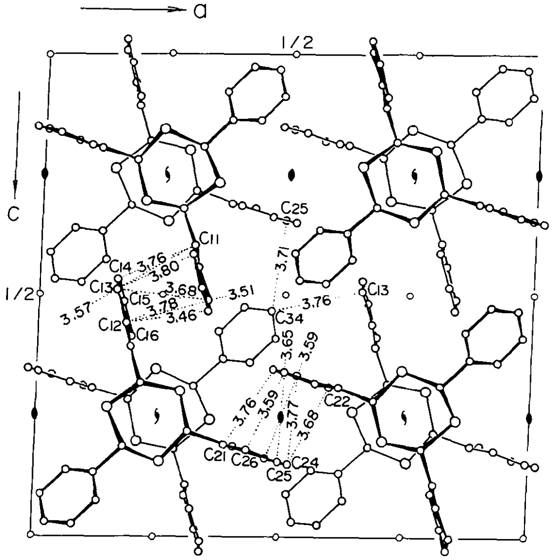

Fig. 2. The molecular packing viewed down **b**, showing all intermolecular distances (involving non-hydrogen atoms) less than 3·81 Å. Each e.s.d. is no greater than 0·01 Å.

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Structure of *N*-[1′-(9-Adenyl)-β-D-ribofuranuronosyl]-L-phenylalanine Water Ethanol (1/½/¼), $C_{19}H_{20}N_6O_6.\frac{1}{2}H_2O.\frac{1}{4}C_2H_6O$

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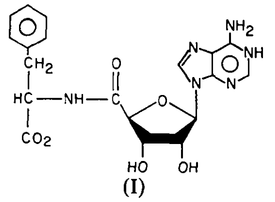
Abstract. $M_r = 448{\cdot}94$, monoclinic, $P2_1$, $a = 9{\cdot}207$ (1), $b = 10{\cdot}503$ (2), $c = 22{\cdot}208$ (3) Å, $\beta = 101{\cdot}4$ (1)°, $V = 2105{\cdot}2$ (9) Å^3, $Z = 4$, $D_x = 1{\cdot}416$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 9{\cdot}3$ cm^{-1}, $F(000) = 942$, $T = 293$ K. Final $R = 0{\cdot}053$ for 4132 observed intensities. Both independent molecules in the asymmetric unit are zwitterions. One molecule has an extended conformation with the base *anti* and the sugar C(2′) *endo* (^2E); the other molecule has a closed conformation with the base *syn* and the sugar C(3′) *endo* (^3E).

Introduction. Nucleoside peptides are found in a variety of biological systems. *S*-Adenosylmethionine, the cofactor responsible for methylation, is one example, as are a wide variety of nucleoside antibiotics (Suhadolnik, 1970). Amino acids were first shown to bind covalently to RNA in 1958 (Akashi & Yokoi, 1958). Covalent protein–nucleic acid attachments have been demonstrated in adenovirus (Rekosh, Russell, Bellet & Robinson, 1977) and polyovirus (Rothberg, Harris, Nomoto & Wimmer, 1978). As one method to aid in the identification of nucleoside peptides in DNA and RNA, model compounds have been synthesized (Robins *et al.*, 1971). The crystal structure of one, *N*-[1′-(9-adenyl)-β-D-ribofuranuronosyl]-L-phenylalanine (I) (Kawana, Rousseau & Robins, 1972), has been determined as part of our program to understand the detailed geometry of these molecules as well as their intermolecular interactions.



(I)

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Table 1. *Fractional atomic coordinates and isotropic temperature factors*

For non-H atoms $B = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B(Å^2)
N(1A)	0·0279 (3)	0·5126 (3)	0·5707 (1)	3·00
C(2A)	0·0689 (4)	0·4115 (3)	0·6083 (2)	3·08
N(3A)	0·1815 (3)	0·4074 (3)	0·6534 (1)	3·02
C(4A)	0·2592 (4)	0·5186 (3)	0·6603 (2)	2·64
C(5A)	0·2253 (4)	0·6274 (3)	0·6255 (2)	2·91
C(6A)	0·1013 (4)	0·6254 (3)	0·5771 (2)	2·91
N(6A)	0·0542 (4)	0·7194 (3)	0·5393 (2)	3·98
N(7A)	0·3297 (4)	0·7215 (3)	0·6442 (1)	3·50
C(8A)	0·4221 (4)	0·6684 (3)	0·6891 (2)	3·22
N(9A)	0·3863 (3)	0·5446 (3)	0·7010 (1)	2·67
C(1′A)	0·4735 (4)	0·4641 (3)	0·7476 (1)	2·65
C(2′A)	0·4033 (4)	0·4351 (3)	0·8036 (2)	3·11
C(3′A)	0·3519 (4)	0·2977 (3)	0·7909 (1)	2·82
C(4′A)	0·4725 (4)	0·2436 (3)	0·7593 (1)	2·55
C(5′A)	0·4238 (3)	0·1232 (3)	0·7231 (1)	2·40
O(1′A)	0·4978 (3)	0·3462 (2)	0·7197 (1)	2·76
O(2′A)	0·5131 (4)	0·4382 (2)	0·8572 (1)	4·27
O(3′A)	0·3248 (3)	0·2283 (3)	0·8413 (1)	3·76
O(5′A)	0·4628 (3)	0·0196 (2)	0·7465 (1)	3·45
N(6′A)	0·3319 (3)	0·1373 (2)	0·6697 (1)	2·58
C(7′A)	0·2608 (4)	0·0274 (3)	0·6352 (2)	2·73
C(8′A)	0·2062 (4)	0·0623 (3)	0·5684 (2)	2·80
O(8′A)	0·2009 (3)	0·1759 (2)	0·5519 (1)	3·54
O(8″A)	0·1613 (3)	−0·0301 (3)	0·5326 (1)	3·62
C(9′A)	0·1336 (4)	−0·0244 (4)	0·6635 (2)	3·43
C(P1A)	0·0061 (5)	0·0662 (4)	0·6613 (2)	3·74
C(P2A)	−0·1020 (5)	0·0774 (5)	0·6091 (3)	4·89
C(P3A)	−0·2224 (7)	0·1603 (7)	0·6066 (4)	6·95
C(P4A)	−0·2322 (8)	0·2306 (7)	0·6580 (4)	7·80
C(P5A)	−0·128 (1)	0·2206 (6)	0·7083 (4)	7·92
C(P6A)	−0·0040 (7)	0·1405 (5)	0·7124 (3)	5·34
N(1B)	−0·0173 (3)	0·2892 (3)	0·9202 (1)	3·30
C(2B)	−0·0666 (4)	0·3963 (4)	0·8887 (2)	4·20
N(3B)	0·0084 (3)	0·5014 (3)	0·8878 (2)	3·78
C(4B)	0·1464 (3)	0·4921 (3)	0·9226 (1)	2·48
C(5B)	0·2060 (3)	0·3893 (3)	0·9574 (1)	2·31
C(6B)	0·1183 (4)	0·2807 (3)	0·9577 (1)	2·61
N(6B)	0·1556 (4)	0·1772 (3)	0·9900 (2)	3·51
N(7B)	0·3498 (3)	0·4141 (3)	0·9863 (1)	2·98
C(8B)	0·3746 (3)	0·5285 (3)	0·9679 (2)	2·75
N(9B)	0·2547 (3)	0·5832 (3)	0·9297 (1)	2·46
C(1′B)	0·2438 (3)	0·7072 (3)	0·8998 (1)	2·30
C(2′B)	0·3216 (4)	0·8148 (3)	0·9395 (1)	2·49
C(3′B)	0·3543 (3)	0·9078 (3)	0·8908 (1)	2·41
C(4′B)	0·3977 (3)	0·8137 (3)	0·8447 (1)	2·31
C(5′B)	0·5627 (3)	0·7842 (3)	0·8612 (1)	2·30
O(1′B)	0·3124 (3)	0·7008 (2)	0·8478 (1)	2·59
O(2′B)	0·2426 (3)	0·8636 (3)	0·9823 (1)	3·48
O(3′B)	0·2235 (3)	0·9760 (2)	0·8653 (1)	3·19
O(5′B)	0·6109 (3)	0·6900 (2)	0·8920 (1)	2·85
N(6′B)	0·6464 (3)	0·8720 (3)	0·8410 (1)	2·56
C(7′B)	0·8071 (3)	0·8747 (3)	0·8558 (2)	2·69
C(8′B)	0·8630 (4)	0·9834 (4)	0·9008 (2)	3·05
O(8′B)	0·9683 (3)	0·9628 (3)	0·9436 (1)	3·45
O(8″B)	0·8013 (3)	1·0904 (3)	0·8899 (2)	4·62
C(9′B)	0·8673 (4)	0·9000 (4)	0·7975 (2)	3·42
C(P1B)	0·8320 (4)	0·8006 (4)	0·7477 (2)	3·67
C(P2B)	0·8750 (8)	0·6757 (6)	0·7585 (3)	6·25
C(P3B)	0·849 (1)	0·5870 (7)	0·7114 (4)	8·32
C(P4B)	0·7789 (8)	0·6192 (9)	0·6537 (3)	7·93
C(P5B)	0·7354 (8)	0·7454 (9)	0·6424 (3)	7·14
C(P6B)	0·7599 (5)	0·8331 (6)	0·6892 (2)	4·85
O(W1)	0·5651 (4)	0·2002 (3)	0·9255 (1)	4·44
O(1Et)*	0·290 (1)	0·411 (1)	0·5156 (5)	8·32
C(1Et)*	0·447 (3)	0·425 (3)	0·528 (2)	14·59
C(2′Et)*	0·491 (9)	0·555 (9)	0·511 (4)	13·32
C(2″Et)*	0·510 (9)	0·329 (9)	0·491 (4)	16·04
H(N1A)	−0·049 (5)	0·505 (4)	0·536 (2)	3·30
H(C2A)	0·007 (5)	0·335 (5)	0·593 (2)	4·00
H(1)(N6A)	−0·039 (5)	0·704 (6)	0·508 (2)	4·60
H(2)(N6A)	0·095 (6)	0·781 (5)	0·544 (2)	4·60
H(C8A)	0·515 (5)	0·700 (5)	0·714 (2)	4·10
H(C1′A)	0·568 (4)	0·507 (4)	0·763 (2)	2·20
H(C2′A)	0·327 (4)	0·489 (4)	0·808 (2)	3·20
H(C3′A)	0·251 (5)	0·298 (5)	0·761 (2)	3·50
H(C4′A)	0·568 (5)	0·225 (5)	0·790 (2)	3·40
H(O2′A)	0·532 (4)	0·509 (4)	0·869 (2)	2·80
H(O3′A)	0·412 (4)	0·219 (4)	0·867 (2)	2·30
H(N6′A)	0·283 (5)	0·213 (5)	0·651 (2)	4·40
H(C7′A)	0·327 (5)	−0·028 (5)	0·636 (2)	4·40
H(1)(C9A)	0·175 (5)	−0·040 (5)	0·704 (2)	4·20
H(2)(C9A)	0·095 (5)	−0·098 (5)	0·641 (2)	4·00
HC(P2A)	−0·097 (7)	0·021 (6)	0·571 (3)	6·20
HC(P3A)	−0·298 (7)	0·179 (7)	0·563 (3)	6·90
HC(P4A)	−0·34 (1)	0·28 (1)	0·655 (5)	12·70
HC(P5A)	−0·14 (1)	0·26 (1)	0·742 (5)	12·60
HC(P6A)	0·087 (8)	0·139 (8)	0·756 (3)	8·50
H(N1B)	−0·073 (5)	0·231 (5)	0·914 (2)	4·10
H(C2B)	−0·167 (6)	0·391 (6)	0·863 (2)	5·00
H(1)(N6B)	0·109 (6)	0·112 (6)	0·983 (3)	6·10
H(2)(N6B)	0·246 (5)	0·178 (5)	1·018 (2)	4·00
H(C8B)	0·471 (4)	0·573 (4)	0·980 (2)	2·60
H(C1′B)	0·130 (4)	0·718 (4)	0·884 (2)	2·20
H(C2′B)	0·422 (5)	0·790 (5)	0·965 (2)	3·30
H(C3′B)	0·441 (5)	0·962 (5)	0·910 (2)	4·10
H(C4′B)	0·374 (3)	0·848 (3)	0·804 (1)	1·30
H(O2′B)	0·152 (5)	0·891 (5)	0·963 (2)	3·80
H(O3′B)	0·265 (7)	1·044 (7)	0·849 (3)	6·60
H(N6′B)	0·602 (5)	0·929 (5)	0·820 (2)	3·60
H(C7′B)	0·846 (5)	0·788 (4)	0·880 (2)	3·20
H(1)(C9B)	0·983 (5)	0·910 (5)	0·811 (2)	4·50
H(2)(C9B)	0·834 (6)	0·977 (6)	0·780 (2)	5·10
HC(P2B)	0·94 (1)	0·66 (1)	0·796 (5)	13·60
HC(P3B)	0·88 (1)	0·48 (1)	0·731 (4)	11·70
HC(P4B)	0·76 (2)	0·59 (2)	0·605 (6)	18·00
HC(P5B)	0·685 (7)	0·761 (7)	0·601 (3)	6·30
HC(P6B)	0·723 (7)	0·928 (7)	0·683 (3)	6·80
H(1)(OW1)	0·59 (1)	0·31 (1)	0·941 (5)	13·40
H(2)(OW1)	0·649 (8)	0·162 (8)	0·913 (3)	8·30

* The occupancy factors for these atoms are 0·55 (8) for O(1Et) and C(1Et), and 0·28 (8) for C(2′Et) and C(2″Et).

Experimental. Colorless prism, approx. 0·3 × 0·2 × 0·04 mm, obtained by recrystallization from an ethanol–water mixed solution was mounted on a glass fiber oriented approximately along [010]. Cell constants determined using 25 centered reflections widely scattered throughout reciprocal space. Preliminary photographic and counter data indicated a monoclinic system with systematic absences $0k0$ for $k = 2n+1$, uniquely defining the space group as $P2_1$. Two octants ($h\,0\rightarrow 11$, $k\,0\rightarrow 12$, $l\,-26\rightarrow 26$) of data out to $\theta = 70°$ collected, Enraf–Nonius CAD-4 diffractometer (Cu $K\alpha$, graphite monochromator), θ–2θ scan mode. Total number of reflections measured 4895. Lorentz and polarization factors applied. Corrections made for a 0·96 decline in intensity of three standard reflections. Semi-empirical χ-scan technique used to correct for absorption (North, Phillips & Mathews, 1968). 4132 independent F_o data obtained by averaging symmetry-related data ($0kl$ and $0k\bar{l}$).

Initial attempts to solve the structure automatically using the program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) were not successful. Instead, a symbolic addition technique was used. Three origin reflections were selected; five additional reflections were assigned symbols. When the values of several symbols were determined the phase angles were refined and extended by the tangent formula using *MULTAN*78. One E map showed an adenine ring and several other chemically reasonable fragments. Successive difference Fourier syntheses revealed the positions of the 63 atoms in the two independent molecules and that of one water molecule.

Several cycles of isotropic and anisotropic block-diagonal least-squares refinement minimizing

Table 2. *Bond distances* (Å) *and bond angles* (°) *involving non*-H *atoms*

(The e.s.d.'s of the last digits are in parentheses.)

	AP–*A*	AP–*B*		AP–*A*	AP–*B*		AP–*A*	AP–*B*
N(1)–C(2)	1·357 (4)	1·355 (5)	C(1′)–C(2′)	1·541 (5)	1·522 (4)	C(7′)–C(8′)	1·514 (5)	1·537 (5)
N(1)–C(6)	1·357 (5)	1·360 (4)	C(1′)–O(1′)	1·422 (4)	1·423 (4)	C(7′)–C(9′)	1·534 (6)	1·529 (6)
C(2)–N(3)	1·292 (4)	1·304 (5)	C(2′)–C(3′)	1·528 (4)	1·531 (4)	C(8′)–O(8′)	1·246 (4)	1·235 (4)
N(3)–C(4)	1·362 (4)	1·354 (4)	C(2′)–O(2′)	1·402 (4)	1·403 (4)	C(8′)–O(8″)	1·271 (4)	1·261 (6)
C(4)–C(5)	1·380 (5)	1·377 (4)	C(3′)–C(4′)	1·535 (5)	1·532 (4)	C(9′)–C(*P*1)	1·504 (6)	1·509 (6)
C(4)–N(9)	1·357 (4)	1·368 (4)	C(3′)–O(3′)	1·399 (4)	1·419 (4)	C(*P*1)–C(*P*2)	1·376 (7)	1·378 (8)
C(5)–C(6)	1·405 (5)	1·398 (4)	C(4′)–C(5′)	1·518 (4)	1·523 (4)	C(*P*1)–C(*P*6)	1·395 (8)	1·380 (5)
C(5)–N(7)	1·384 (5)	1·377 (4)	C(4′)–O(1′)	1·439 (4)	1·431 (4)	C(*P*2)–C(*P*3)	1·402 (8)	1·39 (1)
C(6)–N(6)	1·313 (5)	1·310 (4)	C(5′)–O(5′)	1·228 (4)	1·234 (4)	C(*P*3)–C(*P*4)	1·38 (1)	1·36 (1)
N(7)–C(8)	1·301 (4)	1·304 (5)	C(5′)–N(6′)	1·322 (3)	1·335 (4)	C(*P*4)–C(*P*5)	1·32 (1)	1·39 (1)
C(8)–N(9)	1·380 (5)	1·378 (4)	N(6′)–C(7′)	1·466 (4)	1·451 (4)	C(*P*5)–C(*P*6)	1·41 (1)	1·374 (9)
N(9)–C(1′)	1·450 (4)	1·456 (4)						
C(2)–N(1)–C(6)	123·1 (2)	123·0 (3)	N(9)–C(1′)–C(2′)	115·5 (3)	114·7 (2)	C(5′)–N(6′)–C(7′)	121·4 (2)	124·6 (3)
N(1)–C(2)–N(3)	125·9 (3)	125·9 (3)	N(9)–C(1′)–O(1′)	108·0 (2)	109·0 (2)	N(6′)–C(7′)–C(8′)	110·4 (2)	110·9 (3)
C(2)–N(3)–C(4)	112·4 (3)	111·7 (3)	C(2′)–C(1′)–O(1′)	107·9 (2)	105·8 (2)	N(6′)–C(7′)–C(9′)	111·3 (3)	109·6 (3)
N(3)–C(4)–C(5)	126·2 (3)	127·0 (3)	C(1′)–C(2′)–C(3′)	101·6 (3)	101·6 (2)	C(8′)–C(7′)–C(9′)	110·8 (3)	106·9 (3)
N(3)–C(4)–N(9)	127·7 (3)	126·6 (3)	C(1′)–C(2′)–O(2′)	109·5 (3)	114·6 (3)	C(7′)–C(8′)–O(8′)	120·4 (3)	118·8 (4)
C(5)–C(4)–N(9)	106·0 (3)	106·4 (2)	C(3′)–C(2′)–O(2′)	108·9 (2)	116·5 (3)	C(7′)–C(8′)–O(8″)	115·6 (3)	117·2 (3)
C(4)–C(5)–C(6)	118·4 (3)	118·4 (2)	C(2′)–C(3′)–C(4′)	102·0 (3)	100·0 (2)	O(8′)–C(8′)–O(8″)	123·9 (3)	124·0 (4)
C(4)–C(5)–N(7)	110·9 (3)	110·7 (3)	C(2′)–C(3′)–O(3′)	116·3 (3)	109·5 (3)	C(7′)–C(9′)–C(*P*1)	114·6 (3)	116·0 (3)
C(6)–C(5)–N(7)	130·6 (3)	130·9 (3)	C(4′)–C(3′)–O(3′)	115·6 (3)	111·8 (2)	C(9′)–C(*P*1)–C(*P*2)	120·8 (4)	121·2 (4)
N(1)–C(6)–C(5)	113·9 (3)	113·9 (3)	C(3′)–C(4′)–C(5′)	112·7 (3)	110·5 (2)	C(9′)–C(*P*1)–C(*P*6)	120·3 (4)	120·8 (4)
N(1)–C(6)–N(6)	119·7 (3)	120·0 (3)	C(3′)–C(4′)–O(1′)	102·8 (3)	106·5 (2)	C(*P*2)–C(*P*1)–C(*P*6)	119·0 (5)	117·9 (5)
C(5)–C(6)–N(6)	126·4 (3)	126·2 (3)	C(5′)–C(4′)–O(1′)	111·5 (2)	110·5 (2)	C(*P*1)–C(*P*2)–C(*P*3)	121·4 (6)	120·5 (6)
C(5)–N(7)–C(8)	103·5 (3)	103·9 (3)	C(4′)–C(5′)–O(5′)	118·9 (2)	121·9 (3)	C(*P*2)–C(*P*3)–C(*P*4)	118·7 (7)	121·6 (7)
N(7)–C(8)–N(9)	113·9 (3)	114·1 (3)	C(4′)–C(5′)–N(6′)	116·8 (3)	113·2 (3)	C(*P*3)–C(*P*4)–C(*P*5)	120·2 (7)	118·2 (7)
C(4)–N(9)–C(8)	105·6 (3)	104·9 (3)	O(5′)–C(5′)–N(6′)	124·1 (3)	124·9 (3)	C(*P*4)–C(*P*5)–C(*P*6)	122·9 (8)	120·2 (6)
C(4)–N(9)–C(1′)	129·9 (3)	126·1 (2)	C(1′)–O(1′)–C(4′)	109·1 (3)	109·6 (2)	C(P1)–C(*P*6)–C(*P*5)	117·7 (6)	121·5 (6)
C(8)–N(9)–C(1′)	124·5 (3)	128·9 (3)						

$\sum w(|F_o|-k|F_c|)^2$ reduced R to 0·09 for all data. $w = 4F_o^2/[\sigma^2 + (0{\cdot}02F_o)^2]$, where σ was obtained from counting statistics. A difference Fourier map showed all hydrogen peaks as well as two other relatively high peaks. The H atoms were added in refinements with isotropic temperature factors. The new difference Fourier map showed the CH_3 group of an ethanol molecule which was disordered around the C—OH bond. The ethanol molecule was refined to an occupancy of 0·55 (8). Final $R = 0{\cdot}053$, $wR = 0{\cdot}055$, $S = [\sum w(|F_o| - k|F_c|)^2/(m-n)]^{1/2} = 1{\cdot}386$ for all data where k, m and n are the scale factor (1·532), number of observations (4132) and number of variables (773). Max. Δ/σ in last block-diagonal least-squares refinement cycle 0·1 (in a coordinate), where the scale factor is in one block and the parameters of each atom are each in one block. Final difference Fourier map featureless. Neutral-atom scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965). All calculations performed on a VAX 11/780 computer at the Fox Chase Cancer Center using programs in the *DNA* system (Takusagawa, 1981, unpublished work).

Discussion. The atomic positional parameters are shown in Table 1.* The distances and angles are in Table 2. The two independent molecules are designated AP–*A* and AP–*B*.

As shown in Fig. 1, the two molecules have very different shapes. The molecule AP–*A* is in a closed conformation. The glycosidic torsion angle (Table 3) is −129·4 (3)° which is in the *syn* range. The pseudorotation angle *P* is 31·8° or C(3′)-*endo*. The conformation about the C(4′)–C(5′) bond is *gauche*⁻ placing the amide N such that it donates a hydrogen bond to N(3) of the adenine. The amide linkage, C(5′)–N(6′), is −170·9 (4)° or *trans*. The AP–*B* molecule is extended with the base in an *anti* conformation [$\chi = 77{\cdot}8$ (3)°], the sugar C(2′)-*endo* ($P = 177{\cdot}8°$) and the conformation about the C(4′)–C(5′) bond *gauche*⁺. This places O(5)′ within 3·4 Å of the C(8) atom of adenine as has been observed in most *anti* nucleosides (Sundaralingam, 1975); as in AP–*A* the amide linkage is

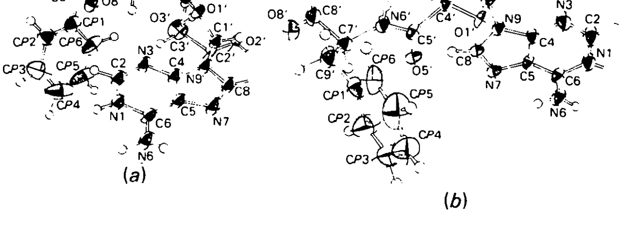

Fig. 1. The two molecules (*a*) AP–*A* and (*b*) AP–*B* in the asymmetric unit illustrating the differences in the conformations.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39743 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Torsion angles* (°)

	AP–*A*	AP–*B*
χ O(1′)–C(1′)–N(9)–C(8)	−129·4 (3)	+77·8 (3)
τ_0 C(4′)–O(1′)–C(1′)–C(2′)	−9·8 (2)	−14·4 (2)
τ_1 O(1′)–C(1′)–C(2′)–C(3′)	−16·2 (2)	+34·4 (2)
τ_2 C(1′)–C(2′)–C(3′)–C(4′)	+34·0 (2)	−39·4 (2)
τ_3 C(2′)–C(3′)–C(4′)–O(1′)	−40·7 (2)	+32·2 (2)
τ_4 C(3′)–C(4′)–O(1′)–C(1′)	+31·7 (2)	−11·7 (2)
C(3′)–C(4′)–C(5′)–O(5′)	−98·9 (3)	+95·4 (2)
C(4′)–C(5′)–N(6′)–C(7′)	−170·9 (4)	173·1 (5)
C(5′)–N(6′)–C(7′)–C(9′)	76·1 (3)	134·6 (3)
N(6′)–C(7′)–C(9′)–C(*P*1)	64·3 (3)	−62·6 (2)
C(7′)–C(9′)–C(*P*1)–C(*P*2)	82·3 (4)	−58·6 (4)
N(6′)–C(7′)–C(8′)–O(8′)	−12·6 (2)	+138·1 (4)

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

X–H···*Y*	*X*···*Y*	*X*–H	H···*Y*	∠*X*–H···*Y*
N(1*A*)–H···O(8″A^{vi})	2·630 (3)	0·94 (4)	1·70 (4)	167 (5)
N(6*A*)–H(1)···O(8′A^{vi})	2·819 (4)	1·00 (4)	1·82 (4)	177 (5)
N(6*A*)–H(2)···O(8″A^{ii})	2·824 (5)	0·75 (5)	2·11 (5)	162 (5)
O(2′*A*)–H···O(5′B^{i})	2·851 (3)	0·80 (4)	2·06 (4)	170 (4)
O(3′*A*)–H···O($W1^{\mathrm{i}}$)	2·616 (4)	0·89 (4)	1·73 (4)	171 (4)
N(6′*A*)–H···N(3A^{i})	3·146 (4)	0·97 (5)	2·25 (5)	154 (4)
N(1*B*)–H···O(8″B^{iv})	2·675 (4)	0·79 (5)	1·89 (5)	173 (5)
N(6*B*)–H(1)···O(8′B^{iv})	2·899 (4)	0·81 (6)	2·11 (6)	166 (6)
N(6*B*)–H(2)···O(5′B^{vii})	3·046 (4)	0·94 (4)	2·17 (4)	156 (4)
O(2′*B*)–H···O(8′B^{v})	2·710 (4)	0·91 (4)	1·82 (5)	165 (4)
O(3′*B*)–H···O(3′A^{ii})	2·894 (4)	0·92 (7)	2·03 (7)	156 (6)
N(6′*B*)–H···O(5′A^{ii})	2·874 (3)	0·82 (5)	2·09 (4)	160 (5)
O(*W*1)–H(1)···O(2′A^{i})	2·914 (4)	1·2 (1)	2·3 (1)	109 (6)
O(*W*1)–H(1)···O(2′B^{vii})	2·973 (4)	1·2 (1)	2·13 (9)	123 (6)
O(*W*1)–H(2)···O(8″B^{iii})	2·714 (5)	0·96 (8)	1·75 (8)	179 (9)
O(1Et)–H···O(8′A^{i})	2·77 (1)	—	—	—

Symmetry code: (i) x, y, z; (ii) $x, y+1, z$; (iii) $x, y-1, z$; (iv) $x-1, y-1, z$; (v) $x-1, y, z$; (vi) $-x, y+\frac{1}{2}, 1-z$; (vii) $1-x, y-\frac{1}{2}, 2-z$.

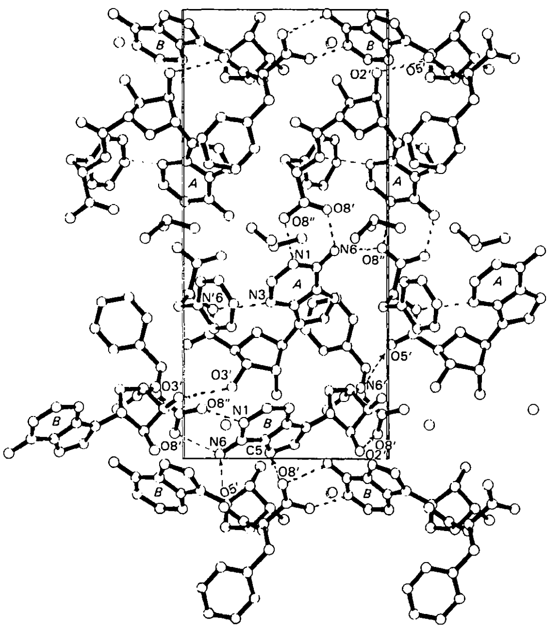

Fig. 2. A view down the *a* axis of the hydrogen bonding and packing. The hydrogen bonds are shown as dotted lines.

trans. The torsion angles involving the amino acid are completely different from one another but otherwise unremarkable.

The tautomeric form of this structure was determined unambiguously because it was possible to locate the H atoms. Both adenine bases are protonated and the carboxylate groups each carry a negative charge. The distances and angles are consistent with this zwitterionic structure. That is, the angles at C(2)–N(1)–C(6) are 123·1 and 123·0°, in excellent agreement with the mean values found in recent structures found in the Cambridge Crystallographic Data File (Allen *et al.*, 1979) as well as those in structures surveyed by Voet & Rich (1970). The N(1)–C(2), N(1)–C(6), N(3)–C(4) and C(8)–N(9) bonds are longer than in neutral adenine rings while the C(2)–N(3) and C(6)–N(6) bonds are shorter.

Each molecule in the asymmetric unit is involved in a hydrogen-bonding network connecting symmetry-related molecules *via* the N(1) and N(6) atoms of the adenine base and the carboxylate group of the amino acid (Table 4 and Fig. 2). Similar types of base/amino acid contacts have been observed in other adenosine peptide structures. In *S*-adenosylhomocysteine (Shieh & Berman, 1982) the N(7) and N(6) atoms of a neutral adenine hydrogen-bond with the charged amino-acid moiety. In adenosyl-glycyl-L-alanine (Narayanan, Berman & Rousseau, 1976) the N(7) and N(6) form similar double hydrogen bonds although with an uncharged carboxyl group. In this structure, the two hydrogen-bonding networks are interconnected *via* sugar–sugar and sugar–amide hydrogen bonds. There are no base–base hydrogen bonds or base–base stacking interactions although the bases are aligned in parallel planes. Interestingly, however, the carboxylate group of AP–*B* stacks above a symmetry-related adenine ring with the carbonyl C(8′)–O(8′) aligned with respect to the adenine ring C(5)–N(7), such that the O(8′)···C(5) contact distance is 3·066 (4) Å. In all probability this is a dipole–dipole interaction that precludes any N(7) hydrogen bonding. The phenyl rings in this structure are arranged in the familiar herring-bone pattern.

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6,6,8-Trinitropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, $C_{10}H_9N_3O_6$

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Abstract. $M_r = 267 \cdot 2$, monoclinic, $P2_1/c$, $a = 9 \cdot 352\ (4)$, $b = 7 \cdot 401\ (2)$, $c = 16 \cdot 070\ (6)$ Å, $\beta = 97 \cdot 76\ (4)°$, $V = 1102 \cdot 1$ Å^3, $Z = 4$, $D_x = 1 \cdot 61$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 1 \cdot 19$ mm^{-1}, $F(000) = 552$, $T = 292$ K, $R = 0 \cdot 059$, $R_w = 0 \cdot 051$ for 1495 observed reflections. The molecule is substantially distorted from a cubane geometry; two of the six sides of the framework are four-membered rings and four sides are five-membered rings. The average C—C—C angles in the four- and five-membered rings are 89·2 and 102·9°, respectively. C—C bond lengths show the effects of the nitro substituents: the average of the two bonds linked to $C(NO_2)_2$ is 1·507 (4) Å, and the three bonds joined to $C(NO_2)$ average 1·560 (4) Å.

Introduction. There is considerable interest in the synthesis and chemistry of strained energetic compounds (*e.g.* Sollott & Gilbert, 1980; Eaton, Ravi Shankar, Price, Pluth, Gilbert, Alster & Sandus, 1984; Marchand & Suri, 1984). Polynitropolycyclic compounds are potential members of this important class. In this paper, we report the structure of the first polynitrobishomocubane (I) to have been prepared (Marchand & Suri, 1984). The structure of one other homocubane (homocubanecarboxylic acid *p*-bromoanilide; Pettersen, 1967) has been reported; these structural data, however, are not readily available.

Experimental. Six-sided parallelepiped crystal, 0·49 × 0·23 × 0·19 mm, from ethyl acetate–hexane; cell parameters determined and intensity measurements made with a Picker FACS-I diffractometer, graphite monochromator, Cu radiation; unit-cell parameters determined by least squares from 2θ values of 14 reflections automatically centered at $\pm 2\theta$; intensities measured with θ–2θ scan technique, 2° min^{-1} 2θ scan speed, 10 s backgrounds, 2θ scan width = 1·6° + 0·3° tanθ; four standards monitored at 100 reflection intervals, maximum intensity variation <2%; 2θ maximum of 126°, *h,k,l* range 0–10, 0–8, −18–18; 2111 total reflections measured, 1901 unique (excluding systematic absences), 1495 3σ above background; Gaussian quadrature (8 × 8 × 8 grid) absorption correction ($A^*_{\max}/A^*_{\min} = 1 \cdot 558/1 \cdot 234$); structure solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); H atoms located in difference map; full-matrix least-squares structure refinement minimized $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F)$; C, N, and O atoms refined with anisotropic

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