adenosinium 3,5-dinitrosalicylate

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The crystal structure of adenosinium 3,5-dinitrosalicylicate, $[(C_{10}H_{14}N_5O_4)^+ (C_7H_3N_2O_7)^-]$ shows results from protonation of N1 of the purine ring, with subsequent formation of cyclic $R^2_2(8)$ hydrogen-bonding interactions between this and the adjacent amino group with the two carboxylate oxygen acceptors of the anionic species. Other hydrogen-bonding associations as well as heteromolecular π–π interactions give a chain polymer structure.

Experimental

Crystal data

$C_{10}H_{14}N_5O_4{\cdot}C_7H_3N_2O_7$
M_r = 495.38
Monoclinic, $P2_1$
a = 15.297 (2) Å
b = 8.8543 (14) Å
c = 7.2805 (8) Å
β = 92.321 (10)°
V = 985.3 (2) Å^3
Z = 2
Mo $K\alpha$ radiation, λ = 0.71069 Å
μ = 0.14 mm^{-1}
T = 298 K
0.40 × 0.35 × 0.03 mm

Data collection

Rigaku AFC 7R diffractometer
Absorption correction: ψ scan *TEXSAN* for Windows(Molecular Structure Corporation, 1999)
T_{min} = 0.945, T_{max} = 0.995
2690 measured reflections
2406 independent reflections
1873 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
3 standard reflections every 150 min
intensity decay: 0.0%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.122
S = 0.88
2406 reflections
317 parameters
1 restraint
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1

Selected bond angles (º)

C11—O41—C41	110.4 (3)

Table 2

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O7*B*	0.9237	1.6118	2.438 (5)	146.80
N12—H12···O7*A*^{i}	0.9033	1.8683	2.763 (4)	170.34
O21—H21*A*···O7*A*^{xi}	0.9090	1.8990	2.782 (4)	163.18
O31—H31*A*···N72^{ix}	0.9306	1.9280	2.785 (4)	152.24
O51—H51*C*···O5*B*^{xi}	1.0122	2.1973	2.955 (5)	130.39
O51—H51*C*···O5*A*^{xii}	1.0122	2.3369	3.164 (5)	138.17
N62—H62*A*···O21^{iii}	0.8433	2.1153	2.886 (4)	151.72
N62—H62*B*···O7*B*^{i}	0.8834	1.9160	2.785 (5)	167.30
C22—H22···O2^{viii}	0.96	2.22	3.041 (5)	142
C82—H82···O51	0.97	2.42	3.278 (5)	148

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1; (iii) *x*, *y*−1, *z*; (viii) −*x*+1, *y*+1/2, −*z*+1; (ix) *x*, *y*+1, *z*; (xi) *x*, *y*, *z*+1; (xii) −*x*+2, *y*+1/2, −*z*+2.

Data collection: MSC/AFC Data Collection Software(Molecular Structure Corporation, 1999); cell refinement: MSC/AFC Data Collection Software(Molecular Structure Corporation, 1999); data reduction: *TEXSAN* for Windows(Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SIR92* (Altomare, 1994); molecular graphics: *PLATON* for Windows (Spek, 1999); software used to prepare material for publication: *PLATON* for Windows (Spek, 1999).

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supplementary materials

adenosinium 3,5-dinitrosalicylate

Graham Smith,* Urs D. Wermuth and Peter C. Healy

Comment

Adenosine (6-amino-9β-D-ribofuranosyl-9H-purine) is an important biological molecule, in its di- and tri-phosphorolated form being associated with energy transfer processes in muscle tissue. The structures of many neutral adenosine molecules have been reported, including the parent (Lai & marsh, 1972), adenosine-5'-phosphate (Kraut & Jensen, 1963), adenosine-3'-phosphate (Sundaralingam, 1966), deoxyadenosine monohydrate (Watson *et al.*, 1965), and 3'-O-acetyladenosine (Rao & Sundaralingam, 1970). As a base (pK_a =), adenosine will react with the stronger carboxylic acids resulting in protonation at the N1 position of the purine ring, giving salts with enhanced crystallinity due to hydrogen-bonding interactions. Examoles of these include adenosinium chloride (Shikata *et al.*, 1973), Adenosinium picrate has been known for some time (Budavari, 198x) but its crystal structure has only just been reported (Goto *et al.*, 2004). In this structure, stability is enhanced by the presence of significant heteromolecular π–π ring interactions as well as the expected conventional cation–anion hydrogen bonding interactions. We report here the crystal structure of a similar compound formed from the reaction of adenosine with 3,5-dinitrosalicylic acid (DNSA), adenosinium 3,5-dinitrosalicylate (I). We have previously completed the structures of more than 40 charge-transfer compounds of DNSA with both aliphatic and aromatic Lewis bases (Smith *et al.*, 2000; Smith *et al.*, 2002; Smith *et al.*, 2004), with the incidence of π–π interactions being limited to those examples with the bicyclic hetero-aromatic bases, quinoline, 2,2'-bipyridine and 1,10-phenanthroline (Smith *et al.*, 2004).

In the structure of (I), proton transfer to N1 of the purine ring occurs with subsequent formation of an $R^2_2(8)$ cyclic hydrogen-bonded dimer, similar to that formed in the common symmetric carboxylate–pyrimidine interaction (Lynch *et al.*, 1994; Smith *et al.*, 1995; Lynch *et al.*, 1997; Smith *et al.*, 2002) [N—H···O^i, 2.763 (5), 2.785 (5) Å].This links the cation and anion molecules head-to-tail.

in (I) are the only ones present in the structure, apart from the homomolecular π–π stacking of the six-membered C51–C101 portions of the centrosymmetrically related 8-AQ cation rings [perpendicular separation, 3.38 (1) Å; Cg–Cg 3.72 (1) Å]. These result in a sheet polymer structure extending across the ac cell direction (Fig. 2).

Experimental

The title compound was synthesized by heating under reflux for 10 min, 1 mmol quantities of adenosine and 3,5-dinitrosalicylic acid (DNSA) in 50 mL of 50% ethanol/water. After concentration to ca. 30 mL, partial room temperature evaporation of the hot-filtered solution gave thin pale yellow crystal plates, m. p. 4xx.5–425.0 K.

Refinement

Hydrogen atoms potentially involved in hydrogen-bonding inetractions were located by difference methods while others were included in the refinement at calculated positions (C—H = 0.96 Å) as riding models with and U_{iso}(H) = 1.2U_{eq} (C). The absolute configuration from the parent adenosine [C11(R), C21(R), C31(S), C41(R)] was invoked.

(723GS13_DNSAAD)

Crystal data

$C_{10}H_{14}N_5O_4 \cdot C_7H_3N_2O_7$	$F(000)$ = 512
M_r = 495.38	D_x = 1.670 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, λ = 0.71069 Å
Hall symbol: P 2yb	Cell parameters from 25 reflections
a = 15.297 (2) Å	θ = 12.5–16.9°
b = 8.8543 (14) Å	μ = 0.14 mm^{-1}
c = 7.2805 (8) Å	T = 298 K
β = 92.321 (10)°	Plate, Pale yellow
V = 985.3 (2) Å^3	0.40 × 0.35 × 0.03 mm
Z = 2	

Data collection

Rigaku AFC 7R diffractometer	1873 reflections with $I > 2\sigma(I)$
Radiation source: Rigaku rotating anode	R_{int} = 0.018
graphite	θ_{max} = 27.5°, θ_{min} = 2.7°
ω–2θ scans	h = −8→19
Absorption correction: ψ scan *TEXSAN* for Windows(Molecular Structure Corporation, 1999)	k = 0→11
T_{min} = 0.945, T_{max} = 0.995	l = −9→9
2690 measured reflections	3 standard reflections every 150 min
2406 independent reflections	intensity decay: 0.0%

Refinement

Refinement on F^2	Secondary atom site location: Difference Fourier map
Least-squares matrix: Full	Hydrogen site location: Inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.037	H-atom parameters not refined
$wR(F^2)$ = 0.122	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.5029P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.88	$(\Delta/\sigma)_{max}$ = 0.003
2406 reflections	$\Delta\rho_{max}$ = 0.20 e Å^{-3}
317 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
1 restraint	Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: Structure-invariant direct methods	Extinction coefficient: 0.013 (3)

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All esds are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.60981 (18)	0.1756 (4)	0.3497 (5)	0.0449 (10)
O3A	0.6826 (2)	−0.0660 (4)	0.5133 (5)	0.0530 (11)
O3B	0.8175 (2)	−0.0836 (4)	0.4380 (5)	0.0516 (11)
O5A	0.9774 (2)	0.3746 (4)	0.6546 (5)	0.0581 (11)
O5B	0.9495 (2)	0.5597 (4)	0.4672 (4)	0.0505 (10)
O7A	0.62995 (19)	0.6321 (3)	0.2930 (5)	0.0420 (9)
O7B	0.54980 (18)	0.4236 (4)	0.2720 (5)	0.0493 (10)
N3	0.7517 (2)	−0.0119 (4)	0.4699 (5)	0.0380 (10)
N5	0.9304 (2)	0.4413 (4)	0.5402 (5)	0.0380 (10)
C1	0.6965 (2)	0.3985 (4)	0.3833 (5)	0.0276 (10)
C2	0.6854 (2)	0.2404 (5)	0.3972 (5)	0.0312 (11)
C3	0.7581 (3)	0.1533 (4)	0.4576 (5)	0.0318 (11)
C4	0.8377 (3)	0.2184 (5)	0.5037 (5)	0.0337 (11)
C5	0.8454 (2)	0.3730 (5)	0.4892 (5)	0.0302 (10)
C6	0.7761 (2)	0.4645 (4)	0.4297 (5)	0.0295 (10)
C7	0.6208 (2)	0.4938 (5)	0.3118 (6)	0.0323 (11)
O21	0.70934 (18)	0.8539 (3)	1.0866 (4)	0.0360 (8)
O31	0.8179 (2)	1.0044 (3)	0.8598 (4)	0.0419 (9)
O41	0.84577 (16)	0.6698 (3)	0.7672 (4)	0.0320 (8)
O51	0.9662 (2)	0.6129 (4)	1.0694 (5)	0.0490 (10)
N12	0.5273 (2)	0.2793 (4)	0.7750 (5)	0.0348 (10)
N32	0.5874 (2)	0.5264 (4)	0.7650 (5)	0.0359 (10)
N62	0.5965 (2)	0.0651 (4)	0.8899 (5)	0.0393 (10)
N72	0.75235 (19)	0.2820 (4)	0.9702 (4)	0.0303 (9)
N92	0.73744 (19)	0.5268 (4)	0.8934 (4)	0.0285 (8)
C11	0.7654 (2)	0.6817 (4)	0.8549 (5)	0.0276 (9)
C21	0.7839 (2)	0.7775 (4)	1.0275 (5)	0.0285 (10)
C22	0.5248 (2)	0.4296 (5)	0.7334 (6)	0.0377 (11)
C31	0.8551 (2)	0.8849 (4)	0.9644 (5)	0.0306 (10)
C41	0.9063 (2)	0.7848 (4)	0.8354 (5)	0.0310 (10)
C42	0.6591 (2)	0.4599 (4)	0.8464 (5)	0.0278 (10)
C51	0.9868 (3)	0.7075 (5)	0.9208 (7)	0.0429 (14)
C52	0.6693 (2)	0.3099 (4)	0.8945 (5)	0.0289 (10)
C62	0.5992 (2)	0.2097 (4)	0.8555 (5)	0.0288 (10)
C82	0.7898 (2)	0.4153 (5)	0.9659 (6)	0.0319 (11)
H2	0.568400	0.250100	0.328000	0.0330*
H4	0.885900	0.157900	0.546000	0.0400*
H6	0.783800	0.571500	0.417800	0.0340*

H11	0.723100	0.731000	0.775300	0.0330*
H12	0.479500	0.221500	0.751400	0.0330*
H21	0.807500	0.713800	1.123300	0.0340*
H21A	0.689600	0.789700	1.173100	0.0330*
H22	0.471300	0.468100	0.676900	0.0450*
H31	0.891300	0.920600	1.065600	0.0350*
H31A	0.808700	1.090900	0.929000	0.0330*
H41	0.923100	0.844900	0.733800	0.0370*
H51A	1.028000	0.782700	0.963100	0.0540*
H51B	1.013900	0.648000	0.829000	0.0540*
H51C	0.983800	0.648600	1.197700	0.0330*
H62A	0.642600	0.026000	0.936100	0.0330*
H62B	0.553200	0.007600	0.846600	0.0330*
H82	0.849500	0.432800	1.010400	0.0380*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0298 (14)	0.0317 (15)	0.072 (2)	−0.0026 (12)	−0.0143 (13)	0.0037 (15)
O3A	0.0529 (19)	0.0355 (17)	0.070 (2)	−0.0073 (15)	−0.0059 (16)	0.0095 (16)
O3B	0.0544 (19)	0.0373 (17)	0.062 (2)	0.0159 (16)	−0.0127 (16)	−0.0100 (16)
O5A	0.0405 (16)	0.049 (2)	0.082 (2)	0.0012 (16)	−0.0312 (17)	−0.0012 (18)
O5B	0.0396 (16)	0.056 (2)	0.0559 (18)	−0.0174 (16)	0.0034 (14)	0.0052 (17)
O7A	0.0332 (14)	0.0321 (15)	0.0603 (19)	0.0047 (12)	−0.0028 (13)	0.0084 (14)
O7B	0.0291 (14)	0.0352 (16)	0.082 (2)	0.0028 (13)	−0.0187 (14)	0.0063 (17)
N3	0.0424 (18)	0.0295 (18)	0.0408 (18)	0.0044 (15)	−0.0128 (15)	−0.0019 (15)
N5	0.0273 (15)	0.040 (2)	0.0463 (19)	−0.0027 (15)	−0.0022 (13)	−0.0101 (16)
C1	0.0244 (16)	0.0275 (18)	0.0305 (17)	0.0008 (14)	−0.0022 (13)	0.0004 (14)
C2	0.0258 (17)	0.0282 (19)	0.039 (2)	0.0002 (15)	−0.0052 (14)	−0.0009 (15)
C3	0.0362 (19)	0.0261 (19)	0.0327 (18)	0.0012 (15)	−0.0041 (15)	−0.0019 (15)
C4	0.0275 (17)	0.036 (2)	0.037 (2)	0.0072 (16)	−0.0050 (15)	−0.0006 (16)
C5	0.0239 (16)	0.035 (2)	0.0316 (18)	−0.0004 (15)	−0.0017 (14)	−0.0027 (16)
C6	0.0284 (17)	0.0265 (18)	0.0332 (18)	−0.0021 (14)	−0.0033 (14)	0.0007 (15)
C7	0.0265 (17)	0.029 (2)	0.041 (2)	0.0044 (15)	−0.0029 (14)	0.0025 (16)
O21	0.0350 (13)	0.0297 (14)	0.0437 (15)	0.0050 (12)	0.0047 (12)	0.0019 (12)
O31	0.0592 (18)	0.0221 (14)	0.0441 (15)	0.0053 (14)	−0.0022 (13)	0.0014 (13)
O41	0.0267 (12)	0.0295 (13)	0.0398 (14)	−0.0051 (11)	0.0026 (10)	−0.0076 (12)
O51	0.0490 (17)	0.0401 (18)	0.0561 (18)	0.0072 (15)	−0.0186 (14)	0.0025 (15)
N12	0.0241 (14)	0.0270 (16)	0.0528 (19)	−0.0031 (13)	−0.0063 (13)	−0.0015 (15)
N32	0.0261 (15)	0.0299 (17)	0.051 (2)	0.0011 (13)	−0.0073 (13)	0.0040 (15)
N62	0.0280 (16)	0.0289 (17)	0.060 (2)	−0.0053 (14)	−0.0111 (15)	−0.0030 (16)
N72	0.0269 (14)	0.0246 (15)	0.0388 (16)	0.0020 (13)	−0.0075 (12)	−0.0024 (13)
N92	0.0240 (14)	0.0221 (14)	0.0391 (16)	0.0011 (12)	−0.0025 (12)	−0.0015 (13)
C11	0.0241 (15)	0.0246 (17)	0.0339 (17)	0.0013 (14)	−0.0027 (13)	−0.0006 (15)
C21	0.0284 (17)	0.0241 (17)	0.0327 (17)	0.0029 (15)	−0.0020 (13)	0.0014 (15)
C22	0.0272 (18)	0.0280 (19)	0.057 (2)	0.0040 (16)	−0.0078 (16)	0.0013 (18)
C31	0.0311 (17)	0.0235 (17)	0.0367 (18)	−0.0055 (14)	−0.0056 (14)	−0.0038 (15)
C41	0.0282 (17)	0.0240 (17)	0.0407 (19)	−0.0071 (15)	0.0012 (14)	0.0005 (16)
C42	0.0237 (15)	0.0260 (18)	0.0336 (17)	0.0011 (14)	−0.0009 (13)	−0.0027 (14)
C51	0.0281 (19)	0.037 (2)	0.063 (3)	−0.0012 (17)	−0.0074 (17)	−0.002 (2)
C52	0.0249 (16)	0.0237 (18)	0.0380 (18)	−0.0006 (14)	−0.0001 (14)	−0.0018 (15)

C62	0.0264 (17)	0.0233 (18)	0.0364 (18)	−0.0001 (14)	−0.0014 (14)	−0.0043 (15)
C82	0.0268 (17)	0.0275 (18)	0.041 (2)	0.0029 (15)	−0.0049 (14)	0.0008 (16)

Geometric parameters (Å, º)

O2—C2	1.324 (5)	N92—C11	1.467 (5)
O3A—N3	1.214 (5)	N12—H12	0.9033
O3B—N3	1.220 (5)	N62—H62B	0.8834
O5A—N5	1.229 (5)	N62—H62A	0.8433
O5B—N5	1.216 (5)	C1—C2	1.414 (6)
O7A—C7	1.241 (5)	C1—C7	1.508 (5)
O7B—C7	1.275 (5)	C1—C6	1.380 (5)
O2—H2	0.9237	C2—C3	1.409 (6)
O21—C21	1.408 (4)	C3—C4	1.376 (6)
O31—C31	1.410 (4)	C4—C5	1.378 (6)
O41—C11	1.412 (4)	C5—C6	1.389 (5)
O41—C41	1.450 (4)	C4—H4	0.9524
O51—C51	1.414 (6)	C6—H6	0.9591
O21—H21A	0.9090	C11—C21	1.533 (5)
O31—H31A	0.9306	C21—C31	1.530 (5)
O51—H51C	1.0122	C31—C41	1.530 (5)
N3—C3	1.469 (5)	C41—C51	1.520 (6)
N5—C5	1.468 (5)	C42—C52	1.381 (5)
N12—C62	1.371 (5)	C52—C62	1.412 (5)
N12—C22	1.365 (6)	C11—H11	0.9564
N32—C42	1.359 (5)	C21—H21	0.9563
N32—C22	1.299 (5)	C22—H22	0.9633
N62—C62	1.306 (5)	C31—H31	0.9573
N72—C52	1.386 (4)	C41—H41	0.9549
N72—C82	1.313 (5)	C51—H51A	0.9590
N92—C42	1.368 (4)	C51—H51B	0.9584
N92—C82	1.364 (5)	C82—H82	0.9690
O2···O3A	2.670 (5)	N32···H11	2.7539
O2···O7B	2.438 (5)	N72···H31A^{iii}	1.9280
O2···N3	2.842 (5)	N72···H62A	2.8257
O2···C22^{i}	3.041 (5)	C1···C42	3.485 (5)
O3A···O21^{ii}	3.229 (5)	C1···C82^{vi}	3.412 (5)
O3A···O2	2.670 (5)	C1···N72^{vi}	3.324 (5)
O3A···O7A^{iii}	3.203 (5)	C2···N72^{vi}	3.333 (5)
O3B···O21^{ii}	3.041 (5)	C3···O31^{iii}	3.306 (5)
O3B···C41^{iii}	3.355 (5)	C4···O31^{iii}	3.235 (5)
O3B···O31^{iii}	3.168 (5)	C5···O41	3.317 (5)
O3B···C21^{ii}	3.253 (5)	C6···C42	3.584 (5)
O5A···O51^{iv}	3.164 (5)	C6···C82^{vi}	3.420 (6)
O5A···O5B^{v}	3.145 (5)	C6···O41	3.204 (5)
O5B···O41	2.919 (4)	C7···C22	3.502 (6)
O5B···O51^{vi}	2.955 (5)	C7···C42^{vi}	3.475 (6)
O5B···O5A^{vii}	3.145 (5)	C7···N32	3.372 (6)
O7A···C21^{vi}	3.363 (5)	C7···N12^{viii}	3.436 (5)
O7A···N12^{viii}	2.763 (4)	C7···C52^{vi}	3.552 (6)

O7A···O21^{vi}	2.782 (4)	C21···O51	3.150 (5)
O7A···O3A^{ix}	3.203 (5)	C21···O3B^{x}	3.253 (5)
O7B···C22	3.397 (6)	C21···O7A^{xi}	3.363 (5)
O7B···O2	2.438 (5)	C22···O2^{viii}	3.041 (5)
O7B···N62^{viii}	2.785 (5)	C22···C7	3.502 (6)
O21···N92	3.256 (4)	C22···O7B	3.397 (6)
O21···O31	2.735 (4)	C31···O51^{xii}	3.415 (5)
O21···N3^{x}	3.078 (5)	C41···O3B^{ix}	3.355 (5)
O21···N62^{ix}	2.886 (4)	C42···C6	3.584 (5)
O21···O7A^{xi}	2.782 (4)	C42···C1	3.485 (5)
O21···O3B^{x}	3.041 (5)	C42···C7^{xi}	3.475 (6)
O21···O3A^{x}	3.229 (5)	C52···C7^{xi}	3.552 (6)
O31···O41	3.072 (4)	C82···C6^{xi}	3.420 (6)
O31···N3^{ix}	2.979 (5)	C82···O51	3.278 (5)
O31···C4^{ix}	3.235 (5)	C82···C1^{xi}	3.412 (5)
O31···O3B^{ix}	3.168 (5)	C7···H62B^{viii}	2.8602
O31···C3^{ix}	3.306 (5)	C7···H2	2.3065
O31···N72^{ix}	2.785 (4)	C7···H12^{viii}	2.5639
O31···O21	2.735 (4)	C7···H21A^{vi}	3.0129
O41···O5B	2.919 (4)	C52···H31A^{iii}	2.8856
O41···O51	2.857 (4)	C82···H51A^{iv}	3.0491
O41···C6	3.204 (5)	C82···H21	2.8891
O41···O31	3.072 (4)	C82···H31A^{iii}	2.9004
O41···C5	3.317 (5)	H2···H22^{i}	2.5696
O41···N5	2.945 (4)	H2···C7	2.3065
O51···O5A^{xii}	3.164 (5)	H2···O7B	1.6118
O51···C21	3.150 (5)	H4···O3B	2.4937
O51···C82	3.278 (5)	H4···O31^{iii}	2.8881
O51···C31^{iv}	3.415 (5)	H4···O5B^{v}	2.6692
O51···O5B^{xi}	2.955 (5)	H4···O5A	2.4852
O51···O41	2.857 (4)	H6···O41	2.8163
O2···H22^{i}	2.2210	H6···H21^{vi}	2.5257
O3A···H21A^{ii}	2.7929	H6···O5B	2.5478
O3A···H11^{iii}	2.6753	H6···O7A	2.5454
O3A···H22^{i}	2.6994	H11···O3A^{ix}	2.6753
O3B···H21A^{ii}	2.9155	H11···O31	2.8756
O3B···H4	2.4937	H11···N32	2.7539
O3B···H41^{iii}	2.7141	H12···H62B	2.2968
O3B···H21^{ii}	2.9090	H12···O7A^{i}	1.8683
O5A···H51A^{iv}	2.9042	H12···O7B^{i}	2.6798
O5A···H51C^{iv}	2.3369	H12···C7^{i}	2.5639
O5A···H4	2.4852	H21···O3B^{x}	2.9090
O5A···H51B	2.7797	H21···O51	2.6311
O5A···H31^{iv}	2.8317	H21···C82	2.8891
O5B···H51C^{vi}	2.1973	H21···H6^{xi}	2.5257
O5B···H51B	2.8827	H21A···O3A^{x}	2.7929
O5B···H6	2.5478	H21A···O3B^{x}	2.9155
O5B···H4^{vii}	2.6692	H21A···O7A^{xi}	1.8990
O7A···H6	2.5454	H21A···N3^{x}	2.9140
O7A···H21A^{vi}	1.8990	H21A···C7^{xi}	3.0129
O7A···H12^{viii}	1.8683	H22···O2^{viii}	2.2210
O7B···H12^{viii}	2.6798	H22···O3A^{viii}	2.6994

O7B···H2	1.6118	H22···H2^{viii}	2.5696
O7B···H62B^{viii}	1.9160	H31···H51A	2.5587
O21···H62A^{ix}	2.1153	H31···O5A^{xii}	2.8317
O21···H31A	2.8586	H31···H51B^{xii}	2.5799
O31···H4^{ix}	2.8881	H31A···O21	2.8586
O31···H11	2.8756	H31A···N72^{ix}	1.9280
O31···H62A^{ix}	2.7671	H31A···C52^{ix}	2.8856
O41···H82	2.7448	H31A···C82^{ix}	2.9004
O41···H6	2.8163	H41···O3B^{ix}	2.7141
O51···H82	2.4191	H51A···H31	2.5587
O51···H21	2.6311	H51A···O5A^{xii}	2.9042
N3···O2	2.842 (5)	H51A···C82^{xii}	3.0491
N3···O21^{ii}	3.078 (5)	H51A···H82^{xii}	2.2991
N3···O31^{iii}	2.979 (5)	H51B···O5A	2.7797
N5···O41	2.945 (4)	H51B···O5B	2.8827
N12···C7^{i}	3.436 (5)	H51B···H31^{iv}	2.5799
N12···O7A^{i}	2.763 (4)	H51C···O5B^{xi}	2.1973
N32···C7	3.372 (6)	H51C···O5A^{xii}	2.3369
N62···O7B^{i}	2.785 (5)	H62A···O21^{iii}	2.1153
N62···N72	3.099 (5)	H62A···O31^{iii}	2.7671
N62···O21^{iii}	2.886 (4)	H62A···N72	2.8257
N72···C2^{xi}	3.333 (5)	H62B···H12	2.2968
N72···N62	3.099 (5)	H62B···O7B^{i}	1.9160
N72···C1^{xi}	3.324 (5)	H62B···C7^{i}	2.8602
N72···O31^{iii}	2.785 (4)	H82···O41	2.7448
N92···O21	3.256 (4)	H82···O51	2.4191
N3···H21A^{ii}	2.9140	H82···H51A^{iv}	2.2991

C2—O2—H2	108.71	N92—C11—C21	114.0 (3)
C11—O41—C41	110.4 (3)	O41—C11—N92	106.4 (3)
C21—O21—H21A	101.96	O21—C21—C31	112.8 (3)
C31—O31—H31A	113.07	C11—C21—C31	102.0 (3)
C51—O51—H51C	117.51	O21—C21—C11	113.0 (3)
O3B—N3—C3	116.7 (3)	N12—C22—N32	126.2 (3)
O3A—N3—C3	118.0 (3)	O31—C31—C21	110.6 (3)
O3A—N3—O3B	125.3 (4)	O31—C31—C41	108.0 (3)
O5B—N5—C5	118.1 (3)	C21—C31—C41	102.3 (3)
O5A—N5—O5B	124.5 (3)	O41—C41—C31	106.3 (2)
O5A—N5—C5	117.5 (3)	O41—C41—C51	108.6 (3)
C22—N12—C62	123.2 (3)	C31—C41—C51	115.9 (3)
C22—N32—C42	111.6 (3)	N32—C42—N92	127.2 (3)
C52—N72—C82	102.9 (3)	N32—C42—C52	127.4 (3)
C11—N92—C82	125.4 (3)	N92—C42—C52	105.3 (3)
C11—N92—C42	128.0 (3)	O51—C51—C41	112.2 (4)
C42—N92—C82	106.1 (3)	N72—C52—C62	130.1 (3)
C22—N12—H12	119.67	C42—C52—C62	118.4 (3)
C62—N12—H12	117.11	N72—C52—C42	111.4 (3)
C62—N62—H62B	121.72	N12—C62—N62	119.4 (3)
C62—N62—H62A	116.53	N62—C62—C52	127.4 (3)
H62A—N62—H62B	120.57	N12—C62—C52	113.1 (3)
C2—C1—C7	119.1 (3)	N72—C82—N92	114.2 (3)
C6—C1—C7	120.3 (3)	O41—C11—H11	109.89

C2—C1—C6	120.6 (3)	N92—C11—H11	110.31
C1—C2—C3	117.9 (3)	C21—C11—H11	110.00
O2—C2—C3	120.9 (4)	O21—C21—H21	110.30
O2—C2—C1	121.1 (3)	C11—C21—H21	108.86
N3—C3—C2	120.7 (4)	C31—C21—H21	109.46
N3—C3—C4	117.6 (4)	N12—C22—H22	117.09
C2—C3—C4	121.7 (4)	N32—C22—H22	116.72
C3—C4—C5	118.3 (4)	O31—C31—H31	112.09
N5—C5—C4	117.9 (3)	C21—C31—H31	111.76
N5—C5—C6	119.7 (4)	C41—C31—H31	111.67
C4—C5—C6	122.4 (3)	O41—C41—H41	108.31
C1—C6—C5	118.9 (3)	C31—C41—H41	108.25
O7B—C7—C1	116.2 (4)	C51—C41—H41	109.20
O7A—C7—O7B	123.7 (4)	O51—C51—H51A	109.24
O7A—C7—C1	120.1 (3)	O51—C51—H51B	108.91
C3—C4—H4	120.59	C41—C51—H51A	109.26
C5—C4—H4	121.06	C41—C51—H51B	109.18
C1—C6—H6	120.43	H51A—C51—H51B	107.96
C5—C6—H6	120.61	N72—C82—H82	122.82
O41—C11—C21	106.1 (3)	N92—C82—H82	122.98

C41—O41—C11—C21	−17.4 (4)	C7—C1—C2—O2	−0.4 (5)
C11—O41—C41—C31	−5.4 (4)	C7—C1—C2—C3	177.6 (3)
C41—O41—C11—N92	−139.1 (3)	C7—C1—C6—C5	−177.8 (3)
C11—O41—C41—C51	119.9 (3)	C2—C1—C7—O7B	1.6 (5)
O3B—N3—C3—C4	−32.0 (5)	O2—C2—C3—C4	178.6 (4)
O3A—N3—C3—C2	−34.3 (5)	O2—C2—C3—N3	−0.2 (6)
O3B—N3—C3—C2	146.8 (4)	C1—C2—C3—N3	−178.2 (3)
O3A—N3—C3—C4	146.9 (4)	C1—C2—C3—C4	0.6 (5)
O5A—N5—C5—C4	−27.6 (5)	N3—C3—C4—C5	178.6 (3)
O5A—N5—C5—C6	152.0 (4)	C2—C3—C4—C5	−0.1 (6)
O5B—N5—C5—C4	152.6 (4)	C3—C4—C5—C6	−0.1 (6)
O5B—N5—C5—C6	−27.8 (5)	C3—C4—C5—N5	179.5 (4)
C62—N12—C22—N32	−1.0 (7)	C4—C5—C6—C1	0.0 (6)
C22—N12—C62—C52	1.4 (5)	N5—C5—C6—C1	−179.6 (3)
C22—N12—C62—N62	−179.6 (4)	N92—C11—C21—O21	−89.0 (3)
C42—N32—C22—N12	0.4 (6)	O41—C11—C21—C31	32.8 (3)
C22—N32—C42—C52	−0.2 (6)	O41—C11—C21—O21	154.2 (3)
C22—N32—C42—N92	177.8 (4)	N92—C11—C21—C31	149.5 (3)
C82—N72—C52—C62	177.2 (4)	O21—C21—C31—O31	−41.5 (4)
C52—N72—C82—N92	0.0 (4)	O21—C21—C31—C41	−156.3 (3)
C82—N72—C52—C42	0.1 (4)	C11—C21—C31—C41	−34.7 (3)
C11—N92—C42—C52	173.1 (3)	C11—C21—C31—O31	80.1 (3)
C82—N92—C11—C21	−71.4 (4)	O31—C31—C41—C51	148.1 (3)
C11—N92—C42—N32	−5.3 (6)	O31—C31—C41—O41	−91.1 (3)
C42—N92—C11—C21	116.9 (4)	C21—C31—C41—O41	25.6 (3)
C82—N92—C42—N32	−178.3 (4)	C21—C31—C41—C51	−95.2 (3)
C42—N92—C11—O41	−126.6 (3)	O41—C41—C51—O51	−60.4 (4)
C82—N92—C42—C52	0.1 (4)	C31—C41—C51—O51	59.2 (5)
C11—N92—C82—N72	−173.3 (3)	N92—C42—C52—C62	−177.6 (3)
C42—N92—C82—N72	0.0 (4)	N92—C42—C52—N72	−0.1 (4)
C82—N92—C11—O41	45.2 (5)	N32—C42—C52—N72	178.3 (4)

C6—C1—C2—O2	−178.7 (4)	N32—C42—C52—C62	0.7 (6)
C6—C1—C2—C3	−0.7 (5)	N72—C52—C62—N62	2.8 (7)
C6—C1—C7—O7A	0.6 (6)	C42—C52—C62—N12	−1.2 (5)
C6—C1—C7—O7B	179.9 (5)	C42—C52—C62—N62	179.9 (5)
C2—C1—C7—O7A	−177.7 (4)	N72—C52—C62—N12	−178.2 (4)
C2—C1—C6—C5	0.4 (5)		

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1; (ii) *x*, *y*−1, *z*−1; (iii) *x*, *y*−1, *z*; (iv) −*x*+2, *y*−1/2, −*z*+2; (v) −*x*+2, *y*−1/2, −*z*+1; (vi) *x*, *y*, *z*−1; (vii) −*x*+2, *y*+1/2, −*z*+1; (viii) −*x*+1, *y*+1/2, −*z*+1; (ix) *x*, *y*+1, *z*; (x) *x*, *y*+1, *z*+1; (xi) *x*, *y*, *z*+1; (xii) −*x*+2, *y*+1/2, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O7*B*	0.9237	1.6118	2.438 (5)	146.80
N12—H12···O7*A*^{i}	0.9033	1.8683	2.763 (4)	170.34
O21—H21*A*···O7*A*^{xi}	0.9090	1.8990	2.782 (4)	163.18
O31—H31*A*···N72^{ix}	0.9306	1.9280	2.785 (4)	152.24
O51—H51*C*···O5*B*^{xi}	1.0122	2.1973	2.955 (5)	130.39
O51—H51*C*···O5*A*^{xii}	1.0122	2.3369	3.164 (5)	138.17
N62—H62*A*···O21^{iii}	0.8433	2.1153	2.886 (4)	151.72
N62—H62*B*···O7*B*^{i}	0.8834	1.9160	2.785 (5)	167.30
C22—H22···O2^{viii}	0.96	2.22	3.041 (5)	142
C82—H82···O51	0.97	2.42	3.278 (5)	148

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1; (iii) *x*, *y*−1, *z*; (viii) −*x*+1, *y*+1/2, −*z*+1; (ix) *x*, *y*+1, *z*; (xi) *x*, *y*, *z*+1; (xii) −*x*+2, *y*+1/2, −*z*+2.

Figure 1

Fig. 1. Molecular configuration and atom numbering scheme for the adeninium cation and the DNSA anion in (I). Atoms are shown as 30% probability ellipsoids

Figure 2

Fig. 2. The packing of (I) in the unit cell viewed down c, showing hydrogen-bonding associations as broken lines.