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Structural Studies of the Interaction between Indole Derivatives and Biologically Important Aromatic Compounds. I. The Crystal and Molecular Structure of the Indole-3-acetic Acid-Nicotinamide (1:1) Complex

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The title complex crystallizes in the monoclinic space group $P2_1/c$. The unit-cell dimensions are $a=11.287(5)$, $b=5.110(3)$, $c=26.391(3)$ Å, and $\beta=107.07(2)°$. The crystal structure was solved by a direct method. By block-diagonal least-squares refinements, the R-value dropped to 0.069. All the nitrogen and oxygen atoms in the complex participate in the hydrogen bonding. No prominent overlapping between pyridine and indole rings is observed in the crystal. Both molecules are hydrogen-bonded to form infinite-layered structures perpendicular to the c-axis; those structures are held together by van der Waals contacts.

Pullman and Pullman[1] showed that the indole moiety of tryptophan was the best electron donor in amino acids, and Isenberg and Szent-Györgyi[2] presented evidence of charge-transfer interaction in the complex of tryptophan and NAD. Since then, a number of investigations have been undertaken to establish the precise mechanism of such interactions as indole derivatives and NAD or FAD as a model for protein-coenzyme interaction,[3–7] and indole derivatives and nucleic acid or its constituent as a model for protein-nucleic acid interaction.[8–12] As a result, it has been suggested that one of the main factors controlling these interactions is a charge-transfer force between the indole ring and the aromatic ring.[13] Recently, Herriott *et al.*[14] determined the crystal structure of 1-[2-(3-indolyl)ethyl]-3-carbamoylpyridinium chloride as a model of tryptophan–NAD interaction and observed the overlapping of the indole ring and the cationic pyridinium ring. To investigate to what extent a protonation is actually important for the interaction of the indole ring and the pyridinium ring, we tried to crystallize the molecular complex, with indole-3-acetic acid (IAA) as a donor and nicotinamide (NA) or *N*-methylnicotinamide as an acceptor. The crystal size of the IAA: *N*-methylnicotinamide complex is not suitable for X-ray analysis at present. We wish to report here the crystal structure of a 1:1 molecular complex of NA and IAA.

Experimental

Equimolar amounts of NA and IAA were dissolved in a 99.5% ethanol solution. After evaporation at room temperature, light-brown, plate-shaped crystals were obtained. The melting point of the crystals is 138—139 °C. Preliminary oscillation and Weissenberg photographs showed the crystals to be monoclinic and the space group to be $P2_1/c$, judging from the systematic absent spectra.

The crystallographic data are shown in Table 1. The density was measured by the floatation method in a benzene-carbon tetrachloride mixture. Three-dimensional intensity data were collected with a computer-controlled four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. By means of the $\omega/2\theta$ scan technique, a total of 1918 independent reflections were collected within $\sin\theta/\lambda$ less than 0.54 Å^{-1}. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption. The intensities of three standard reflections measured for every 50 reflections of the data set showed no decrease in intensity during the run. The scan speed was 4°/min, and 5-s background measurements were performed at each terminus of the scan. All the numerical calculations were carried out on an NEAC 2200-700 computer of the Computation Center of Osaka University using "UNICS" programs (1973).[15] Atomic scattering factors in "International Tables for X-Ray Crystallography," Vol. 4 (1974)[16] were used.

Table 1. Crystal data

$C_6H_6ON_2\cdot C_{10}H_9O_2N$	
$a=11.287$ (5) Å	*F.W.* 297.31
$b=5.110$ (3)	Space group $P2_1/c$
$c=26.391$ (3)	$Z=4$
$\beta=107.07$ (2)°	$V=1455.1$ Å^3
$D_m=1.353$ g cm^{-3}	$\mu(\text{Cu } K\alpha)=9.21$ cm^{-1}
$D_x=1.357$	

Determination and Refinement of the Structure

The structure was solved by the direct method with the "MULTAN" program[17] using 443 reflections with $|E|\geqq 1.20$. An E-map computed with the phase set of the highest figure of merit, 1.302, revealed the positions of all the non-hydrogen atoms. After least-squares refinement, a difference map revealed the positions of all fifteen hydrogen atoms (peak height: 0.3—0.5 e Å^{-3}), which were included in all subsequent refinements with isotropic temperature factors.

The final least-squares refinement was made with a weighting scheme of this form: $w=0.15$ for $F_o=0$, $w=1.0$ for $0<F_o\leqq 34.0$, and $w=\{1+0.776(|F_o|-34.0)\}^{-1}$ for $F_o>34.0$. In the last cycle of refinement, none of the positional parameters shifted more than one-third of the estimated standard deviation. The final R-value including $F_o=0$ is 0.069. The observed and calculated structure factors are listed in Table 2.[18]

Results and Discussion

A perspective view of the NA and IAA molecules projected on each ring plane is presented in Fig. 1,

Table 3. Atomic coordinates ($\times 10^4$) and their standard deviations of heavy atoms

Atom	x	y	z
NN1	5296(2)	4156(6)	721(1)
NC2	4079(3)	4036(6)	486(1)
NC3	3249(2)	5789(6)	597(1)
NC4	3695(3)	7754(6)	966(1)
NC5	4965(3)	7866(7)	1213(2)
NC6	5711(3)	6048(7)	1083(2)
NC7	1899(3)	5405(6)	338(1)
NN8	1181(2)	7508(5)	258(1)
NO9	1478(2)	3177(4)	214(1)
IN1	1026(2)	−3312(6)	2340(1)
IC2	−59(3)	−3385(8)	1928(1)
IC3	−16(3)	−1569(8)	1564(1)
IC4	1744(4)	1812(8)	1568(2)
IC5	2924(4)	2541(8)	1864(2)
IC6	3524(4)	1310(9)	2334(2)
IC7	2975(3)	−691(8)	2531(1)
IC8	1791(3)	−1424(6)	2239(1)
IC9	1153(3)	−251(7)	1752(1)
IC10	−989(4)	−1030(10)	1048(1)
IC11	−2058(3)	602(7)	1082(1)
IO12	−2849(2)	1109(6)	613(1)
IO13	−2239(2)	1307(6)	1484(1)

Table 4. Anisotropic thermal parameters ($\times 10^4$) and their standard deviations of heavy atoms

The anisotropic temperature factors are expressed in this form: $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
NN1	63(2)	426(13)	21(1)	54(9)	13(2)	24(4)
NC2	66(3)	347(14)	16(1)	42(10)	16(2)	16(5)
NC3	62(3)	247(11)	15(1)	00(9)	15(2)	11(4)
NC4	82(3)	303(13)	20(1)	−11(11)	9(2)	−7(5)
NC5	88(3)	366(15)	24(1)	−38(12)	−4(2)	−20(6)
NC6	67(3)	446(17)	25(1)	−31(12)	−1(2)	38(6)
NC7	64(3)	267(12)	13(1)	7(9)	16(2)	−1(4)
NN8	64(2)	226(10)	24(1)	29(8)	16(2)	0(4)
NO9	67(2)	226(8)	20(1)	6(6)	10(1)	−10(3)
IN1	92(3)	419(13)	17(1)	30(10)	17(2)	26(4)
IC2	86(3)	543(18)	17(1)	31(13)	20(2)	7(6)
IC3	87(3)	618(19)	13(1)	185(13)	21(2)	−8(5)
IC4	182(5)	486(18)	20(1)	174(16)	75(3)	53(6)
IC5	195(6)	480(19)	29(1)	−93(18)	97(4)	−5(7)
IC6	138(4)	591(21)	26(1)	−142(16)	57(3)	−43(7)
IC7	97(3)	561(19)	19(1)	7(14)	21(2)	−7(6)
IC8	88(3)	347(14)	15(1)	79(11)	26(2)	11(5)
IC9	108(3)	403(15)	14(1)	152(12)	40(2)	26(5)
IC10	108(4)	1076(31)	14(1)	382(19)	15(2)	2(7)
IC11	69(3)	500(16)	14(1)	47(12)	17(2)	2(5)
IO12	93(2)	921(18)	15(1)	249(11)	16(2)	35(4)
IO13	89(2)	720(15)	17(1)	177(10)	7(2)	−65(4)

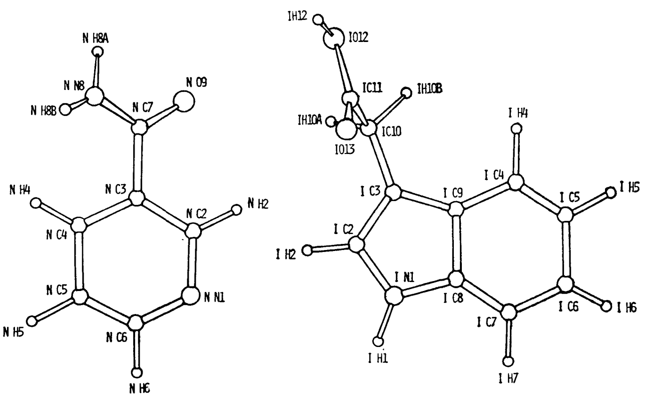

Fig. 1. The perspective view of NA and IAA molecules with the atomic numbering.

Table 5. Hydrogen atom coordinates ($\times 10^3$) and isotropic temperature factors, with their standard deviations

Atom	x	y	z	B(Å^2)
NH2	376(3)	255(8)	20(1)	3.8(9)
NH4	307(3)	909(8)	108(1)	4.3(9)
NH5	532(3)	940(8)	152(1)	4.3(9)
NH6	669(3)	608(7)	126(1)	3.6(8)
NH8A	28(3)	729(8)	10(1)	3.8(9)
NH8B	146(4)	919(10)	28(2)	8.1(14)
IH1	121(4)	−450(8)	268(2)	5.4(10)
IH2	−78(3)	−478(8)	192(1)	4.0(9)
IH4	127(4)	287(8)	121(2)	5.4(10)
IH5	335(4)	408(9)	171(2)	5.5(11)
IH6	439(4)	192(8)	253(2)	5.1(10)
IH7	342(3)	−156(8)	289(1)	4.7(10)
IH10A	−132(4)	−274(10)	87(2)	7.6(13)
IH10B	−62(3)	2(8)	78(2)	4.6(9)
IH12	−359(4)	223(8)	66(2)	5.6(10)

Table 6. Bond lengths and their standard deviations

	NA		
NN1–NC2	1.332(4)Å	NN1–NC6	1.341(5)Å
NC2–NC3	1.388(4)	NC3–NC4	1.387(5)
NC3–NC7	1.489(4)	NC4–NC5	1.391(5)
NC5–NC6	1.364(6)	NC7–NN8	1.325(4)
NC7–NO9	1.240(4)		
	IAA		
IN1–IC2	1.380(5)	IN1–IC8	1.372(4)
IC2–IC3	1.347(6)	IC3–IC9	1.434(5)
IC3–IC10	1.504(6)	IC4–IC5	1.382(7)
IC4–IC9	1.408(6)	IC5–IC6	1.379(7)
IC6–IC7	1.374(6)	IC7–IC8	1.384(5)
IC8–IC9	1.409(5)	IC10–IC11	1.492(6)
IC11–IO12	1.323(5)	IC11–IO13	1.192(5)

along with the atomic numbering. The atomic coordinates and thermal parameters, with their estimated standard deviations for non-hydrogen atoms are given in Tables 3 and 4 respectively. The coordinates and isotropic thermal parameters for hydrogen atoms are given in Table 5.

The Molecular Structure. Tables 6 and 7 show the bond lengths and angles, with their standard deviations.

NA Molecule: The NC5–NC6 bond length, 1.364 Å, is apparently smaller than the averaged C–C bond length in the pyridine ring;[19] this tendency is also observed in the crystal structures of 3,3′-dicarbamoyl-1,1′-trimethylenedipyridinium dichloride monohy-

Table 7. Bond angles and their standard deviations

NA	
NC2–NN1–NC6	117.5(3)°
NC2–NC3–NC4	119.2(3)
NC4–NC3–NC7	122.0(3)
NC4–NC5–NC6	118.7(4)
NC3–NC7–NN8	117.5(3)
NN8–NC7–NO9	122.3(3)
NN1–NC2–NC3	122.6(3)
NC2–NC3–NC7	118.8(3)
NC3–NC4–NC5	118.1(3)
NC5–NC6–NN1	123.9(4)
NC3–NC7–NO9	120.2(3)
IAA	
IC2–IN1–IC8	109.2(3)
IC2–IC3–IC9	107.4(3)
IC9–IC3–IC10	125.6(4)
IC4–IC5–IC6	121.5(4)
IC6–IC7–IC8	117.5(4)
IC7–IC8–IN1	130.0(3)
IC8–IC9–IC3	106.7(3)
IC3–IC9–IC4	135.5(4)
IC10–IC11–IO12	112.8(3)
IO12–IC11–IO13	122.0(3)
IN1–IC2–IC3	109.5(3)
IC2–IC3–IC10	127.0(4)
IC5–IC4–IC9	118.9(4)
IC5–IC6–IC7	121.5(4)
IC7–IC8–IC9	122.9(3)
IN1–IC8–IC9	107.1(3)
IC8–IC9–IC4	117.8(3)
IC3–IC10–IC11	115.8(4)
IC10–IC11–IO13	125.2(4)

drate,20) 3-carbamoyl-1-methylpyridinium 9-adenylacetate dihydrate21) and 3-carbamoyl-1-methylpyridinium picrate, chloride, and iodide.22)

The bond angles are reasonable compared with those of the other pyridine derivatives.23–27) The dimensions of the amide group are similar to those cited by Bracher and Small.28) The planarity of the NA molecule is given in Table 8. The NC7 atom deviates slightly from the pyridine-ring plane (0.09 Å). The amide group is almost planar, and the dihedral angle between the amide group and the pyridine-ring plane is 30.6°. The conformation of NA in the complex is different from that of the isolated molecule.24)

The torsion angle, τ(NC2–NC3–NC7–NO9), is 29.3° in this complex and 155.9° in the isolated molecule, and they are in opposite directions to each other. The torsional angles found in the pyridine derivatives can be grouped into three angles: 150, 35, and 0°. A theoretical calculation of the conformation of the NA molecule29) predicts that the most stable conformation has the torsional angle, τ, at 150°, and the next one, at 35°. The conformation of the present NA molecule belongs to the second stable conformation.

IAA Molecule: The bond lengths and angles are similar to those reported for IAA30–32) and indole derivatives.33) The planar carboxyl group is not in a resonance state because the IC11–IO13 bond has a strong double-bond character (1.192 Å). The IC10 atom is slightly out of the indole-ring plane (0.08 Å), contrary to 5-methoxyindole-3-acetic acid31) and the isolated IAA.30) The dihedral angle between the carboxyl group and the indole ring is 104.9°.

Table 8. Deviations of atoms from the least-squares planes

Equations of the best planes with the $m_1X+m_2Y+m_3Z=d$ formula in an orthogonal space.

Plane	m_1	m_2	m_3	d
Pyridine ring	0.3342	0.6048	−0.7229	1.7750
Amide group	0.4199	0.1155	−0.9002	0.3345
Indole ring	−0.5644	0.6652	0.4889	2.1097
Carboxyl group	0.5459	0.8368	−0.0430	−1.6023

Deviations (in Å) from the best planes

NA		IAA	
Pyridine ring		Indole ring	
NN1*	−0.006	IN1*	−0.020
NC2*	0.001	IC2*	0.002
NC3*	0.003	IC3*	0.021
NC4*	−0.002	IC4*	−0.015
NC5*	−0.002	IC5*	−0.005
NC6*	0.007	IC6*	0.010
NC7	0.092	IC7*	0.012
NH2	−0.006	IC8*	−0.007
NH4	0.049	IC9*	0.003
NH5	0.034	IC10	0.080
NH6	0.007	IH1	−0.063
Amide group		IH2	0.033
NC3*	0.002	IH4	−0.072
NC7*	−0.007	IH5	−0.003
NN8*	0.003	IH6	0.018
NO9*	0.003	IH7	−0.017
NH8A	0.022	Carboxyl group	
NH8B	−0.185	IC10*	−0.005
		IC11*	0.017
		IO12*	−0.005
		IO13*	−0.007
		IH12	−0.004

Atoms with asterisks define the plane.

The torsion angle, χ(IC2–IC3–IC10–IC11), is 80.4° in this complex, 97.7° in the isolated IAA, and 113.4° in the 5-methoxytryptamine: IAA complex,32) while the torsional angle, Ψ(IC3–IC10–IC11–IO13), is −6.4° in this complex, −11.7° in the isolated IAA, and −29.4° in the 5-methoxytryptamine: IAA complex. These facts show that such a conformation of the IAA molecule would be most stable regardless of the environmental changes in the crystal.

The Crystal Structure. Figure 2 shows the packing diagram viewed down the b-axis, where the dotted lines represent the hydrogen bonds (see Table 9). All the nitrogen and oxygen atoms in the complex participate in hydrogen bonding. The neighboring NA molecules related by a center of symmetry form a hydrogen-bonded dimer (NN8···NO9=2.913 Å, NN8–NN8HA···NO9=179.4°), similar to that found in a number of amide compounds,34) but not in the isolated NA. The NN8

Table 9. Hydrogen bonds and short contacts less than 3.5 Å

Superscribed numbers represent symmetry operators.

Hydrogen bonds

Donor	Acceptor	Distance D···A	Distance H···A	Angle D–H···A
IO12$^{1)}$	NN1$^{2)}$	2.691(4)Å	1.64(4)Å	176(4)°
IN1$^{1)}$	IO13$^{7)}$	3.008(4)	2.22(4)	131(3)
NN8$^{1)}$	NO9$^{4)}$	2.913(3)	1.93(4)	179(3)
NN8$^{1)}$	NO9$^{5)}$	2.922(3)	2.04(5)	161(5)

Short contacts

IC11$^{1)}$	NN1$^{2)}$	3.385(5)Å
IO13$^{1)}$	NN1$^{2)}$	3.261(4)
IO13$^{1)}$	IC7$^{3)}$	3.328(5)
NC7$^{1)}$	IO12$^{4)}$	3.493(4)
IO12$^{1)}$	NC3$^{4)}$	3.473(4)
IC4$^{1)}$	IN1$^{5)}$	3.462(5)
NC5$^{1)}$	IO13$^{6)}$	3.498(5)
NC6$^{1)}$	IO12$^{6)}$	3.471(5)
NO9$^{1)}$	IC10$^{8)}$	3.394(6)
IO12$^{1)}$	NC6$^{2)}$	3.425(5)
IO13$^{1)}$	NC6$^{2)}$	3.303(5)
IO13$^{1)}$	IC8$^{3)}$	3.457(4)
NN8$^{1)}$	IO12$^{4)}$	3.446(4)
IC4$^{1)}$	IC2$^{5)}$	3.492(6)
IC5$^{1)}$	IN1$^{5)}$	3.499(6)
NC6^{1}	IC11$^{6)}$	3.429(5)
NC6$^{1)}$	IO13$^{6)}$	3.502(5)

Symmetry code

Superscript	Symmetry operator		
1)	x	y	z
2)	$-1+x$	y	z
3)	$-x$	$0.5+y$	$0.5-z$
4)	$-x$	$1-y$	$-z$
5)	x	$1+y$	z
6)	$1+x$	$1+y$	z
7)	$-x$	$-0.5+y$	$0.5-z$
8)	$-x$	$-y$	$-z$

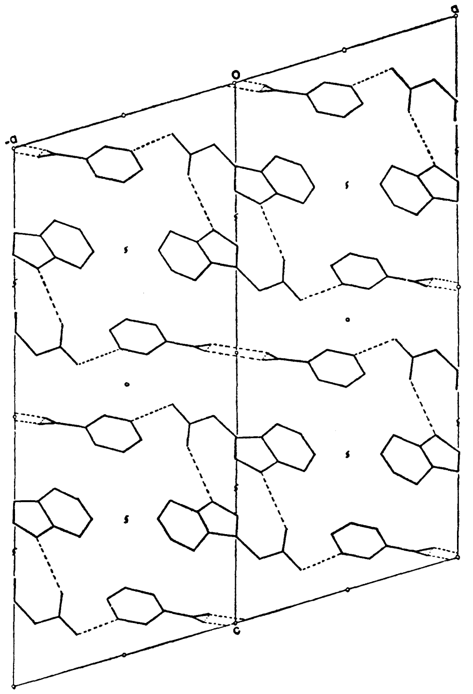

Fig. 2. Molecular packing of IAA–NA viewed down the b-axis. The dotted lines represent the possible hydrogen bonds.

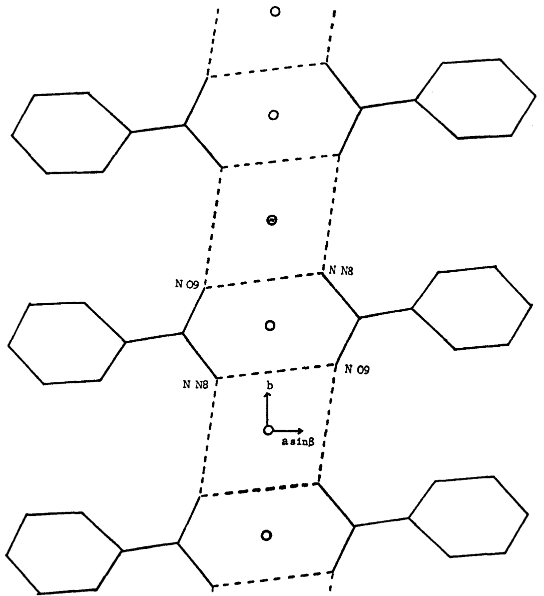

Fig. 3. The hydrogen bond network connected the NA molecules on the ab-plane.

atom is also hydrogen-bonded to the NO9 atom of the NA molecule, translated to the b-axis by one unit. Therefore, these hydrogen bonds form a network system connecting the NA molecules on the ab-plane, as is shown in Fig. 3.

On the other hand, the IO12 atom of the IAA molecule participates in a strong hydrogen bond[35] with the NN1 of the NA molecule, with a distance of 2.691 Å and the IO12–IO12H···NN1 angle of 176.3°; then, the IO13 atom is hydrogen-bonded to the IN1 atom of the neighboring indole ring, related by a diad screw axis with a distance of 3.008 Å. The hydrogen bonds and short contacts of less than 3.5 Å found in the crystal are listed in Table 9. Many short contacts were found between the carboxyl group in IAA and the pyridine ring in the neighboring NA molecule.

As a whole, both NA and IAA molecules are hydrogen-bonded to form infinite-layered structures perpendicular to the c-axis, structures which are held together by van der Waals contacts. The prominent overlapping between the pyridine and indole rings was not observed in this crystal, contrary to our expectations, but Ash *et al.*[36] recently found a prominent overlapping between the pyridinium and indole rings, arising from the π-π interactions in the crystal of the 3-carbamoyl-1-methylpyridinium *N*-acetyl-*l*-tryptophanate complex. This fact may indicate that the quaternary nitrogen atom in 1-methylnicotinamide, similar to NAD$^+$, is a necessity in the case of a specific charge-transfer interaction between the indole ring and the pyridine ring.

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