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Restrained Refinement of Disodium Adenosine 5'-Triphosphate Trihydrate*

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The crystal structure parameters of 5'-ATP have been further refined using the bond-restraints model. The final R indices are marginally improved while the final model for the 5'-ATP molecule is significantly more consistent with other notions of the chemistry.

Introduction

The crystal structure of disodium adenosine 5'-triphosphate trihydrate was determined by Kennard, Isaacs, Motherwell, Coppola, Wampler, Larson & Watson (1971), hereafter KIM. Because the data were of marginal quality due to small crystal size and a very large mosaicity about the c axis, the original refinement was carried out using the rigid-body model described by LaPlaca & Ibers (1965) and by Doedens (1970) with the constraints being applied to only the adenine portion of the ion. In Los Alamos the problem of poor data was normally addressed through the use of the distance-restraints model advocated by Waser (1963) and described by Rollett (1970), by Pawley (1972), and by Cady & Larson (1975). This model allows one to retain the complete parameterization of the molecule while restraining the bond lengths to values close to those predetermined by increasing the number of equations of condition.

The results of the refinement of 2'-O-tetrahydropyranyladenosine (Kennard, Motherwell, Coppola, Griffin, Reese & Larson, 1971) were available as a reasonable model for the adenosine portion of the molecules and the data from the structure of guanosine 5'-phosphate trihydrate (Murayama, Nagashima & Shimizu, 1969) were chosen as a model for the phosphate. These two structures were thought to give the best estimate available of the necessary bond lengths.

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Experimental details

The diffraction data used are those of KIM.‡ The space group is $P2_12_12_1$ with $a = 30\cdot45$ (4), $b = 20\cdot88$ (3), $c = 7\cdot07$ (1) and $Z = 8$. This data set consisted of the 1118 reflections found to be observable on crystals 2 and 3, out of the 1139 reflections indicated to be observable in an examination of the 3193 reflections out to 120° 2θ with Cu $K\alpha$ radiation (minimum d spacing 0·9 Å) from crystal 1.

The bond lengths used in the restrained model of the adenosine came from 2'-O-tetrahydropyranyladenosine for the adenosine and from guanosine 5'-phosphate trihydrate for the phosphate. The assumption was made that the bridging P—O bond lengths would be similar to that in the linkage to the ribose. Nearest-neighbor bond lengths were used to define the bonds throughout the ion and second-neighbor distances were used to define bond angles in the adenine and phosphate portions of the molecule. All atoms were given individual isotropic thermal parameters. No constraints were placed on either the Na ions or on the water of hydration. The sigmas used to determine the weights of the bond constraints were 0·010 for C—C, C—N, and C—O bonds, 0·020 for C—C, C—N, and C—O second neighbors, 0·020 for P—O bonds, and 0·050 for O—O distances defining O—P—O angles. The quantity minimized was $\sum w(|F_o| - |F_c|)^2 + K \sum (D_{ij}^2 - d_{ij}^2)^2/\sigma_{ij}$, where K was set to $[\sum w(|F_o| - |F_c|)^2/(N -$

$M)]^{1/2}$ and D_{ij} is the constraint distance and d_{ij} the calculated distance. The final positional and thermal parameters are given in Table 1 along with the shift of each atom from the positions given by KIM. The distances used in the restraints are given in Table 2 along with the final distances. The final values of the reliability indices $R = \sum ||F_o| - |F_c||/|F_o|$ and $R_2 = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|$ are 0·120 and 0·046. These compare with the values of 0·123 and 0·053 reported by KIM. The atom designations and atom orders used in KIM have been retained in Tables 1 and 2 for ease of comparison.

All calculations reported herein were carried out on a Control Data Corporation, CDC 7600, using the programs *GENLES* (Larson, 1977).

Discussion

The conformation of the ATP ions was well covered in KIM and as there is no major revision of those conclusions, they will not be discussed here.

The major points for discussion are the improved bond lengths in the ribose and phosphate portions of the ions and the waters of hydration. In this refinement all atoms were given individual isotropic thermal parameters and with the exception of O(W)4 all refined to reasonable values.

The improved consistency of the bond lengths in the phosphate groups is evident from the greatly decreased spread of chemically similar distances. The non-bridging P—O bonds now range from 1·482 to 1·514

Table 1. *Disodium adenosine 5'-triphosphate trihydrate final fractional parameters* $\times 10^4$, *final thermal parameters* (B, Å^2) *and the shift,* Δ (Å), *from the positions of KIM*

	Molecule A					Molecule B				
	x	y	z	B	Δ	x	y	z	B	Δ
P(1)	1386 (5)	−3495 (7)	12243 (19)	3·0 (4)	0·054	1410 (5)	1920 (7)	5303 (20)	2·7 (4)	0·017
P(2)	1145 (5)	−4538 (8)	9580 (22)	4·4 (4)	0·051	1024 (5)	3011 (7)	3170 (19)	2·7 (4)	0·013
P(3)	509 (5)	−3797 (7)	7149 (19)	2·5 (4)	0·070	503 (5)	2112 (6)	731 (19)	1·9 (3)	0·028
O(1)	925 (7)	−3397 (16)	12850 (42)	3·8 (9)	0·125	994 (8)	1807 (15)	6395 (39)	4·0 (9)	0·090
O(11)	1677 (9)	−3737 (14)	13781 (35)	3·3 (9)	0·167	1810 (9)	1912 (19)	6549 (47)	8·6 (15)	0·159
O(6')	1417 (10)	−3927 (14)	10381 (38)	10·2 (16)	0·139	1390 (8)	2623 (11)	4398 (41)	6·0 (11)	0·083
O(2)	1496 (9)	−5007 (12)	8963 (42)	3·7 (9)	0·142	1266 (10)	3597 (12)	2513 (45)	5·3 (11)	0·172
O(22)	801 (8)	−4744 (14)	10950 (38)	2·7 (9)	0·069	661 (8)	3152 (16)	4531 (39)	4·1 (9)	0·055
O(7')	933 (8)	−4233 (14)	7703 (34)	5·2 (11)	0·105	906 (8)	2535 (13)	1506 (36)	5·8 (12)	0·138
O(3)	727 (9)	−3224 (12)	6270 (40)	4·0 (10)	0·216	743 (8)	1584 (11)	−0300 (36)	2·0 (8)	0·058
O(33)	270 (9)	−4131 (15)	5598 (38)	4·5 (10)	0·117	244 (9)	2516 (13)	−0591 (37)	2·4 (8)	0·086
O(333)	268 (9)	−3664 (14)	8938 (31)	2·7 (8)	0·064	249 (8)	1886 (14)	2396 (32)	2·4 (8)	0·064
O(5')	1597 (8)	−2825 (11)	11450 (38)	2·4 (8)	0·088	1441 (10)	1445 (12)	3587 (32)	2·3 (8)	0·113
C(1')	1631 (8)	−1602 (25)	7814 (54)	5·6 (18)	0·237	1515 (8)	−0101 (17)	2349 (51)	2·0 (12)	0·070
C(2')	1777 (11)	−2032 (21)	6196 (58)	4·3 (16)	0·097	1778 (13)	105 (16)	4080 (54)	3·5 (14)	0·139
O(2')	2201 (10)	−1859 (16)	5520 (48)	3·5 (9)	0·094	1940 (10)	−0497 (16)	4730 (43)	2·4 (8)	0·023
C(3')	1876 (14)	−2645 (19)	7291 (55)	2·7 (13)	0·088	2143 (13)	460 (20)	3051 (59)	2·8 (13)	0·157
O(3')	2101 (9)	−3126 (15)	6226 (40)	1·7 (7)	0·050	2469 (12)	37 (19)	2312 (43)	3·9 (9)	0·089
C(4')	2081 (15)	−2389 (18)	9097 (59)	4·9 (17)	0·161	1933 (13)	838 (20)	1465 (66)	5·6 (18)	0·108
O(1')	1862 (10)	−1777 (17)	9489 (47)	3·1 (9)	0·100	1565 (10)	410 (15)	1029 (45)	2·9 (8)	0·092
C(5')	2044 (9)	−2780 (24)	10901 (58)	1·8 (11)	0·106	1767 (14)	1482 (23)	2160 (59)	4·6 (17)	0·088
N(1)	347 (9)	−0011 (12)	8537 (52)	2·5 (11)	0·036	267 (9)	−1567 (12)	4362 (45)	1·1 (8)	0·076
C(2)	759 (10)	65 (11)	7924 (60)	1·1 (11)	0·070	646 (10)	−1691 (11)	3478 (62)	3·1 (14)	0·156
N(3)	1088 (8)	−0362 (14)	7824 (56)	3·4 (11)	0·055	975 (7)	−1283 (11)	3077 (42)	0·4 (8)	0·072
C(4)	920 (9)	−0955 (11)	8048 (66)	4·2 (15)	0·128	823 (7)	−0681 (10)	3255 (63)	2·2 (13)	0·118
C(5)	521 (9)	−1099 (11)	8858 (68)	3·8 (14)	0·052	401 (8)	−0492 (11)	3671 (70)	3·6 (15)	0·044
C(6)	211 (8)	−0603 (13)	9026 (65)	2·5 (12)	0·052	101 (7)	−0969 (13)	4235 (61)	1·7 (11)	0·030
N(7)	492 (9)	−1755 (11)	9216 (52)	2·2 (9)	0·054	357 (9)	168 (11)	3405 (49)	2·0 (10)	0·101
C(8)	887 (10)	−1971 (12)	8836 (69)	3·5 (15)	0·091	739 (11)	341 (12)	2700 (67)	3·1 (14)	0·166
N(9)	1164 (7)	−1511 (14)	8121 (49)	2·2 (10)	0·021	1049 (8)	−0136 (14)	2756 (60)	3·8 (12)	0·093
N(10)	−0205 (8)	−0721 (17)	9572 (47)	1·2 (8)	0·061	−0319 (7)	−0849 (17)	4732 (44)	1·0 (9)	0·076
Na(1)	220 (7)	2256 (10)	5717 (32)	3·8 (6)	0·066					
Na(2)	259 (7)	−3960 (11)	2077 (26)	2·8 (5)	0·060					
Na(3)	1636 (8)	3853 (13)	−0468 (39)	7·5 (8)	0·038					
Na(4)	2535 (11)	1215 (15)	7014 (48)	10·7 (10)	0·104					
O(W1)	2095 (11)	2844 (17)	−0889 (56)	4·7 (10)	0·142					
O(W2)	1159 (12)	4808 (18)	4111 (55)	5·7 (11)	0·197					
O(W3)	1032 (11)	3463 (17)	7903 (48)	4·5 (10)	0·111					
O(W4)	2085 (24)	5068 (41)	5186 (119)	27·7 (39)	1·100					
O(W5)	2133 (21)	3834 (29)	6475 (92)	16·4 (25)	0·185					
O(W6)	2222 (21)	4175 (32)	2426 (99)	18·2 (27)	0·733					

Table 2. *Interatomic distances used to restrain the structure refinement, restrained values, and the final observed values* (Å)

Constraint		d(A)	d(B)	Constraint		d(A)	d(B)
P(1)–O(1)	1·508	1·482 (16)	1·503 (16)	N(7)–C(8)	1·313	1·314 (9)	1·316 (9)
O(11)	1·508	1·491 (16)	1·504 (16)	C(8)–N(9)	1·376	1·373 (9)	1·374 (9)
O(6′)	1·608	1·599 (16)	1·602 (15)	C(2)–C(4)	2·200	2·188 (16)	2·184 (16)
O(5′)	1·608	1·638 (16)	1·571 (16)	C(6)	2·300	2·312 (15)	2·306 (16)
P(2)–O(6′)	1·608	1·622 (16)	1·629 (16)	C(4)–C(6)	2·376	2·385 (15)	2·384 (15)
O(2)	1·508	1·514 (16)	1·504 (16)	C(8)	2·195	2·195 (14)	2·185 (14)
O(22)	1·508	1·490 (16)	1·496 (16)	N(7)	2·275	2·274 (14)	2·272 (13)
O(7′)	1·608	1·607 (15)	1·582 (15)	C(5)–C(8)	2·138	2·135 (14)	2·136 (14)
P(3)–O(7′)	1·608	1·628 (15)	1·608 (15)	N(1)	2·354	2·343 (15)	2·334 (15)
O(3)	1·508	1·504 (16)	1·510 (16)	N(3)	2·430	2·425 (16)	2·442 (15)
O(33)	1·508	1·490 (16)	1·485 (16)	N(9)	2·203	2·200 (14)	2·207 (14)
O(333)	1·508	1·489 (16)	1·486 (16)	N(1)–N(3)	2·428	2·424 (14)	2·414 (15)
O(5′)–C(5′)	1·419	1·420 (10)	1·417 (10)	N(7)–N(9)	2·248	2·247 (13)	2·248 (14)
C(1′)–C(2′)	1·519	1·522 (10)	1·523 (10)	O(5′)–O(1)	2·525	2·566 (29)	2·524 (29)
O(1′)	1·422	1·427 (10)	1·425 (10)	O(11)	2·525	2·531 (28)	2·570 (31)
N(9)	1·447	1·450 (10)	1·451 (10)	O(6′)	2·587	2·484 (28)	2·531 (29)
C(2′)–O(2′)	1·425	1·423 (10)	1·426 (10)	O(1)–O(11)	2·438	2·486 (28)	2·498 (30)
C(3′)	1·522	1·527 (10)	1·523 (10)	O(6′)	2·525	2·552 (30)	2·521 (30)
C(3′)–O(3′)	1·430	1·431 (10)	1·429 (10)	O(11)–O(6′)	2·525	2·564 (29)	2·482 (30)
C(4′)	1·515	1·519 (10)	1·514 (10)	O(6′)–O(2)	2·525	2·480 (28)	2·462 (28)
C(4′)–O(1′)	1·462	1·468 (10)	1·466 (10)	O(22)	2·525	2·565 (31)	2·483 (29)
C(5′)	1·519	1·519 (10)	1·518 (10)	O(7′)	2·587	2·484 (30)	2·529 (29)
N(1)–C(2)	1·336	1·337 (9)	1·339 (9)	O(2)–O(22)	2·438	2·599 (27)	2·510 (29)
C(6)	1·346	1·349 (9)	1·350 (9)	O(7′)	2·525	2·519 (27)	2·575 (27)
C(2)–N(3)	1·345	1·342 (9)	1·345 (9)	O(22)–O(7′)	2·525	2·564 (28)	2·607 (29)
C(4)–N(3)	1·342	1·350 (9)	1·346 (9)	O(7′)–O(3)	2·525	2·422 (29)	2·413 (26)
C(5)	1·375	1·376 (9)	1·377 (9)	O(33)	2·525	2·517 (29)	2·501 (28)
N(9)	1·376	1·379 (9)	1·375 (9)	O(333)	2·525	2·504 (28)	2·498 (29)
C(5)–C(6)	1·404	1·408 (9)	1·409 (9)	O(3)–O(33)	2·438	2·399 (30)	2·476 (27)
N(7)	1·397	1·395 (9)	1·397 (9)	O(333)	2·438	2·522 (28)	2·511 (27)
C(6)–N(10)	1·344	1·346 (9)	1·349 (9)	O(33)–O(333)	2·438	2·557 (28)	2·489 (28)

with an average value of 1·496 (10) Å while the KIM values range from 1·38 to 1·62 with an average of 1·48 (8) Å. The bridging P–O bond lengths now range from 1·571 to 1·638 with an average of 1·609 (21) Å compared with a range of 1·46 to 1·75 and an average of 1·62 (11) Å. (All averages and their standard deviations in this section were computed using the Hewlett Packard HP-45 hand-held computer.)

The improvement in the internal consistency of the bond lengths in the ribose groups is also rather dramatic. The C–C distances now range from 1·514 to 1·527, average 1·521 (4) Å compared with 1·38 to 1·61, average 1·51 (9) Å and the ribose carbon–oxygen distances now range from 1·417 to 1·468, average 1·433 (8) Å compared with 1·37 to 1·59, average 1·48 (8) Å.

Two of the water O atoms have moved fairly large distances from the positions of KIM. One, O(W)6, has moved 0·73 Å and the other, O(W)4, has moved 1·10 Å. An examination of the ΔF Fourier map computed using these final parameters shows several small peaks of ~0·6 e Å^{-3} near the final O(W)6 position with no pronounced peak at the KIM location for this atom. In the region of O(W)4, however, there is only one peak in the F map and it is at the location of this atom in the KIM data. This peak is ~1·6 e Å^{-2}. Considering the

fact that the crystals seemed to lose water and that the data were collected from two crystals, it is probable that the loss of water is from these positions and that there may be some disorder in the location of these water molecules. The list of interatomic distances computed with the positions given in this paper shows no unreasonable contact distances for the water molecules. However, the large shifts in the location of these two water molecules would require a modification of the hydrogen-bonding scheme proposed by KIM. Owing to the uncertainty in the knowledge of the water positions, no attempt has been made to establish a new hydrogen-bonding scheme and it is believed that no such attempt can be warranted.

There still seems to be a need for further work on this compound. The data published by KIM are now highly overworked and no reason can be seen for further analyses using it. However, if better data can be obtained it would seem that a justification for further work on this compound can be found.

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Molecular Complexes Exhibiting Polarization Bonding. XII. The Crystal Structure of the 2:1 Complex between 9-Ethylcarbazole and Tetracyanoethylene

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The complex, $2(C_{14}H_{13}N).C_6N_4$, crystallizes as blue-black laths in the orthorhombic space group *Pbca* with $Z = 4$ and $a = 8.941$ (2), $b = 17.253$ (3), $c = 17.888$ (3) Å. The structure consists of centrosymmetric groups of two carbazole donor molecules and one tetracyanoethylene acceptor molecule within which the tetracyanoethylene molecule is disordered unequally in two orientations. The mean perpendicular separation between donor and acceptor is 3.24 Å.

Experimental

Blue-black crystals of the complex were prepared by refluxing together, for ten minutes, solutions of 9-ethylcarbazole (EtCBZ) and tetracyanoethylene (TCNE), concentrating the resulting deep-blue solution by evaporation under reduced pressure and allowing it to cool. The crystals were washed with cold acetonitrile and dried *in vacuo*. The space group and unit-cell dimensions were found from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. A crystal of approximate dimensions $0.2 \times 0.5 \times 0.6$ mm was mounted so as to rotate about its longest (*a*) axis on a Hilger & Watts, four-circle, computer-controlled diffractometer. The cell dimensions were refined and intensities were measured using a $\theta/2\theta$ scan, a scintillation counter and Mo $K\alpha$ radiation for 3814 reflections up to $\theta = 25°$. Of these, 3334 had significant intensities $[I > 3\sigma(I)]$ but only the 2142 largest values were used in the solution and refinement of the structure. The disorder in the structure, which became apparent during refinement, indicated that the computing difficulties involved in using all the significant data

would not be warranted. The intensities were corrected for Lorentz and polarization factors but not for absorption. The solution and refinement of the structure were carried out on the University's ICL 1906A computer using the XRAY system of programs edited by Stewart, Kundell & Baldwin (1970).

Crystal data

$2(C_{14}H_{13}N).C_6N_4$, $M_r = 518.6$; orthorhombic, $a = 8.941$ (2), $b = 17.253$ (3), $c = 17.888$ (3) Å; $U = 2759$ (1) Å³, $D_m = 1.25$ (1), $D_c = 1.248$ g cm⁻³, $Z = 4$, $F(000) = 1088$, Mo $K\alpha$ ($\lambda = 0.71069$ Å), $\mu = 0.826$ cm⁻¹, space group *Pbca* from systematic absences.

The structure was solved by direct methods with the *MULTAN* program (Germain, Main & Woolfson, 1971) using 203 $|E| > 1.86$. The Σ_1 relationship gave positive signs for four reflections and four further reflections were used as a starting set to be given all combinations of positive and negative signs. An E map based on the set of phases with the highest figure of merit gave chemically reasonable peak positions for all 20 non-hydrogen atoms in the asymmetric unit (EtCBZ