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# NMR analysis of thione-thiol tautomerization of a triazine derivative in the solid state and in acetone solution

Akira Mizuno<sup>a,\*</sup>, Yoshihisa Toda<sup>a</sup>, Masaaki Itoh<sup>a</sup>, Katsunori Kojima<sup>b</sup>, Yoshinori Kadoma<sup>b</sup>

<sup>a</sup>San Analysis and Consulting Service Limited, 6 Waki, Waki-cho, Kuga-gun, Yamaguchi-ken 740, Japan <sup>b</sup>Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, 2 Kandasurugadai, Chiyoda-ku, Tokyo 101, Japan

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#### Abstract

The important dental material referred to as 6-[(4-vinylbenzyl)propylamino]-1,3,5-triazine-2,4-dithione (VBATDT), which may have the thione-thiol tautomerization, was confirmed for the first time to have the dithione structure in the solid state by using <sup>15</sup>N CP/MAS NMR with the dipolar dephasing technique. VBATDT was also shown to have the dithione structure in acetone solution by comparison of the <sup>13</sup>C NMR spectrum with the corresponding solid state spectrum. © 1998 Elsevier Science B.V.

Keywords: Triazine derivative; Dithione structure; <sup>15</sup>N CP/MAS NMR; Dipolar dephasing

# **1. Introduction**

It is well known that the surface treatment of dental noble metal alloys or noble metals with the compound referred to as 6-[(4-vinylbenzyl)propylamino]-1,3,5triazine-2,4-dithione (VBATDT), which is practically used in 0.5% acetone solution, demonstrates the excellent durability against water in adhesion of resins to these metals [1]. On the other hand, this triazine derivative was reported to have a dithiol structure in the study of protection of the copper surface against corrosion [2]. While VBATDT is in this way an important adhesive bonding promoter, its structure is somewhat ambiguous, because it may have some tautomers such as triazine-dithiol (I), triazinedithione (II) and triazine-thione-thiol (III) shown by structure 1: 0022-2860/98/\$19.00 © 1998 Elsevier Science B.V. All rights reserved *PII* \$0022-2860(97)00253-6

<sup>\*</sup> Corresponding author.

The preliminary structural analysis conducted by IR and <sup>1</sup>H NMR spectroscopy suggested that the dithione structure (II) was dominant among the possible tautomer structures in the solid state or in  $CDCl_3/DMSO-d_6$  mixed solution because neither IR nor NMR spectra showed the peaks clearly assigned to the mercapto group [1]. However, no direct spectroscopic proof has been reported so far concerning these tautomers.

In the heterocyclic rings, the number of NH is 0, 2 and 1 for the dithiol (I), dithione (II) and thiol-thione (III) structure, respectively, as shown in structure 1. Therefore, the analysis of the chemical states of these nitrogen atoms is expected to provide the most useful information about the structure of VBATDT. Furthermore, the structure of VBATDT may be well investigated in the solid state, because the exchange rate among the tautomers is presumed to be considerably or completely suppressed.

Thus, we have studied the chemical structure of VBATDT in the solid state by the high resolution <sup>15</sup>N NMR spectroscopy. Thereafter, <sup>13</sup>C NMR spectra in the solid state and in acetone-d<sub>6</sub> solution have been also compared to examine the VBATDT structure in acetone solution.

# 2. Experimental

#### 2.1. Sample

VBATDT was synthesized in the following manner acording to the literature [1,2]. First, 4-vinylbenzyl n-propyl amine was prepared by reacting 4-vinylbenzyl chloride (80 g, 0.54 mol) with n-propyl amine (150 g, 2.54 mol) in methanol solution of NaOH (21.4 g, 0.54 mol/200 g) at 50°C for 2 h, boiling point 99-100.5°C/1.8 mmHg. A THF solution of 4-vinylbenzyl n-propyl amine (17.5 g, 0.1 mol/20g) was reacted with a tetrahydrofuran (THF) solution of cyanuric chloride (18.45 g, 0.1 mol/100 g) at 0°C for 1 h, followed by the addition of an aqueous solution of  $Na_2CO_3$  (5.3 g, 0.05 mol/60 g). The reaction mixture was treated with an aqueous solution of NaSH (24 g, 0.3 mol), and acidified with 5% HCl acqeous solution to give VBATDT. The white crystalline product obtained has a melting point of 171–172°C.

#### 2.2. NMR measurements

Cross polarization (CP)/magic angle spinning (MAS) <sup>15</sup>N and <sup>13</sup>C NMR spectra of VBATDT were recorded at room temperature on a Chemagnetics CMX 300-Infinity NMR spectrometer. The <sup>15</sup>N spectrum was obtained under the following conditions; spectral width: 20 kHz; data points: 8 k; contact time: 4 ms; pulse delay: 4 s; 90° pulse width: 7  $\mu$ s; MAS rate: 3 kHz; and accumulation time: 10,000. Chemical shifts were calibrated using solid Na<sub>4</sub>Cl (18 ppm). <sup>13</sup>C measurement conditions were as follows; spectral width: 30 kHz; data points: 16 k; contact time: 2 ms; pulse delay: 4 s; 90° pulse: 6.2  $\mu$ s; MAS rate: 8 kHz; number of accumulations: 2000. Chemical shifts were externally referenced to the CH<sub>2</sub> peak of solid adamantane (29.5 ppm).

As to solid state <sup>15</sup>N experiments, the <sup>15</sup>N-<sup>1</sup>H heteronuclear dipolar dephasing technique [3–5] was used for discrimination of the type of nitrogen species. In this measurement, an additional delay of 200  $\mu$ s was inserted between the nitrogen–proton contact period and the data acquisition period.



Fig. 1. CP/MAS <sup>15</sup>N NMR spectra of VBATDT: (A) without dipolar dephasing, (B) with dipolar dephasing.

 $^{13}$ C NMR spectra of VBATDT in acetone-d<sub>6</sub> solution were measured at room temperature and at 55°C, using a JEOL LA 500 NMR spectrometer under instrumental conditions of pulse angle 45°, spectral width 30 kHz, 64 k data points, pulse delay 10 s and number of accumulations 50,000–100,000.

# 3. Results and discussion

#### 3.1. VBATDT structure in the solid state

The <sup>15</sup>N CP/MAS spectrum is shown in Fig. 1(A). Here four nitrogen peaks with equal intensities are observed, corresponding to nitrogen atoms in four different chemical environments. This indicates that VBATDT has a single chemical structure in the solid state rather than the mixture of the tautomers. The

Table 1 <sup>15</sup>N chemical shifts of VBATDT

Peak no.	Nitrogen species	Chemical shifts/ppm 78.1	
1	N(aliphatic)		
2	NH(1, heterocyclic)	124.4	
3	NH(3, heterocyclic)	160.3	
4	N(5, heterocyclic)	183.6	

Note: Chemical shift reference NH<sub>4</sub>Cl-18 ppm.

peak at 78.1 ppm is easily assigned to the aliphatic nitrogen atom directly bonded to the heterocyclic ring. However, other nitrogen peaks are difficult to assign from the present data alone. The CP/MAS <sup>15</sup>N spectrum with dipolar dephasing was, therefore, measured to determine the nitrogen species. The spectrum obtained is presented in Fig. 1(B). It is noticeable that two peaks at 124.4 ppm and 160.3 ppm



Fig. 2. CP/MAS <sup>13</sup>C NMR spectrum of VBATDT.



Fig. 3. 13C NMR spectra of VBATDT in the range of 150-200 ppm: (A) at 55°C in solution, (B) at room temperature in solution, (C) in the solid state.

of the spectrum shown in Fig. 1(A) disappear by dipolar dephasing. These disappearing peaks are assigned to NH, while the remaining ones at 78.1 ppm and 183.6 ppm to nitrogen atoms having no hydrogen. It is, therefore, concluded from the number of NH that VBATDT has the dithione structure.

All the nitrogen peaks were assigned on the basis of these solid state  $^{15}N$  NMR measurements with the aid of the related compounds found in literature [6]. The results are summarized in Table 1. The NH(1) and N(5) of VBATDT are observed in the different resonance positions (124.4 ppm and 183.6 ppm), suggesting that the proton of NH(1) does not migrate to the position of N(5) in the solid state.

Since VBATDT has the dithione structure, the chemical shifts of two thione carbons were studied by CP /MAS <sup>13</sup>C NMR measurement. The obtained spectrum is exhibited in Fig. 2, where two thione carbons(C = S) are observed at 175.2 ppm and 182.1 ppm, respectively. This separate observation of two thione carbon peaks is in accord with the result that the proton migration from NH(1) to N(5) does not happen in the solid state. The thione carbon conjugated with N = C resonates at the higher field from the empirical chemical shift rule [7] (Fig. 2).

# 3.2. VBATDT structure in acetone solution

<sup>13</sup>C NMR spectra of VBATDT in acetone- $d_6$  solution were measured at room temperature and 55°C. A comparison between the spectra for the heterocyclic carbon region in the solid state and in acetone- $d_6$  solution is most interesting, because this region in VBATDT directly reflects the tautomeric isomer structure (see Fig. 3). The C(6) peak, which is assigned to the quarternary carbon bonded with three nitrogen atoms in the heterocyclic ring, resonates at the same position, regardless of the

<sup>3</sup> C chemical	shifts of	C(2), C(4	) and C(6)	of VBATDT

Table 2

Peak no.	Chemical shifts/ppm				
	55°C in soln.	r.t. in soln.	Solid state		
C(2)	180.6	182.7	182.1		
C(4)	176.2	174.9	175.2		
C(6)	150.4	150.4	150.6		

solid state or acetone solution. As to the two thione carbon peaks, C(2) and C(4), their chemical shifts in solution are in good accord with those in the solid state at room temperature. However, the shift difference between these two lines becomes slightly smaller at 55°C, although their averaged value is unchanged. The chemical shift values of C(2), C(4) and C(6) are summarized in Table 2. These findings indicate that the dithione structure is maintained even in acetone solution and no proton migration occurs from NH(1) to N(5). Moreover, this migration is hardly observed at 55°C.

#### 3.3. Storage stability of VBATDT

When the surfaces of noble metals are treated with N-(4-mercaptophenyl)methacrylamide(MPMA), which is a functional monomer having a mercapto group, the strong adhesion is obtainable between resins and these metals [8]. Such strong adhesion is explained by the chemical reaction between the mecapto group and the metal surface. However, MPMA is labile on storage because the addition reaction of the mercapto group takes place to the double bond of the methacryloyl group.

On the other hand, VBATDT is confirmed to be quite stable on storage by our present result that VBATDT has the dithione structure instead of the dithiol structure. The reason that VBATDT acts as a prominent adhesive bonding promoter is probably due to mercapto groups formed by rearrangement of the dithione structure in contact with the metal surface. A further study is anticipated for the elucidation of this mechanism.

# 4. Conclusions

VBATDT structure in the solid state was investigated by CP/MAS <sup>15</sup>N NMR methods including the dipolar dephasing technique. These NMR studies provided the first conclusive proof that VBATDT has the dithione structure. A comparison between <sup>13</sup>C NMR spectra of VBATDT in the solid state and in acetoned<sub>6</sub> solution shows that the dithione structure is maintained in acetone solution as well.

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