

Structure of the 1/2 Complex of Adenine and *N*-Methyl-2-pyrrolidone, C₅H₅N₅·2C₅H₉NO

By V. LANGER AND K. HUML

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Praha 6, Czechoslovakia

AND J. ZACHOVÁ

Institute of Physics, Charles University, 121 16 Praha 2, Czechoslovakia

(Received 3 April 1984; accepted 23 August 1984)

Abstract. $M_r = 333.40$, monoclinic, $P2_1/c$, $a = 9.907$ (5), $b = 21.962$ (7), $c = 7.994$ (2) Å, $\beta = 100.73$ (3)°, $V = 1709$ (1) Å³, $Z = 4$, $D_m = 1.275$ (5), $D_x = 1.296$ (1) Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.699$ mm⁻¹, $F(000) = 712$, $T = 295$ K, $R = 0.057$ for 1097 observed reflections. The adenine molecule is neutral and this feature is reflected in the geometry of the pyrimidine ring, in comparison with protonated molecules. There is an overlap of adenine with *N*-methyl-2-pyrrolidone but none between adenine molecules. A net of hydrogen bonds, forming adenine dimers, is found in the structure.

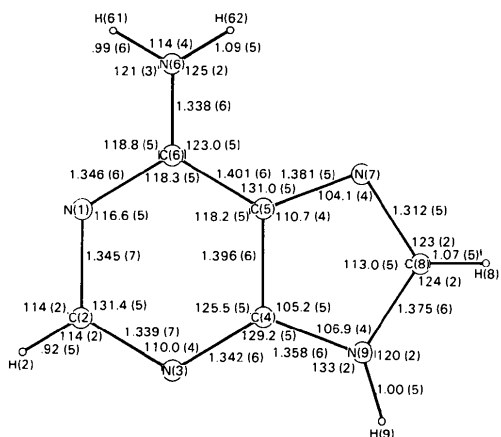
Introduction. The crystal and molecular structure of the title compound has been determined as part of a study of the transfer of energy and information in nucleic acids and their components. Single crystals serve as a model for the interpretation of the results obtained by various methods of low-temperature reflection and emission spectroscopy for polynucleotides, carried out at the Institute of Physics, Charles University, Praha. This communication is a continuation of our studies concerned with the structures of adeninium sulfate (Langer & Huml, 1978*a*), adenine hydrobromide hemihydrate (Langer & Huml, 1978*b*), adeninium hemisulfate hydrate (Langer, Huml & Lessinger, 1978) and adeninium phosphate (Langer, Huml & Zachová, 1979).

Experimental. Crystals grown from twice-recrystallized adenine (Lachema) and redistilled *N*-methyl-2-pyrrolidone by cooling in a special crystallizer. Starting temperature of saturated solution was 295 K, the final was (after one to two weeks) 277 K; a seed crystal was used. Single crystals were colourless plates with max. dimensions 12 × 9 × 4 mm. They are unstable in air and within minutes transmute into amorphous adenine. Their lifetime is much longer in *N*-methyl-2-pyrrolidone atmosphere. Molecular formula confirmed by elemental analysis and purity by HPLC method. D_m by flotation in bromoform/*N*-methyl-2-pyrrolidone mixture. Cell dimensions refined from setting angles of 25 reflections with $11.9 < 2\theta < 27.8^\circ$. Crystal 0.7 × 0.5 × 0.5 mm in Lindemann capillary in *N*-methyl-2-pyrrolidone

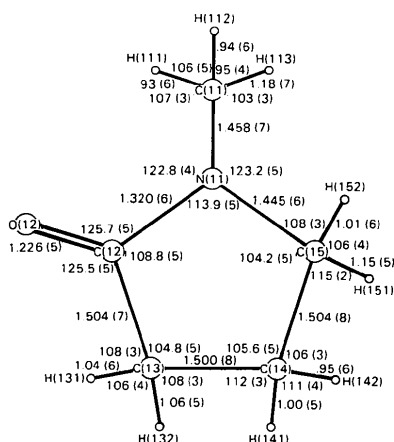
atmosphere. Syntex $P2_1$ automated diffractometer, graphite monochromator, max. $\sin\theta/\lambda$ in intensity measurement 0.4382 Å⁻¹, θ - 2θ scan technique, min. scan speed 2° min⁻¹ in 2θ , $-8 \leq h \leq 8$, $0 \leq k \leq 19$, $0 \leq l \leq 6$. Three standard reflections measured after every 47 reflections (approx. 90 min interval) to monitor crystal decay. When any of the standard reflections dropped below 50% of initial value, a new crystal was mounted. During data collection four crystals of similar dimensions were used. Measurements reduced to same scale with *INTER* (Langer, 1973). In range up to $2\theta = 85^\circ$, 1196 unique reflections measured, 1098 with $I > 1.96 \sigma_I$ regarded as observed. Correction for Lorentz and polarization factors, not for absorption. Phase problem solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), taking advantage of knowledge of geometry of molecules in structure. Best E map clearly revealed positions of all non-H atoms. Refinement based on $|F|^2$'s by full-matrix least squares using *SHELX76* (Sheldrick, 1976). During refinement one reflection, 102, apparently suffering from secondary extinction was excluded. H atoms in calculated positions. Refinement (anisotropic for non-H and isotropic for H atoms) stopped when max. $\Delta/\sigma < 0.15$. 309 parameters refined. Final $R = 0.0566$, $wR = 0.0597$ for observed reflections. $w = [\sigma_F^2 + (0.02F)^2]^{-1}$, σ_F from counting statistics. Final $\Delta\rho$ map shows no significant feature, max. 0.16 and min. -0.30 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The numbering scheme, bond distances and bond angles and their e.s.d.'s are given in Fig. 1. The fractional atomic coordinates and B_{eq} values for non-H atoms are given in Table 1.* The molecule of adenine can be considered planar as indicated by a χ^2 test,

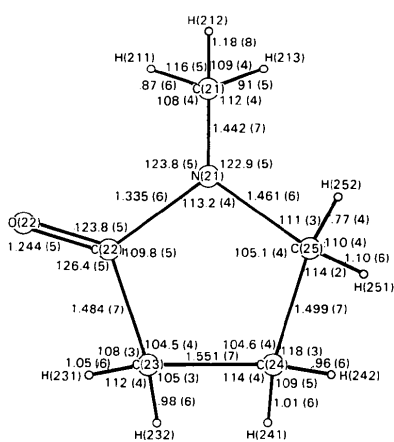
* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, some bond angles involving H atoms and weighted-mean-plane tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39692 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(a)



(b)



(c)

Fig. 1. Numbering scheme, bond distances (Å) and angles (°) for (a) adenine, (b) first and (c) second molecules of *N*-methyl-2-pyrrolidone.

Table 1. Fractional positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses, for non-H atoms

$$B_{eq} = (\frac{1}{3})\pi^2 \sum U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
N(1)	2173 (5)	6474 (2)	3696 (5)	4.9 (2)
C(2)	3374 (7)	6376 (4)	3186 (7)	5.7 (2)
N(3)	4048 (4)	5861 (3)	2985 (5)	5.2 (1)
C(4)	3350 (6)	5380 (3)	3416 (5)	4.1 (2)
C(5)	2089 (6)	5406 (2)	3953 (5)	3.9 (2)
C(6)	1500 (5)	5979 (2)	4099 (5)	4.0 (2)
N(6)	297 (5)	6054 (2)	4606 (5)	4.7 (1)
N(7)	1647 (4)	4829 (2)	4277 (4)	4.3 (1)
C(8)	2608 (6)	4468 (3)	3914 (5)	4.4 (2)
N(9)	3659 (4)	4778 (2)	3386 (4)	4.5 (2)
N(11)	3073 (5)	2675 (2)	8806 (4)	4.7 (1)
C(11)	4168 (7)	2278 (3)	8460 (11)	6.7 (2)
C(12)	1910 (6)	2464 (3)	9160 (5)	4.2 (2)
O(12)	1610 (3)	1926 (2)	9258 (4)	6.2 (1)
C(13)	1003 (6)	2994 (2)	9400 (9)	6.1 (2)
C(14)	1897 (7)	3545 (3)	9384 (9)	7.0 (2)
C(15)	3119 (7)	3331 (3)	8677 (8)	6.1 (2)
N(21)	7599 (4)	1175 (2)	6515 (4)	4.5 (1)
C(21)	7545 (8)	1825 (3)	6750 (11)	6.6 (3)
C(22)	6595 (6)	794 (2)	6730 (5)	4.4 (2)
O(22)	5527 (4)	958 (1)	7209 (4)	5.9 (1)
C(23)	6945 (5)	166 (2)	6280 (8)	5.2 (2)
C(24)	8464 (5)	205 (2)	6057 (9)	5.4 (2)
C(25)	8728 (7)	873 (3)	5902 (8)	5.0 (2)

Table 2. Hydrogen-bond geometry

<i>X</i>	<i>H</i>	<i>Y</i>	<i>X</i> - <i>H</i> (Å)	<i>X</i> ... <i>Y</i> (Å)	<i>H</i> ... <i>Y</i> (Å)	<i>X</i> - <i>H</i> ... <i>Y</i> (°)
N(6)	H(61)	O(12 ⁱ)	0.99 (6)	2.949 (6)	2.13 (5)	139 (4)
N(6)	H(62)	N(7 ⁱⁱ)	1.09 (5)	2.985 (6)	1.91 (5)	168 (4)
C(8)	H(8)	O(12 ⁱⁱⁱ)	1.07 (5)	3.245 (7)	2.24 (5)	156 (3)
N(9)	H(9)	O(22 ⁱⁱⁱ)	1.00 (5)	2.751 (6)	1.76 (5)	169 (4)

For symmetry codes see Fig. 3.

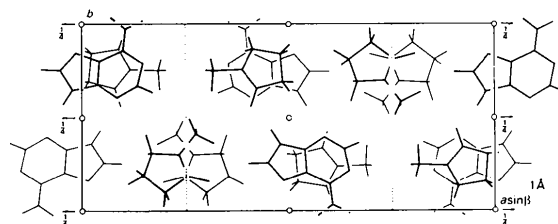


Fig. 2. Projection of the structure along *c*.

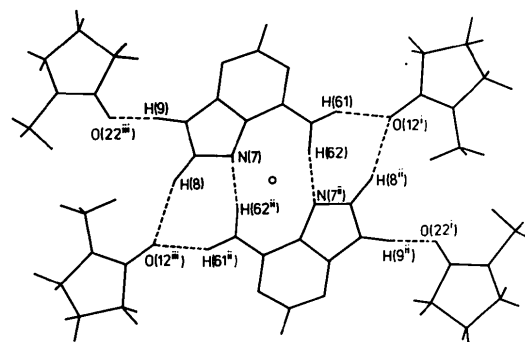


Fig. 3. Hydrogen-bond scheme. Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$, (ii) $-x, -y + 1, -z + 1$, (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

whereas both *N*-methyl-2-pyrrolidone molecules are significantly nonplanar. A projection of the structure along the *c* axis is given in Fig. 2. The molecules of adenine form, *via* H-bonds, (see Table 2) dimers related by a centre of symmetry (see Fig. 3). The perpendicular separation of planes formed by adenines in the dimer is 0.049 (4) Å and that of the other pair of adenines related by a centre of symmetry is 3.141 (4) Å. There is an overlap of adenine with *N*-methyl-2-pyrrolidone; distances of atoms of *N*-methyl-2-pyrrolidone from the adenine mean plane are in the range 3.281 (7) to 3.590 (6) Å. There is no overlap between adenine and *N*-methyl-2-pyrrolidone molecules themselves.

A comparison of the bond distances and angles for adenine with those in similar structures (Langer & Huml, 1978*a, b*; Langer, Huml & Lessinger, 1978; Langer, Huml & Zachová, 1979) shows significant differences in geometry, mainly in distances C(6)–N(1), N(1)–C(2), C(2)–N(3), N(3)–C(4), C(6)–N(6) and angles C(6)–N(1)–C(2), N(1)–C(2)–N(3) in the pyrimidine ring [mean weighted values for the above structures are 1.369 (4), 1.359 (3), 1.305 (4), 1.362 (2), 1.303 (2) Å and 123.6 (2), 125.7 (3)°]. These changes occur because in the present case the adenine molecule is neutral; this is supported by the mean values for the neutral molecule as given by Voet & Rich (1970), *i.e.* 1.35 (3), 1.33 (2), 1.315 (8), 1.35 (1), 1.34 (2) Å and 119 (1), 129 (2)°. The slight difference in the distance C(8)–N(9) is possibly due to

different crystal packing. The same explanation holds for a difference in bond lengths C(13)–C(14) and C(23)–C(24) for the two symmetrically independent molecules of *N*-methyl-2-pyrrolidone, although from a statistical point of view both molecules as a whole do not significantly differ.

The authors thank Professor V. Prosser for suggesting the problem and for his interest in the crystal growth and structure determination.

References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LANGER, V. (1973). *Crystallographic Programs* (ÚMCH-111 INTER). Institute of Macromolecular Chemistry, Praha, Czechoslovakia.
- LANGER, V. & HUML, K. (1978*a*). *Acta Cryst.* B34, 1157–1163.
- LANGER, V. & HUML, K. (1978*b*). *Acta Cryst.* B34, 1881–1884.
- LANGER, V., HUML, K. & LESSINGER, L. (1978). *Acta Cryst.* B34, 2229–2234.
- LANGER, V., HUML, K. & ZACHOVÁ, J. (1979). *Acta Cryst.* B35, 1148–1152.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- VOET, D. & RICH, A. (1970). *Prog. Nucleic Acid Res. Mol. Biol.* 10, 183–265.

Acta Cryst. (1984). C40, 2082–2084

Structure of (Di-*tert*-butylmethyleneamino)diphenylborane, C₂₁H₂₈BN*

BY WILLIAM CLEGG

Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, England

AND STEPHEN J. BRYAN AND KENNETH WADE

Department of Chemistry, Durham University, South Road, Durham DH1 3LE, England

(Received 8 June 1984; accepted 28 August 1984)

Abstract. $M_r = 305.3$, orthorhombic, *Pbca*, $a = 11.534$ (1), $b = 14.875$ (1), $c = 22.909$ (3) Å, $V = 3930.5$ Å³, $Z = 8$, $D_x = 1.032$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.54$ cm⁻¹, $F(000) = 132$, $T = 291$ K, $R = 0.077$ for 1638 observed reflections. The allene-like molecule has a dihedral angle of 94.4° between the

C₂BN and NCC₂ planes. B–N and N–C bond lengths of 1.366 (6) and 1.244 (5) Å, together with a B–N–C angle of 178.2 (4)° indicate substantial π -contribution to both bonds.

Introduction. Compounds in which a methyleneamino (ketimino) group $R_2C=N-$ is bonded to a metal or metalloid atom *M* are of interest because of the question of π -bonding between the N and *M* atoms. Such

* Azomethine derivatives. 21. Part 20: Clegg, Snaith, Shearer, Wade & Whitehead (1983).