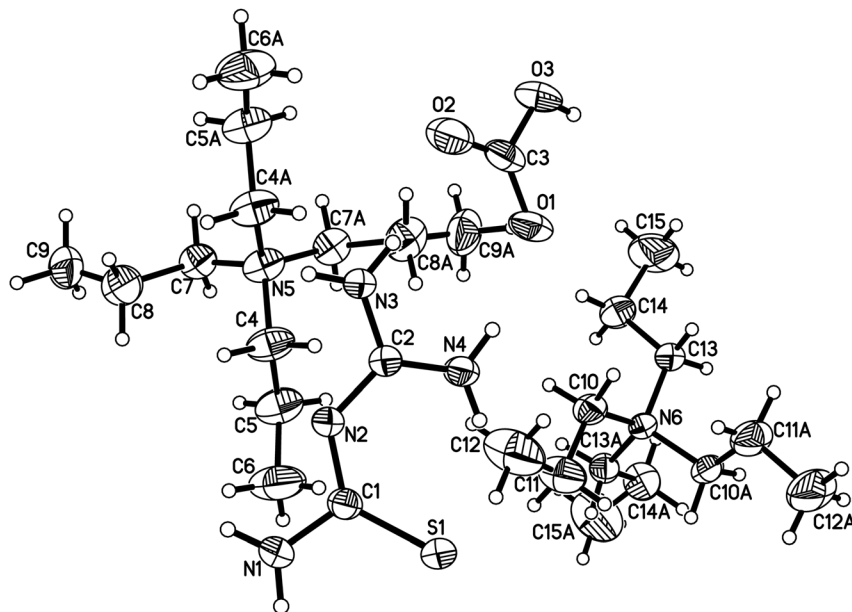


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Crystal structure of tetrapropylammonium bicarbonate-1-(diaminomethylene)thiourea(1/1)



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Abstract

$C_{60}H_{140}N_{20}O_{12}S_4$, monoclinic, $P2_1/n$ (no. 13), $a = 15.6996 \text{ \AA}$, $b = 8.5361 \text{ \AA}$, $c = 15.8896 \text{ \AA}$, $\beta = 94.722^\circ$, $V = 2122.19(10) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0440$, $wR_{\text{ref}}(F^2) = 0.1366$, $T = 296(2) \text{ K}$.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

Amidinothiourea and tetrapropylammonium (25 % aqueous solution), which are commercially available, were mixed in a

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.55 × 0.20 × 0.17 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.17 mm ⁻¹
Diffraction, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.0°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8726, 3732, 0.014
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2963
$N(\text{param})_{\text{refined}}$:	221
Programs:	SHELX ^{1,2}

molar ratio of 1:1. The mixture was dissolved in a minimum amount of ethanol and water, the mixture was vigorously stirred for about 30 min. Subsequently the solution was set aside to allow it slow evaporation at room temperature. Colorless block crystals were obtained about 10 days later. It can be concluded that the bicarbonate anions are present in the crystal structure due to the absorption of CO₂ of the air under basic conditions.

2 Comment

Amidinothiourea is a common pharmaceutical intermediate and can be applied in different research fields including

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}
S1	0.47835 (3)	0.96085 (10)	0.13282 (3)	0.0870 (3)
N1	0.61809 (11)	0.9261 (3)	0.05772 (10)	0.0757 (5)
H1A	0.6716	0.9073	0.0552	0.091*
H1B	0.5872	0.9544	0.0131	0.091*
C1	0.58273 (11)	0.9114 (2)	0.13134 (11)	0.0510 (4)
O1	0.54271 (11)	0.6313 (2)	0.44523 (8)	0.0796 (5)
N2	0.63837 (9)	0.86661 (17)	0.19522 (8)	0.0483 (4)
C2	0.61646 (10)	0.81978 (19)	0.27152 (10)	0.0458 (4)
O2	0.67249 (12)	0.7058 (2)	0.49895 (10)	0.0901 (5)
N3	0.68014 (9)	0.80424 (19)	0.33107 (9)	0.0560 (4)
H3A	0.6702	0.7703	0.3803	0.067*
H3B	0.7314	0.8281	0.3205	0.067*
C3	0.60601 (17)	0.6280 (3)	0.49978 (12)	0.0672 (6)
O3	0.59999 (12)	0.5312 (2)	0.56550 (9)	0.0826 (5)
H3	0.5523 (15)	0.476 (4)	0.562 (2)	0.124*
N4	0.53920 (10)	0.7818 (2)	0.29060 (10)	0.0635 (5)
H4A	0.5313	0.7481	0.3404	0.076*
H4B	0.4966	0.7906	0.2533	0.076*
C4	0.70342 (17)	0.4379 (3)	0.18468 (16)	0.0819 (7)
H4C	0.6648	0.5045	0.2132	0.098*
H4D	0.7451	0.5055	0.1612	0.098*
N5	0.7500	0.3326 (2)	0.2500	0.0666 (6)
C5	0.65283 (19)	0.3567 (3)	0.11274 (18)	0.0964 (8)
H5A	0.6893	0.2833	0.0860	0.116*
H5B	0.6062	0.2984	0.1341	0.116*
N6	0.2500	0.1710 (2)	0.2500	0.0495 (5)
C6	0.6178 (2)	0.4755 (5)	0.0491 (2)	0.1356 (13)
H6A	0.5857	0.4230	0.0035	0.203*
H6B	0.5813	0.5472	0.0757	0.203*
H6C	0.6642	0.5322	0.0276	0.203*
C7	0.81228 (14)	0.2265 (2)	0.20890 (15)	0.0692 (6)
H7A	0.8441	0.1672	0.2531	0.083*
H7B	0.7794	0.1521	0.1733	0.083*
C8	0.87542 (18)	0.3048 (3)	0.1564 (2)	0.0953 (8)
H8A	0.8456	0.3502	0.1063	0.114*
H8B	0.9045	0.3884	0.1885	0.114*
C9	0.93919 (18)	0.1873 (4)	0.1313 (2)	0.1070 (10)
H9A	0.9794	0.2376	0.0978	0.160*
H9B	0.9689	0.1435	0.1810	0.160*
H9C	0.9102	0.1053	0.0990	0.160*
C10	0.32994 (12)	0.2707 (3)	0.25268 (13)	0.0638 (5)
H10A	0.3363	0.3242	0.3067	0.077*
H10B	0.3788	0.2017	0.2501	0.077*
C11	0.33276 (19)	0.3912 (3)	0.18390 (17)	0.0984 (9)
H11A	0.3340	0.3387	0.1299	0.118*
H11B	0.2815	0.4548	0.1820	0.118*
C12	0.4079 (3)	0.4921 (5)	0.1979 (2)	0.1540 (18)
H12A	0.4079	0.5676	0.1531	0.231*
H12B	0.4062	0.5455	0.2509	0.231*
H12C	0.4587	0.4295	0.1988	0.231*
C13	0.25313 (12)	0.0721 (2)	0.32951 (12)	0.0596 (5)
H13A	0.2595	0.1420	0.3777	0.072*
H13B	0.1985	0.0197	0.3311	0.072*
C14	0.32238 (17)	−0.0501 (3)	0.34027 (17)	0.0859 (7)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H14A	0.3188	−0.1195	0.2918	0.103*
H14B	0.3780	0.0001	0.3441	0.103*
C15	0.3121 (3)	−0.1423 (4)	0.4187 (2)	0.1507 (16)
H15A	0.3563	−0.2202	0.4256	0.226*
H15B	0.3163	−0.0733	0.4666	0.226*
H15C	0.2573	−0.1926	0.4144	0.226*

supramolecular architecture³ and membrane materials.⁴ Obviously, these varied applications should thank to the unique structure of amidinothiourea. It can be seen as a planar configuration that can form plentiful hydrogen bonds due to various functional groups. Thus, the related organic crystal structures of amidinothiourea have been explored. Till now, the similar organic crystal structure of tetrapropylammonium sulfanilate-1-(diaminomethylene)thiourea,⁵ bis (tetrapropylammonium)terephthalate-1-(diaminomethylene)thiourea – water⁶ and tetrapropylammonium bicarbonate-1-(diaminomethylene)thiourea – water⁷ have been reported.

Compared with the analogous structure of tetrapropylammonium bicarbonate-1-(diaminomethylene)thiourea – water, the asymmetric unit of the title compound only contains one independent 1-(diaminomethylene)thiourea, one bicarbonate anion and two tetrapropylammonium cations that are arranged at special positions. Analyzing the crystal structure, the amidinothiourea molecule firstly connects with the neighboring molecule to generate the amidinothiourea dimer by typical N–H...N hydrogen bonding, and the two adjacent bicarbonate anions also form the bicarbonate dimer by classical O–H...O hydrogen bonds, then these different dimers links with each other to obtain a 3-dimensional hydrogen-bonded framework with rhombic cavities that can accommodate tetrapropylammonium cations. Clearly, in the similar crystal structures of the title compound and tetrapropylammonium bicarbonate-1-(diaminomethylene)thiourea – water, the bicarbonate and amidinothiourea both tend to form the related dimers by classical hydrogen bonding, but the absence of water molecules existing in the lattice of the title compound leads to the final stable 3-dimensional structure that is very different from the sandwich-like structure of tetrapropylammonium bicarbonate-1-(diaminomethylene)thiourea – water.

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