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Crystal structure of caffenium triiodide – caffeine (1/1), $C_{16}H_{21}I_3N_8O_4$

Table 1: Data collection and handling.

Crystal:	Orange-brown block
Size:	$0.37 \times 0.22 \times 0.09$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	3.99 mm^{-1}
Diffractometer, scan mode:	APEX-II with Ims 2.0, φ and ω -scans
$\theta_{\max}$, completeness:	28.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	50390, 6007, 0.031
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5051
$N(\text{param})_{\text{refined}}$:	298
Programs:	Bruker programs [1], SHELX [2, 3], DIAMOND [4]

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound caffeine triiodide – caffeine (1/1) [systematic name: 1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-9-ium triiodide – 1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (1/1)] was obtained from a mixing solution of ethanol and equimolar amounts of caffeine triiodide hydrate and caffeine. The crystals show an orange colour and are easily distinguishable from the dark caffeine triiodide hydrate crystals.

Experimental details

The crystal used for the study was harvested directly from the mother liquor. Data collection followed the standard procedures of the Bruker APEX2 software [1]. Absorption correction was applied using the SADABS program implemented in the APEX2 program system [1]. Structure solution with the SHELXT [2] yielded all non-hydrogen atoms. During the latter stages of the refinement [3] a slight disorder of the triiodide anion was taken into account (not shown in the figure). The largest difference electron density peaks and holes are 0.99 and $-0.88 \text{ e \AA}^{-3}$, respectively. The largest difference electron peaks (down to $0.51 \text{ e \AA}^{-3}$) are less than $0.84 \text{ \AA}$ away from iodine positions. Coordinates and U_{iso} of the H4 hydrogen atom (*cf.* the figure) were refined freely. All other hydrogen

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Abstract

$C_{16}H_{21}I_3N_8O_4$, monoclinic, $P2_1/n$ (no. 14), $a = 14.7257(7) \text{ \AA}$, $b = 10.5712(5) \text{ \AA}$, $c = 16.7501(8) \text{ \AA}$, $\beta = 114.408(2)^\circ$, $V = 2374.4(2) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0254$, $wR_{\text{ref}}(F^2) = 0.0760$, $T = 290(2) \text{ K}$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.49960(15)	0.7740(2)	0.92598(12)	0.0515(5)
N1	0.34313(15)	0.8568(2)	0.86300(13)	0.0355(4)
C1	0.42266(19)	0.7887(2)	0.86069(16)	0.0357(5)
O2	0.19363(14)	0.9609(2)	0.79700(13)	0.0476(5)
N2	0.41061(14)	0.73470(19)	0.78165(13)	0.0323(4)
C2	0.32494(16)	0.7579(2)	0.71023(15)	0.0283(4)
O3	0.57340(16)	0.1957(2)	0.58374(15)	0.0543(5)
N3	0.17760(14)	0.83646(19)	0.62699(13)	0.0319(4)
C3	0.25052(16)	0.8314(2)	0.71241(15)	0.0291(4)
O4	0.38498(16)	0.54937(19)	0.55667(13)	0.0465(5)
N4	0.29786(15)	0.7182(2)	0.62603(14)	0.0330(4)
H4	0.324(2)	0.669(3)	0.608(2)	0.048(10)*
C4	0.25565(18)	0.8905(2)	0.79041(16)	0.0330(5)
N5	0.47505(16)	0.36861(19)	0.56947(14)	0.0345(4)
C5	0.20813(18)	0.7681(2)	0.57761(16)	0.0355(5)
H5	0.17266(1)	0.75590(4)	0.51763(5)	0.043*
N6	0.45126(18)	0.2348(2)	0.44954(15)	0.0405(5)
C6	0.3573(3)	0.9101(3)	0.94827(18)	0.0546(8)
H6A	0.39484(3)	0.98718(4)	0.95813(7)	0.082*
H6B	0.39283(6)	0.85058(3)	0.99380(4)	0.082*
H6C	0.29346(2)	0.92736(2)	0.94863(2)	0.082*
N7	0.27222(17)	0.4727(2)	0.36275(16)	0.0460(5)
C7	0.49322(19)	0.6655(3)	0.77591(19)	0.0432(6)
H7A	0.46943(2)	0.61778(0)	0.72236(7)	0.065*
H7B	0.52131(8)	0.60890(4)	0.82489(8)	0.065*
H7C	0.54335(2)	0.72411(4)	0.77667(6)	0.065*
N8	0.3187(2)	0.2992(3)	0.31194(16)	0.0532(6)
C8	0.0848(2)	0.9092(3)	0.5969(2)	0.0469(7)
H8A	0.10000(3)	0.99797(0)	0.60331(4)	0.070*
H8B	0.04878(1)	0.88701(3)	0.63133(5)	0.070*
H8C	0.04474(1)	0.89045(4)	0.53635(6)	0.070*
C9	0.5049(2)	0.2611(2)	0.53707(18)	0.0375(5)
C10	0.3755(2)	0.3121(3)	0.39890(18)	0.0396(6)
C11	0.34984(19)	0.4176(2)	0.43303(18)	0.0365(5)
C12	0.40038(18)	0.4536(2)	0.52121(17)	0.0330(5)
C13	0.2569(3)	0.3978(3)	0.2937(2)	0.0569(8)
H13	0.20759(7)	0.41325(4)	0.23798(2)	0.068*
C14	0.5278(2)	0.3913(3)	0.66411(19)	0.0472(7)
H14A	0.55855(2)	0.47329(0)	0.67388(3)	0.071*
H14B	0.57808(0)	0.32772(7)	0.68967(1)	0.071*
H14C	0.48121(2)	0.38778(1)	0.69066(0)	0.071*
C15	0.4778(3)	0.1235(3)	0.4119(3)	0.0656(10)
H15A	0.46290(2)	0.13915(7)	0.35126(8)	0.098*
H15B	0.44009(0)	0.05195(9)	0.41644(8)	0.098*
H15C	0.54769(5)	0.10648(5)	0.44311(6)	0.098*
C16	0.2194(3)	0.5896(3)	0.3628(3)	0.0618(9)
H16A	0.18843(1)	0.62243(2)	0.30424(2)	0.093*
H16B	0.26572(7)	0.65056(6)	0.40025(7)	0.093*
H16C	0.16916(5)	0.57247(5)	0.38400(5)	0.093*
I1A ^a	0.46702(3)	1.10662(5)	0.79487(3)	0.05997(11)
I2A ^a	0.32749(2)	1.09822(2)	0.61021(2)	0.04423(7)
I3A ^a	0.19370(2)	1.07608(8)	0.42627(3)	0.07731(17)
I1B ^b	0.4784(10)	1.0801(14)	0.7790(9)	0.05997(11)
I2B ^b	0.32749(2)	1.09822(2)	0.61021(2)	0.04423(7)
I3B ^b	0.1870(8)	1.137(2)	0.4414(8)	0.07731(17)

^a Occupancy: 0.967(2); ^b Occupancy: 0.033(2).

atoms were included using the standard riding models of the SHELX System (AFIX 43; 137) [3].

Comment

A report on the first triiodide (strychninium triiodide) dates back to the beginning of the 19th century [5]. A reinvestigation by combustion analysis in 1865 verified these findings [6]. In the course of the aforementioned study caffeinium triiodide monohydrate (caffHI₃ · H₂O) was identified. Further investigations in the 19th century on the caffeine/HI system followed with a view to analytical aspects [7, 8]. A preliminary structure determination of caffHI₃ · H₂O has been reported [9] and a reconsideration of this compound is in progress [10]. As part of a study on polyiodides trapped in hydrogen bonded surroundings [11–13], we have reinvestigated the system caffeine/HI/H₂O/I₂. In the course of this study, the new compound caffHI₃ · caff was obtained. The appearance of this compound was expected, as we have already shown that depending on the pH value organic aminium halogenides co-crystals containing the organic aminium cation, the counter anion and one additional equivalent of the neutral organic amine can be easily obtained [11, 14, 15]. Even though caffeine has been known for many decades, studies on the medical and biological properties are still in progress [16]. Despite this interest in caffeine, we were surprised that structures of the *N*-protonated caffeine are still rare.

The asymmetric unit of the title crystal structure contains one *N*-protonated caffeinium cation, one triiodide counter anion and one caffeine molecule (*cf.* the figure). Bond lengths and angles in the title crystal structure are in the expected ranges. Caffeine is a weak base, a property which is expressed by its structural chemistry. Protonation at the 9-position of the purine moiety (in the title structure at N4) only takes place on reaction with strong acids [17–21]. Weak organic acids form co-crystals without any transfer of the proton from the organic acid to the caffeine molecule [22, 23]. In the title structure the protonated N atom of the caffeinium cation donates one hydrogen bond to the adjacent neutral caffeine molecule (*cf.* the figure; N–H = 0.78(3) Å; N ··· O = 2.722(3) Å). The caffeinium cation as well as the caffeine molecule are almost planar [*rms* deviation of fitted atoms (N1–N4; C1–C5) = 0.022 Å; *rms* deviation of fitted atoms (N5–N8; C9–C13) = 0.010 Å]. The dihedral angle is 21.37(9)°. In the packing scheme of the title crystal structure there is one triiodide anion above and another one below each caffeinium cation, which rules out any kind of π–π interactions. This feature of packing has been reported earlier [24]. The neutral caffeine molecules are pairwise arranged with an interplanar distance of 3.319(6) Å. The I–I distances in the triiodide anion are in the typical range for triiodide anions not involved in strong secondary interactions [11–13]. A detailed discussion of the geometric parameters of

the anion based on the crystal structure is ruled out by its disorder. Furthermore, there are no intermolecular $I \cdots I$ halogen bonds as the shortest $I \cdots I$ distances are >4.3 Å.

To obtain more information about the geometry of the triiodide anion in the title structure a Raman spectrum was recorded (MultiRAM, Bruker Optics, range: $4000\text{--}50\text{ cm}^{-1}$). A strong Raman signal at $\sim 110\text{ cm}^{-1}$ was detected, which features a shoulder towards higher wavenumbers, and a weak signal at 216 cm^{-1} . Both signals are in perfect accord with a roughly symmetrical I_3^- anion [25–27]. A significant asymmetry, which may be introduced by halogen [28–30] or hydrogen bonds [12] shifts the strongest Raman signals into the $150\text{--}165\text{ cm}^{-1}$ range.

This contribution forms part of the general interest on stacking properties of caffeine [31–33].

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