Preparation and Chemical Reactions of Trifluoroacetaldehyde Azine (1,1,1,6,6,6-Hexafluoro-3,4-diaza-2,4-hexadiene)

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Trifluoroacetaldehyde azine (TFAcAz) was prepared and its reactivity was investigated. TFAcAz is readily attacked by nucleophiles such as trialkylamines, methanol, and water. The structures of the products were studied by ^{1}H, ^{13}C, and ^{19}F NMR, IR, Raman, and EI-mass spectroscopies and X-ray crystallographic analysis. A cyclic dimer containing a 1,4-dihydro-1,2,4,5-tetrazine ring was obtained by the reactions of TFAcAz with trialkylamines. 1,2-Adducts were found to be produced by the reactions of TFAcAz with methanol and with water.

Many papers have been published concerning the polymerization of compounds with a C=C or C=O double bond. However, only a few papers[1—7] have been reported on the polymerizability of the C=N double bond. We therefore investigated the polymerizations of the C=N double bond,[8—15] and found that alkanal azines (RCH=N–N=CHR, R=CH_3, C_2H_5, C_3H_7) could be polymerized with Grignard reagents to form crystalline 1,4-polymers.[13,14] However, typical anionic initiators, such as butyllithium and naphthylsodium, gave only soluble oligomers of alkanal azines. The formation of oligomers is due to a chain-transfer reaction, in which protons on α-carbons of aldehyde are extracted by propagating anions.

In order to retard the chain-transfer reaction we prepared trifluoroacetaldehyde azine (R=CF_3, TFAcAz), which had no protons on the α-carbons of aldehyde, and investigated the polymerizability of TFAcAz. It has been found that TFAcAz can be polymerized in a frozen state (at −20 °C) to form a crystalline 1,2-polymer with triethylamine, which does not react with the alkanal azines.[15] During the course of the study we found that a pale-yellow crystalline product was obtained without the formation of the 1,2-polymer when the polymerization was performed at 20 °C.

Although several papers have been reported concerning the syntheses of azine compounds containing fluorine atoms,[16—21] to our knowledge no paper has been published on the preparation and chemical reactions of TFAcAz. Only few papers have been published concerning the chemical reactivity of alkanal azines.[22,23] We found that the chemical reactivity of TFAcAz was remarkably different from that of alkanal azines. In this paper we report on the reactions of TFAcAz with bases and protic compounds, and discuss the chemical reactivity of TFAcAz based on the structures of the obtained products.

Experimental

Materials. TFAcAz was prepared from trifluoroacetaldehyde hydrate[24] and hydrazine monohydrate, and was purified by successive distillations, as described in a previous paper.[15] Acetic acid and trifluoroacetic acid were dried with phosphorus pentaoxide and separated from the phosphorus pentaoxide by decantation just before use. Triethylamine (Et_3N) and tributylamine (n-Bu_3N) were dried with calcium hydride and distilled under reduced pressure. Tridecylamine (n-Dec_3N) was dried with calcium hydride and separated from the calcium hydride by decantation just before use. Distilled water was used. Other reagents were used without further purification.

Reactivities of TFAcAz. A given amount of a reagent was added to TFAcAz (50 mg, 0.26 mmol) with a microsyringe. The change in the reaction mixture was detected by means of gas chromatography.

Preparation of a Cyclic Dimer of TFAcAz. Et_3N (0.375 mL, 2.63 mmol) was added to TFAcAz (1.0 mL, 5.26 mmol) in an ampule at about 20 °C. After 1 d, a cyclic dimer of TFAcAz was isolated as pale-yellow crystals by using a gas chromatograph with a silicone (DC550, Gasukuro Kogyo Inc.) column. Yield: 142 mg, 14.2%. Mp 26.8—27.1 °C. IR (KBr) 1160 (C–F), 1280 (C–F), 1336 (C–F), 1633 cm^{-1} (C=N). Raman 1680 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$, 270 MHz) δ=4.04 (q, J=8.1 Hz, CH_2). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ=53 (qq, J=35.1, 3.1 Hz, CH_2N), 117 (q, J=277.1 Hz, CF_3), 123 (q, J=278.9 Hz, CF_3), 139 (q, J=35.7 Hz,

C=N). ^{19}F NMR ($CDCl_3$, 470.5 MHz) $\delta=-65.5$ (q, $J=1.8$ Hz, CF_3), -72.2 (tq, $J=8.1$, 1.8 Hz, CF_3). ^{14}N NMR ($CDCl_3$, 36.1 MHz) $\delta=-81$ (bs, C=N), -250 (bs, CH_2N). Found: C, 25.37; H, 1.32; N, 14.93%. Calcd for $C_8H_4N_4F_{12}$: C, 25.01; H, 1.05; N, 14.59; F, 59.35%. Found: M^+, m/z 384. Calcd for $C_8H_4N_4F_{12}$: M, 384.

X-Ray Crystallographic Analysis of the Cyclic Dimer. Single crystals of the cyclic dimer were grown under reduced pressure (ca. 10^{-1} mmHg) in sealed tubes.

Details of the crystal data, intensity collection, and refinement are given in Table 1. The intensity data were collected at about -12.5 °C on a Rigaku NL-1 diffractometer using Cu $K\alpha$ radiation. Accurate cell constants for the cyclic dimer were determined using 25 general reflections ($28.65° < \theta < 30.12°$).

The intensities were measured by the ω ($0° < 2\theta < 80°$) and 2θ–ω ($80° \leq 2\theta \leq 120°$) scan techniques with background counts being made at the beginning and end of each scan for a total of half the scan time. The stability of the crystal was checked by monitoring the intensities of standard reflections every 100 measurements. Only minor variations were observed. The structure was solved by a direct method (MULTAN80[25]) and refined by least-squares methods in consideration of anomalous dispersion terms. All of the hydrogen atoms were located in difference Fourier syntheses, and were included in the refinement in an unconstrained isotropic form. The final refinement was carried out using full-matrix-least-squares techniques.

The atomic coordinates and temperature factors are listed in Table 2.[26]

Preparation of an Adduct of TFAcAz with Methanol. Methanol (1.0 mL, 24.7 mmol) was added to TF-

Table 1. Crystal Data

Molecular formula	$C_8F_{12}H_4N_4$
Molecular weight	384.13
Crystal system	Tetragonal
Space group	$P4_32_12$
a/Å	9.5598(8)
c/Å	14.532(1)
V/Å^3	1328.2(2)
Z	4
D_c/g cm^{-3}	1.921
μ(Cu $K\alpha$)/cm^{-1}	22.2
Crystal size/mm	0.3×0.3×0.2
Scan method	ω, 2θ–ω
Scan speed/deg min^{-1}	4.0
Scan width/deg	1.8
2θ range/deg	0—120
Standard reflections	−1 4−7, 6−1 2, 4 4−4
Standard variation/%	±2.3
Number of measured reflections	2229
Number of observation reflections $I \geq 3\sigma(I)$	892
Final R, R_w	0.0415, 0.0448
Largest shift/error in final cycle; Δ/σ	0.001

Table 2. Final Fractional Atomic Coordinates for the Cyclic Dimer of TFAcAz

Atom	x	y	z	B_{eq}[a)]/Å^2
F(1)	0.0493(4)	0.7579(4)	0.1882(2)	7.7
F(2)	0.2224(4)	0.6243(4)	0.1552(3)	8.5
F(3)	0.0454(4)	0.6394(4)	0.0663(2)	7.6
F(4)	0.2232(4)	0.9927(4)	−0.2029(2)	8.2
F(5)	0.2269(4)	0.7925(4)	−0.1376(2)	7.3
F(6)	0.3537(4)	0.9584(4)	−0.0853(3)	8.5
N(1)	0.1016(4)	0.9230(4)	0.0291(3)	4.3
N(2)	0.0644(4)	1.0292(4)	0.0923(3)	4.6
C(1)	0.1127(5)	0.9744(5)	−0.0606(3)	4.2
C(2)	0.2024(5)	0.8264(6)	0.0693(4)	4.9
C(3)	0.1281(6)	0.7115(6)	0.1190(4)	5.5
C(4)	0.2325(7)	0.9287(6)	−0.1219(4)	6.2
H(1)	0.256(5)	0.870(5)	0.111(3)	2.2
H(2)	0.274(6)	0.783(5)	0.028(3)	3.7

a) $B_{eq}=(4/3)\sum_i B_{ii} a_i^2$.

AcAz (1.0 mL, 5.26 mmol) in an ampule at about 20 °C. After 1 d, an adduct of TFAcAz with methanol was isolated as colorless needles by using a gas chromatograph with a diethyleneglycol succinate (DEGS, Gasukuro Kogyo Inc.) column. Mp 25.1—25.5 °C. IR (KBr) 1138 (C–F), 1275 (C–F), 1325 (C–F), 1630 cm^{-1} (C=N). Raman 1135 (C–F), 1277 (C–F), 1620 cm^{-1} (C=N). ^1H NMR ($CDCl_3$, 270 MHz) δ=3.50 (s, 3H, CH_3O), 4.92 (m, 1H, CHN), 6.40 (d, 1H, J=7.5 Hz, NH), 7.00 (q, 1H, J=4.2 Hz, CH=N). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ=57.3 (s, CH_3O), 88.6 (q, J=33.6 Hz, CHN), 120.4 (q, J=269.8 Hz, CF_3), 122.1 (q, J=282.0 Hz, CF_3), 126.5 (q, J=39.7 Hz, CH=N). ^{19}F NMR ($CDCl_3$, 84.5 MHz) δ=−80.7 (d, J=4.9 Hz, CF_3), −64.8 (d, J=4.3 Hz, CF_3). Found: C, 26.56; H, 2.80; N, 12.94%. Calcd for $C_5F_6H_6N_2O$: C, 26.80; H, 2.70; N, 12.50%. Found: M^+, m/z 224. Calcd for $C_5F_6H_6N_2O$: M, 224.

Preparations of an Adduct of TFAcAz with Water. Water (1.0 mL, 55.5 mmol) was added to TFAcAz (1.0 mL, 5.26 mmol) in an ampule at about 20 °C. After 1 d, colorless needles were deposited and separated from the solution by decantation. After recrystallization from diethyl ether–chloroform, an adduct of TFAcAz with H_2O was obtained as sublimable colorless needles. Mp 98.0—99.0 °C (in a sealed tube). IR (KBr) 1140 (C–F), 1278 (C–F), 1625 cm^{-1} (C=N). Raman 1040 (C–F), 1280 (C–F), 1630 cm^{-1} (C=N). ^1H NMR (DMSO-d_6, 270 MHz) δ=5.22 (m, 1H, CHN), 7.21 (q, 1H, J=5.0 Hz, CH=N), 7.40 (d, 1H, J=5.8 Hz, NH), 9.20 (d, 1H, J=8.3 Hz, OH). ^{13}C NMR (DMSO-d_6, 67.9 MHz) δ=80.1 (q, J=32.9 Hz, CHN), 121.4 (q, J=278.3 Hz, CF_3), 123.2 (q, J=283.2 Hz, CF_3), 123.7 (q, J=36.6 Hz, CH=N). ^{19}F NMR (DMSO-d_6, 84.5 MHz) δ=−80.0 (d, J=5.6 Hz, CF_3), −64.8 (d, J=4.6 Hz, CF_3). Found: M^+, m/z 210. Calcd for $C_4F_6H_4N_2O$: M, 210.

Measurements. The infrared spectra were recorded on a JASCO FT/IR-3 spectrometer. Raman spectra were obtained on a JASCO R-800 spectrometer by using an argon-laser 5145 Å excitation line. A frequency calibration of the spectra was carried out with the natural emission of a neon lamp from 0 to 2000 cm^{-1}. ^1H NMR spectra were analyzed on a JEOL JNM-FX90Q at 90 MHz under a neat condition. ^1H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270. ^{19}F NMR spectra were measured on a JEOL JNM-GX500 or a JEOL JNM-90Q as a $CDCl_3$ or DMSO-d_6 solution. A GPC analysis was performed in THF with a TOSOH CO-8011 system by using TSK gel. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. Mass spectra were recorded on a JEOL JMS SX-102 mass spectrometer by the electron-impact (EI) method. The mass number was calibrated by using cesium iodide (CsI). The absorption spectrum of TFAcAz was obtained on a Shimadzu UV-2100 spectrometer in cyclohexane at 20 °C.

Results and Discussion

Characterization of TFAcAz. TFAcAz was prepared from trifluoroacetaldehyde hydrate and hydrazine monohydrate, and purified by successive distillations as a pale-yellow liquid (λ_{max}=209 (ε=4.1×10^3) and 226 nm (ε=1.4×10^3)). [15] TFAcAz freezes at a relatively high temperature (mp −4 to −6 °C). Although the molecular weight of TFAcAz (MW=192) is larger than that of acetaldehyde azine (CH_3CH=N–N=$CHCH_3$, AcAz, MW=84), TFAcAz is much more volatile (bp 54—56 °C) than AcAz (bp 98—100 °C), suggesting that the substitution with fluorine atoms reduces the intermolecular interactions.

Since there is no paper concerning the synthesis of TFAcAz, TFAcAz was characterized by means of elemental analysis and ^1H, ^{13}C, and ^{19}F NMR, IR, Raman, and EI-mass spectroscopies. The C, H, and N contents of TFAcAz (C, 24.53; H, 1.07; N, 14.39%) were consistent with the calculated values (C, 25.01; H, 1.05; N, 14.59; F, 59.35%). The EI-mass spectrum of TFAcAz showed a protonated molecular ion peak at m/z=193. Only one signal was observed at 7.56 ppm, which split into a quartet (J=3.7 Hz) due to coupling with three fluorine nuclei of a trifluoromethyl group in the ^1H NMR spectrum of TFAcAz. In the ^{13}C NMR spectrum of TFAcAz (Fig. 3, upper), two kinds of quartets are observed at 119 (J=273.4 Hz) and 147 ppm (J=39.1 Hz). The former is assignable to the carbon of the trifluoromethyl group; the latter is assignable to the carbon atom of the azine bond bound to the trifluoromethyl group.[27] In the ^{19}F NMR spectrum of TFAcAz we can observe only one signal due to the fluorine of trifluoromethyl group at −70.2 ppm,[27] which is split into a doublet (J=3.7 Hz) due to coupling with one proton. Although the absorption band assignable to the stretching vibration of the C=N double bond is not observed in the IR spectrum of TFAcAz, it is clearly observed at 1640 cm^{-1} in the Raman spectrum. Since the stretching vibration of the C=N double bond is IR-inactive and Raman-active, the TFAcAz molecule is considered to have exclusively an s-trans structure.[28]

Polymerizability of TFAcAz. Since TFAcAz is a new monomer, polymerizations of TFAcAz with various types of initiators have been carried out to study the polymerizability of TFAcAz. The results are shown in Table 3. No polymer was obtained by radical and cationic initiators, such as AIBN and $AlCl_3$. When a catalytic amount of n-BuLi, CH_3MgI, CH_3OK/18-crown-6, or DBU was added to TFAcAz under an argon atmosphere, only oligomers ($\overline{M}_w \approx$1200—1800) were obtained. However, when Et_3N was added to TFAcAz in a frozen state (at −20 °C), poly (TFAcAz) was obtained as a pale-yellow powder, whose structure was previously reported.[15] However, when catalytic amounts of amines, such as Et_3N, n-Bu_3N, and n-Dec_3N, were added to TFAcAz at room temperature (20 °C), a crystalline product was selectively formed. No reaction occurred with pyridine, which is a weaker base than Et_3N. When catalytic amounts of acids, such as acetic acid and trifluoroacetic acid, were added to TFAcAz, no change was detected by means of gas chromatography. No polymer was obtained by methanol or water. However, TFAcAz quantitatively reacted with a small excess of methanol or with water to form a colorless crystalline product, whose structure is mentioned later.

Table 3. Reactions and Polymerizations of TFAcAz

Reagent (mol %)	Temperature/°C	Time/h	Conversion[a)]/%	Product
				Oligomers
n-BuLi (0.57)	−20	30	42[b)]	$\overline{M}_w \approx 1800$[b)]
CH_3MgI (0.57)	−20	30	23[b)]	$\overline{M}_w \approx 1300$[b)]
CH_3OK/18-crown-6 (1.0)	−20	30	49[b)]	$\overline{M}_w \approx 1800$[b)]
DBU (9.1)	−20	48	81[b)]	$\overline{M}_w \approx 1200$[b)]
Et_3N (2.4)	−20	72	59[c)]	An insoluble polymer
Et_3N (5)	20	18	60	A pale yellow crystal Mp 26.8—27.1°C
Et_3N (33)	20	6	88	
n-Bu_3N (5)	20	48	41	
n-Dec_3N (5)	20	168	25	
Pyridine (9.1)	−20	72	0[d)]	—
CH_3COOH (5)	20	10	0	—
CF_3COOH (5)	20	10	0	—
				Colorless crystals
H_2O (66)	20	200	ca. 100	Mp 98.0—99.0 °C
CH_3OH (66)	20	200	99.9	Mp 25.1—25.5 °C

a) By GC. b) By GPC. c) Acetone insoluble fraction. d) By NMR.

Chemical Reactions of TFAcAz. a) Reactions of TFAcAz with Et_3N: As shown above, TFAcAz was polymerized with Et_3N in a frozen state to form a crystalline 1,2-polymer. When the reaction of TFAcAz with Et_3N was carried out at room temperature (20 °C), no polymerization took place, and a crystalline compound was formed.

When a catalytic amount of Et_3N was added to TFAcAz at 20 °C, the reaction mixture gradually changed from pale-yellow to red-orange. The reaction was followed by ^1H NMR spectroscopy. The results are shown in Fig. 1. The spectra show that the signal of the product increases and that of TFAcAz decreases with an elapse of time, suggesting that TFAcAz selectively converts to the product. Furthermore, there is no change in the signals of Et_3N during the reaction, suggesting that Et_3N is just a catalyst for the reaction. The reaction was also followed by gas chromatography. Figure 2 shows that most of the TFAcAz converts to the product.

The product was isolated as pale-yellow crystals by preparative gas chromatography; the structure of the crystalline product was studied in detail by means of elemental analysis and EI-mass, IR, Raman, and ^1H, ^{19}F, and ^{13}C NMR spectroscopies.

The C, H, and N contents of the product shown in the Experimental Section are consistent with those of TFAcAz, indicating that the product is an oligomer (dimer, trimer, and so on) of TFAcAz. The EI-mass

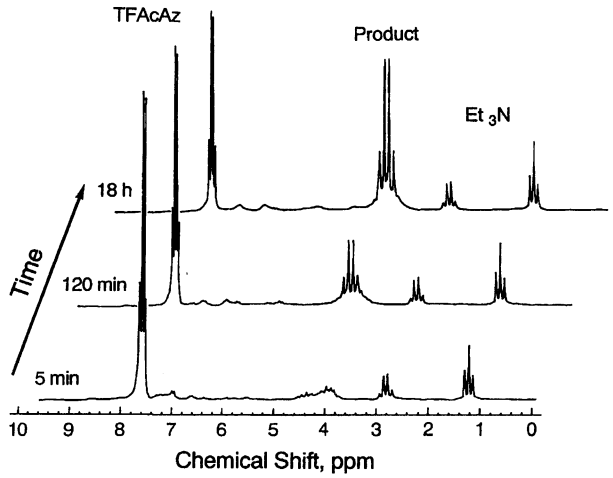


Fig. 1. 90 MHz ^1H NMR spectra of TFAcAz–Et_3N (neat, molar ratio TFAcAz : Et_3N=20 : 1).

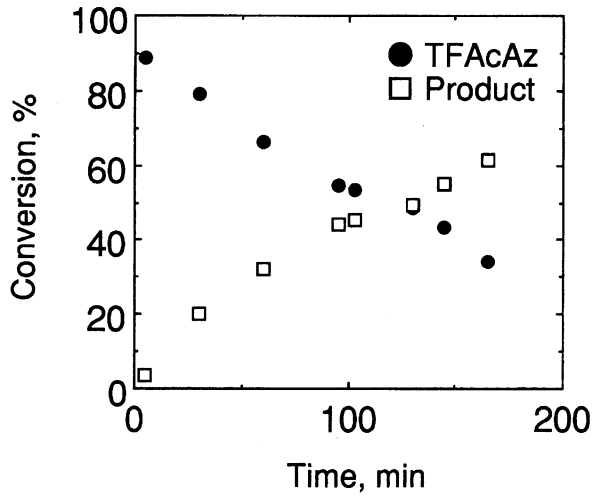


Fig. 2. Time conversion of the reaction of TFAcAz with Et_3N (neat, molar ratio TFAcAz : Et_3N=20 : 1).

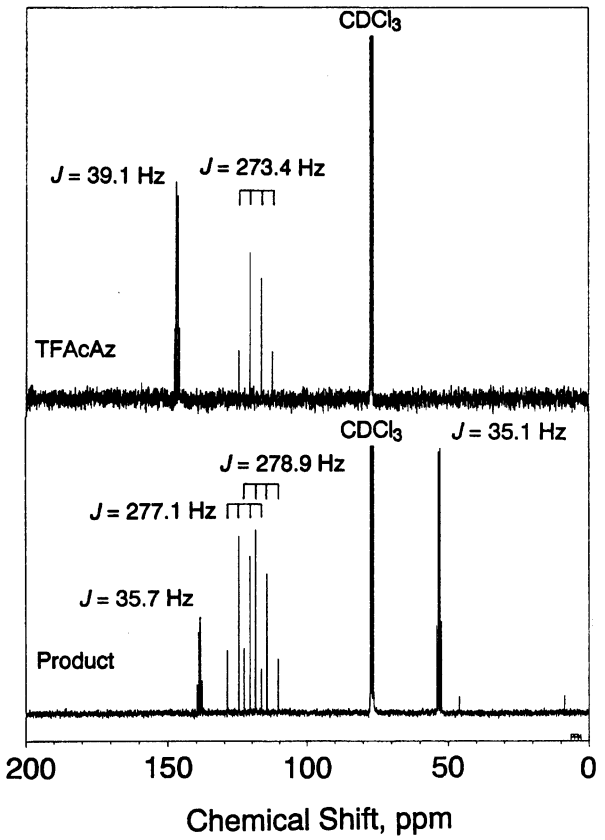


Fig. 3. 67.9 MHz ^{13}C NMR spectra of TFAcAz and the product.

spectrum of the product showed a peak at m/z=384 as a molecular ion peak (see the Experimental Section). On the basis of these data, we can conclude that the crystalline product is a dimer of TFAcAz.

In the ^{1}H NMR spectrum of the product, only one quartet signal (J=8.1 Hz) is observed at 4.04 ppm, whose coupling constant of the signal is larger than that of TFAcAz (J=3.7 Hz). These results show that the carbon bound to the hydrogen in TFAcAz changes to sp^3-carbon in the product.[27]

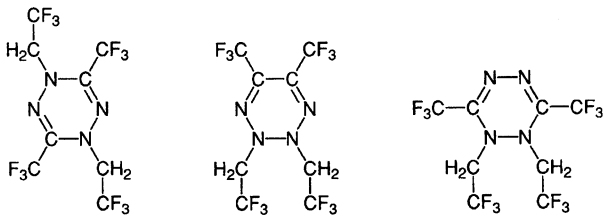
In the ^{19}F NMR spectrum of the product, singlet and triplet signals are observed at −65.5 and at −72.2 ppm, respectively. The triplet signal is due to coupling with two protons. A long-range coupling of the trifluoromethyl group is observed in each signal. These results show that the product has two kinds of trifluoromethyl groups that bind the carbon containing no hydrogen and a methylene group, respectively.

The ^{13}C NMR spectra of TFAcAz and the product are shown in Fig. 3. In the spectrum of the product, four kinds of signals are observed. Two of them, at 117 and 123 ppm (J=277.1 and 278.9 Hz, respectively), are ascribed to the carbons of the trifluoromethyl groups. The other two, at 53 and 139 ppm (J=35.1 and 35.7 Hz, respectively), are due to the carbons bound to the trifluoromethyl groups. From the data shown above we can conclude that the product has two kinds of trifluoromethyl groups and two kinds of carbons bound to the trifluoromethyl group. Furthermore, we can also conclude that the resonance bands observed at 53 and 139 ppm can be assigned to a single bond and a double bond, respectively.[29]

In the IR and Raman spectra of the product, the bands due to the stretching vibration of the C=N double bond are clearly observed at 1633 and 1680 cm^{-1}, respectively. These results show that the product has a C=N double bond. In the Raman spectra, the band due to the C=N double bond shifts to a higher wavenumber in the product. Therefore, the C=N double bond in the product is considered to be no longer conjugated, or to suffer stress.[30] Furthermore, the IR and Raman spectra show no band at around 1550 cm^{-1}, indicating that the product has no N=N double bond.[30]

These spectroscopic data show that the product comprises two units, CF_3CH_2N– and CF_3C=N–. Since the product is a dimer, the three structures shown in Scheme 1 are considered to be the structure of the product.

In order to confirm the structure of the product, an X-ray crystallographic analysis was performed (Tables 1 and 2). The result is shown in Fig. 4. It is consistent with the structure **1** (Scheme 1). The result shows that the reaction of TFAcAz with Et_3N at 20 °C gave the



1 **2** **3**

Scheme 1. Proposed structures of the product.

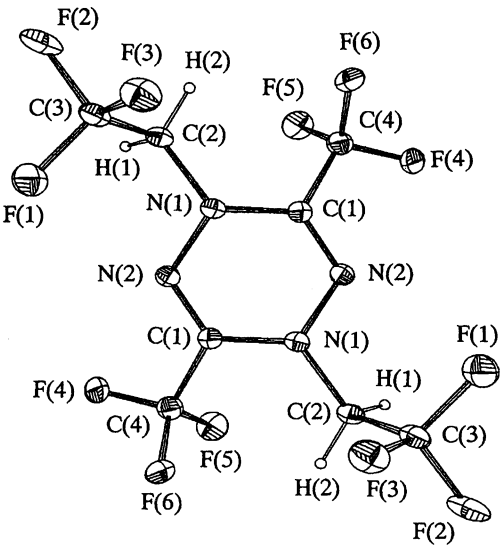
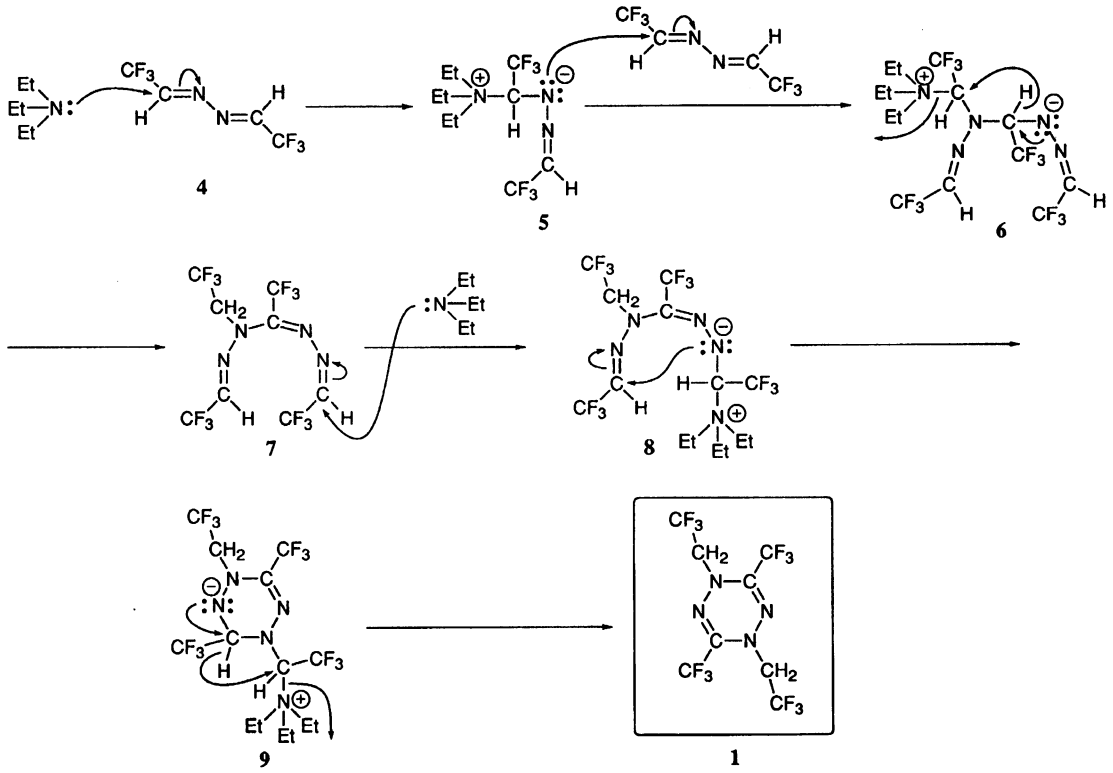


Fig. 4. Molecular structure (ORTEP[31]) of the product.



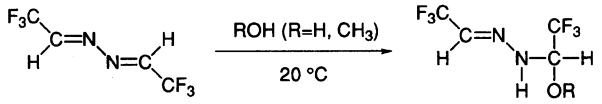
Scheme 2. A proposed mechanism of formation of the cyclic dimer.

1,4-dihydro-1,2,4,5-tetrazine derivatives. Various kinds of syntheses of 1,4-dihydro-1,2,4,5-tetrazine derivatives have been reported so far.[32,33] However, to our knowledge, the formation of a 1,4-dihydro-1,2,4,5-tetrazine ring from azine compounds has never been reported so far.

A tentatively proposed mechanism is shown in Scheme 2. Et_3N attacks the carbon of the C=N double bond of TFAcAz to form a zwitter ion (step **4** to **5**), whose anion attacks another TFAcAz molecule to form a 1,2-dimer (step **5** to **6**). A conjugated double bond is reformed by the hydride shift to the carbon bound to the ammonium ion. Then Et_3N comes off (step **6** to **7**). Et_3N attacks the obtained conjugated C=N double bond to form a ring through an intramolecular 1,2-addition (step **7** to **8**). After the 1,3-hydride shift and elimination of the Et_3N, a cyclic dimer is formed (step **9** to **1**).

b) Reactions of TFAcAz with Protic Compounds: The reactions of TFAcAz with protic compounds were also performed in order to investigate the chemical reactivity of TFAcAz.

When a small excess of methanol was added to TFAcAz, a certain product was quantitatively formed (Table 3). This product was isolated as colorless needles by preparative gas chromatography. The structure of the product was investigated by means of ^1H, ^{13}C, and ^{19}F NMR, IR, Raman, and EI-mass spectroscopies and elemental analysis. The EI-mass spectrum of the product shows the peak at $m/z=224$ as being a molecular ion peak, suggesting that the product is an adduct of TFAcAz (MW=192) with methanol (MW=32). An elemental analysis of the product also indicates that the product is an adduct of TFAcAz with methanol. The IR and Raman spectra of the product show signals due to the stretching vibration of the C=N double bond at 1630 and 1620 cm^{-1}, respectively. These results reveal that the product has a C=N double bond, suggesting that the product is formed through a 1,2-addition of methanol to TFAcAz. The ^1H, ^{13}C, and ^{19}F NMR spectra also support the idea that the product is formed through a 1,2-addition. We can thus conclude that the product is the 1,2-adduct shown in Scheme 3.



Scheme 3. Reactions of TFAcAz with protic compounds.

Similarly, the formation of a 1,2-adduct with water was confirmed by ^1H, ^{13}C, and ^{19}F NMR, IR, Raman and EI-mass spectroscopies (Scheme 3).

These results suggest that it is easy for TFAcAz to be attacked by nucleophiles, and that TFAcAz is more subject to a 1,2-addition than to a 1,4-addition. The suggestion that TFAcAz is subject to a 1,2-addition is consistent with the formation of the 1,2-polymer and with the proposed mechanism for the formation of a cyclic dimer.

Conclusion. TFAcAz was prepared and its chemi-

cal reactivity was investigated. Consequently, we found that TFAcAz easily reacts with nucleophiles, such as Et_3N, methanol, and water. The reactions of TFAcAz with Et_3N produced a cyclic dimer containing a 1,4-dihydro-1,2,4,5-tetrazine ring; that with methanol and water gave 1,2-adducts.

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