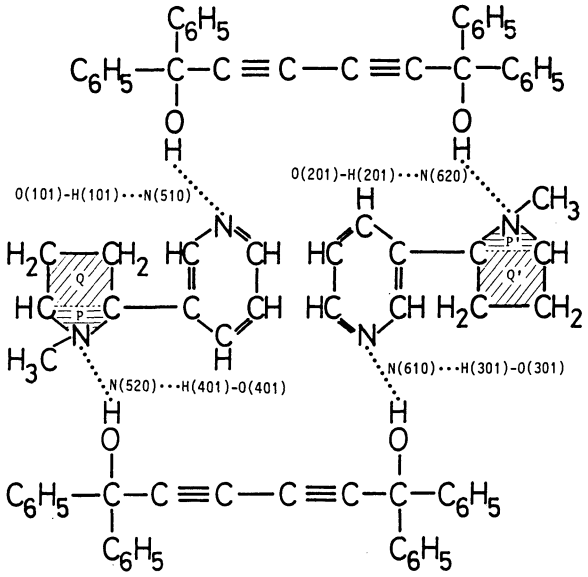
The Crystal and Molecular Structure of 2:2 Complex of 1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol (DD) with 1-Methyl-2-(3-pyridyl)pyrrolidine (Nicotine)

Ken-ichi FUKAWA, Shigeharu HARADA, Nobutami KASAI,* Mari TODA (née SEGAWA),†
Koji MORI,† and Fumio TODA*,†
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565
†Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
(Received March 22, 1989)

Synopsis. X-Ray crystal structure analysis of the title complex is described. $2(C_{30}H_{22}O_2),2(C_{10}H_{14}N_2)$, *F.W.* 1153.5, monoclinic, space group $P2_1$, a=28.913(2), b=12.353(1), c=9.340(1) Å, β=98.20(1)°, V=3301.7(6) Å^3, D_c=1.16 g cm^{-3} for Z=2. Two DD molceules are bound by two nicotine by four O-H···N hydrogen bonds to form a 2:2 complex. The crystal consists of these asymmetric 2:2 complexes.

Host-guest complexation method has been applied for the isolation of natural products.[1] Among them is the isolation of nicotine from tobacco leaves. In order to obtain structural informations on the complexation the crystal structure of the title 2:2 complex has been determined by means of X-ray diffraction.



Experimental

A crystal with approximate dimensions of 0.5×0.3×0.2 mm was mounted on a goniometer head attached to a Rigaku rotating anode four-circle diffractometer at the Institute for Protein Research, Osaka University. Intensity data were collected using nickel filtered Cu $K\alpha$ radiation by the θ-2θ scan technique up to 2θ=120°. The scan rate was 12° min^{-1} and the scan width $\Delta\theta$=(1.2+0.15 tanθ)°. Backgrounds were counted for 3 s at both ends of a scan. Three standard reflections measured after every 100 reflections to monitor the stability and orientation of the crystal showed slight change through the experiment. Of the 5175 reflections measured, number of reflections observed is 4640 ($|F_o|>2\sigma(F_o)$), where σ is the standard deviation obtained from the counting statistics). Usual Lorentz and polarization corrections were applied but absorption effect was ignored [μ(Cu $K\alpha$)=5.64 cm^{-1}].

Structure Solution and Refinement

The structure was established by the direct method. First the *MULTAN* 78[2] program was used to solve the structure. It seemed that all the non-hydrogen atoms of DD molecules and several non-hydrogen atoms of

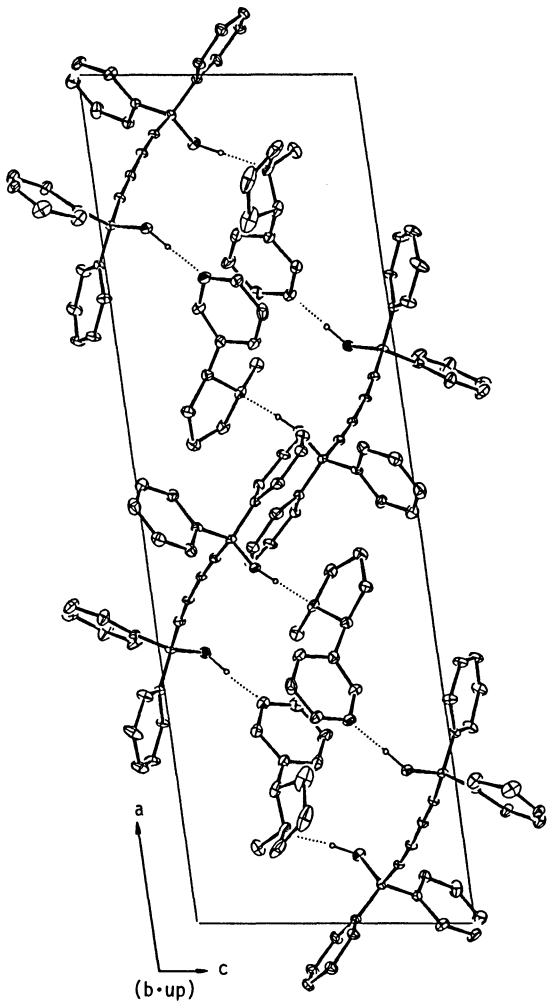


Fig. 1. Crystal structure projected along the b axis.[7] Non-hydrogen atoms are drawn as thermal ellipsoids with 10% probability level, and hydrogen atoms as spheres (B=1.0 Å). Hydrogen atoms not engaged in hydrogen bondings (shown by dotted lines) are omitted for clarity.

Table 1. Final Atomic Coordinates and Equivalent Isotropic Temperature Factors[5] for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
C(101)	0.8807(2)	0.1255(5)	0.1372(6)	4.3	C(313)	0.6360(3)	−0.4719(7)	1.3017(9)	7.8
C(102)	0.8551(2)	0.1982(4)	0.0881(6)	3.9	C(314)	0.6264(3)	−0.3659(9)	1.2939(10)	8.8
C(103)	0.8228(2)	0.2890(5)	0.0418(6)	4.1	C(315)	0.6397(3)	−0.3033(6)	1.1842(8)	7.0
C(104)	0.8412(2)	0.3619(5)	−0.0665(6)	4.2	O(301)	0.6809(2)	−0.3454(3)	0.8370(4)	5.1
C(105)	0.8668(3)	0.3197(6)	−0.1708(7)	6.3	C(401)	0.5910(2)	−0.0332(5)	0.8103(6)	4.2
C(106)	0.8787(3)	0.3865(7)	−0.2838(8)	7.1	C(402)	0.5696(2)	0.0414(4)	0.7536(6)	4.1
C(107)	0.8678(3)	0.4933(6)	−0.2861(7)	5.9	C(403)	0.5475(2)	0.1389(4)	0.6868(6)	3.8
C(108)	0.8420(4)	0.5299(7)	−0.1968(11)	10.4	C(404)	0.5340(2)	0.2137(5)	0.8026(6)	4.3
C(109)	0.8316(3)	0.4669(6)	−0.0696(9)	7.6	C(405)	0.4960(3)	0.1897(6)	0.8751(7)	6.1
C(110)	0.7754(2)	0.2438(5)	−0.0212(6)	4.1	C(406)	0.4839(3)	0.2526(9)	0.9802(8)	8.3
C(111)	0.7363(2)	0.3094(6)	−0.0211(8)	6.2	C(407)	0.5090(4)	0.3437(8)	1.0177(9)	8.5
C(112)	0.6926(2)	0.2716(7)	−0.0777(8)	6.4	C(408)	0.5473(3)	0.3751(7)	0.9462(8)	7.8
C(113)	0.6869(2)	0.1676(7)	−0.1365(8)	6.8	C(409)	0.5605(3)	0.3095(5)	0.8381(7)	6.2
C(114)	0.7240(3)	0.1079(6)	−0.1326(9)	7.0	C(410)	0.5034(2)	0.1120(5)	0.5790(6)	4.7
C(115)	0.7692(3)	0.1410(6)	−0.0796(8)	6.3	C(411)	0.4843(2)	0.0084(5)	0.5586(6)	5.0
O(101)	0.8193(2)	0.3555(3)	0.1671(4)	4.7	C(412)	0.4470(2)	−0.0088(7)	0.4523(8)	6.6
C(201)	0.9076(2)	0.0404(5)	0.1910(6)	4.2	C(413)	0.4250(3)	0.0644(9)	0.3758(8)	7.7
C(202)	0.9304(2)	−0.0345(5)	0.2442(6)	4.1	C(414)	0.4427(3)	0.1732(9)	0.3876(8)	8.5
C(203)	0.9530(2)	−0.1343(5)	0.3142(6)	4.5	C(415)	0.4823(3)	0.1975(6)	0.4905(8)	6.5
C(204)	0.9951(2)	−0.1045(5)	0.4272(5)	3.8	O(401)	0.5809(2)	0.1932(3)	0.6137(4)	4.3
C(205)	1.0169(2)	−0.1867(6)	0.5069(7)	5.6	C(510)	0.7254(3)	0.1999(6)	0.3148(8)	6.1
C(206)	1.0554(3)	−0.1666(6)	0.6087(7)	6.4	C(520)	0.6866(2)	0.1885(5)	0.3769(6)	5.2
C(207)	1.0720(2)	−0.0669(7)	0.6307(6)	6.4	C(530)	0.6846(3)	0.2539(7)	0.4978(8)	7.3
C(208)	1.0524(3)	0.0213(6)	0.5403(7)	6.2	C(540)	0.7205(4)	0.3168(8)	0.5433(8)	8.5
C(209)	1.0126(2)	−0.0040(5)	0.4430(6)	5.0	C(550)	0.7573(3)	0.3289(8)	0.4674(8)	7.5
C(210)	0.9666(2)	−0.2060(5)	0.1942(6)	4.7	C(560)	0.6466(3)	0.1137(6)	0.3123(7)	5.9
C(211)	0.9443(3)	−0.3022(5)	0.1568(7)	5.5	C(570)	0.6032(3)	0.1688(7)	0.2239(8)	7.1
C(212)	0.9589(4)	−0.3699(8)	0.0502(9)	8.4	C(580)	0.5654(3)	0.0832(8)	0.2272(8)	7.8
C(213)	0.9933(3)	−0.3423(8)	−0.0193(10)	8.6	C(590)	0.5855(3)	−0.0020(7)	0.3422(8)	7.4
C(214)	1.0137(3)	−0.2466(10)	0.0088(9)	8.8	C(500)	0.6582(3)	−0.0288(6)	0.4950(8)	7.0
C(215)	1.0014(3)	−0.1710(8)	0.1184(8)	7.4	N(510)	0.7606(2)	0.2670(6)	0.3514(7)	6.8
O(201)	0.9188(2)	−0.1897(3)	0.3840(4)	5.2	N(520)	0.6257(2)	0.0516(5)	0.4224(5)	5.3
C(301)	0.6190(2)	−0.1175(5)	0.8703(6)	4.0	C(610)	0.7733(3)	−0.1883(6)	0.6893(7)	6.3
C(302)	0.6441(2)	−0.1908(5)	0.9117(6)	4.8	C(620)	0.8088(3)	−0.1662(7)	0.6058(7)	6.3
C(303)	0.6768(2)	−0.2794(4)	0.9562(6)	3.7	C(630)	0.8109(3)	−0.2295(9)	0.4876(8)	8.3
C(304)	0.7259(2)	−0.2332(5)	1.0206(6)	4.2	C(640)	0.7794(3)	−0.3202(9)	0.4465(9)	9.2
C(305)	0.7318(3)	−0.1327(5)	1.0737(8)	6.3	C(650)	0.7424(3)	−0.3217(9)	0.5308(9)	8.9
C(306)	0.7753(3)	−0.0909(6)	1.1351(9)	9.2	C(660)	0.8415(3)	−0.0741(7)	0.6495(8)	7.5
C(307)	0.8152(3)	−0.1629(7)	1.1277(9)	8.3	C(670)	0.8294(6)	0.0257(8)	0.5429(13)	14.3
C(308)	0.8082(2)	−0.2635(9)	1.0802(9)	8.1	C(680)	0.8757(6)	0.0851(9)	0.5592(11)	14.8
C(309)	0.7639(2)	−0.2990(6)	1.0231(6)	5.5	C(690)	0.9112(4)	0.0135(10)	0.6712(11)	12.5
C(310)	0.6596(2)	−0.3473(4)	1.0783(6)	4.0	C(600)	0.9104(4)	−0.1713(10)	0.7434(9)	10.6
C(311)	0.6684(3)	−0.4593(6)	1.0811(9)	8.0	N(610)	0.7410(2)	−0.2663(6)	0.6513(6)	7.4
C(312)	0.6559(4)	−0.5212(6)	1.1826(9)	8.7	N(620)	0.8889(2)	−0.0944(6)	0.6370(6)	7.7

nicotine appeared on an E map, but the rest of non-hydrogen atoms of nicotine could not be located in spite of all possible efforts. The trial to solve the structure from the beginning by using the *SHELX-76*[3] program was successful. The structure was refined anisotropically by the least-squares procedure (*HBLS* V).[4] Hydrogen atoms except those of methyl groups were included in the refinements with isotropic temperature factors: R=0.063 for 4640 reflections ($|F_o|>2\sigma$). The function minimized in the refinement was $\sum w\Delta F^2$, and the weighting scheme used in the final stage of the refinement was $w=[\sigma^2(F_o)+0.01971|F_o|+0.00198|F_o|^2]^{-1}$. However, about one third of the hydrogen atoms could not be refined reasonably. All the hydrogen atoms refined were then relocated at the calculated positions, and the temperature factor of each hydrogen atom was assumed equal to the equivalent isotropic temperature factor of the non-hydrogen atom to which the hydrogen atom attached. Structure factor calculation gave the R value of 0.065. Atomic scattering factors used were taken from International Tables for X-Ray Crystallography.[6] Computations were done on an ACOS S930 computer at the Protein Engineering Center, Institute for Protein Research, Osaka University.

Final atomic parameters are given in Table 1.[††] Thermal parameters of atoms belong to the pyrrole ring of a nicotine molecule are fairly large. These might limit the accuracy of the result.

[††] Tables of anisotropic thermal parameters of non-hydrogen atoms, atomic parameters of hydrogen atoms, and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8890.

Results and Discussion

As seen in Fig. 1 the crystal is composed of a loose packing of 2:2 complex units of DD molecules with nicotine molecules. No close atomic contact less than 3.8 Å is observed between non-hydrogen atoms of adjacent complex units and also between those of pyridine rings of nicotine molecules in the complex unit.

The 2:2 complex has a sandwitch structure. The C-C≡C-C≡C-C backbone of each DD molecule bent inwardly in a small extent with the two hydroxyl groups inside and four phenyl groups outside. The two -C≡C- bond distances are 1.210(7) and 1.203(7) Å in one molecule and 1.190(7) and 1.191(7) Å in the other, whereas the central C-C distances in two molecules are 1.361(7) and 1.387(7) Å. All the bond angles on -C≡C-C≡C- linkages are slightly smaller than 180° [174.6(5), 177.2(6), 177.0(6), and 172.5(6)° in one molecule and 176.6(6), 174.9(6), 175.4(6), and 174.4(5)° in the other]. Two nicotine molecules are captured inside two DD molecules connected by four O-H···N hydrogen bonds. The nitrogen atom of the pyridine ring is bound to one of the hydroxyl groups of one DD by an approximately linear O-H···N hydrogen bond [O(101)···N(510)=2.806(7) and O(301)···N(610)=2.800 (8) Å]. The nitrogen atom of the pyrrole ring of the same nicotine molecule is also hydrogen bonded to the other hydroxyl group of the second DD [O(201)···N(620)=2.881(7) and O(401)···N(520)=2.930 (6) Å]. The pyrrole ring of nicotine takes an envelope form: the dihedral angle between planes defined by the nitrogen and two carbon atoms (Plane P or P′) and that made by the four carbon atoms(Plane Q or Q′) is 42.6(6) or 53.8(8)°. The pyridine ring and the Q plane (or Q′ plane) in the nicotine molecule makes approximately right angle [86.8(4) and 83.8(5)°]. Two pyridine rings of the different nicotine molecules are nearly parallel in the complex [dihedral angle: 7.9(3)°].

The present study was partially supported by a Grand-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) M. Segawa, K. Mori, and F. Toda, *Chem. Lett.*, **1988**, 1755.

2) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, *MULTAN* 78, "A System Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univs. of York, England and Louvain, Belgium, 1978.

3) G. M. Sheldrick, *SHELX*-76, "Program for Crystal Structure Determination, Univ. of Cambridge, England, 1976.

4) T. Ashida, *HBLS* V, "The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University, 1979.

5) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

6) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1974, Vol. IV, p. 71.

7) C. K. Johnson, *ORTEP* II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.