# Thermal stability of quaternary ammonium salts used as charge-control agents as viewed from their crystal structure

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## Abstract

*Quaternary ammonium salts are well-known charge-control agents (CCAs) used widely in electrophotography. Aside from the CCA performance, a high thermal stability is also required because pulverized toners are prepared by kneading CCA with various toner components at 130-180 ℃. Therefore, thermal stability has been studied in the present investigation in various quaternary ammonium salts with naphtholsulfonates in terms of structure analysis as well as IR spectra. As a result, the anions are found to play the key role in raising the melting point due to the formation of intermolecular OH···O hydrogen bonds between the OH group of one anion and the sulfonic O atom of the neighboring one. The hydrogen bonds bridge anions either in the form of a one-dimensional chain or a dimer.*

## Introduction

Quaternary ammonium salts are widely used in practice as supporting electrolytes in the field of electrochemistry. On the other hand, similar salts that possess high melting points are also used in electrophotograpy as charge-control agents (CCAs) for toners.

Previously, we have been involved in the charge-control mechanism of CCA that assumes an appreciable temperature increase at the "toner/carrier" interface due to the tribo-electrification [1]. Because of the present local heating, the electrical conductivity of CCA (which resides on the surface of both toner and carrier) is remarkably increased to give a conductive channel, through which the carrier-flow occurs effectively to charge the toner. In the course of this investigation, we have analyzed the crystal structure of benzyltributylammonium 4-hydroxy-naphthalene-1-sulfonate (P-51 from Orient Chemical Industries, Ltd: Fig. 1) in an attempt to elucidate its high melting point (about 190 °C) from the structural point [2]. The ORTEP plots of P-51 are shown in Figs. 2(a) and 2(b). To our surprise, there are OH···O intermolecular hydrogen bonds in anions between the OH group of the one anion and the sulfonic O atom of the neighboring one (Fig. 2(b)). The hydrogen bond forms a one-dimensional polymer chain along the *b* axis. It is actually the present hydrogen bond network that imparts a polymer-like stabilization to P-51, resulting in the increase of the melting point.

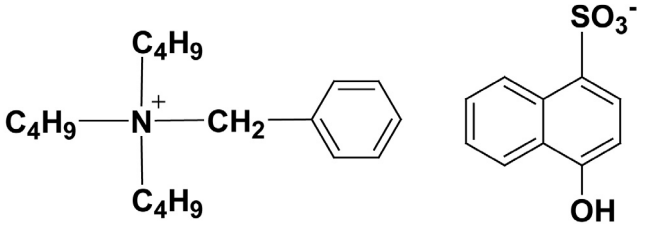


***Figure 1.*** *Molecular structure of P-51*

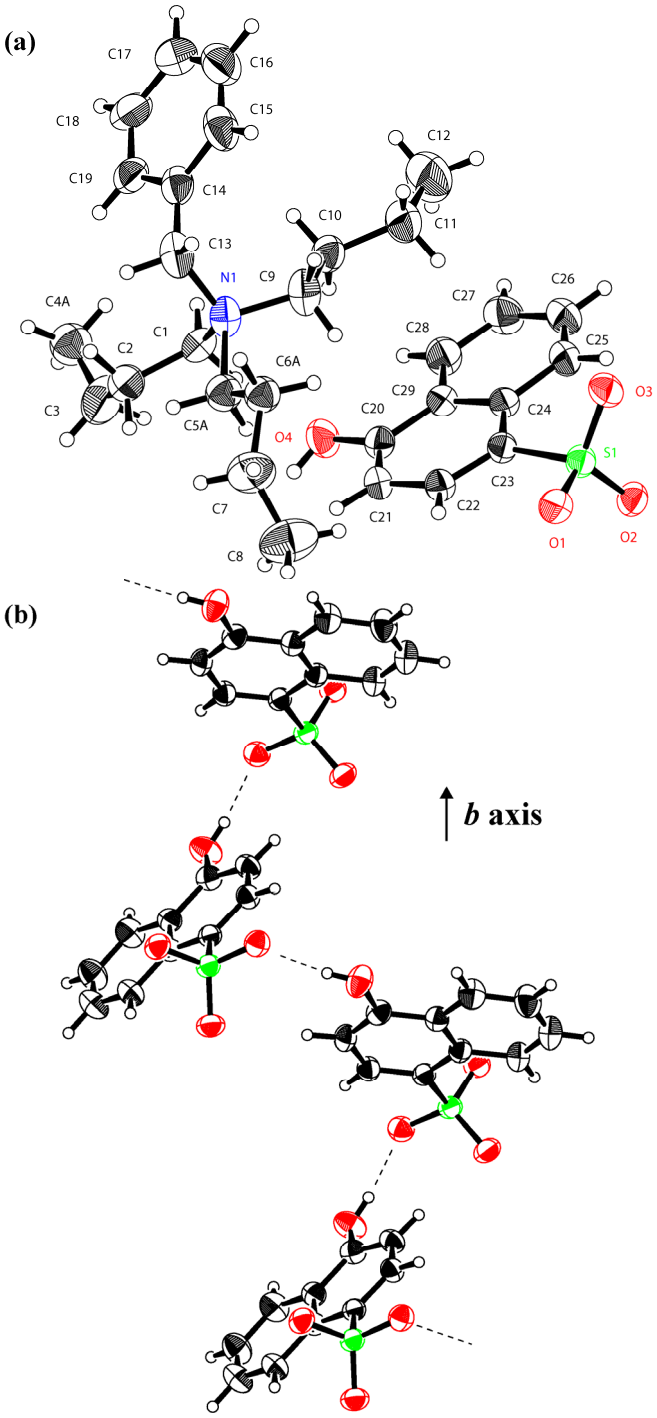


***Figure 2.*** *(a) ORTEP plot of P-51 and (b) one dimensional polymer chain along the b axis*

The above results motivated us to study a series of P-51 derivatives with different anions while retaining the cation structure (YNU1-4) as shown in Fig. 3. The purpose of the present investigation is to study the thermal stability of the derivatives in terms of DSC (Differential scanning calorimetry) and IR spectra from the view point of intermolecular OH···O hydrogen bonds. This paper also presents the crystal structure for YNU1 which has been successfully isolated as single crystals.

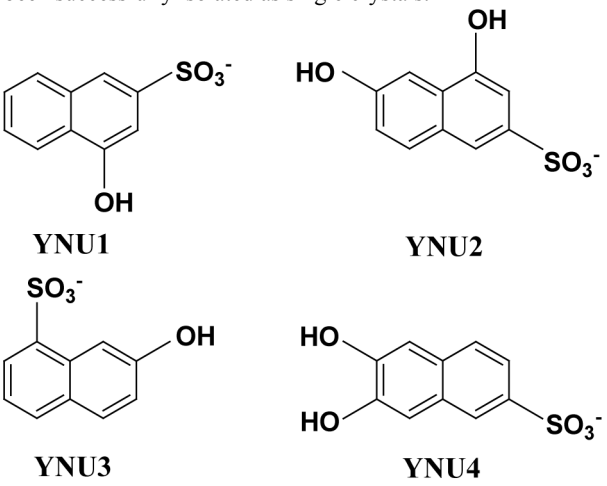


***Figure 3.*** *Anions of YNU1-4*

## Experiment

### *Materials and crystal growth*

Single crystals of YNU1 were grown by recrystallization from an acetonitrile solution. After 48 h, a number of light brown crystals were obtained in the form of blocks (size: 0.44×0.40×0.25 $mm^3$).

### *Collection of reflection data and X-ray structure analysis*

Reflection data were collected on an R-AXIS RAPID-F diffractometer from Rigaku using Cu$K\alpha$ as the radiation source ($\lambda$ =1.5418 Å) at room temperature. The structure was solved by direct methods (SHELXS97 [3]) and refinement was carried out by the full-matrix least-squares method of $F^2$ (SHELXL97 [3]).

### *Equipment*

DSC analysis was made on powdered P-51 derivatives in air by means of a Thermo Plus 2 DSC-8230 from Rigaku at a heating rate of 10 °C/min. Infrared (IR) spectra were measured with a JASCO MET-2000 on P-51 derivatives.

## Result and discussion

### *Hydrogen bonds and melting points*

Fig. 4 shows the DSC curves for P-51 and YNU1-4. The melting points of these compounds are listed in Table 1 together with their OH stretching bands. Fig. 5 shows the IR spectra for P-51 and YNU1-4 in the wavenumber region between 2500 and 3500 $cm^{-1}$. The broad absorption bands around 3100 $cm^{-1}$ are assigned to the hydrogen-bonded OH stretching band. Both the high melting point and the hydrogen-bonded OH stretching band indicate that the anions in YNU1-4 are indicative of the formation of intermolecular OH···O hydrogen bonds between the OH group of one anion and the sulfonic O atom of the neighboring one.

Among YNU1-4, only YNU1 gave single crystals which were sufficiently big for structure analysis.

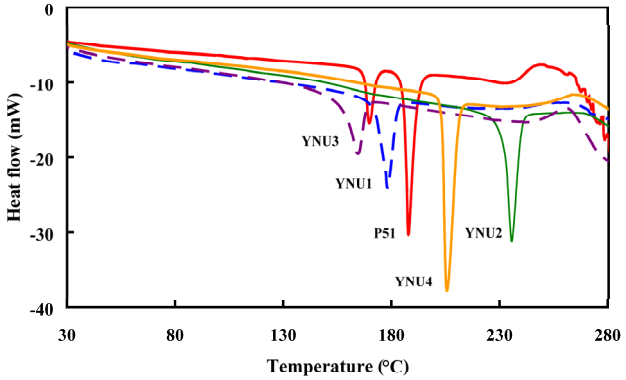


***Figure 4.*** *DSC curves of P-51 and YNU1-4*

**Table 1: Melting point and OH stretching band of P-51 and YNU1-4**

| | m. p. (°C) | OH band ($cm^{-1}$) |
|---|---|---|
| P-51 | 189 | 3080 |
| YNU1 | 178 | 3080 |
| YNU2 | 235 | 3120 |
| YNU3 | 166 | 3150 |
| YNU4 | 205 | 3100 |

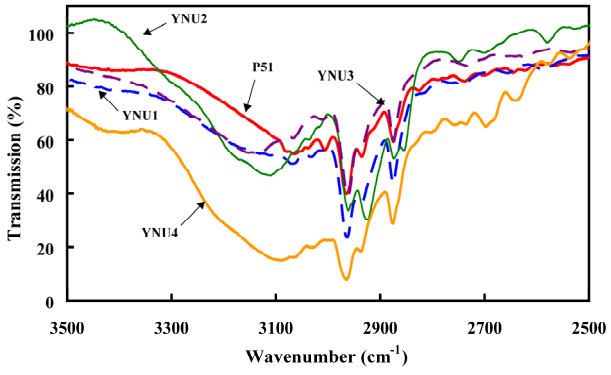


***Figure 5.*** *IR spectra of P-51 and YNU1-4*

### *Crystallographic parameters and molecular conformation of YNU1*

Table 2 details the crystallographic parameters of YNU1. YNU1 is found to crystallize in the space group of $P2_12_12_1$. There are six independent molecules in the asymmetric unit, and the $Z$ value is 4. Therefore, there are 24 molecules in the unit cell.

**Table 2: Crystallographic parameters of YNU1**

| | YNU1 |
|---|---|
| Formula | $C_{29}H_{41}N\,O_4S$ |
| Molecular Weight | 499.71 |
| $Z$ | 24 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| $a$ (Å) | 13.3610(5) |
| $b$ (Å) | 22.9336(10) |
| $c$ (Å) | 55.6900(2) |
| Density (g/cm$^3$) | 1.167 |

Fig. 6 shows the ORTEP plot of YNU1. The molecule has no center of symmetry (*i.e.* $C_1$). No significant difference is recognized in the S-O bond length. This indicates that the electrons are delocalized in the sulfonic group. As expected from the structure of P-51, there exists OH···O intermolecular hydrogen bond between anions. However, this time, the two anions are dimerized through OH···O intermolecular hydrogen bonds as shown in Fig. 7. Table 3 summarizes the intermolecular hydrogen bonds. The present intermolecular hydrogen bonds ensure the thermal stability, leading to a high melting point.

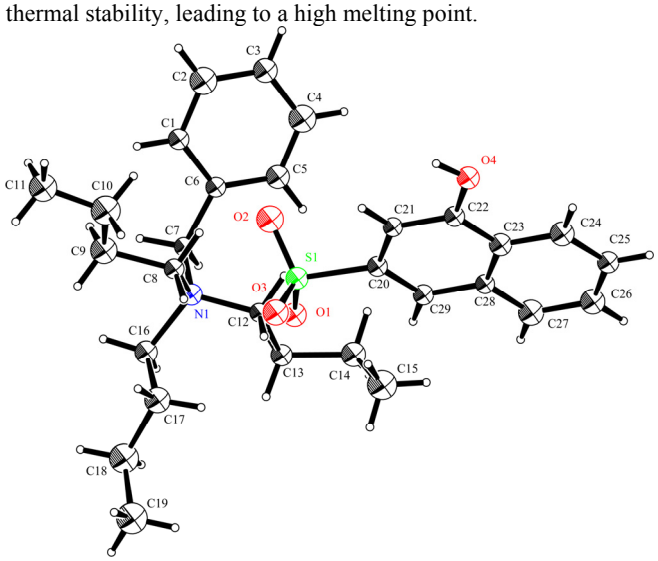


***Figure 6.*** *ORTEP plot of YNU1*

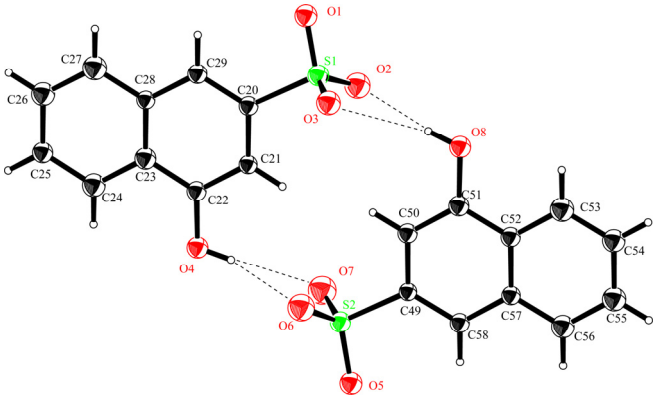


***Figure 7.*** *Hydrogen-bonded dimer of YNU1*

**Table 3: Distance (Å) and angle (°) of hydrogen bonds in dimer**

| D — H···A | D — H | H···A | D···A | D — H···A |
|---|---|---|---|---|
| O4 — H4···O6 | 0.82 | 2.11 | 2.88 | 156.4 |
| O4 — H4···O7 | 0.82 | 2.59 | 3.30 | 145.5 |
| O8 — H8···O2 | 0.82 | 2.05 | 2.85 | 164.8 |
| O8 — H8···O3 | 0.82 | 2.90 | 3.55 | 138.6 |

### *Tribo-electrification of toners which include P-51 or YNU1*

A tribo-electric charging experiment was carried out on toners composed of styrene-acryl resin (100 parts), carbon black (6 parts), wax (2 parts) and CCA (1 part) in accordance with the standard procedure specified by Imaging Society of Japan. YNU1 or P-51 was added externally to the toner/carrier system. Fig. 8 shows the charging characteristics as a function of time. YNU1 exhibits a similar performance to that of P-51. More accurate experiments are now in progress for all derivatives shown in Fig. 3.

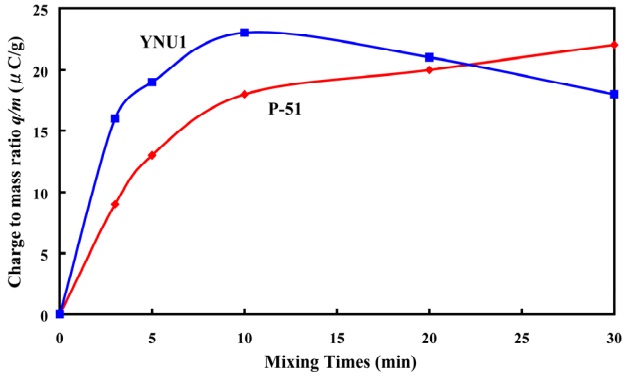


***Figure 8.*** *Tribo-electrification of toners which include P-51 or YNU1*

## Conclusions

The conclusions drawn from the present investigation can be summarized as follows.

1. The possibility of forming OH···O intermolecular hydrogen bonds has been studied for YNU1-4 by means of DSC and IR spectra. All derivatives show relatively high melting points which are nearly equivalent to that of P-51.
2. YNU1 is found to crystallize in the space group of $P2_12_12_1$. There are 24 molecules in the unit cell. Two anions are dimerized through OH···O intermolecular hydrogen bonds. The present dimerization contributes to the stabilization of the structure, raising the melting point.
3. The charging characteristic of YNU1 exhibits a similar performance to that of P-51.

## References


[1] J. Mizuguchi, A. Hitachi, Y. Sato and K. Uta, "A study on the charge-control mechanism of charge-control agents," J. Imag. Sci. Tech., (2008) in print.

[2] J. Mizuguchi, Y. Sato, K. Uta, and K. Sato, "Benzyltributylammonium 4-hydroxy-naphthalene-1-sulfonate," Acta Cryst. E63, o2509-o2510 (2007).

[3] G. M. Sheldrick, "A short history of SHELX," Acta Crystallogr. A64, 112-122 (2008).


## Author Biography


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