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Crystal Structure of the Adduct of Thiourea with 2,6-Diethylnaphthalene

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The crystal structure of 2,6-diethylnaphthalene thiourea adduct was solved by single crystal X-ray diffraction method. The crystal is monoclinic, space group $P2_1/c$, with $a=12.571(3)$, $b=9.282(2)$, $c=14.634(3)$ Å, $\beta=92.14(2)°$, $V=1706.3(6)$ Å^3 and $Z=2$. The final R value was 0.083. The structure was composed of thiourea (host) molecules enclosing channels with hexagonal-prism and 2,6-diethylnaphthalene (guest) molecules in the channels. The cross-section of the channel was deformed hexagon. In the channel, the occupying channel length of the guest molecule was 12.571(3) Å

It is strongly hoped to develop effective separation methods of 2,6-diethylnaphthalene, since 2,6-diethylnaphthalene is expected as a feed stock of speciality high-performance polymers such as poly(ethylene 2,6-naphthalenedicarboxylate). The sources of 2,6-diethylnaphthalene are light cycle oils form catalytic cracking of gas oil fractions, light oils from coal derived liquids, and alkylation products of naphthalene. Since the physical properties of diethylnaphthalene isomers are quite similar, it is difficult to isolate 2,6-isomer by conventional methods, i.e., distillation and crystallization. Thiourea selectively forms the crystal of the adduct with 2,6-isomer. In this connection, it is interesting to apply the thiourea adduction for the separation of 2,6-isomer from the mixture of its isomers. Structural information of the crystal of the adduct is strongly needed for the fundamental understandings of adductibility of thiourea with 2,6-isomer.

In relation to the structure of thiourea adducts, crystal systems were only determined by powder X-ray analysis in the early investigations.[1] Recently, the structure of thiourea inclusion compounds of organometalics such as (benzene)$Cr(CO)_3$/thiourea,[2] (1,3-cyclohexadiene)$Fe(CO)_3$/thiourea,[2] and ferrocene/thiourea[3] were solved by single crystal X-ray analysis. In addition to these, the structure of thiourea inclusion complexes of organic compounds such as cyclohexane,[4] adamantane,[5] and chlorocyclohexane[6] were also studied. According to the results of these studies, crystal system of these thiourea inclusion compounds was trigonal or orthorhombic. The shape of the channel formed by thiourea molecules of these inclusion compounds was a regular hexagon in which disordered guest molecules were located. In contrast to these, distorted hexagonal channel of thiourea molecules was observed in the case of 2,3-dimethyl-1,3-butadiene thiourea adduct.[7] Crystal system of this adduct was monoclinic and ordered 2,3-dimethyl-1,3-butadiene (guest) molecules were accommodated in the distorted hexagonal channel formed by thiourea (host) molecules.

In the present study, single crystal of 2,6-diethylnaphthalene thiourea adduct was prepared and was subjected to the X-ray diffraction method in order to get detailed information of the crystal structure of the adduct.

Experimental

Sample and Reagents. A fraction of diethylnaphthalene isomers (ethylnaphthalene 0.53 wt%, diethylnaphthalenes 94.09 wt%, triethylnaphthalenes 2.12 wt% and others 3.26 wt%) was obtained from ethylation products of naphthalene by a conventional distillation method. By some repeated thiourea adductions of this fraction, 2,6-diethylnaphthalene was isolated. The purity of 2,6-diethylnaphthalene in the sample was more than 99.9 wt% by GC analysis. Trace amounts of impurity in the sample was 2,7-isomer.

Thiourea, methanol, pentane, and diethyl ether were extra pure grade reagents (Nacalai Tesque, Inc.) and they were dried to remove trace amounts of water prior to use.

Preparation of Single Crystal of the Adduct. Preparation of single crystal of the adduct was as follows: 2,6-Diethylnaphthalene (0.3 g) was added to a thiourea saturated methanol solution (20 g) at 10 °C. This solution was heated at 50 °C for the dissolution of 2,6-diethylnaphthalene, followed by the gradual cooling with the rate of 4 °C min^{-1} down to 10 °C, and was kept at this temperature for 1 h. The crystals of the adduct formed during this period were separated from a mother liquor by filtration. The mother liquor was kept at 5 °C for several days. After these treatment, tiny crystals of the adduct were newly formed in the mother liquor. These crystals were isolated and were subjected to the X-ray diffraction analysis. The molar ratio of 2,6-diethylnaphthalene thiourea adduct was determined to be 1:6 on the basis of the elemental analysis. Found: C, 37.31; H, 6.34; N, 26.16; S, 30.19%. Calcd for $(C_{14}H_{16})6((NH_2)_2CS)$: C, 37.48; H, 6.29; N, 26.22; S, 30.01%. The density of the adduct was measured to be 1.254 g cm^{-3} by a conventional flotation method.

X-Ray Experimental. A colorless crystal with sizes of 0.2×0.25×0.25 mm was used for the data collection on a Rigaku automated four circle diffractometer (AFC5PR), equipped with a rotating anode (45 kV, 200 mA), using graphite-monochromated Cu $K\alpha$ radiation ($\lambda=1.54178$ Å). Crystal data are as follows; $a=12.571(3)$, $b=9.282(2)$, $c=14.634(3)$ Å, $\beta=92.14(2)°$, $V=1706.3(6)$ Å^3, the space group $=P2_1/c$, $Z=2$, $D_{calcd}=1.257$ g cm^{-3}, μ(Cu $K\alpha$)$=38.98$ cm^{-1}. The ω–2θ scan mode with a scan rate of 4 ° min^{-1} was employed with ω scan range (1.2+0.30

$\tan\theta)°$. A total of 2976 reflections within $2\theta=128°$ were collected. Azimuthal scans of several reflections indicated no need for an absorption correction.

The structure was solved by the direct method and refined by the full-matrix least squares method. Three thiourea molecules are first defined and the remaining naphthalene molecules involving ethyl carbons are found by two steps weighted fourier syntheses. All non-hydrogen atoms were refined with anisotropic temperature factors. Although some positions of hydrogen atoms were located in a difference Fourier map, the geometrically calculated ones were included in the refinement. The final cycle of refinement was based on 2222 observed reflections within $I>\sigma(I)$ and 166 variable parameters and converge to the final R ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) value of 0.083 and R_w ($R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}$) of 0.113. The weighting scheme is $4F_o^2/\sigma^2(F_o^2)$. The maximum and minimum peaks on the final difference Fourier map correspond to 0.60 and -0.54 e Å^{-3}, respectively. The final atomic coordinates are given in Table 1.

All computations were performed using Rigaku Texsan software package system.[8)]

Results and Discussion

Molecular Structure. Bond lengths and bond angles of thiourea (host) molecules of the adduct are shown in Table 2. Three nonequivalent thiourea molecules exist in the crystal structure, but have no significant difference with the experimental errors, and almost the same of ordinary thiourea molecule. This indicates the formation of host–guest inclusion system give no effective structural change. The structural parameters of 2,6-diethylnaphthalene (guest) molecule are also shown in Table 2. Their standard deviations are relatively larger than those for thiourea molecules, and the noteworthy finding is that the temperature factors of ethyl carbons are extraordinary large, thus indicating the large motion in the crystal structure. Despite of this uncertainty, the conformation of ethyl group gives an important information. By the inspection of the planarity and bond torsion angles (Table 2), the ethyl group is not coplanar with the naphthalene moiety. The C(16) atom deviates by 0.12 Å from the naphthalene plane, implying the bending of *exo* C(15)–C(16) bond. In contrast, the deviation of the terminal C(17) atom is only -0.04 Å, indicating the rotation toward the plane. As the result, the largest torsion is $-13.9°$ in the C(17)–C(16)–C(15)–C(14′), while the torsion of C(11)–C(15)–C(16)–C(17) is 171.9°. Probably, in the free molecule, occur no bending of C(16) *exo* bond and instead the larger rotation of C(17) atom. Thus, it can be said the present guest molecule is forced to a planar conformation so as to be included within a channel.

Table 1. Fractional Atomic Coordinates and Equivalent Temperature Factors (Å) for Non-Hydrogen Atoms

Atom	x	y	z	B_{eq}
S(1)	−0.0602(1)	0.1028(2)	0.1390(1)	4.80(7)
S(2)	0.2784(1)	0.0809(2)	0.2128(1)	5.85(7)
S(3)	−0.3900(1)	−0.0029(2)	0.1632(1)	5.27(8)
N(11)	−0.1398(5)	−0.1098(6)	0.2360(4)	6.5(3)
N(12)	0.0382(4)	−0.0693(6)	0.2587(4)	6.0(3)
N(21)	0.1835(5)	0.0313(7)	0.0520(3)	5.9(3)
N(22)	0.3598(4)	−0.0220(7)	0.0630(4)	6.2(3)
N(31)	−0.4735(4)	0.2361(6)	0.2277(4)	6.6(3)
N(32)	−0.2962(4)	0.2450(6)	0.2026(5)	6.8(3)
C(1)	−0.0531(5)	−0.0347(7)	0.2172(4)	4.9(3)
C(2)	0.2725(5)	0.0260(6)	0.1008(4)	4.6(3)
C(3)	−0.3873(5)	0.1703(7)	0.2001(4)	4.9(3)
C(11)	−0.161(1)	0.130(1)	0.450(1)	9.5(8)
C(12)	−0.060(2)	0.160(1)	0.4463(8)	9.8(8)
C(13)	0.016(1)	0.0653(9)	0.4801(5)	7.0(5)
C(14)	0.127(1)	0.093(1)	0.4765(8)	8.5(7)
C(15)	−0.202(1)	0.001(1)	0.489(1)	9.8(8)
C(16)	−0.326(5)	−0.009(4)	0.496(5)	20(2)
C(17)	−0.369(8)	−0.139(6)	0.523(6)	35(3)

$B_{eq}=(4/3)\sum_{ij}\beta(a_i\cdot a_j)$.

Crystal Structure of the Adduct. The inclusion way of the present adduct can be best seen by the view along a axis (Fig. 1). The channels are expanded infinitely along with the crystallographic a axis. This channel structure is commonly seen in the other thiourea adducts, but the noteworthy feature in the mono-

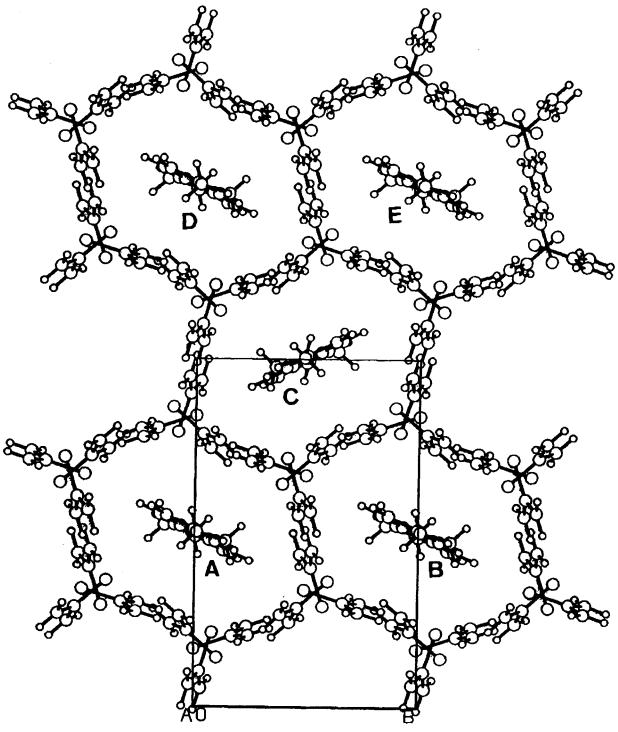

Fig. 1. Crystal structure of 2,6-diethylnaphthalene thiourea adduct viewed along a axis, in which symmetry operations of guest molecules are as follows;

A : x, y, z; $-x$, $-y$, $1-z$
B : x, $1+y$, z; $-x$, $1-y$, $1-z$
C : $-x$, $1/2+y$, $3/2-z$; x, $1/2-y$, $1/2+z$
D : x, y, $1+z$; $-x$, $-y$, z
E : x, $1+y$, $1+z$; $-x$, $1-y$, z

Table 2. Structural Parameters

a) Bond lengths and angles of nonhydrogen atoms

Atom	Atom	Lengths (Å)	Atom	Atom	Atom	Angles (°)
S(1)	C(1)	1.714(6)	S(1)	C(1)	N(11)	120.4(5)
S(2)	C(2)	1.716(6)	S(1)	C(1)	N(12)	120.7(5)
S(3)	C(3)	1.696(7)	N(11)	C(1)	N(12)	118.9(6)
N(11)	C(1)	1.331(8)	S(2)	C(2)	N(21)	121.1(5)
N(12)	C(1)	1.318(8)	S(2)	C(2)	N(22)	119.5(5)
N(21)	C(2)	1.305(8)	N(21)	C(2)	N(22)	119.4(6)
N(22)	C(2)	1.324(7)	S(3)	C(3)	N(31)	121.0(5)
N(31)	C(3)	1.321(7)	S(3)	C(3)	N(32)	120.5(5)
N(32)	C(3)	1.339(8)	N(31)	C(3)	N(32)	117.6(6)
C(11)	C(12)	1.31(2)	C(12)	C(11)	C(15)	125(1)
C(11)	C(15)	1.43(2)	C(11)	C(12)	C(13)	121(1)
C(12)	C(13)	1.38(2)	C(12)	C(13)	C(13)′	119(2)
C(13)	C(13)′	1.41(2)	C(12)	C(13)	C(14)	123(1)
C(13)	C(14)	1.42(2)	C(13)′	C(13)	C(14)	118(1)
C(14)	C(15)′	1.37(2)	C(13)	C(14)	C(15)′	122(1)
C(15)	C(16)	1.56(2)	C(11)	C(15)	C(14)′	115(1)
C(16)	C(17)	1.38(2)	C(11)	C(15)	C(16)	117(1)
			C(14)′	C(15)	C(16)	128(1)
			C(15)	C(16)	C(17)	118.1(6)

b) Atom deviations from the plane involving naphthalene moiety

Atom	Deviations (Å)
C(11)	0.005
C(12)	−0.005
C(13)	−0.002
C(14)	0.003
C(15)	−0.000
C(16)[a)]	−0.124
C(17)[a)]	0.039

a) Indicates atoms not including in the planarity.

c) Bond torsion angles in 2,6-diethylnaphthalene molecule

Atom	Atom	Atom	Atom	Angle (°)
C(11)	C(12)	C(13)	C(14)	179
C(11)	C(15)	C(16)	C(17)	172
C(12)	C(11)	C(15)	C(16)	174
C(12)	C(11)	C(15)	C(14′)	−1
C(13)	C(12)	C(11)	C(15)	1
C(17)	C(16)	C(15)	C(14′)	−14

C(14′) indicates atom related by symmetry operation $(x, y, 1-z)$.

clinic system is that the hexagon can distort so as to accommodate the guest molecules. To recognize this distortion in detail, only one channel structure is shown in Fig. 2a. The lengths of three diagonals are 11.6, 9.7, and 9.6 Å. They mean the hexagonal shape is represented by the longest axis of 11.6 Å and shortest width of 8.1 Å (Fig. 1). In contrast, in 2,3-dimethyl-1,3-butadiene thiourea adduct the corresponding lengths are 11.5, 10.6, and 8.6 Å, and the hexagonal shape is represented by the shortest axis of 8.6 Å and longest width 9.8 Å.[7] Thus, apparently the distortion way depends on the shape of the guest molecule. It is interesting to note that the change in both the shape and the dimensions of the channel of thiourea adduct can be permitted in accordance with the size, shape and/or the packing mode of guest molecules. This makes contrast to the fact that the shape and the dimensions of channel of urea adduct are strictly limited.[9]

The network mode can be well seen in Fig. 2b which is a projection chart around one channel. The network forms spiral chains of hydrogen bonds. However, unique feature in the monoclinic lattice is that the thiourea molecules do not locate at equal intervals along the channel, the intervals of which are ca. 1/9 and ca. 2/9 of a axis. Figure 2c shows side view of the present adduct perpendicular to the naphthalene plane. It is important that ethyl groups are surrounded by thioureas of 1/9 interval. A length of 2,6-diethylnaphthalene in the channel, the length of the guest molecule projected to the channel axis, is almost equal to a=12.571(3) Å.

Visualization of the Structure of 2,6-Diethylnaphthalene Thiourea Adduct. Figure 3 shows the space filling model of the present adduct. The shape of the cavity formed by the thiourea molecules is almost an ellipse. There are, however, concavo–convex surfaces inside the cavity. It is clear that 2,6-diethylnaphthalene is well situated within the cavity with the mode that hydrogen atom attached to C(12) and hydrogen atoms of ethyl group of 2,6-diethylnaphthalene are held in hollow spaces in the cavity.

Conclusion

In order to get the fundamental understandings on the thiourea adductibility of 2,6-diethylnaphthalene, X-ray crystallographic investigation of single crystal of the thiourea adduct was studied. The concluding remarks

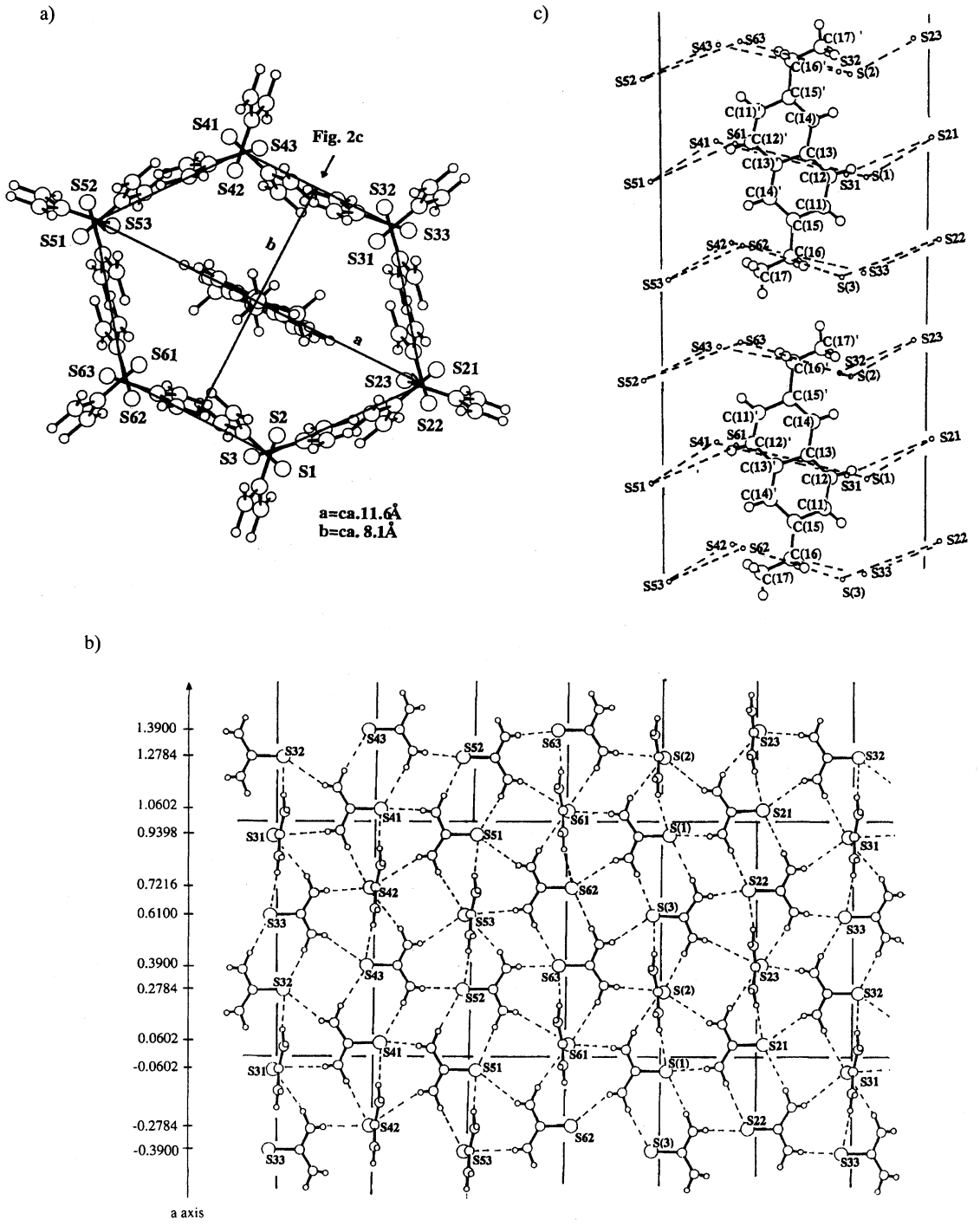

Fig. 2. Three views for inclusion behavior in one channel. (a) distorsion way of hexagonal channel. (b) a projection chart of host network around one channel, showing all S–HN hydrogen bonds. (c) inclusion way of guest molecules viewed parallel to the naphthalene plane, connecting thioureas of 1/9 intervals in dot lines. There are shown atom numbering scheme of guest molecules and S atoms, in which symmetry operations are as follows.

S(1),	S(2),	S(3),	:	x,	y,	z
S21,	S22,	S23,	:	$-x$,	$1/2+y$,	$1/2-z$
S31,	S32,	S33,	:	x,	$1/2-y$,	$1/2+z$
S41,	S42,	S43,	:	$-x$,	$-y$,	$1-z$
S51,	S52,	S53,	:	x,	$-1/2-y$,	$1/2+z$
S61,	S62,	S63,	:	$-x$,	$-1/2+y$,	$1/2-z$
C11—C17			:	x,	y,	z
C11′—C17′			:	$-x$,	$-y$,	$1-z$

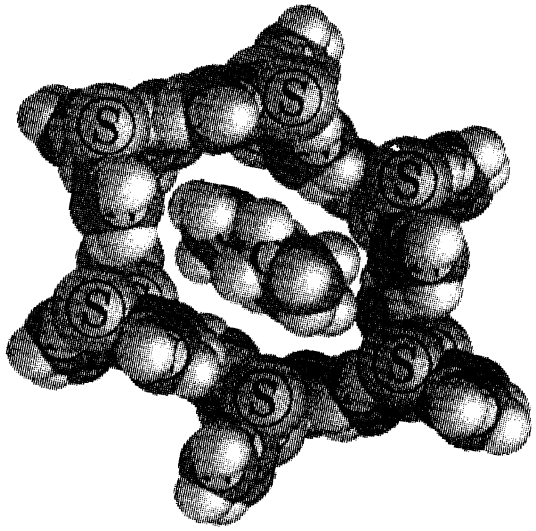

Fig. 3. Space filling model representation of inclusion behavior in one channel. The atomic radii are used 1.7, 1.55, 1.6, and 1.15 Å for S, N, O, and H atoms, respectively.

are summarized: Monoclinic $P2_1/c$ space group is another suitable lattice for the formation of channel structure in which plate-like guest such as 2,6-diethylnaphthalene can be included. This lattice exhibits the capability of deforming the hexagon and as the result, the guest molecules can be embedded within the channel without the disordered conformation.

Tables of experimental details, final atomic coordinates, anisotropic temperature factors, bond lengths and angles, and the observed and calculated structure factors are deposited as Document No. 66025 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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