⁱⁱⁱ	1.00	2.18	3.139 (2)	159

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

In the refinement, H atoms bonded to C atoms were treated as riding (C—H = 1.00 Å), with isotropic displacement parameters allowed to vary. The methyl group of the acetate ion was allowed to rotate. H atoms bonded to N atoms were located in difference Fourier calculations and refined isotropically. All H-atom displacement parameters refined to realistic values, with somewhat high values only for the acetate methyl group (ammonium-H atoms have *U* in the range 0.030–0.043 Å², cyclohexyl-H atoms have *U* in the range 0.018–0.037 Å², the ethynyl-H atom has *U* = 0.052 Å², and the acetate methyl-H atoms have *U* in the range 0.102–0.113 Å²).

Cell refinement: *EVAL14* (Duisenberg, 1998). Data reduction: *EVAL14*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1330). Services for accessing these data are described at the back of the journal.

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