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The Crystal Structures of 2-Aminoperimidine

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The structures of both 2-perimidinylammonium ethyl sulfate (PDAEtSO$_4$) and 2-perimidinylammonium bromide (PDABr) were determined by single-crystal X-ray diffractometry. PDAEtSO$_4$ crystallized in the monoclinic system, space group $P2_1/c$, with a=7.229(2), b=8.329(1), c=22.404(1) Å, β=91.94(1)°, V=1348.1(3) Å^3, Z=4. PDABr crystallized in the orthorhombic system, space group $Pbca$ with a=15.441(1), b=23.877(1), c=7.468(1) Å, V=2754.9(4) Å^3, Z=8. The dimer of PDA was observed in both of the crystals. Also, four hydrogen bonds between the PDA ions and the ethyl sulfate ions for PDAEtSO$_4$ were observed. The ions pack in the crystal held together by the dimer of PDA and strong hydrogen bonds between the oxygen atoms of the ethyl sulfate ion and the hydrogen atoms of the amino groups of the PDA ions. The results are discussed along with giving a reason why PDA is an excellent precipitant for the sulfate ion.

The 2-perimidinylammonium ion (PDA) is an excellent precipitant for the sulfate ion. This reagent has been applied to the nephelometric determination of 0.1—5 ppm of the sulfate ion,$^{1)}$ to the spectrophotometric determination of 2—500 ppm of the sulfate ion,$^{2,3)}$ and to the indirect spectrophotometric determination of 4—120 ppm of the sulfate ion.$^{4-6)}$ The selectivity and sensitivity of PDA to the sulfate ion are excellent, although phosphate and fluoride ions slightly interfere. The reason that PDA specifically forms precipitation with the sulfate ion is not yet obvious.

There are two important factors concerning the formation of the precipitation of a cation with an anion in an aqueous solution. One is the hydration energies of ions in solution; the other is the lattice energy in the crystal. In the case of the hydration energy, the difference between the hydration energies of anions causes the formation of precipitation for PDA with an anion, because the PDA of the precipitant is a cation. The hydration energy of the sulfate ion is generally larger than that of such anions as halide ions.$^{7)}$ However, although the formation of precipitation for PDA with the sulfate ion occurrs, that for PDA with halide ions does not.$^{1)}$ It is therefore considered that the ability to form precipitation for PDA with sulfate ion causes the lattice energy in the crystal. If the crystal structure of 2-perimidinylammonium sulfate were determined, it would be obvious. Since the crystal structure of PDA has not been reported, a determination of the structure has been requested. The crystal of PDA with the sulfate ion is too small to be measured using a single-crystal X-ray diffractometry. Although we have examined the precipitation of PDA with some sulfonates, such as Methyl orange, Sulfonazo III and Dinitrosulfonazo III, instead of the sulfate ion, the proper single crystals were not available. Therefore, the formation of a single crystal of PDA with anions possessing the sulfonate or sulfate group has been investigated. The single crystal X-ray structures of PDA with ethyl sulfate ion and with bromide ion were determined together.

Experimental

2-Perimidinylammonium bromide (PDABr) was synthesized according to a method described in the literature.$^{8)}$ A single crystal of PDABr·EtOH was made from the saturated PDABr ethanol (EtOH) solution at room temperature. Though an aqueous solution of PDABr was directly mixed with aqueous solutions of sulfonates or sulfates, single crystals of PDA with sulfonates or sulfates for the determination of the single-crystal X-ray structure were not available.

Diethyl sulfate is a liquid which is insoluble to water. The specific gravity of diethyl sulfate is larger than that of water. When an aqueous acid solution was added to diethyl sulfate, the solution was separated into the aqueous phase with the diethyl sulfate phase. The diethyl sulfate was hydrolyzed at the interface, generating the sulfate ion and a couple of ethanol molecules. The crystal of PDA with the sulfate ion grew up the interface between the aqueous acid solution of PDA and diethyl sulfate. However, the hydrolysis rate of diethyl sulfate in an aqueous acid solution was too fast to obtain a large single crystal of PDA with the sulfate ion for a determination of the single-crystal X-ray structure. We then used an aqueous PDA solution of pH 7 without acid. The hydrolysis of diethyl sulfate with the aqueous solution of pH 7 slowly generated an ethyl sulfate ion, not the sulfate ion, and an ethanol molecule at the interface. The crystal of 2-perimidinylammonium ethyl sulfate (PDAEtSO$_4$) obtained from standing the aqueous PDABr solution of pH 7 with diethyl sulfate at room temperature for one week was of sufficient size to be measured by single-crystal X-ray

Table 1. Crystal Data for PDAEtSO$_4$ and PDABr·EtOH

	PDAEtSO$_4$	PDABr·EtOH
Formula	$C_{13}H_{15}N_3O_4S$	$C_{13}H_{16}N_3OBr$
Formula weight	309.34	310.19
Crystal color	Colorless	Colorless
Crystal size/mm^3	$0.20\times0.20\times0.30$	$0.20\times0.20\times0.30$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a/Å	7.229(2)	15.451(1)
b/Å	8.329(1)	23.877(1)
c/Å	22.404(1)	7.468(1)
β/deg	91.94(1)	—
V/Å^3	1348.1(3)	2754.9(4)
Z	4	8
D_{calcd}/g cm^{-3}	1.524	1.466
μ(Cu $K\alpha$)/cm^{-1}	23.40	40.10
Radiation	Cu $K\alpha$ (λ=1.54178 Å)	Cu $K\alpha$ (λ=1.54178 Å)
Temperature/K	293	293
Scan type	ω–2θ	ω–2θ
Scan rate/deg min^{-1}	16	16
Scan width/deg	$1.57+0.30\tan\theta$	$1.68+0.30\tan\theta$
$2\theta_{\text{max}}$/deg	120.1	120.2
Measured reflections	2372	2395
Observed reflections ($I>3\sigma(I)$)	1686	1701
$R^{\text{a)}}$	0.078	0.038
$R_w{}^{\text{b)}}$	0.082	0.044

a) $R=||F_o|-|F_c||/|\Sigma F_o|$. b) $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/[\Sigma(|F_o|)+g(|F_o|^2)]$.

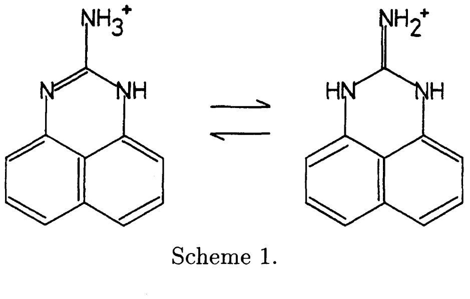
diffractometry.

The single crystals were enclosed within a glass capillary tube, and the X-ray reflections were collected using a Rigaku AFC7R diffractometer. The single-crystal structure solution was carried out using the program SHELXS86. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were isotropically refined. Two hydrogen atoms of the ethanol molecule were not found. The coordinates of these two hydrogen atoms were determined by a calculation. Table 1 summarizes the crystallographic data.

Results and Discussion

The atomic coordinates and thermal parameters for PDAEtSO$_4$ and PDABr·EtOH are presented in Tables 2 and 3, respectively. The bond lengths and angles for PDAEtSO$_4$ and PDABr·EtOH are presented in Tables 4 and 5, respectively. Figures 1 and 2 show the labeling diagrams for PDAEtSO$_4$ and PDABr·EtOH, respectively. The types of $-NH_3^+$ and $=NH_2^+$ were found for PDAEtSO$_4$ and PDABr·EtOH, respectively.

The bond lengths of N(1)–C(1) (1.411 Å and 1.409 Å) are the same as those of N(2)–C(8) (1.416 Å and 1.409 Å) within 0.07 Å in PDAEtSO$_4$ and PDABr·EtOH, respectively. These values are shorter than the typical single-bond length (1.47 Å) and longer than the typical partial double-bond length (1.35 Å), such as that of pyridine.[9] On the other hand, the bond lengths of N(1)–C(11) (1.329 Å and 1.330 Å), N(2)–C(11) (1.337 Å and 1.327 Å) and N(3)–C(11) (1.314 Å and 1.328 Å) are close to the distance of the typical partial double bond in PDAEtSO$_4$ and PDABr·EtOH, respectively. Consequently, when the bond lengths and angles between non-hydrogen atoms of PDA in the PDAEtSO$_4$ crystal are compared with those in the PDABr·EtOH crystal, there are no differences. The structure for the non-hydrogen atoms of PDA in PDAEtSO$_4$ is the same as that of PDA in PDABr·EtOH. As the results show concerning the resonance of the perimidine ring, it is recognized that PDA has tautomers, such as shown in Scheme 1. It is considered that the $=NH_2^+$ tautomer would be more preferential than the $-NH_3^+$ one, because the geometry of the $=NH_2^+$ tautomer is more symmetrical than that of the $-NH_3^+$ one. If only the $=NH_2^+$ tautomer existed, the lengths of N(1)–C(11) and N(2)–C(11) would have to be close to the length of the typical single bond. Also, if only the $-NH_3^+$ tautomer existed, the length



Scheme 1.

Table 2. Atomic Coordinates and Temperature Factors ($B^{a)}$) for PDAEtSO$_4$

Atom	x	y	z	B
S(1)	0.3830(3)	0.9779(2)	0.18062(8)	3.26(4)
O(1)	0.2446(8)	1.0292(6)	0.2312(2)	4.9(1)
O(2)	0.4848(7)	0.8485(6)	0.2097(2)	4.3(1)
O(3)	0.2675(8)	0.9292(6)	0.1298(2)	4.7(1)
O(4)	0.4952(7)	1.1175(6)	0.1688(2)	4.5(1)
N(1)	0.6979(8)	1.1230(7)	0.4170(2)	2.9(1)
N(2)	0.6254(9)	0.8516(8)	0.4128(3)	2.9(2)
N(3)	0.576(1)	1.011(1)	0.3310(3)	3.7(2)
C(1)	0.7577(9)	1.1102(8)	0.4774(3)	2.6(2)
C(2)	0.822(1)	1.2405(10)	0.5080(3)	3.3(2)
C(3)	0.877(1)	1.223(1)	0.5681(4)	3.9(2)
C(4)	0.864(1)	1.080(1)	0.5971(3)	3.9(2)
C(5)	0.784(1)	0.7867(10)	0.5525(4)	4.0(2)
C(6)	0.722(1)	0.662(1)	0.5594(4)	4.0(2)
C(7)	0.667(1)	0.6786(9)	0.4986(3)	3.4(2)
C(8)	0.6801(9)	0.8245(9)	0.4732(3)	2.8(2)
C(9)	0.7438(9)	0.9605(8)	0.5053(3)	2.7(2)
C(10)	0.7990(10)	0.9411(9)	0.5661(3)	3.1(2)
C(11)	0.6344(9)	0.9959(9)	0.3869(3)	2.8(2)
C(12)	0.124(1)	1.165(1)	0.2185(5)	4.8(2)
C(13)	−0.062(2)	1.126(2)	0.2358(7)	7.0(4)
H(1)	0.820(8)	1.326(7)	0.489(2)	1(1)
H(2)	0.919(9)	1.304(8)	0.586(3)	3(1)
H(3)	0.937(10)	1.077(9)	0.638(3)	5(1)
H(4)	0.852(9)	0.763(8)	0.634(3)	3(1)
H(5)	0.700(9)	0.568(8)	0.570(3)	2(1)
H(6)	0.619(9)	0.590(8)	0.478(3)	3(1)
H(7)	0.558(9)	0.793(9)	0.401(3)	2(2)
H(8)	0.53(1)	0.94(1)	0.311(4)	3(2)
H(9)	0.47(2)	1.03(2)	0.307(7)	16(6)
H(10)	0.57(1)	1.097(10)	0.317(3)	2(2)
H(11)	0.19(1)	1.24(1)	0.251(5)	9(3)
H(12)	0.08(3)	1.13(2)	0.164(8)	29(7)
H(13)	−0.06(1)	1.08(1)	0.267(4)	6(3)
H(14)	−0.14(1)	1.04(1)	0.204(5)	10(3)
H(15)	−0.16(1)	1.20(1)	0.217(4)	7(2)

a) Non-hydrogen atoms are anisotropic and hydrogen atoms are isotropic.

of N(3)–C(11) would have to be close to the length of the typical single bond. The observed bond lengths are the distance of the typical partial double bond. Therefore, it cannot be characterized whether PDA is the =NH$_2{}^+$ or –NH$_3{}^+$ tautomer in the crystals. This means that a proton could easily transfer from –NH of =NH$_2{}^+$ to –NH$_3{}^+$ without having any influence on the perimidine ring. It is considered that the difference between the proton position of PDA in PDAEtSO$_4$ and that in PDABr·EtOH, i.e., –NH$_3{}^+$ and =NH$_2{}^+$ types, might cause the counterions. The –NH$_3{}^+$ and =NH$_2{}^+$ types in both of the crystals are discussed below.

The packing diagrams for PDAEtSO$_4$ and PDABr·EtOH including generated hydrogen-bonding interactions of distance within 2.4 Å between hydrogen and oxygen atoms are shown in Figs. 3 and 4, respectively. Each of the perimidine rings is a plane. The mean deviation of non-hydrogen atom coordinates from the plane is 0.0105 Å. The perimidine rings form layers and the amino group of each PDA is placed on the opposite direction from each other. The adjacent distances between the parallel planes of the perimidine ring are 3.407(11) Å and 3.413(7) Å in PDAEtSO$_4$ and PDABr·EtOH, respectively. The adjacent distance between the parallel planes of the pyrene ring in the crystal according to a π–π interaction was 3.53 Å.[10] Therefore, there is a considerable π–π interaction between the perimidine rings. It is considered that the strength of the π–π interaction in the PDAEtSO$_4$ crystal would be the same as that in the PDABr·EtOH crystal. Both of the crystals comprise units of the parallel PDA dimer, causing the π–π interaction shown in Fig. 5. The dimer is more effective for forming a hydrogen-bonding network, as described later. The parameters of the hydrogen bonds are given in Table 6. Considering the distance of the hydrogen bond within 2.4 Å, the hydrogen bonds of the even large B values for the hydrogen atoms (i.e., H(9) for

Table 3. Atomic Coordinates and Temperature Factors ($B^{a)}$) for PDABr·EtOH

Atom	x	y	z	B
Br(1)	0.40457(4)	0.43238(2)	0.11178(8)	4.89(1)
O(1)	0.2986(4)	0.0734(3)	0.2460(8)	7.4(1)
N(1)	0.6789(3)	0.3453(2)	−0.1750(6)	3.9(1)
N(2)	0.5429(3)	0.3424(2)	−0.0480(6)	3.8(1)
N(3)	0.6060(4)	0.4270(2)	−0.1037(8)	5.9(1)
C(1)	0.6853(3)	0.2864(2)	−0.1810(6)	3.2(1)
C(2)	0.7571(3)	0.2602(2)	−0.2455(7)	4.0(1)
C(3)	0.7596(4)	0.2014(2)	−0.2447(7)	4.5(1)
C(4)	0.6923(4)	0.1706(2)	−0.1838(7)	4.4(1)
C(5)	0.5426(4)	0.1676(2)	−0.0533(7)	4.3(1)
C(6)	0.4735(4)	0.1961(2)	0.0088(8)	4.7(1)
C(7)	0.4710(3)	0.2546(2)	0.0150(7)	3.9(1)
C(8)	0.5405(3)	0.2835(2)	−0.0474(6)	3.1(1)
C(9)	0.6145(3)	0.2559(2)	−0.1146(6)	2.98(10)
C(10)	0.6163(3)	0.1966(2)	−0.1173(6)	3.5(1)
C(11)	0.6099(3)	0.3715(2)	−0.1097(7)	4.0(1)
C(12)	0.3547(9)	0.0544(4)	0.111(1)	9.0(3)
C(13)	0.362(1)	−0.0068(4)	0.102(2)	9.3(3)
H(1)	0.802(3)	0.282(2)	−0.307(6)	4(1)
H(2)	0.816(3)	0.182(2)	−0.305(6)	6(1)
H(3)	0.696(3)	0.129(2)	−0.180(7)	5(1)
H(4)	0.545(4)	0.124(2)	−0.061(7)	7(1)
H(5)	0.422(3)	0.176(2)	0.047(6)	3(1)
H(6)	0.422(3)	0.274(2)	0.055(6)	4(1)
H(7)	0.717(4)	0.365(2)	−0.203(8)	5(1)
H(8)	0.503(3)	0.360(2)	0.001(7)	5(1)
H(9)	0.644(3)	0.441(2)	−0.148(7)	2(1)
H(10)	0.550(6)	0.454(3)	−0.05(1)	24(3)
H(11)	0.266(9)	0.057(4)	0.31(2)	32(5)
H(12)	0.332(6)	0.064(3)	0.01(1)	15(3)
H(13)	0.391(5)	−0.023(4)	−0.01(1)	12(3)
H(14)	0.300(5)	−0.015(3)	0.11(1)	23(3)
H(15)[b]	0.424(5)	0.058(3)	0.12(1)	31(3)
H(16)[b]	0.396(5)	−0.018(3)	0.22(1)	14(3)

a) Non-hydrogen atoms are anisotropic and hydrogen atoms are isotropic. b) Calculated values.

Table 4. Bond Lengths and Bond Angles for $PDAEtSO_4$

Distances (Å)			
N(1)–C(1)	1.411(8)	N(1)–C(11)	1.329(8)
N(2)–C(8)	1.416(9)	N(2)–C(11)	1.337(9)
N(3)–C(11)	1.314(9)	C(1)–C(2)	1.358(10)
C(1)–C(9)	1.400(9)	C(2)–C(3)	1.40(1)
C(3)–C(4)	1.36(1)	C(4)–C(10)	1.42(1)
C(5)–C(6)	1.35(1)	C(5)–C(10)	1.422(10)
C(6)–C(7)	1.41(1)	C(7)–C(8)	1.347(10)
C(8)–C(9)	1.410(9)	C(9)–C(10)	1.415(9)
S(1)–O(1)	1.596(5)	S(1)–O(2)	1.448(5)
S(1)–O(3)	1.448(5)	S(1)–O(4)	1.446(5)
C(12)–C(13)	1.45(1)	C(12)–O(1)	1.447(9)
Angles (°)			
C(1)–N(1)–C(11)	121.1(6)	N(2)–C(8)–C(9)	115.8(6)
C(8)–N(2)–C(11)	122.9(7)	C(7)–C(8)–C(9)	122.5(7)
N(1)–C(1)–C(2)	120.9(7)	C(1)–C(9)–C(8)	121.0(6)
N(1)–C(1)–C(9)	118.1(6)	C(1)–C(9)–C(10)	120.6(6)
C(2)–C(1)–C(9)	121.0(7)	C(8)–C(9)–C(10)	118.3(6)
C(1)–C(2)–C(3)	118.9(8)	C(4)–C(10)–C(5)	124.1(7)
C(2)–C(3)–C(4)	122.0(8)	C(4)–C(10)–C(9)	117.1(7)
C(3)–C(4)–C(10)	120.4(7)	C(9)–C(10)–C(5)	118.8(7)
C(6)–C(5)–C(10)	119.8(8)	N(1)–C(11)–N(2)	121.1(6)
C(5)–C(6)–C(7)	122.3(8)	N(1)–C(11)–N(3)	120.1(7)
C(6)–C(7)–C(8)	118.3(8)	N(2)–C(11)–N(3)	118.8(7)
N(2)–C(8)–C(7)	121.8(7)		
O(1)–S(1)–O(2)	101.6(3)	O(2)–S(1)–O(4)	113.7(3)
O(1)–S(1)–O(3)	106.0(3)	O(2)–S(1)–C(12)	131.3(3)
O(1)–S(1)–O(4)	106.5(3)	O(3)–S(1)–O(4)	113.2(3)
O(2)–S(1)–O(3)	114.6(3)	S(1)–O(1)–C(12)	117.1(5)

Table 5. Bond Lenghts and Bond Angles for PDABr•EtOH

Distances (Å)			
N(1)–C(1)	1.409(6)	N(1)–C(11)	1.330(6)
N(2)–C(8)	1.409(6)	N(2)–C(11)	1.327(6)
N(3)–C(11)	1.328(7)	C(1)–C(2)	1.363(6)
C(1)–C(9)	1.406(6)	C(2)–C(3)	1.405(7)
C(3)–C(4)	1.352(7)	C(4)–C(10)	1.418(7)
C(5)–C(6)	1.349(7)	C(5)–C(10)	1.415(7)
C(6)–C(7)	1.398(7)	C(7)–C(8)	1.359(6)
C(8)–C(9)	1.412(6)	C(9)–C(10)	1.416(6)
C(12)–C(13)	1.47(1)	O(1)–C(12)	1.41(1)
Angles (°)			
C(1)–N(1)–C(11)	122.5(5)	N(2)–C(8)–C(9)	116.3(4)
C(8)–N(2)–C(11)	123.0(5)	C(7)–C(8)–C(9)	121.7(4)
N(1)–C(1)–C(2)	121.8(5)	C(1)–C(9)–C(8)	120.9(4)
N(1)–C(1)–C(9)	116.9(4)	C(1)–C(9)–C(10)	119.9(4)
C(2)–C(1)–C(9)	121.3(4)	C(8)–C(9)–C(10)	119.2(4)
C(1)–C(2)–C(3)	118.7(5)	C(4)–C(10)–C(5)	124.8(5)
C(2)–C(3)–C(4)	121.6(5)	C(4)–C(10)–C(9)	117.3(5)
C(3)–C(4)–C(10)	121.2(5)	C(5)–C(10)–C(9)	117.9(5)
C(6)–C(5)–C(10)	120.4(5)	N(1)–C(11)–N(2)	120.4(5)
C(5)–C(6)–C(7)	122.5(5)	N(1)–C(11)–N(3)	121.2(5)
C(6)–C(7)–C(8)	118.2(5)	N(2)–C(11)–N(3)	118.4(5)
N(2)–C(8)–C(7)	121.9(5)	O(1)–C(12)–C(13)	113.6(10)

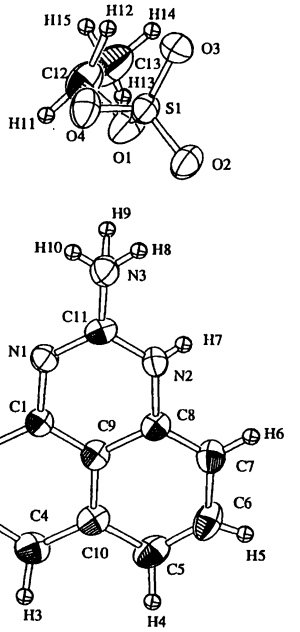


Fig. 1. ORTEP drawing of $PDAEtSO_4$ with the labeling system used.

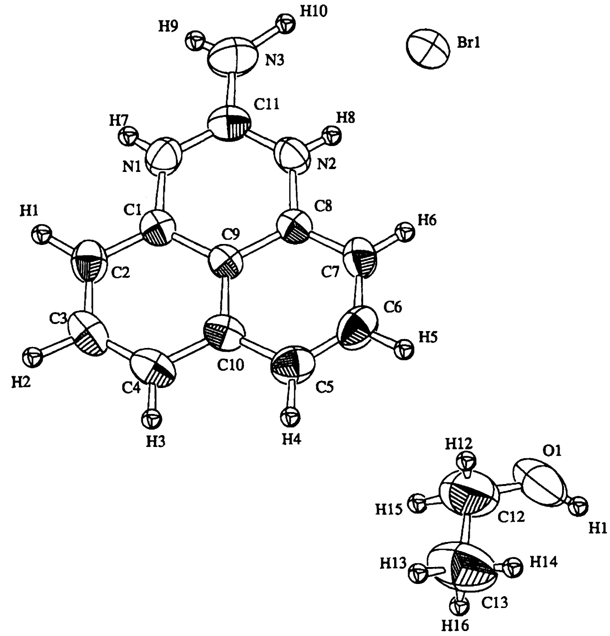


Fig. 2. ORTEP drawing of PDABr•EtOH with the labeling system used.

$PDAEtSO_4$ and H(10) for PDABr•EtOH) are reasonable. There are great differences between $PDAEtSO_4$ and PDABr•EtOH with respect of the hydrogen-bonding interaction.

First, in the case of $PDAEtSO_4$, three oxygen atoms of one ethyl sulfate ion form four strong hydrogen bonds with NH protons of three PDA ions in addition to the electrostatic interaction. The ethyl sulfate ion could hydrogen-bond with a plural PDA dimer because of hydrogen-bonding sites of the PDA dimer placed on the oppo-

Table 6. Hydrogen-bond Lengths (Å) for PDAEtSO$_4$ and PDABr•EtOH

A	H	B	A–H	H···B	A···B	Transformation
				PDAEtSO$_4$		
N(3)	H(8)	O(2)	0.84(10)	2.40(9)	3.087(9)	x, y, z
N(3)	H(9)	O(1)	1.0(2)	2.3(2)	3.223(9)	x, y, z
N(2)	H(7)	O(4)	0.73(7)	2.17(7)	2.792(8)	$1-x$, $1/2+y$, $1/2-z$
N(3)	H(10)	O(2)	0.78(8)	2.21(8)	2.98(1)	$1-x$, $-1/2+y$, $1/2-z$
				PDABr•EtOH		
N(1)	H(7)	O(1)	0.78(5)	1.97(5)	2.733(6)	$-1/2+x$, $1/2-y$, $-z$

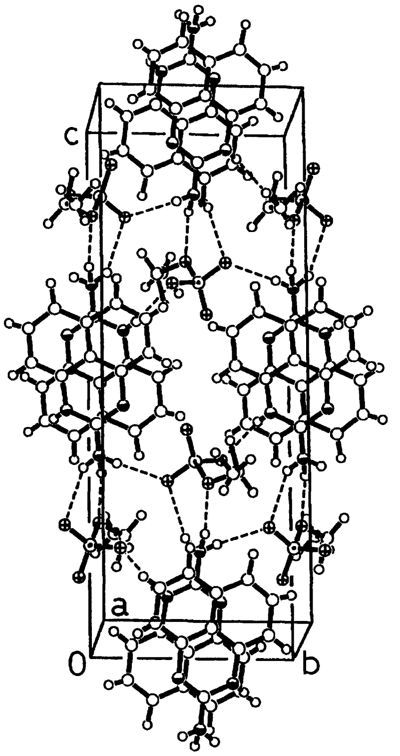


Fig. 3. View of the packing of the ethyl sulfate ion and PDA in PDAEtSO$_4$ including generated hydrogen-bonded interactions; ○, carbon atom; ◒, nitrogen atom; ⊕, oxygen atom; ⊙, sulfur atom; small open circle, hydrogen atom.

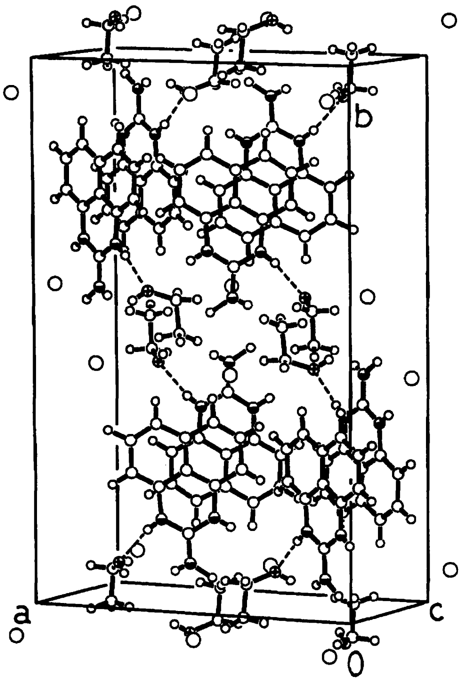


Fig. 4. View of the packing of the bromide ion and PDA in PDABr•EtOH including generated hydrogen-bonded interactions: ○, carbon atom; ◒, nitrogen atom; ⊕, oxygen atom; small open circle, hydrogen atom; large open circle, bromide atom.

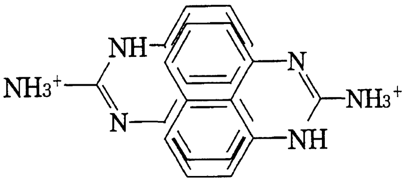


Fig. 5. Dimer of PDA in the crystals of PDAEtSO$_4$ and PDABr•EtOH.

site direction. There is no hydrogen-bonding interaction between the PDA and the O(3) atom for PDAEtSO$_4$, since the nearest distance of the O(3) atom with NH protons is 3.21(8) Å of N(3)–H(10)···O(3) transformed by ($1-x$, $-1/2+y$, $1/2-z$). Consequently, the hydrogen-bonding network of PDA ions in Fig. 3 is formed by the ethyl sulfate ion.

If the PDA is of the $=NH_2^+$ type, the O(3) atom would have a hydrogen-bonding interaction because the non-bonded contact distance between N(1) and O(3) transformed by ($1-x$, $-1/2+y$, $1/2-z$) is 2.771(8) Å. The number of hydrogen bonds for the $=NH_2^+$ type is the same as that for the $-NH_3^+$ one. The $-NH_3^+$ type is predominant over the $=NH_2^+$ one in PDAEtSO$_4$. This suggests that the hydrogen-bonding network due to the formation of four strong hydrogen bonds for $-NH_3^+$ protons and a single imino proton is preferred to that due to the formation of four strong hydrogen bonds for $=NH_2^+$ and two imino protons in PDAEtSO$_4$. Therefore, anions forming strong hydrogen bonds have a tendency to give the $-NH_3^+$ type.

On the other hand, PDABr•EtOH is greatly different from PDAEtSO$_4$ in respect of the interactions between PDA and anions. Generally, it is considered that the bromide ion only interacts with PDA electrostatically because of the low surface-charge density of the bromide ion. However, since the distance between an imino proton of H(8) for PDA and the bromide ion is 2.45(5) Å for PDABr·EtOH, it would be a sufficient distance for a hydrogen-bonding interaction to exist. The distance of 2.60(10) Å between H(10) for PDA and the bromide ion, in spite of the large B value of H(10), suggests a weak hydrogen-bonding interaction. The hydrogen-bonding interactions of N(3)–H(10)···Br(1) and N(3)–H(9)···Br(1) transformed by $(1-x, 1-y, -z)$ are weaker than that of N(2)–H(8)···Br(1), because the distances of H(10)···Br(1) and H(9)···Br(1) are 2.85(9) Å and 3.14(5) Å, respectively. The H(7) atom of another imino group of PDA forms a hydrogen bond with the oxygen atom of an ethanol of solvent molecule. It is considered that the one bromide ion weakly hydrogen-bonds with a single PDA, and not with a plural PDA.

The hydrogen-bonding interactions on the $=NH_2^+$ type are slightly different from that on the $-NH_3^+$ one for PDABr·EtOH, because the hydrogen-bonding interactions for the bromide ion with the proton attached the N(3) atom in the PDABr·EtOH crystal are as weak as N(3)–H(10)···Br(1) and N(3)–H(9)···Br(1), mentioned above. Therefore, PDA prefers the symmetrical $=NH_2^+$ to the $-NH_3^+$ type in respect of the proton position. The hydrogen-bonding network is never observed in the crystal of PDABr·EtOH.

In the case of the sulfate ion, it is considered that it would form more than four complex hydrogen bonds with a plural PDA dimer like the hydrogen bonds in the $PDAEtSO_4$ crystal. This is because there is no steric hindrance of the ethyl group for the sulfate ion, compared with the ethyl sulfate ion. Therefore, the sulfate ion, which has some hydrogen-bonding acceptor sites like those of the ethyl sulfate ion, forms an ion pair with PDA, making a cluster structure. This cluster structure causes a fine precipitation of PDA to form with the sulfate ion, because the formation rate of the cluster is relatively fast. Also, the hydrogen-bonding interactions of the $=NH_2^+$ type are essentially little different from that of the $-NH_3^+$ one in relation to the formation of the hydrogen-bonding network, although the $-NH_3^+$ type might be predominant over the $=NH_2^+$ one because of the strong hydrogen bonds of the sulfate ion. Accordingly, PDA is an effective precipitant for the sulfate ion.

Conclusions

The PDA ions form a layer crystal having amino groups placed on the opposite direction to each other. The amino groups would form some hydrogen bonds with the four oxygens of the sulfate ion. It is considered that the hydrogen bonds would take the π–π interaction of the perimidine rings easily. The property that PDA forms the dimer with the amino group on the opposite direction is most effective for the formation of a hydrogen-bonding network. Unless the dimer of PDA existed, the hydrogen-bonding network could not be formed. The reason that PDA is an excellent precipitant of the sulfate ion is referred to the complex hydrogen bonds in addition to the π–π interaction of each perimidine ring of PDA, namely, the PDA dimer. Consequently, PDA can be used as an excellent nephelometric reagent for the sulfate ion.

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References

1) W. I. Stephen, *Anal. Chim. Acta*, **50**, 413 (1970).

2) P. K. Dasgupta, L. G. Hanley, Jr., and P. W. West, *Anal. Chem.*, **50**, 1793 (1978).

3) K. Tôei, H. Miyata, and Y. Yamawaki, *Anal. Chim. Acta*, **94**, 485 (1977).

4) P. A. Jones and W. I. Stephen, *Anal. Chim. Acta*, **64**, 85 (1973).

5) K. Aihara, M. Kaneko, and Y. Wada, *Taikiosen-gakkaishi*, **13**, 223 (1978).

6) T. Yokoyama, H. Ohnuma, K. Ohmura, and M. Zenki, *Bull. Hiruzen Res. Inst.*, *Okayama Univ. of Sci.*, **19**, 123 (1993).

7) Y. Marcus, *J. Chem. Soc.*, *Faraday Trans.*, **87**, 2995 (1991).

8) G. L. McClure, *Anal. Chim. Acta*, **64**, 289 (1973).

9) "CRC Handbook of Chemistry and Physics," 62nd ed, ed by R. C. Weast and M. J. Astle, CRC Press, Boca Raton (1981—1982).

10) E. A. Silinsh, "Organic Molecular Crystals," Springer-Verlag, Berlin, Heidelberg, and New York (1980).