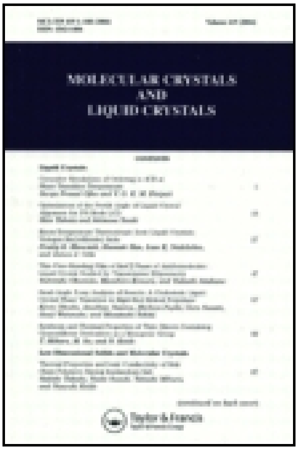

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# DIELECTRIC PROPERTY OF HYDROGEN-BONDED SQUARIC ACID DERIVERTIVES

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Abstract The crystal of squaric acid (SQ) shows dielectric property caused by tautomerization coupled with intermolecular proton transfer. We prepared a squaric acid derivative, 1,4-phenylenebis(squaric acid) (PBSQ), and determined its crystal structure. In the unit cell one PBSQ molecule and two water molecules are incorporated. There are one dimensional hydrogen-bonded chains PBSQ molecules. The distance between hydrogen-bonded O···O is very short (2.48Å). The result suggests that PBSA exists as mono deprotonated species accompanied by a counter cation of protonated $2H_2O$ molecules (O···O distance of 2.45Å).

## INTRODUCTION

Organic molecules sometimes show a prominent dielectric property even in the solid state. In crystals of succinonitrile or *d*-camphor, which are known as plastic crystals, reorientational motions of the polar molecules can occur, leading to a dielectric property[1].

In these years, we have been interested in developing novel organic dielectrics of which reversible dipole moment is derived from proton dynamics along the hydrogen bond. The tautomerization of *s*-cis form of 3-hydroxyenones, which is an enol form of 1,3-diketones, is a prototype for observing such a phenomenon, because the transverse component of the 3-hydroxyenones inverts coupled with proton transfer along with intramolecular hydrogen bond (Fig. 1a).

Recently we discovered that the crystal of 5-bromo-9-hydroxyphenalenone (Br-HPN) shows a characteristic dielectric response derived from proton dynamics in the solid state. The tautomerization of Br-HPN was concluded to occur through a tunnelling mechanism, because dielectric constant of Br-HPN showed little temperature dependence and the dielectric response was not quenched even at 4 K[2]. When the hydroxy proton of Br-HPN was deuterated, the deuterium-induced phase transitions were observed in the deuterated compound[3].

We are now interested in observing proton transfer along the intermolecular hydrogen bond coupled with π-bond switching of the s-trans form of 3-hydroxyenones as shown in Fig 1 (b). The crystal of squaric acid may be the sole example in which such an intermolecular proton transfer takes place coupled with tautomerization. Although a distinct dielectric response was observed at higher temperatures than 375 K, the dielectric response was quenched at lower temperatures[4]. Besides it is necessary to apply higher pressures than 3 GPa in order to suppress this antiferroelectric phase transition[5].

Thus it is of great significance to develop organic intermolecular hydrogen-bonded crystals which exhibit dielectric response derived from proton dynamics under ambient temperature and pressure. This paper reports the characteristic hydrogen-bonded crystal structures of phenyl squaric acid (PSQ)[6] and 1,4-phenylenebis (squaric acid) (PBSQ) which we prepared for the above purpose.

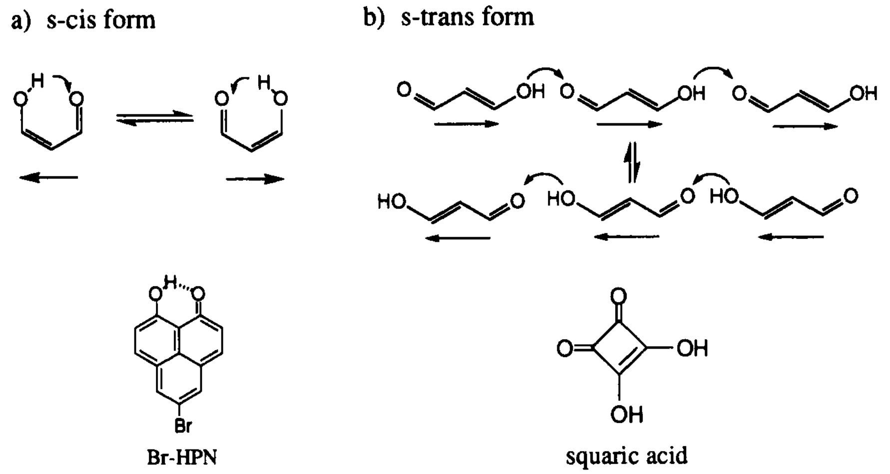

a) s-cis form
b) s-trans form
Br-HPN
squaric acid

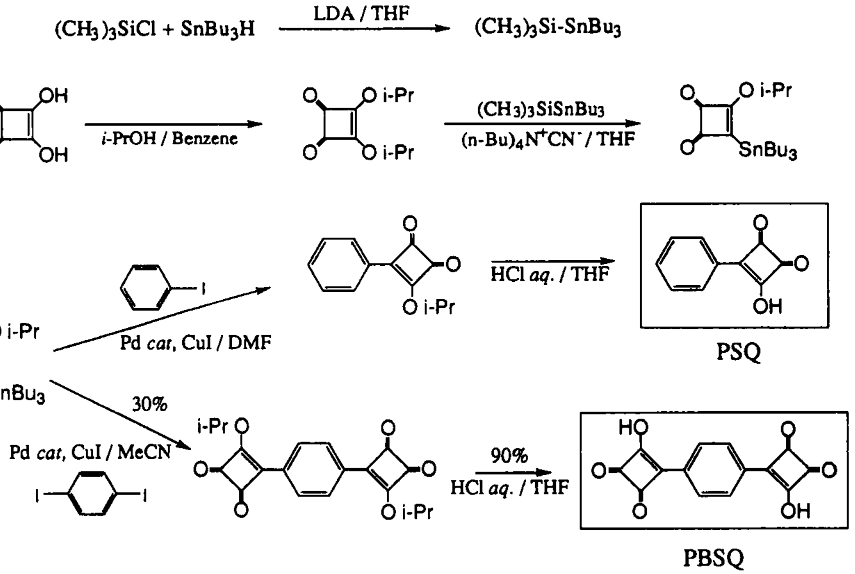
Fig. 1 Tautomerization of 3-hydroxyenones coupled with proton transfer along the hydrogen bond
a) Intramolecular proton transfer in s-cis form
b) Intermolecular proton transfer in s-trans form

## EXPERIMENTAL

Phenyl squaric acid (PSQ)[7] and 1,4-phenylene-bis (squaric acid) (PBSQ) were prepared according to the following reaction scheme (Scheme 1).

The crystal structure were determined by an X-ray diffraction method. The crystal was mounted on Rigaku AFC-5 four-circle diffractometer. PSQ : triclinic, $P\bar{1}$ , $a$ = 7.177(2), $b$ = 9.343(2), $c$ = 6.494(2) Å, $\alpha$ = 101.67(2), $\beta$ = 102.47(3), $\gamma$ = 105.71(2) °, V

= 393.2(2) Å$^3$, Z = 2. Final R = 0.0426 for 2793 reflections. PBSQ • $2H_2O$ : triclinic, P1, $a$ = 8.115(2), $b$ = 8.119(3), $c$ = 5.327(1) Å, $\alpha$ = 96.56(2), $\beta$ = 96.04(2), $\gamma$ = 112.91(2) °, V = 316.8(2) Å$^3$, Z = 1. Final R = 0.0428 for 1618 reflections. Both structure were solved by direct methods using the program SAPI-85[8] and Shelxs-86[9], refined by a block-diagonalized least-square method using UNICS-III system[10].



Scheme 1 Synthetic routes of PSQ and PBSQ

## RESULTS AND DISCUSSION

### Molecular Design

The crucial factors are as follows for constructing an intermolecular hydrogen bond along which a facile proton transfer can occur. First, construct a strong hydrogen bond which consists of a strongly acidic hydrogen-bond donor and a strongly basic hydrogen-bond acceptor. Second, construct a hydrogen bond which has energetically equivalent forms before and after the proton transfer. Combining these two factors, an appropriate proton potential of a symmetrical double well with a low barrier may be achieved. Then it may become possible to observe reversible proton transfer which occurs through a proton-tunnelling mechanism.

In order to construct one-dimensional strongly hydrogen-bonded crystal, phenyl squaric acid (PSQ), in which one of the hydroxy groups of squaric acid was replaced by phenyl, has become into consideration. Phenyl squaric acid (PSQ) is even more acidic (pKa = -0.22)[11] than squaric acid (pKa = 0.54)[12]. Besides, 1,4-phenylenebis(squaric acid) (PBSQ), in which two squaric acid moieties are connected with a benzene ring, has been prepared, because one of the squaric acid moieties exerts as a hydrogen-bond donor and the other exerts as a hydrogen-bond acceptor, especially when it exists as a mono-deprotonated species.

## Crystal Structure of Phenyl Squaric Acid (PSQ)

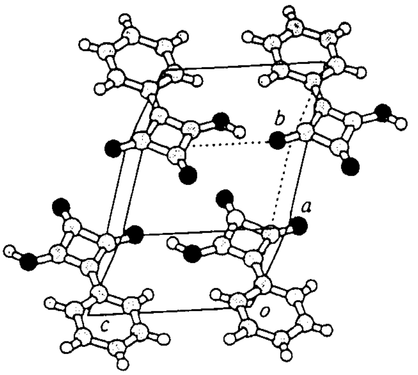


Fig. 2 Sheet structure of PSQ crystal

Although PSQ forms an intermolecular one-dimensional hydrogen bond between hydroxyl group and carbonyl group of the adjacent molecule with the O···O distance of 2.62Å. The configuration of the hydrogen bond in the 3-hydroxyenone moiety is an asymmetric *syn-anti* type.

Thus the shape of the double-well potential is also asymmetric in respect to proton transfer along the intermolecular hydrogen bond.

This configurational situation should lead to the localization of the proton along the hydrogen bond. In fact the proton is localized on the hydroxyl group and there is no sign for the proton dynamics in this crystal.

## Crystal Structure of 1,4-phenylenebis (squaric acid) PBSQ · $2H_2O$

The crystal of PBSQ • $2H_2O$ is characterized by a layered structure. In the unit cell, one PBSQ molecule and two water molecules are incorporated. Each water molecule forms a dimer with a water molecule located above or below respectively. The O···O distance within the dimer is only 2.45Å, which is fairly shorter than that in the case of crystal ice (O···O distance of 2.76Å), suggesting that the dimeric water molecules are bridged by a proton, existing as $H_5O_2^+$. The direction of the hydrogen bond is almost perpendicular to the layer. There are one-dimensional strong hydrogen-bonded chains which consist of PBSQ molecules on the plane. The distance between the hydrogen-bonded O···O is also very short (2.48Å) even compared with that of SQ (2.55Å)[13]. Thus a PBSQ molecule is considered to exist as a mono-deprotonated species as a result of donation of a proton to the dimeric water molecules, forming a strong intermolecular hydrogen bond with hydroxy group of the adjacent molecule (Fig. 4).

Net atomic charges was calculated by a PM3 method. The negative charge was found to be localized up to 80% on one of the SQ moieties of which hydroxy group is deprotonated. Although around 20% of the negative charge is delocalized to the other SQ moiety, the proton donating ability of the hydroxy group of this moiety is not lessened significantly. This is the reason why the aforementioned hydrogen bond is so strong.

It is certain that the hydrogen bond configuration of PBSQ does not change before and after proton transfer. Moreover, the arrangement of atoms around the O···O is almost symmetric. Consequently, the hydrogen bond potential in this crystal is symmetrical and a barrier to proton transfer should be low. The crystal structure of PBSQ • $2H_2O$ is, therefore, almost ideal for observing the reversible intermolecular proton transfer.

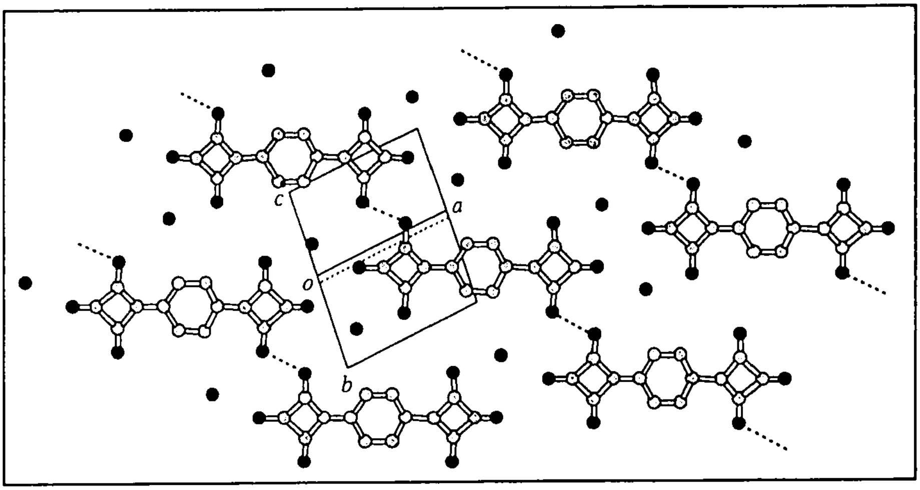


Fig. 3 Sheet structure of PBSQ · $2H_2O$ crystal (Black balls represent oxygen atoms)

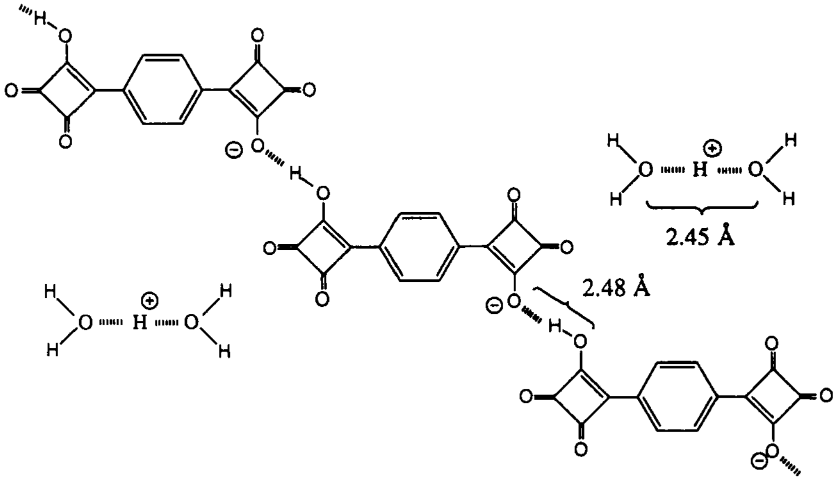


Fig. 4 Scheme of one-dimensional hydrogen-bonded chain of PBSQ · $2H_2O$ (The protonated water molecules are located perpendicular to the plane the hydrogen-bonded chain)

## CONCLUSION

Judged from the crystal structure of PBSQ • $2H_2O$, the hydrogen bonding scheme is considered to be most appropriate for observing reversible intermolecular proton transfer coupled with tautomerization. The detail of the dielectric measurement of PBSQ • $2H_2O$ and the deuterated compound will be published elsewhere.

## ACKNOWLEDGMENT

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## REFERENCES

1 D. E. William and C. P. Smith, J. Amer. Chem. Soc., 84, 1808, (1962)
2 T. Mochida, A. Izuoka, T. Sugawara, Y. Moritomo, and Y. Tokura, J. Chem. Phys., 101, 7971 (1994)
3 Y. Moritomo, Y. Tokura, T. Mochida, A. Izuoka, and T. Sugawara, J. Phys. Soc. Jpn., 64, 1892 (1995)
4 D. Semmingsen and J. Feder, Solid State Commun. 15, 1369 (1974)
5 Y. Moritomo, Y. Tokura, H. Takahashi, and N. Mori, Phys. Rev. Lett., 67, 2041 (1991)
6 E. J. Smutny, M.C. Casario and J. D. Roberts, J. Amer. Chem. Soc. 83, 1793 (1959)
7 L. S. Kiebeskind and R. W. Fengl, J. Org. Chem., 55, 5359 (1990)
8 H. F. Fan, J. X. Yao, and J. Z. Qian, Acta Cryst., A44, 688 (1986)
9 "SHELXS86, Program for the solution of Crystal structures", Univ. of Gottingen, Fedral Republic of Germany (1986)
10 T. Sakurai and K. Kobayashi, Rep. Inst. Phys. Chem. Res., 55, 69 (1979 )
11 E. Patton and R. West, J. Amer. Chem Soc., 95, 8703 (1973)
12 R. West, Oxocarbons (Academic press, New York, 1980)
13 D. Semmingan, Acta Chem. Scand., 27, 3961 (1973)