ANALYTICAL SCIENCES 2004, VOL. 20

X-ray Structure Analysis Online

Crystal Structure of 4-Dimethylaminoazobenzene-4′-sulfonyl-L-tryptophan Dimethylsulfoxide Solvate

Chizuru SASAKI, Soh-ichi KITOH, Hiroshige HAYASHI, and Ko-Ki KUNIMOTO†

Division of Applied Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920–1192, Japan

Crystals of 4-dimethylaminoazobenzene-4′-sulfonyl-L-tryptophan dimethylsulfoxide solvate (Dabs-Trp·DMSO) are monoclinic, space group $P2_1$ with a = 12.941(6)Å, b = 7.760(3)Å, c = 14.131(7)Å, β = 103.161(8)° and Z = 2. The structure was solved by direct methods (SIR88) and refined to a final R value of 0.058 for 3152 reflections ($I > 2.00\sigma(I)$). The molecular geometries and conformations are comparable to the typical values of azobenzene and L-tryptophan. The DMSO molecule is involved in the intermolecular hydrogen bonds with the sulfonamide NH and the carboxyl OH groups of different Dabs-Trp molecules. The hydrogen-bonded chains propagate along the b axis, and are constructed from molecules related by a two-fold screw axis. The sulfonamide S=O and the carboxyl C=O groups do not participate in hydrogen bonding.

(Received May 27, 2004; Accepted July 12, 2004; Published on web September 8, 2004)

4-Dimethylaminoazobenzene-4′-sulfonyl chloride (Dabs-Cl) reacts with primary amines to form sulfonamide derivatives. Since the dabsylated amino acids have strong and stable absorption in the visible region, Dabs-Cl is used for the pre-column detection of amino acids and protein hydrolyzates by reverse-phase HPLC, as well as by gel and capillary electrophoresis.[1]

4-Dimethylaminoazobenzene dyes are widely used as pH indicators, and their color changes upon pH changes are related to the chemical equilibrium of the molecular species. We studied the resonance Raman spectra of methyl orange (MO) and characterized the vibrational features of the molecular species responsible for UV-vis absorption.[2,3] Dabsyl amino acids possess a 4-dimethylaminoazobenzene chromophore similar to MO. In our study on the UV-vis absorption spectra, dabsyl amino acids with aromatic side chains show new UV absorption bands at around 370 nm, in addition to ordinary visible absorption at 460 nm, in a neutral aqueous solution at concentrations as low as 50 μM. It seems important to study the ground state structures of aromatic dabsyl amino acids in order to obtain information on this abnormal UV absorption. In this study, we analyzed the crystal structure of 4-dimethylaminoazobenzene-4′-sulfonyl-L-tryptophan (Dabs-Trp) as a representative example.

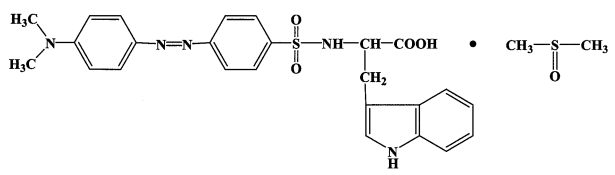

Fig. 1 Chemical structure of Dabs-Trp·DMSO.

† To whom correspondence should be addressed.

Dabs-Trp was purchased from Tokyo Kasei Co., Japan and purified through recrystallization from an ethanol solution several times. Orange prism crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of an aqueous DMSO solution at room temperature.

All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located by a difference Fourier synthesis and a geometrical calculation, with the H atoms bonded to N(1), N(2) and O(1) atoms also being refined isotropically. An ORTEP diagram of Dabs-Trp DMSO solvate with the atomic-labeling scheme is shown in Fig. 2. The crystal and experimental data are listed in Table 1. The final fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 2. Selected bond distances are listed in Table 3.

The azo chromophore part has a trans geometry about the azo linkage. The bond lengths and angles are similar to those of other azobenzene compounds.[4] The N=N and the C–N bond lengths [N(3)–N(4) 1.242(6)Å, N(3)–C(15) 1.452(7)Å and N(4)–C(18) 1.447(6)Å] are in the normal range of azobenzene compounds. The steric repulsion between the C(16)··N(4), and

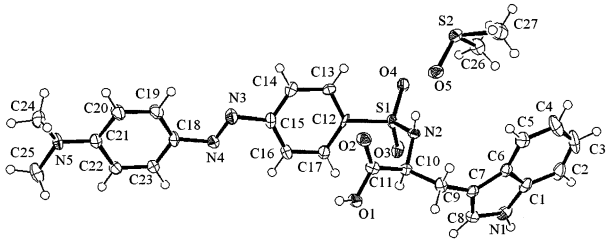

Fig. 2 Molecular structure of Dabs-Trp·DMSO with the atom numbering. Thermal ellipsoids of the non-hydrogen atoms are scaled to enclose 50% probability. The spheres of the hydrogen atoms are drawn on an arbitrary scale.

Table 1 Crystal and experimental data

Formula: $C_{27}H_{31}N_5O_5S_2$
Formula weight = 569.69
Crystal color, Habit: orange, prism
Crystal size: 0.25 × 0.15 × 0.05 mm
Crystal system: monoclinic
Space group: $P2_1$ (#4) $Z = 2$
a = 12.941(6)Å
b = 7.760(3)Å β = 103.161(8)°
c = 14.131(7)Å
V = 1381(1)Å^3
D_{calc} = 1.369 g/cm^3
F(0 0 0) = 600.00
μ(Mo K_α) = 2.39 cm^{-1}
T = 123 K
Radiation: Mo K_α (0.71069 Å)
$2\theta_{max}$ = 55.0°
No. observations = 3152 ($I > 2.00\sigma(I)$)
No. variables = 364
R, R_w = 0.058, 0.067
Goodness-of-fit = 1.42
Flack parameter = – 0.1(1)
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.19 eÅ^{-3}
$(\Delta\rho)_{min}$ = – 0.19 eÅ^{-3}
Measurement: Rigaku/MSC Mercury CCD
Program system: teXsan
Structure determination: direct method (SIR88)
Refinement: full-matrix least-squares

Table 2 Positional parameters of non-hydrogen atoms

Atom	x	y	z	B_{eq}(Å^2)
S(1)	0.28799(8)	0.1547	0.48905(7)	1.47(2)
S(2)	0.14412(9)	0.3364(2)	0.75569(8)	2.18(2)
O(1)	0.0872(3)	-0.2941(4)	0.4141(2)	2.08(7)
O(2)	0.0331(2)	-0.0640(4)	0.4841(2)	2.01(6)
O(3)	0.3771(2)	0.0716(4)	0.4646(2)	2.01(6)
O(4)	0.3005(2)	0.3203(4)	0.5347(2)	1.97(6)
O(5)	0.1123(2)	0.1776(4)	0.6926(2)	2.26(7)
N(1)	0.5264(3)	-0.3223(5)	0.7070(3)	2.16(8)
N(2)	0.2446(3)	0.0286(5)	0.5622(3)	1.50(7)
N(3)	-0.0552(3)	0.2178(5)	0.1294(3)	2.04(8)
N(4)	-0.0401(3)	0.1438(5)	0.0557(3)	1.98(7)
N(5)	-0.3707(3)	0.1773(6)	-0.2795(2)	2.11(7)
C(1)	0.5076(4)	-0.2364(6)	0.7856(4)	2.01(8)
C(2)	0.5762(4)	-0.1830(7)	0.8707(4)	2.9(1)
C(3)	0.5346(5)	-0.0928(8)	0.9379(4)	3.6(1)
C(4)	0.4237(5)	-0.0606(8)	0.9201(3)	3.3(1)
C(5)	0.3564(4)	-0.1136(6)	0.8360(3)	2.14(9)
C(6)	0.3960(3)	-0.2020(6)	0.7661(3)	1.70(8)
C(7)	0.3517(3)	-0.2741(6)	0.6727(3)	1.55(7)
C(8)	0.4318(3)	-0.3435(7)	0.6387(3)	2.02(8)
C(9)	0.2367(3)	-0.2671(6)	0.6191(3)	1.83(8)
C(10)	0.2169(3)	-0.1483(6)	0.5311(3)	1.51(7)
C(11)	0.1014(3)	-0.1620(6)	0.4733(3)	1.63(8)
C(12)	0.1899(3)	0.1727(6)	0.3801(3)	1.30(7)
C(13)	0.1078(3)	0.2905(5)	0.3754(3)	1.61(8)
C(14)	0.0290(3)	0.2996(6)	0.2908(3)	1.72(8)
C(15)	0.0329(4)	0.1941(5)	0.2127(3)	1.65(8)
C(16)	0.1137(4)	0.0746(6)	0.2169(3)	1.73(8)
C(17)	0.1927(4)	0.0621(6)	0.3016(3)	1.77(9)
C(18)	-0.1279(3)	0.1640(7)	-0.0277(3)	1.82(7)
C(19)	-0.2196(4)	0.2525(7)	-0.0290(3)	2.34(9)
C(20)	-0.3008(4)	0.2568(7)	-0.1115(4)	2.60(10)
C(21)	-0.2915(3)	0.1722(6)	-0.1981(3)	1.81(8)
C(22)	-0.1952(4)	0.0828(6)	-0.1941(3)	1.83(8)
C(23)	-0.1165(4)	0.0791(6)	-0.1104(3)	2.09(9)
C(24)	-0.4768(4)	0.2271(7)	-0.2733(4)	2.61(10)
C(25)	-0.3621(4)	0.0749(8)	-0.3631(3)	3.0(1)
C(26)	0.2846(4)	0.3525(7)	0.7736(3)	2.37(8)
C(27)	0.1408(4)	0.2725(7)	0.8759(4)	3.0(1)

$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table 3 Selected bond lengths (Å)

Atom	Atom	Distance	Atom	Atom	Distance
S(1)	O(3)	1.431(4)	S(1)	O(4)	1.431(4)
S(1)	N(2)	1.614(5)	S(1)	C(12)	1.764(4)
O(1)	C(11)	1.309(7)	O(2)	C(11)	1.202(6)
N(2)	C(10)	1.461(7)	N(3)	N(4)	1.242(6)
N(3)	C(15)	1.452(7)	N(4)	C(18)	1.447(6)
N(5)	C(21)	1.356(6)	N(5)	C(24)	1.447(8)
N(5)	C(25)	1.450(8)	C(7)	C(9)	1.508(7)
C(9)	C(10)	1.522(8)	C(10)	C(11)	1.535(7)

Estimated standard deviations in the least-significant figure are given in parentheses.

between the C(19)··N(3) is sufficient to distort the angles about the bridgehead atoms. The repulsive effect increases the angle at the azo nitrogen atoms from a normal tetrahedral value to *ca.* 112° [N(4)–N(3)–C(15) 112.1(4)° and N(3)–N(4)–C(18) 112.8(4)°]. The angles between the C–N bond and the phenyl ring appears to be distorted by a steric repulsion [N(3)–C(15)–C(16) 124.3(5)° and N(4)–C(18)–C(19) 125.7(5)°]. In spite of the steric repulsion, the azobenzene moiety is approximately planar, with all carbon and nitrogen atoms lying within 0.173(5)Å. Both the phenyl rings are inclined at an angle of 12.3(2)° to each other.

Molecular geometries and conformations of the tryptophan part of the compound are comparable to the reported values.[5]

The DMSO solvent molecule is involved in the intermolecular hydrogen bonds with the sulfonamide NH and the carboxyl OH groups of different Dabs-Trp molecules [O(1)···O(5)$^{i)}$ 2.687(6)Å, O(1)–H···O(5)$^{i)}$ 176(6)°; N(2)···O(5) 3.017(6)Å, N(2)–H···O(5) 161(6)°; symmetry code i) $-x$, $-1/2+y$, $1-z$]. The hydrogen-bonded chains propagate along the b axis and are constructed from molecules related by a two-fold screw axis. The sulfonamide S=O and the carboxyl C=O groups do not participate in hydrogen bonding, as is evident by the lack of any notable intermolecular contacts of less than 3.6 Å.

References

1. J. Y. Chang, R. Knecht, and D. G. Braum, Biochem. *J.*, **1981**, *199*, 547.
2. H. Lee, K. Machida, A. Kuwae, and Y. Saito, *J. Mol. Struct*., **1980**, *68*, 51.
3. H. Lee, K. Machida, A. Kuwae, and I. Harada, *J. Raman Spectrosc*., **1983**, *14*, 126.
4. C. Sasaki, S. Kitoh, K. Yamada, K.-K. Kunimoto, S. Maeda, A. Kuwae, and K. Hanai, *Anal. Sci*., **2003**, *19*, x1.
5. B. Khawas, *Indian J. Phys*., **1985**, *59A*, 219.