Investigation of Intermolecular Interaction in Molecular Complex of Tryptamine and Benzoic Acid by Solid-State 2D NMR

Akira TERAKITA,*[,a] Hirokazu MATSUNAGA,[a] Takahiro UEDA,[b] Taro EGUCHI,[b] Midori ECHIGOYA,[a] Kazuichi UMEMOTO,[a] and Masayuki GODO[a]

[a] *Analytical Development Laboratories, Takeda Chemical Industries, Ltd.; 2–17–85 Jusohonmachi, Yodogawa-ku, Osaka 532–8686, Japan: and* [b] *The Museum of Osaka University and Department of Chemistry, Graduate School of Science, Osaka University; 1–16 Machikaneyama, Toyonaka, Osaka 560–0043, Japan.*
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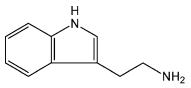
Solid-state NMR spectra and powder X-ray diffraction of the two-component molecular complex composed of tryptamine and benzoic acid were observed to investigate the intermolecular interaction in the molecular complex. 1D ^{13}C CP/MAS NMR spectrum and powder X-ray diffraction pattern of the complex was clearly different from the convolution of each spectrum of the single component. 2D ^{1}H–^{13}C heteronuclear-correlation (HETCOR) NMR technique indicated that the intermolecular interaction between the primary amine of tryptamine and the carboxyl group of benzoic acid must be related to the complex formation.

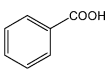
Key words solid-state NMR; molecular complex; intermolecular interaction; cross-polarization/magic angle spinnig (CP/MAS); heteronuclear-correlation (HETCOR)

In the course of drug development, it is a great concern to understand an intermolecular interaction, such as hydrogen bonding and electrostatic interaction, between an active ingredient and excipients in a drug formulation, because the interaction may affect the physicochemical properties of the formulation, such as polymorphism,[1)] chemical reactivity,[2,3)] and dissolution.[4)] The influence of the interaction can be either preferable to the quality of formulation or not.[3,4)] Therefore there is possibility to design drug formulation for better quality by utilizing or avoiding the intermolecular interaction intentionally. For such an intentional formulation design, the compatibility testing with various combinations of components is usually necessary to investigate whether an active ingredient interacts with any excipients or not, and reveal the mechanism and influence of the interaction on the quality if any. Although the analytical method such as powder X-ray diffraction (PXRD) and IR could be often used for such a research, it would be difficult to evaluate the interaction in drug formulation containing some components since the coexistent matrix would complicate the results.

Recently the solid-state NMR technique has been commonly used for research on the drug conformation as represented by polymorphism studies.[1,5,6)] In the conformational study for drug formulation, solid-state NMR has intrinsic advantages as follows: 1) This method is less destructive so that the sample probably remains in the original conformation. 2) It is more possible to avoid the interference of coexistent excipients with evaluation because some chemical shifts of an active ingredient, which mostly has some unsaturated bonds, likely separate from those of excipients used commonly for solid dosage form, many of which have no unsaturated bonds. In addition, 2D heteronuclear-correlation (HETCOR) method is expected to provide still more information about the geometry of molecules than 1D proton or carbon solid-state NMR does.[7,8)] Since the heteronuclear dipolar coupling just depends on the distance between the nuclei, the correlated peak intensity of HETCOR spectrum correlate mainly with the distance of nuclei.[8—10)] Therefore 1D and 2D solid-state NMR can be one of powerful methods for investigation of intermolecular interaction in formulation. In order to verify the usefulness of the solid-state NMR technique for the interaction study, we measured 1D ^{13}C CP/MAS NMR and 2D HETCOR spectra of the molecular complex of tryptamine and benzoic acid, found by Koshima *et al.*,[11,12)] as a model sample. Although the crystal structure of the complex has not been determined, the complex was predicted to have hydrogen bonding and/or electrostatic interaction from the results of X-ray crystallographic analysis for other analogous complexes. Since such interactions could be generated in drug formulation and its structure was unknown, it was selected as a model sample.



Tryptamine



Benzoic acid

Experimental

Materials Tryptamine was purchased from Tokyo Kasei Kogyo Co., Ltd. Benzoic acid was purchased from Wako Pure Chemical Industries, Ltd. Benzoic acid (carboxyl-^{13}C, 99% enriched) was purchased from Cambridge Isotope Laboratories, Inc. Methanol was special grade purchased from Wako Pure Chemical Industries, Ltd.

Sample Preparation With the same manner as described in previous report by Koshima *et al.*,[11,12)] the molecular complex of tryptamine and benzoic acid was prepared by crystallization from equimolar solution of the two compounds in methanol. The crystallization was performed by removing solvent with nitrogen gas stream followed by air-drying at ambient temperature (about 25 °C), resulting in plenty of crystalline powder for PXRD and NMR measurement. Additionally tiny single crystals for crystallographic analysis were obtained by slow-growing crystallization from the same equimolar solution in methanol vapor in a closed container. The physical mixture of the two components was obtained by gently mixing equimolecular quantities of the components in an agate mortar.

Powder X-Ray Diffraction (PXRD) PXRD patterns were determined at ambient temperature (about 25 °C) on a Rigaku X-ray diffractometer Rint Ultima^{+} 2100 with Cu$K\alpha$ radiation at 40 kV and 50 mA. The samples were measured at a step size of 0.02° with a scan speed of 6° per minute from 3° to 40°.

Solid State NMR All the experiments were performed at ambient temperature (about 25 °C) on a Bruker DSX-300 spectrometer with a Bruker 4-mmϕ or 7-mmϕ CPMAS probe, operating at the resonance frequencies of 75.47 and 300.13 MHz for ^{13}C and ^{1}H, respectively.

1D ^{13}C CP/MAS NMR High-resolution ^{13}C solid-state NMR spectra

* To whom correspondence should be addressed. e-mail: Terakita_Akira@takeda.co.jp

were obtained using the cross-polarization/magic angle spinning (CP/MAS) technique in conjunction with the proton decoupling by the two pulse phase modulation (TPPM) sequence.[13] Powdered sample (100—200 mg) was packed into a 4-mmϕ zirconia rotor with a Kel-F cap and was rotated at 10 kHz. The ^{13}C spectra were measured under the following conditions: spectral width being 26 kHz, acquisition time 30 ms, recycle delay 10—360 s, contact time 1 ms, and 90° pulse length 3.5 μs. All the chemical shifts are expressed relative to tetramethylsilane (TMS) using the carbonyl carbon of glycine (δ 176.03 ppm) as a secondary reference.

2D ^{1}H–^{13}C HETCOR 2D ^{1}H–^{13}C heteronuclear-correlation spectra were obtained using the previously reported pulse sequence with the BLEW-12/BB-24 combination during the evolution period followed by WIM-24 sequence for 456 μs during the mixing period.[7,8] Powdered sample (400—500 mg) was packed into a 7-mmϕ zirconia rotor with a Kel-F cap and was rotated at 5 kHz. The spinning speed was set to 3—5 kHz in most HETCOR experiments, because of a good compromise between the need to suppress the ^{13}C spinning sidebands and the requirement for CRAMPS that the rotor speed be slow to strengthen peak intensity.[8] In this experiment the spinning speed was set to 5 kHz to avoid a overlap of significant correlation peaks with spinning side bands. In the t_1 period (^{1}H dimension) 64—128 points and in the t_2 period (^{13}C dimension) 1584 points were acquired, and the spectra were zero-filled to a final size of 128×1024. The spectra were measured under the following conditions: recycle delay being 10—360 s, number of scans 16, and 90° pulse length 3.5 μs.

X-Ray Crystallographic Analysis Data were collected using Cu$K\alpha$ radiation on a Bruker Smart Apex CCD diffractometer. The structure was solved by direct methods using the SIR-92[14] program, and refined by full-matrix least-squares on F^2 using all data and the SHELXL-97[15] program. Hydrogen positions were obtained in the mixed mode. Non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included using a riding model.

Results and Discussion

PXRD We measured PXRD patterns in order to confirm whether the molecular complex was formed as demonstrated by Koshima *et al.*[12] before solid-state NMR measurement. As shown in Fig. 1 (A)—(C), each diffraction peak obtained from the physical mixure of tryptamine and benzoic acid was due to each substance. On the other hand, the sample, which was crystallized from the mixed solution containing tryptamine and benzoic acid with equimolar ratio, gave diffraction peaks at different angles (2θ) from those for each substance alone. When individual substance was recrystallized from methanol solution in the same manner, each recrystallized sample showed same PXRD pattern as the original substance, indicating that the crystallization from methanol solution did not give any different polymorphs for tryptamine and benzoic acid, respectively. From these results the sample crystallized from mixed solution was identified as a molecular complex, but not a mixture of individual polymorphs. In addition, since some characteristic peaks of tryptamine and benzoic acid, such as at about 14° (a) and at about 27° (b, c), were not observed in the pattern (D), it was found out that the components with original configuration scarcely remained in the molecular complex sample.

As demonstrated in this result, PXRD method is useful for simple detection of complexation generated by interaction. However with this method the overlaps of peaks may possibly confuse interruption in a multicomponent system and it is impossible to presume the groups relevant to intermolecular interaction.

1D ^{13}C CP/MAS NMR The ^{13}C solid-state NMR spectra were measured using CP/MAS technique with TPPM sequence[13] to investigate what kinds of information about the difference between the physical mixture and the molecular complex could be obtained (Fig. 2). The solution NMR data

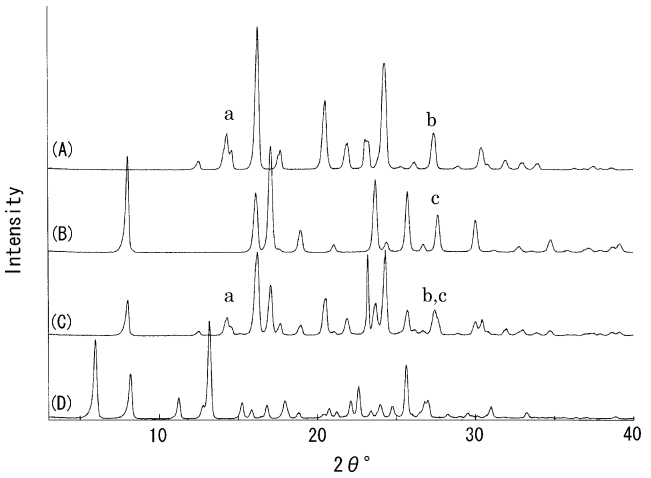


Fig. 1. Powder X-Ray Diffraction Patterns

(A) Tryptamine, (B) benzoic acid, (C) physical mixture, (D) sample crystallized from mixed solution.

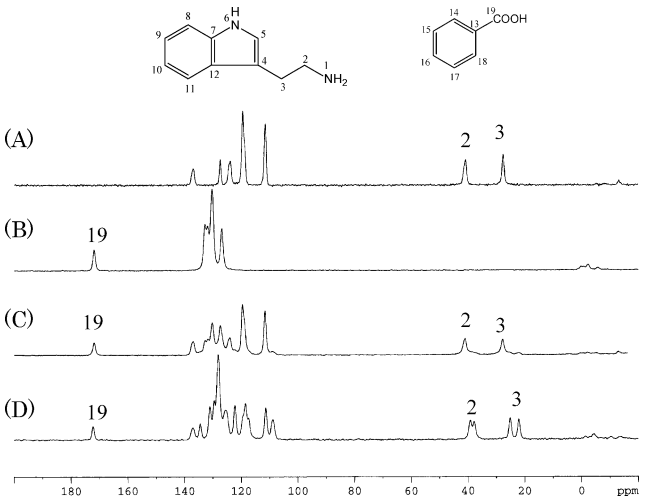


Fig. 2. ^{13}C CP/MAS NMR Spectra with TPPM[13]

Rotation speed: 10 kHz, samples and recycle delay: (A) tryptamine; 60 s, (B) benzoic acid; 360 s, (C) mixture; 360 s, (D) molecular complex; 10 s.

could provide useful information for assignments of chemical shifts in solid-state NMR although it is necessary to notice those in solid state are largely influenced by configuration of the compound unlike those in solution. Table 1 shows chemical shifts of original substances and molecular complex in solid state along with those of original substances in solution. The signals of methylene carbons (2-C and 3-C) and carboxyl carbon (19-C) was unambiguously assigned for both original substances and complex in solid state in reference to solution NMR data (Table 1), although it was difficult to assign close and overlapped aromatic carbons. The distorted signal shape of 2-C at δ 40.88 ppm in tryptamine (Fig. 2 (A)) was caused by the dipolar interaction between ^{13}C and nearby quadrupole ^{14}N.

The signals of two methylene carbons moved upfield from δ 27.62 and 40.88 ppm (Fig. 2 (A), (C)) to δ 23.64 and 38.51 ppm (Fig. 2 (D)), and those of carboxyl carbons moved downfield from δ 171.80 ppm (Fig. 2 (B), (C)) to δ 172.24 ppm (Fig. 2 (D)) due to the complexation, respectively, although all the signals in the spectrum of the mixture

Table 1. Solid-State and Solution ^{13}C-NMR Peak Assignment

Solid-state NMR				Solution NMR[16]		
Carbon	Chemical shift (ppm)			Carbon	Chemical shift (ppm)	
	Try.	B.A.	Comp.		Try.[a]	B.A.[b]
C19	—	171.80	172.24	C19	—	172.77
				C7	136.34	—
	136.85,		137.03,	C16	—	133.83
		132.72,	134.45,	C14, C18	—	130.28
		131.85,	131.04,	C13	—	129.44
		130.25,	129.52,	C15, C17	—	128.49
C4—C18	127.36,		128.11,	C12	127.40	—
		126.83	125.42,	C5	122.53	—
	123.78,		122.22,	C10	120.75	—
	119.45,		118.54,	C9	118.30	—
	111.49		111.34,	C11	118.06	—
			108.80	C4	112.60	—
				C8	111.29	—
C2	40.88	—	38.51	C2	42.71	—
C3	27.62	—	23.64	C3	29.55	—

Try.: Tryptamine, B.A.: Benzoic acid, Comp.: Molecular complex. *a*) DMSO-d_6,[16] *b*) $CDCl_3$.[16]

are identical with the superposition of trptamine and benzoic acid. The chemical shifts of most aromatic carbons in the range of δ 100—140 ppm moved due to complexation, although each change could not be traced because of the overlap of some signals. From the results that the chemical shifts moved in 1D NMR spectra, it was clear that there was drastic change in configuration due to complexation. In addition, the signals of methylenes in the complex were both doublets, although those in tryptamine were both singlets. These splittings were presumably caused by the fact that there were spatially nonequivalent carbons as to each methylene in the lattice of the complex, which was consistent with the results of single crystal X-ray analysis as discussed later.

Furthermore it is also of concern that the recycle delay time, which is an interval of each pulse repetition and dependent on the spin-lattice relaxation time (T_1) of proton, was influenced clearly by intermolecular interaction as described in the footnote of Fig. 2. The shorter the relaxation time of protons in the system, the shorter time can be set for the delay time in CP/MAS measurement. A long interval of 360 s was necessary for the measurement of the physical mixture, which was consistent with that for benzoic acid, because it was longer between the components (tryptamine: 60 s, benzoic acid: 360 s). On the other hand, an interval of 10 s was long enough for the molecular complex, indicating that the interaction sites would produce much shorter relaxation process than original components (configurationally discussed in 2D NMR section). Thus, if a sample containing some components (*e.g.* mixture of drug and excipients, drug formulation) can be measured with shorter recycle delay time than the individual component, it would indicate that the sample may have configurational changes from the original component by intermolecular interaction or crystal form.

2D ^{1}H–^{13}C HETCOR NMR The 2D ^{1}H–^{13}C HETCOR spectra were measured in order to verify the utility of this method for the intermolecular interaction studies, such as the identification of the interaction sites. Since the correlation peaks are observed by utilizing dipolar coupling-driven magnetization transfer in the HETCOR method, the peak intensity correlates mainly with the distance between the nuclei and therefore it is expected that the method can provide a great deal of the configurational information.[8,10]

Although the cross peaks of directly bound C–H pairs were observed in the HETCOR spectrum of the complex with natural abundance, no signals related to intermolecular interaction were observed unambiguously. Therefore the samples prepared using [^{13}C-19]-benzoic acid were measured instead, on the assumption that the carboxyl group most probably interacted with the other group and the enriched carboxyl carbon would enhance the intensity of signals relevant to interaction including the long-range signals. Figures 3 and 4 show the HETCOR spectra of the physical mixture and the molecular complex, with the corresponding 1D ^{1}H and ^{13}C projections of the spectra displayed along the vertical and horizontal axis, respectively.

As shown in Fig. 3, the mixture exhibited two strong peaks (cross peaks A and B) enhanced by ^{13}C-enriched carboxyl carbon (19-C) and some weak peaks due to directly bound pairs of natural abundance. The 19-C was correlated with H(19-CO) (cross peak A) and with H(14-C) and H(18-C) (cross peak B). Cross peaks D and E were attributed to 2-C/H(2-C) and 3-C/H(3-C), respectively, as discussed regarding the assignment of methylene carbons in 1D NMR section. There was also an unexplained cross peak C in the carboxyl resonance. The sample had no possibilities of complexation as demonstrated in PXRD and 1D NMR sections and there were no potential partners of 19-C for the peak C in benzoic acid. Thus the peak C on the ^{1}H projection is assumed to be caused by the artifacts due to the truncation of time evolution of nuclear spins for the t_1 period. In addition a similar weak peak was also observed in the complex (Fig. 4, cross peak H). Therefore these peaks C and H are decided to be excepted from consideration in this report.

On the other hand, as shown in Fig. 4, the 2D spectrum of the complex differed from that of the mixture in two significant points relevant to configuration. First the peak between the 19-C and the hydroxy proton of 19-C was not observed in the complex (Fig. 4) although the strong correlation peaks A

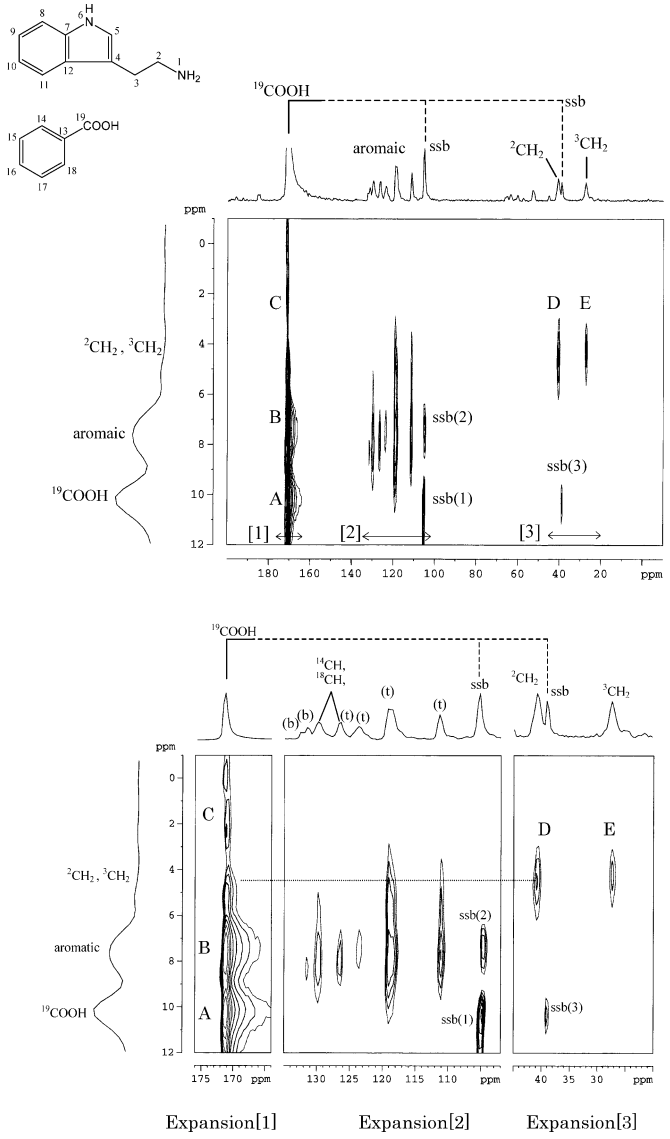


Fig. 3. HETCOR Spectra of Tryptamine/^{13}C-Enriched Benzoic Acid Mixture

Rotation speed: 5 kHz, (t): aromatic carbons in tryptamine, (b): aromatic carbons in benzoic acid, ssb(1) and (3): spinning side band of cross peak A, ssb(2): spinning side band of cross peak B.

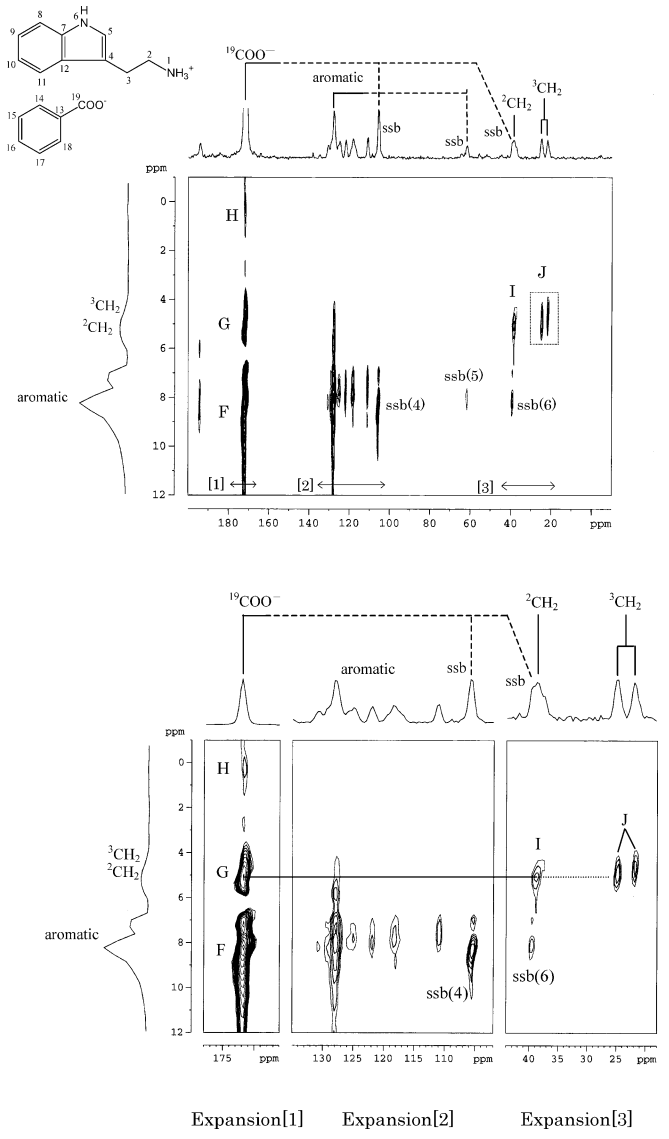


Fig. 4. HETCOR Spectra of Tryptamine/^{13}C-Enriched Benzoic Acid Molecular Complex

Rotation speed: 5 kHz, ssb(4) and (6): spinning side band of cross peak F, ssb(5): spinning side band of cross peak between aromatic carbons and protons.

and B were observed with similar intensity in the mixture (Fig. 3). From the results it was assumed that the carboxyl group in the complex was deprotonated (19-COO$^-$), which was consistent with the crystal data. Secondly a strong correlation peak G arose from long-range C–H pair, indicating intermolecular interaction. The peak G was assigned to be between 19-C and H(2-C) by comparing with the cross peaks in the aliphatic region, whereas the physical mixture exhibited no proton cross peaks in the carboxyl resonance unambiguously as shown in Fig. 3.

Figure 5 shows the cross section along ^{1}H chemical shift axis at the carbonyl ^{13}C resonance frequency for the complex and the mixture. The cross section for the complex showed the signal unambiguously at δ 5.0 ppm, which was the chemical shift of the H(2-C). On the other hand, in the cross section for the mixture, the signal was not observed at δ 4.4 ppm corresponding to H(2-C) except somewhat waved baseline likely because of artifact due to the truncation of FID.

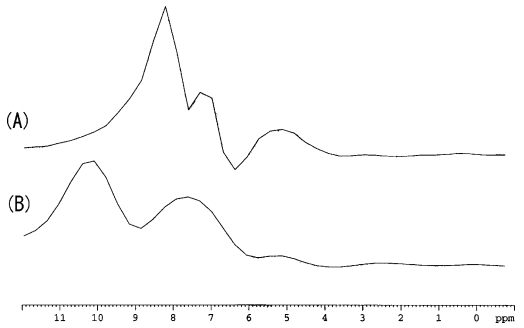


Fig. 5. Cross Section along ^{1}H Chemical Shift Axis at the Carbonyl ^{13}C Resonance Frequency

(A) Complex, (B) mixture.

It is expected that in this HETCOR experiment the correlation peaks would be observed between C–H pairs with dipole interaction of more than 2.2 kHz, which corresponds to inverse of mixing time of 456-μs. The magnitude of this het-

eronuclear dipolar interaction leads to the detectable C–H distance, shorter than about 2.5 Å using the following relation,

$$D_{C-H}=\left(\frac{\mu_0}{4\pi}\right)\frac{\gamma_C\gamma_H h}{r^3_{C-H}}$$

In the molecular complex with natural abundance, the correlation peak between 19-C/H(2-C) was not observed because of the low concentration of ^{13}C nuclei, whereas it was clearly observed in the ^{13}C enriched sample. Furthermore, the intensity of the correlation peak for 19-C/H(3-C) is much weaker than that for 19-C/H(2-C), if any, suggesting that 3-C is located at a longer distance from 19-C than 2-C. These aspects imply that the deprotonated carboxyl carbon is very close to the amino-terminal in tryptamine moiety. In general, a negatively charged carboxyl group is favorable to interact with the positive charge center such as NH_3^+ group. Therefore, it is assumed that the amino-terminal in tryptamine moiety is protonated to be NH_3^+ group and interacts electrostatically with COO^- in benzoic acid moiety, similarly to other analogous complexes composed of tryptamine and carboxylic acids.[11,12] Although additional work is necessary to reveal the reason why correlation peak between the 19-C and the nearby protons, H(1-N), were not observed, there are two possibilities about this phenomenon: One is the effect of the molecular motion of the NH_3^+ group. The rapid rotation of the NH_3^+ group will make the polarization transfer very inefficient as reported by Gu *et al.*[10] Other is the effect of the residual dipolar broadening due to the ^{14}N nuclei. The ^1H signal in the NH_3^+ group will be broadened out by the dipolar coupling with ^{14}N quadrupole nuclei as shown in CRAMPS experiment, in which protons bonded to nitrogen nuclei show broad line shapes due to that effect.[17]

The significant decrease of T_1 was observed in the measurement of 1D ^{13}C CP/MAS spectrum of the complex compared with tryptamine and benzoic acid, probably since the relaxation processes of these samples belong to the region of slow molecular motion as most solids do, where T_1 decreases as the correlation time (τ_c) decreases, and the complex has the NH_3^+ group with rapid rotational motion.

X-Ray Crystallographic Analysis The molecular structure of molecular complex was determined by X-ray diffraction analysis. The crystal data are as follows: $[C_{10}H_{13}N_2]^+$-$[C_7H_5O_2]^-$; M=282.34; monoclinic, space group $P2_1$ (#4), Z=4 with a=6.5104(4) Å, b=15.4015(7) Å, c=14.8764(6) Å, β=98.835°(3); V=1474.0(1) Å^3 and $D_{calc.}$=1.272 g/cm^3. The final R indexes were, respectively: R1=0.0645 for 3254 reflections with $F_o>4s$ (F_o), R2=0.0694 for all the 3516 reflections, wR2=0.1781.

The molecular arrangement of the complex viewed along the *a* axis of the crystal lattice is shown in Fig. 6. There are two pairs of tryptamine and benzoic acid molecules in an asymmetric unit. In other words, there are two non-equivalent pairs of tryptamine and benzoic acid in the crystal. However, major intermolecular interactions between tryptamine and benzoic acid are similar in the two pairs; *i.e.* salt interactions between deprotonated carboxylic groups and protonated ammonium groups, and hydrogen bonds between the carboxylic groups and the indole N–H. It was confirmed that the conclusion on configuration indicated by 1D and 2D NMR agreed well with the crystal structure. According to the atomic coordinates, the nearest neighbor protons (hydrogen atoms) from the carboxylic carbon (19-C) are as follows, quaternary ammonium protons (1-N, 2.6—3.4 Å), indole proton (6-N, 3.2 Å) and methylene protons (2-C, 3.4—3.5 Å). This is consistent with the result of 2D NMR spectra, although the distance between 19-C/H(2-C) determined from the crystal structure was a little longer than the upper limit for the detectable internuclear distance in HETCOR experiment (*ca.* 2.5 Å). The distance from 19-C to nearest proton of another methylene (3-C) was 4.7 Å in crystal lattice, which led no clear correlation peak in HETCOR experiment.

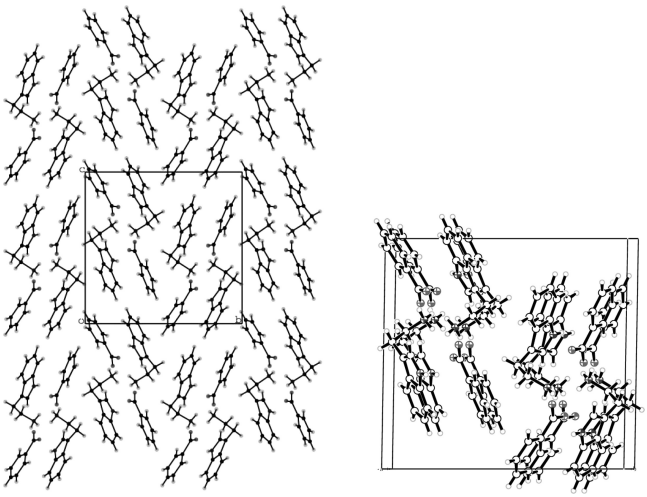


Fig. 6. Molecular Arrangement of the Complex

Conclusion

The 1D and 2D solid-state NMR spectra of a model complex were measured to demonstrate the utility of these methods for the investigation of intermolecular interaction in multicomponent system. According to the 1D ^{13}C CP/MAS measurement, it was possible to discriminate between complex and physical mixture simply and clearly from the comparison of chemical shifts. In addition 1D NMR measurement may provide some information regarding configurational change from the analysis of chemical shift, line shape, splitting and relaxation time. The 2D HETCOR technique provided much more configurational information than 1D technique in the sense of showing the correlated peaks between the neighboring nuclei. The peaks can be observed between C–H pair theoretically within a distance of 2.5 Å using sample of natural abundance under the experimental parameters used in this report, and actually the peak for C–H at a distance of 3.5 Å was not observed. However utilizing ^{13}C-enriched sample enabled the detectable distance to extend to 3.5 Å although the signal with a distance of 4.7 Å was scarcely observed.

Thus it is thought that the solid-state NMR, in particular 2D NMR, is a unique and powerful method besides PXRD to investigate the intermolecular interaction in the solid state, especially in the case that it is difficult to obtain single crystal data. The method is expected to facilitate developing the drug formulation with the specified intermolecular interaction.

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References and Notes

1) Lee G. S. H., Taylor R. C., Dawson M., Kannangara G. S. K., Wilson M. A., *Solid State Nucl. Magn. Reson.*, **16**, 225—237 (2000).
2) Byrn S. R., Xu W., Newman A. W., *Adv. Drug Deliv. Rev.*, **48**, 115—136 (2001).
3) Li J., Guo Y., Zografi G., *J. Pharm. Sci.*, **91**, 229—243 (2002).
4) Gupta M. K., Tseng Y., Goldman D., Bogner R. H., *Pharm. Res.*, **19**, 1663—1672 (2002).
5) Matsunaga H., Eguchi T., Nishijima K., Enomoto T., Sasaoki K., Nakamura N., *Chem. Pharm. Bull.*, **47**, 182—186 (1999).
6) Wenslow R. M., Baum M. W., Ball R. G., Mccauley J. A., Varsolona R. J., *J. Pharm. Sci.*, **89**, 1271—1285 (2000).
7) Burum D. P., Linder M., Ernst R. R., *J. Magn. Reson.*, **44**, 173—188 (1981).
8) Burum D. P., Bielecki A., *J. Magn. Reson.*, **94**, 645—652 (1991).
9) Mirau P. A., White J. L., *Magn. Reson. Chem.*, **32**, S24—S29 (1994).
10) Gu Z., Riedenour C. F., Bronniman C. E., Iwashita T., McDermott A., *J. Am. Chem. Soc.*, **118**, 822—829 (1996).
11) Koshima H., Honke S., *J. Org. Chem.*, **64**, 790—793 (1999).
12) Koshima H., Honke S., Fujita J., *J. Org. Chem.*, **64**, 3916—3921 (1999).
13) Bennet A. E., Rienstra C. M., Auger M., Lakshmi K. V., Griffin R. G., *J. Chem. Phys.*, **103**, 6951—6958 (1995).
14) Altomare A., Burla M. C., Camalli M., Cascarano M., Giacovazzo C., Guagliardi A., Polidori G., *J. Appl. Cryst.*, **27**, 435 (1994).
15) Sheldrick G. M., "Program for the Refinement of Crystal Structuers," University of Goettingen, Germany, 1997.
16) Integrated spectral data base system for organic compounds presented by National Institute of Advanced Industrial Science and Technolology ⟨http://www.aist.go.jp/ RIODB/SDBS/⟩.
17) Naito A., Root A., McDowell C. A., *J. Phys. Chem.*, **95**, 3578—3581 (1991).