Crystal and Molecular Structures of Methoxy and Methylthio Compounds

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The six crystal structures of XCH_2OCH_3 (X = CN, Cl, OCH_3) and XCH_2SCH_3 (X = CN, CH_3, SCH_3), which are liquid at room temperature and atmospheric pressure, have been determined by X-rays. The crystals belong to the monoclinic system and the space groups are $P2_1/c$ or $P2_1/n$. The molecules in all the crystals have the *gauche* conformations, which is consistent with the most populated conformation in the liquid and gaseous state estimated by IR spectra and the most stable conformations obtained by ab initio molecular orbital calculations. Such a *gauche* conformation is probably caused by the anomeric effect in the X–C–O–C or X–C–S–C chains. In all the crystals two molecules are coupled by two antiparallel C–H···O or C–H···S hydrogen bonds to form a four-membered ring. Such a dimer-like pair may be strengthened by the intermolecular interaction between the C–O or C–S bond moments in the four-membered ring.

A crystal structure is the result of an assembly of many intermolecular interactions and the structure analyses provide us with much information about the interactions. In addition, the intermolecular interactions have been studied broadly by the other experimental and theoretical methods. However it is difficult to predict the crystal structure even if the structure of the component molecule is well known. Therefore we should acquire further information about the intermolecular interactions. In this paper, the structure analyses have been focused on the small molecules, for which the prediction of the crystal structure may be possible because the computing time may not be enormous. The prediction of the crystal structure will give us much information about the intermolecular interactions.

Most small molecules have low melting points and exist in the gaseous or liquid state at room temperature. Although the investigations have been made by means of the spectroscopic studies and the molecular orbital calculations, not many crystal structure analyses have been carried out due to the difficulty in getting the single crystals. Recently, we have analyzed the crystal structures of the liquid compounds[1—3] using a new type of diffractometer with two cylindrical imaging plates as detectors (IP-Weissenberg type diffractometer) and a new type of low temperature equipment.[4] In this study the crystal structures of the title compounds which have low melting points were selected since the rotational isomerism may be possible and the relation between the molecular conformation and the crystal packing will be made clear.

The *gauche* preference about a segment X–A–Y–R in cyclic systems is well known as the anomeric effect[5—8] in sugar chemistry, when A is an element of intermediate electronegativities (e.g., C, P, S), X is an atom with more electronegativity than A (e.g., O, N or halogen), Y denotes an element with lone pairs and R is H or C. Although the origin of the term comes from sugar chemistry and there are extensive applications in cyclic systems, this preference is not restricted to carbohydrates or six-membered heterocycles.[8]

At first, if one considers the conformation of molecules of the type XCH_2–OCH_3,[8—12] the molecules exist largely in the *gauche* conformation for methoxyacetonitrile[13—16] and halomethyl methyl ether[17—19] in the liquid or gaseous state. In the case of a molecule with two torsion angles such as dimethoxymethane[20—24] (CH_3O–CH_2–OCH_3), the molecules exist largely in the GG conformation in the liquid or gaseous state. In this paper, the symbols T, G, and G′ will be used to represent the conformation of molecules with two torsion angles. The symbol T corresponds to *trans* conformation and G and G′ correspond to one and the other of two *gauche* conformations, which mean the approximate internal rotation angles 60 and −60° from the *cis* position, respectively. The first symbol of the sequence indicates C–O–C–O torsion angle and the second O–C–O–C. In addtion, ab initio calculations referring to the gaseous state also suggested the *gauche* or GG preference.

Then, the oxygen atom was replaced with the sulfur atom, such as XCH_2–SCH_3 or CH_3S–CH_2–SCH_3. The molecules of XCH_2–SCH_3 and CH_3S–CH_2–SCH_3 have not been studied so often as those of XCH_2–OCH_3 and CH_3O–CH_2–OCH_3. The infrared studies of methylthioacetonitrile gave evidence for the existence of the two conformation in the liquid state, but did not suggest the most stable conformation.[25] For ethylmethylsulfide it was proposed that the *trans* conformation was more stable than the *gauche* conformation.[26] However, later, the energy difference between two conformations was close to zero[27,28] or the *gauche* conformation was considered to be the most stable.[29—31] The conformations of bis(methylthio)methane have not been well

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known so far and the symbols indicating the conformations are the same as those of dimethoxymethane described above.

Experimental

Preparation of the Single Crystal. Each compound was filled in a 0.7 mm glass capillary, which was mounted on the diffractometer. The liquid sample was cooled down at 0.3 K min^{-1} to 10 K below its melting point. When the polycrystals appeared in the capillary, the polycrystalline sample was warmed up to the melting point at 10 K min^{-1}. During this process, sufficient attention was paid not to melt the tiny crystals completely. After several cycles of heating-up and cooling-down process a cylindrical single crystal was obtained in the glass capillary. The sharp diffraction peaks in the oscillation photograph assure the crystallinity. Such a crystallization method is called as in situ crystallization technique.[32]

Crystal Structure Analysis. After several oscillation pho-

Table 1. Crystal Data and Experimental Details for XCH_2OCH_3 (X = CN, Cl, OCH_3)

	$CNCH_2OCH_3$	$ClCH_2OCH_3$	$CH_3OCH_2OCH_3$
Crystal data			
Formula	C_3H_5NO	C_2H_5ClO	$C_3H_8O_2$
Formula weight	71.08	80.51	76.09
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	3.9987(3)	6.2826(8)	6.170(4)
b/Å	12.581(2)	8.0443(13)	8.007(6)
c/Å	7.8559(9)	8.2370(10)	9.255(5)
β/°	98.306(6)	109.968(6)	107.72(5)
V/Å^3	391.06(7)	391.26(9)	435.6(5)
Z	4	4	4
D_x/Mg m^{-3}	1.207	1.367	1.160
$F(000)$	152	168	168
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength/Å	0.71069	0.71069	0.71069
μ/mm^{-1}	0.092	0.753	0.096
Temperature/K	193	123	133
Crystal form	Cylindrical	Cylindrical	Cylindrical
Crystal size/mm	$0.7\phi \times 5$	$0.7\phi \times 5$	$0.7\phi \times 5$
Crystal color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Rigaku R-AXIS-II-CS	Rigaku R-AXIS-II-CS	Rigaku R-AXIS-II-CS
Monochromator	Graphite	Graphite	Graphite
Date collection method	Weissenberg	Weissenberg	Weissenberg
Absorption collection	None	None	None
No. of measured reflections	2895	2894	3122
No. of independent reflections	890	896	967
No. of reflections observed	825	842	892
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{max}/°	27.52	27.48	27.54
Range of h,k,l	$-5 \rightarrow 5$	$-8 \rightarrow 8$	$-8 \rightarrow 8$
	$-15 \rightarrow 16$	$-10 \rightarrow 10$	$-10 \rightarrow 10$
	$-10 \rightarrow 10$	$-10 \rightarrow 10$	$-12 \rightarrow 10$
Refinment			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0415	0.0426	0.0481
$wR(F^2)$	0.1146	0.1036	0.1150
S	1.093	1.075	1.118
No. of reflections used in refinement	890	896	967
No. of parameters	67	57	79
Weighting scheme	$w=1/[\sigma^2(F^2)+(0.0689P)^2+0.0370P]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F^2)+(0.0597P)^2+0.0939P]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F^2)+(0.0631P)^2+0.0478P]$, where $P=(F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.002	0.008
$\Delta\rho_{max}$/e Å^{-3}	0.166	0.356	0.202
$\Delta\rho_{min}$/e Å^{-3}	−0.199	−0.372	−0.304
Extinction correction method	SHELXL-93	None	SHELXL-93
Extinction coefficient	1.15(11)		1.61(11)

tographs were taken to determine the cell dimensions and the crystal orientation, the three-dimensional intensity data were collected with the diffractometer. The crystal data and the experimental details are summarized in Tables 1 and 2. All the structures were solved with the program SHELXS-86,[33] and refined by the full-matrix least squares with the program SHELXL-93.[34] The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located on a difference Fourier map and refined isotropically. The atomic scattering factors were taken from International Tables for Crystallography.[35] The final atomic parameters and equivalent isotropic temperature factors are given in Tables 3 and 4. Lists of the anisotropic temperature factors for non-hydrogen atoms and the observed and calculated structure factors are deposited as Document No. 72035 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained

Table 2. Crystal Data and Experimental Details for XCH_2SCH_3 (X = CN, CH_3, SCH_3)

	$CNCH_2SCH_3$	$CH_3CH_2SCH_3$	$CH_3SCH_2SCH_3$
Crystal data			
Formula	C_3H_5NS	C_3H_8S	$C_3H_8S_2$
Formula weight	87.14	76.15	108.21
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	5.2835(6)	5.2616(3)	7.054(3)
b/Å	8.961(2)	10.7240(9)	10.762(4)
c/Å	9.849(2)	8.3861(5)	7.918(3)
β/°	104.993(10)	101.597(3)	108.99(2)
V/Å^3	450.46(13)	463.53(5)	568.3(3)
Z	4	4	4
D_x/Mg m^{-3}	1.285	1.091	1.265
$F(000)$	184	168	232
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength/Å	0.71069	0.71069	0.71069
μ/mm^{-1}	0.523	0.493	0.777
Temperature/K	168	128	213
Crystal form	Cylindrical	Cylindrical	Cylindrical
Crystal size/mm	$0.7\phi \times 5$	$0.7\phi \times 5$	$0.7\phi \times 5$
Crystal color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Rigaku R-AXIS-II-CS	Rigaku R-AXIS-II-CS	Rigaku R-AXIS-II-CS
Monochromator	Graphite	Graphite	Graphite
Date collection method	Weissenberg	Weissenberg	Weissenberg
Absorption collection	None	None	None
No. of measured reflections	3414	3609	3500
No. of independent reflections	959	987	1282
No. of reflections observed	926	957	1210
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{max}/°	27.51	27.54	27.63
Range of h,k,l	$-6 \rightarrow 5$	$-6 \rightarrow 6$	$-9 \rightarrow 9$
	$-11 \rightarrow 11$	$-13 \rightarrow 13$	$-13 \rightarrow 13$
	$-12 \rightarrow 11$	$-10 \rightarrow 10$	$-10 \rightarrow 10$
Refinment			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0304	0.0279	0.0329
$wR(F^2)$	0.1021	0.0740	0.0932
S	1.240	1.167	1.088
No. of reflections used in refinement	959	987	1281
No. of parameters	67	69	79
Weighting scheme	$w=1/[\sigma^2(F^2)+(0.0632P)^2+0.0506P]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F^2)+(0.0278P)^2+0.1780P]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F^2)+(0.0513P)^2+0.0968P]$, where $P=(F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.006	0.001	0.005
$\Delta\rho_{max}$/e Å^{-3}	0.236	0.192	0.418
$\Delta\rho_{min}$/e Å^{-3}	−0.375	−0.333	−0.297
Extinction correction method	SHELXL-93	None	SHELXL-93
Extinction coefficient	0.64(5)		0.125(13)

Table 3. Positional and Isotropic Thermal Parameters (Å^2) for XCH_2OCH_3 (X = CN, Cl, OCH_3)
The equivalent isotropic thermal parameter (Å^2) is shown for non-hydrogen atoms.

Atom	x	y	z	U or U_{eq}
(a) $CNCH_2OCH_3$				
O1	0.9167(2)	0.46781(6)	0.21040(9)	0.0442
N1	1.4402(3)	0.28076(8)	0.42082(14)	0.0550
C1	1.1182(3)	0.55180(9)	0.2909(2)	0.0500
C2	1.1101(3)	0.38385(8)	0.15892(13)	0.0423
C3	1.2964(2)	0.32563(7)	0.30684(13)	0.0417
HC1A	1.2616(37)	0.5793(13)	0.2134(20)	0.065(4)
HC1B	1.2599(40)	0.5255(13)	0.3989(22)	0.065(4)
HC1C	0.9656(39)	0.6071(13)	0.3151(18)	0.058(4)
HC2A	1.2797(32)	0.4073(10)	0.0887(16)	0.046(3)
HC2B	0.9575(34)	0.3339(11)	0.0992(17)	0.052(3)
(b) $ClCH_2OCH_3$				
C11	0.10332(7)	0.61535(6)	0.86194(5)	0.0419
O1	0.2780(2)	0.5704(2)	0.61270(15)	0.0409
C1	0.1326(3)	0.6733(2)	0.6555(2)	0.0382
C2	0.5122(3)	0.5998(3)	0.7096(3)	0.0430
HC1A	0.1870(36)	0.7831(31)	0.6787(29)	0.046(5)
HC1B	−0.0141(37)	0.6611(26)	0.5732(28)	0.039(5)
HC2A	0.5560(45)	0.7170(35)	0.7029(34)	0.062(7)
HC2B	0.5478(39)	0.5750(33)	0.8305(30)	0.049(6)
HC2C	0.5944(41)	0.5283(33)	0.6543(31)	0.060(7)
(c) $CH_3OCH_2OCH_3$				
O1	0.25502(13)	0.23937(10)	0.65760(9)	0.0388
O2	−0.12573(13)	0.26673(10)	0.65246(10)	0.0386
C1	0.2396(2)	0.32459(15)	0.51992(14)	0.0410
C2	0.1031(2)	0.30121(15)	0.72999(13)	0.0374
C3	−0.1784(2)	0.09302(15)	0.64973(14)	0.0407
HC1A	0.2398(24)	0.4446(22)	0.5358(16)	0.045(3)
HC1B	0.0953(31)	0.2998(20)	0.4435(21)	0.052(4)
HC1C	0.3620(38)	0.2838(25)	0.4879(25)	0.072(6)
HC2A	0.1102(22)	0.4221(19)	0.7368(15)	0.039(3)
HC2B	0.1483(27)	0.2454(18)	0.8289(19)	0.045(4)
HC3A	−0.1239(29)	0.0422(22)	0.7443(21)	0.058(4)
HC3B	−0.1083(28)	0.0339(23)	0.5917(19)	0.062(5)
HC3C	−0.3511(31)	0.0842(26)	0.6113(20)	0.068(5)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j.$$

Table 4. Positional and Isotropic Thermal Parameters (Å^2) for XCH_2SCH_3 (X = CN, CH_3, SCH_3)
The equivalent isotropic thermal parameter (Å^2) is shown for non-hydrogen atoms.

Atom	x	y	z	U or U_{eq}
(a) $CNCH_2SCH_3$				
S1	0.08323(8)	0.15642(4)	0.64114(3)	0.0368
N1	0.7241(3)	0.0867(2)	0.8810(2)	0.0511
C1	0.2876(4)	0.1876(2)	0.5237(2)	0.0416
C2	0.2593(4)	0.0023(2)	0.7425(2)	0.0389
C3	0.5201(3)	0.0469(2)	0.82134(15)	0.0374
HC1A	0.3092(43)	0.1039(28)	0.4699(22)	0.048(5)
HC1B	0.2329(55)	0.2673(33)	0.4660(27)	0.066(7)
HC1C	0.4661(47)	0.2138(26)	0.5746(23)	0.050(5)
HC2A	0.2839(46)	−0.0822(26)	0.6844(23)	0.054(5)
HC2B	0.1769(51)	−0.0255(30)	0.8074(28)	0.067(7)
(b) $CH_3CH_2SCH_3$				
S1	0.47985(7)	0.90918(3)	0.25146(4)	0.0319
C1	0.7121(3)	1.0265(2)	0.2227(2)	0.0407
C2	0.6502(3)	0.83753(14)	0.4382(2)	0.0323
C3	0.8755(3)	0.7555(2)	0.4160(2)	0.0392
HC1A	0.8736(42)	0.9880(20)	0.2201(24)	0.051(5)
HC1B	0.7364(48)	1.0866(20)	0.3104(30)	0.063(7)
HC1C	0.6478(42)	1.0684(19)	0.1215(28)	0.055(6)
HC2A	0.7073(39)	0.9047(17)	0.5151(24)	0.044(5)
HC2B	0.5229(38)	0.7868(18)	0.4769(23)	0.044(5)
HC3A	0.8173(40)	0.6843(19)	0.3397(27)	0.052(6)
HC3B	1.0037(43)	0.8045(20)	0.3746(28)	0.059(6)
HC3C	0.9612(40)	0.7217(19)	0.5193(27)	0.053(5)
(c) $CH_3SCH_2SCH_3$				
S1	1.03167(6)	0.61197(4)	0.22142(6)	0.0491
S2	0.58766(6)	0.67058(4)	0.15375(6)	0.0477
C1	1.0776(4)	0.7763(2)	0.2288(3)	0.0565
C2	0.7777(3)	0.6072(2)	0.0719(2)	0.0446
C3	0.5962(3)	0.5605(2)	0.3262(3)	0.0560
HC1A	1.1991(41)	0.7875(27)	0.3121(36)	0.086(8)
HC1B	0.9710(43)	0.8235(28)	0.2666(37)	0.085(9)
HC1C	1.0774(39)	0.8061(27)	0.1183(41)	0.077(7)
HC2A	0.7654(34)	0.6513(20)	−0.0357(30)	0.055(6)
HC2B	0.7529(28)	0.5249(20)	0.0431(25)	0.051(5)
HC3A	0.7277(38)	0.5571(23)	0.4055(37)	0.072(7)
HC3B	0.5016(47)	0.5912(28)	0.3802(42)	0.089(8)
HC3C	0.5435(41)	0.4809(31)	0.2684(39)	0.083(8)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j.$$

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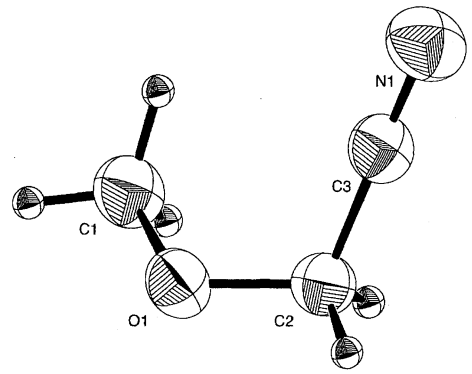
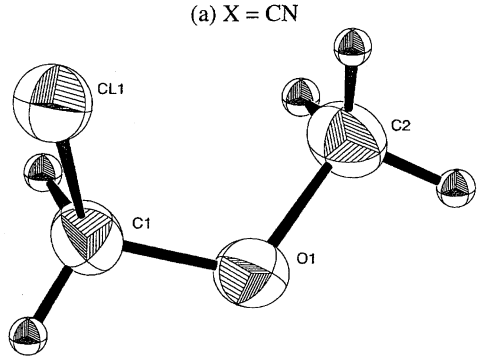
Molecular Orbital Calculations. The ab initio molecular orbital calculation was carried out with the GAUSSIAN 94[36] program for each conformation of all the compounds studied. The geometry of each conformation was optimized with MP2/6-31G* basis set. The calculated energy includes the zero-point energy.

Results and Discussion

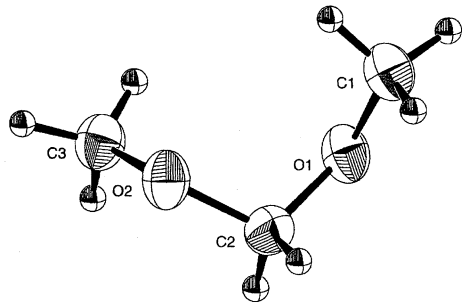
Conformation in the Crystalline State. The ORTEP drawing[37] of the molecular structures of XCH_2OCH_3 (X = CN, Cl, OCH_3) and XCH_2SCH_3 (X = CN, CH_3, SCH_3) with the numbering of the atoms are shown in Figs. 1 and 2. Geometric parameters of each compounds are listed in Tables 5 and 6 together with the results of geometry optimization by the ab initio calculation at the MP2/6-31G* levels. The geometric parameters are in good agreement with the calculated values. The conformations of all the compounds in this study are *gauche* or GG around the C–O or C–S bonds in the crystalline state as shown in Figs. 1 and 2 and Tables 5 and 6. Table 7 shows the most populated conformations obtained by the spectroscopic studies in the gaseous state and the most stable conformations by ab initio molecular orbital calculations together with the energy differences between the most and second most stable conformations. The results indicate that the *gauche* or GG conformations are more stable than *trans* or the other conformations. The conformations in the crystalline state are consistent with the most populated or stable conformations.



(a) X = CN

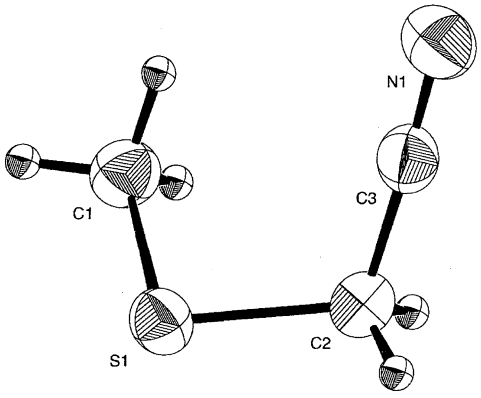


(b) X = Cl

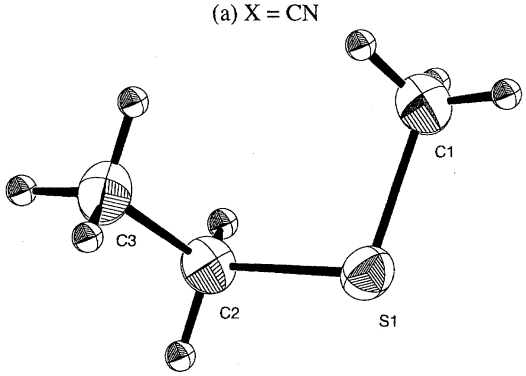


(c) X = OCH_3

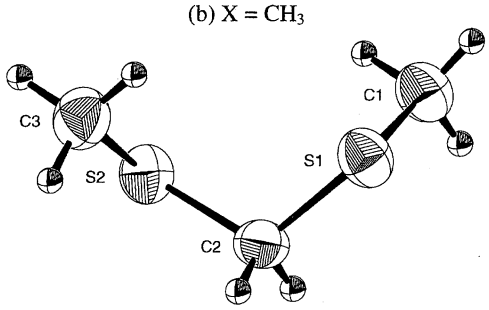
Fig. 1. ORTEP[37] drawing with the numbering of the atoms for XCH_2OCH_3. Thermal ellipsoids of non-hydrogen atoms were scaled to enclose 50% probability and the hydrogen atoms were drawn with arbitrary scale.



(a) X = CN



(b) X = CH_3



(c) X = SCH_3

Fig. 2. ORTEP[37] drawing with the numbering of the atoms for XCH_2SCH_3. Thermal ellipsoids of non-hydrogen atoms were scaled to enclose 50% probability and the hydrogen atoms were drawn with arbitrary scale.

Such *gauche* conformations are probably due to the anomeric effect. The stabilization would be brought about by the interaction of the heteroatom (Y) lone pairs with an antibonding σ^*-orbital (X–A) of the electronegative substituent in X–A–Y–R. The interaction causes the lengthening of the terminal C–O, C–S, and C–X (X: electronegative substituents) bonds by electron transfer to its σ antibonding orbital and the contraction of the central C–O and C–S bonds due to increasing its double-bond character. As shown in Tables 5 and 6 all the bond distances described above tend to be elongated or shortened as compared with the standard values. For example, O1–C2 = 1.403(1) Å of methoxyacetonitrile is shorter than the CH_2–O standard value 1.426 Å and C1–O1 = 1.421(1) and C2–C3 = 1.481(1) Å are longer than the CH_3–O and CH_2–CN standard values 1.416 and 1.470 Å, respectively.[35] The same results were observed in the gaseous state.[8] The interactions between the orbitals were also observed in the crystalline state. The anomeric effect observed in the oxygen-containing compounds is stronger than that in the sulfur-containing compounds. However, the relation between the anomeric effect and the electronegativity of the substituents was not clear.

Crystal Structures. (a) XCH_2OCH_3 (X = CN, Cl, OCH_3). The crystal structure of methoxyacetonitrile viewed along the *a* axis is shown in Fig. 3(a). The molecules make dimer-like pairs through the C–H···O hydrogen bonds. The central C–O bonds in the dimer-like pair orient antiparallel to each other, and the intermolecular O1···C2^i distance is 3.438(1) Å. On the other hand, the CN group directs toward C2 of the neighboring molecule. The intermolecular

Table 5. Bond Distances (Å), Angles (°), and Torsion Angles (°) for XCH_2OCH_3 (X = CN, Cl, OCH_3)

	$CNCH_2OCH_3$		$ClCH_2OCH_3$			$CH_3OCH_2OCH_3$	
	X-ray	MP2/6-31G*	X-ray	MP2/6-31G*		X-ray	MP2/6-31G*
C1–O1	1.4210(13)	1.427	Cl–C1	1.832(2)	1.813	C1–O1	1.423(2)	1.426
C1–C2	1.4030(12)	1.410	C1–O1	1.365(2)	1.380	O1–C2	1.398(2)	1.405
C2–C3	1.4807(14)	1.480	O1–C2	1.434(2)	1.429	C2–O2	1.403(2)	1.405
C3–N1	1.1406(14)	1.181	Cl1–C1–O1	111.94(12)	113.36	O2–C3	1.428(2)	1.426
C1–O1–C2	112.82(8)	112.09	C1–O1–C2	113.99(14)	113.39	C1–O1–C2	112.83(9)	111.90
O1–C2–C3	112.45(8)	112.05	Cl1–C1–O1–C2	75.1(2)	71.6	O1–C2–O2	113.71(10)	113.62
C2–C3–N1	179.94(11)	178.47				C2–O2–C3	112.89(9)	111.90
C1–O1–C2–C3	68.10(11)	66.4				C1–O1–C2–O2	68.98(13)	64.60
						O1–C2–O2–C3	67.13(12)	64.61

(standard values : CH_2–O = 1.426 Å, CH_3–O = 1.416 Å, CH_2–CN = 1.470 Å, CH_2–Cl = 1.790 Å).

Table 6. Bond Distances (Å), Angles (°), and Torsion Angles (°) for XCH_2SCH_3 (X = CN, CH_3, SCH_3)

	$CNCH_2SCH_3$		$CH_3CH_2SCH_3$			$CH_3SCH_2SCH_3$	
	X-ray	MP2/6-31G*	X-ray	MP2/6-31G*		X-ray	MP2/6-31G*
C1–S1	1.796(2)	1.808	C1–S1	1.804(2)	1.808	C1–S1	1.796(2)	1.806
S1–C2	1.813(2)	1.818	S1–C2	1.8112(15)	1.815	S1–C2	1.798(2)	1.812
C2–C3	1.452(2)	1.463	C2–C3	1.518(2)	1.524	C2–S2	1.802(2)	1.812
C3–N1	1.143(2)	1.181	C1–S1–C2	100.41(8)	99.87	S2–C3	1.794(2)	1.806
C1–S1–C2	99.48(8)	98.58	S1–C2–C3	113.78(11)	114.62	C1–S1–C2	100.36(10)	99.09
S1–C2–C3	111.44(11)	112.53	C1–S1–C2–C3	73.75(13)	68.70	S1–C2–S2	116.80(9)	116.99
C2–C3–N1	177.6(2)	177.31				C2–S2–C3	100.30(9)	99.09
C1–S1–C2–C3	63.90(13)	59.17				C1–S1–C2–S2	68.77(12)	66.34
						S1–C2–S2–C3	67.02(12)	66.34

(standard values : CH_2–S = 1.819 Å, CH_3–S = 1.798 Å, CH_2–CN = 1.470 Å, CH_2–CH_3 = 1.513 Å).

Table 7. Conformations Obtained by Each Study for (a) XCH_2OCH_3 (X = CN, Cl, OCH_3) and (b) XCH_2SCH_3 (X = CN, CH_3, OCH_3)
The most populated conformations are shown for the spectroscopic studies in the gaseous state. Energy differences (kJ mol^{-1}) at MP2/6-31G* between *trans* and *gauche* or TG (second stable conformation) and GG are shown in parentheses for ab initio calculations.

(a) XCH_2OCH_3 (X=CN, Cl, OCH_3)

X	X-ray	Spectroscopy	ab initio
CN	*gauche*	*gauche*	*gauche* (6.49)
Cl	*gauche*	*gauche*	*gauche* (16.39)
CH_3O	GG	GG	GG (29.04)

(b) XCH_2SCH_3 (X=CN, CH_3, OCH_3)

X	X-ray	Spectroscopy	ab initio
CN	*gauche*	—	*gauche* (8.25)
CH_3	*gauche*	*trans* or *gauche*	*gauche* (0.02)
CH_3S	GG	—	GG (18.83)

N1···C2^{ii} distance and C3–N1···C2 angle are 3.201(1) Å and 125.11(9)°, respectively. The layers are formed in parallel to the *bc* plane by these interactions.

The crystal structure of chloromethyl methyl ether viewed along the *c* axis is shown in Fig. 3(b). The molecules make columns along the *a* axis coupling through two kinds of C–H···O hydrogen bonds. There are two kinds of the dimer-like pairs. The central and terminal C–O bonds in the respective dimer-like pair orient antiparallel to each other as observed in the crystal of methoxyacetonitrile. The intermolecular O1···C1^{i} and O1···C2^{ii} distances are 3.389(2) and 3.613(2) Å, respectively. The crystal structure is constructed by stacking of the columns through the hydrogen bond O1···C1^{iii} = 3.665(2) Å.

The crystal structure of dimethoxymethane viewed along the *a* axis is shown in Fig. 3(c). There are two hydrogen bonds between one of two oxygen atoms in a molecule and the carbon atoms at both ends of the molecular chain. The intermolecular O2···C1^{i} and O2···C3^{ii} distances are 3.615(2) and 3.603(2) Å, respectively. The molecules make the dimer-like pairs with O2···C1. The molecules are packed by the hydrogen bonds.

The dimer-like pairs through the C–H···O hydrogen bonds are formed in all XCH_2OCH_3 (X = CN, Cl, OCH_3). The dimer-like pair tends to form a four-membered ring except for dimethoxymethane, in which the eight-membered ring (C1–O1–C2–O2···C1^{i}–O1^{i}–C2^{i}–O2^{i}) is formed.

(b) XCH_2SCH_3 (X = CN, CH_3, SCH_3). For the crystals of XCH_2SCH_3 (X = CN, CH_3, SCH_3) the dimer-like pair through the C–H···S hydrogen bonds are formed in the same way as the crystals of XCH_2OCH_3.

The crystal structure of methylthioacetonitrile viewed along the *a* axis is shown in Fig. 4(a). The intermolecular S1···C1^{i} distances is 3.786(2) Å and the four-membered ring is formed. On the other hand, the CN group directs toward C1 of the neighboring molecule. The intermolecular

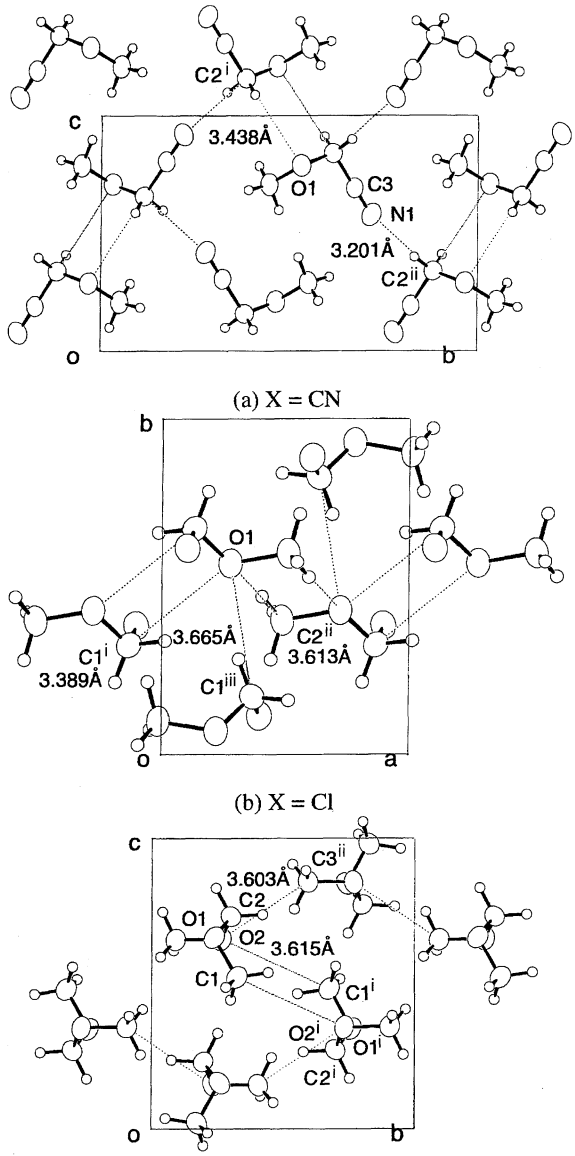


Fig. 3. Crystal structure of XCH_2OCH_3.

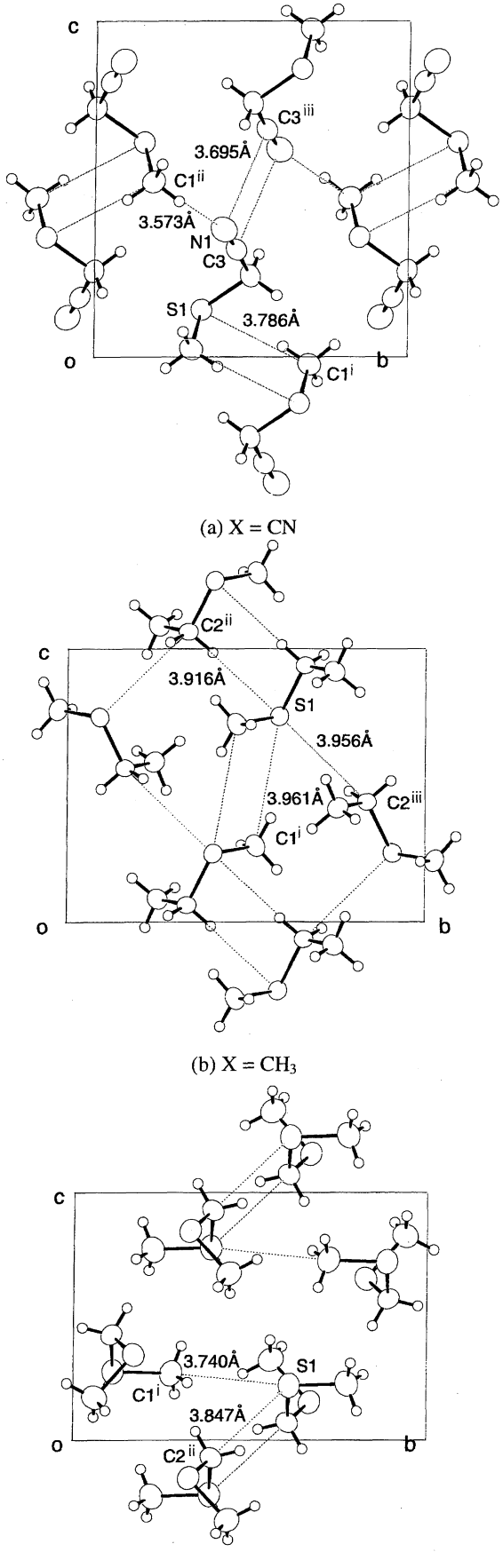


Fig. 4. Crystal structure of XCH_2SCH_3. viewed along *a* axis.

$N1\cdots C1^{ii}$ distance and $C3–N1\cdots C1^{ii}$ angle are 3.573(3) Å and 163.32(13)°, respectively. The CN groups in the dimer-like pair orient antiparallel to each other, and the intermolecular $N1\cdots C3^{iii}$ distance is 3.695(2) Å.

The crystal structure of ethylmethylsulfide viewed along the *a* axis is shown in Fig. 4(b). The molecules make the four-membered rings along the *c* axis through two C–H···S hydrogen bonds. The central and terminal C–S bonds in the dimer-like pair orient antiparallel to each other in the same way as chloromethylmethyl ether. Therefore the crystal structure is very close to that of chloromethylmethyl ether. The intermolecular $S1\cdots C1^{i}$ and $S1\cdots C2^{ii}$ distances are 3.961(2) and 3.916(2) Å, respectively. The crystal structure is constructed by the columns through the hydrogen bond $S1\cdots C2^{iii}$ = 3.956(2) Å.

The crystal structure of bis(methylthio)methane viewed along the *a* axis is shown in Fig. 4(c). There are three hy-

drogen bonds between one of two sulfur atoms in a molecule and the carbon atoms in the same way as dimethoxymethane. The intermolecular S1···C1^{i}, S1···C2^{ii}, and S1···C3 distances are 3.740(3), 3.847(2), and 3.835(3) Å, respectively (S1···C3(symmetry code: $x+1$, y, z) are not shown in Fig. 4(c) because of the a axis projection). The molecules make the four-membered ring with S1···C2^{ii}. The molecules are packed by the hydrogen bonds.

Packing Pattern. For all the compounds, analyzed the molecules form the dimer-like pairs through the C–H···O or C–H···S hydrogen bonds and most of them make the four-membered rings. The bonds in a ring are mutually antiparallel. This type of the four-membered ring is also found in 1, 2-dimethoxyethane, 1-methoxy-2-(methylthio)ethane, and 1, 2-bis(methylthio)ethane.[1] The geometric parameters of these compounds are close to those observed in the present compounds. These rings may stabilize the crystal packing owing to the interaction between the bond moments in addition to the hydrogen bonds.

In order to investigate which bond is preferable to form the antiparallel bond pair, atomic charges are calculated. Table 8 shows the estimation of atomic charges by Mulliken population analyses for the *gauche* or GG conformations at MP2/6-31G*. The values of atomic charges are the sum of hydrogen and heavy atoms. Which bonds form the pair seems to depend on the difference between the atomic charges of both ends of the bond. The bonds with the largest difference, in which the interactions between the bond moments seem to be the largest, always form the pairs in methoxyacetonitrile, chloromethylmethyl ether, methylthioacetonitrile, ethylmethylsulfide, and bis(methylthio)methane. The four-membered rings through the C–H···O or C–H···S hydrogen bonds were observed in four compounds among these five crystals. Since the largest difference is observed in the cyano group for methylthioacetonitrile, the dimer-like pair is formed between the adjacent cyano groups in addition to the four-membered ring through the C–H···S hydrogen bonds. In the case of dimethoxymethane, although the CH_2–O bonds have the largest difference, no antiparallel pair was found in the crystal structure. However, the eight-membered ring was found as an alternative to the antiparallel pair. Moreover, it is noteworthy that although the GG conformations of dimethoxymethane and bis(methylthio)methane having the C_2 symmetry, the symmetry is lost in the crystal structure; i.e. only one of two O or S atoms in a molecule mainly contributes to the C–H···O or C–H···S hydrogen bond. This result is different from the case of 1,2-dimethoxyethane[1] and 1,2-dimethylthioethane.[38]

The dimer-like pair and the four or eight-membered ring are observed in the crystals and play an important role for packing the molecules. The packing patterns are applicable to prediction of the crystal structures.

Table 8. Atomic Charges with Hydrogens Summed into Heavy Atoms for the *Gauche* or GG Conformations by Calculating at MP2/6-31G* for (a) XCH_2OCH_3 (X = CN, Cl, OCH_3) and (b) XCH_2SCH_3 (X = CN, CH_3, OCH_3)

(a) XCH_2OCH_3 (X = CN, Cl, OCH_3)

$CNCH_2OCH_3$		$ClCH_2OCH_3$		$CH_3OCH_2OCH_3$	
Atom		Atom		Atom	
C1	0.281	C11	−0.110	C1	0.262
O1	−0.483	C1	0.278	O1	−0.505
C2	0.315	O1	−0.460	C2	0.485
C3	0.251	C2	0.292	O2	−0.505
N1	−0.364			C3	0.262

(b) XCH_2SCH_3 (X = CN, CH_3, OCH_3)

$CNCH_2SCH_3$		$CH_3CH_2SCH_3$		$CH_3SCH_2SCH_3$	
Atom		Atom		Atom	
C1	−0.023	C1	−0.053	C1	−0.031
S1	0.161	S1	0.099	S1	0.110
C2	−0.066	C2	−0.073	C2	−0.160
C3	0.292	C3	0.027	S2	0.110
N1	−0.364			C3	−0.031

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