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Syntheses of Azobenzene Derivatives Having Fluoroalkyl Chain and Their Monomolecular Film Formation at the Air/Water Interface

Norio Yoshino,* Mitsuharu Kitamura, Tsuyoshi Seto, Yasuhiro Shibata,[†]
Masahiko Abe,*,[†] and Keizo Ogino[†]
Department of Industrial Chemistry, Faculty of Engineering,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
[†]Department of Industrial Chemistry, Faculty of Science and Technology,
Science University of Tokyo, Yamazaki, Noda-shi, Chiba 278

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The compounds, 4-(nonafluorobutyl)aniline, 4-(tridecafluorohexyl)aniline, and 4-(heptadecafluorooctyl)-aniline were prepared by the reaction of corresponding perfluoroalkyl iodide with 4-iodoaniline in the presence of copper bronze. Six azobenzene derivatives (4-(4-fluorophenylazo)phenol, $F(C_6H_4)N=N(C_6H_4)OH$ (**1**) (C_6H_4=*p*-phenylene), 4-(4-trifluoromethylphenylazo)phenol, $CF_3(C_6H_4)N=N(C_6H_4)OH$ (**2**), 4-(4-heptafluoropropylphenylazo)phenol, $C_3F_7(C_6H_4)N=N(C_6H_4)OH$ (**3**), 4-(4-nonafluorobutylphenylazo)phenol, $C_4F_9(C_6H_4)N=N(C_6H_4)OH$ (**4**), 4-(4-tridecafluorohexylphenylazo)phenol, $C_6F_{13}(C_6H_4)N=N(C_6H_4)OH$ (**5**), and 4-(4-heptadecafluorooctylphenylazo)phenol, $C_8F_{17}(C_6H_4)N=N(C_6H_4)OH$ (**6**)) were prepared by the usual diazo coupling reactions using 4-(perfluoroalkyl)aniline and phenol. The monomolecular film formations of the azobenzene derivatives at the air/water interface were investigated by surface pressure measurements to be dependent on the fluoroalkyl chain length (n). The compounds **5** (n=6) and **6** (n=8) formed stable monomolecular films at the air/water interface.

A lot of fluorocarbon compounds exhibit the properties of water and oil repellency, high lubricity, thermal and chemical stability, and so on. The material surface modified with a compound having fluorocarbon chain is protected from chemical and physical pollutions.

On the other hand, the azobenzene compounds containing long hydrocarbon chain have been reported in the viewpoint of the photoisomerism,[1,2] photo-induced potential change,[3] photo-induced ionic-conductivity switching,[4] film structure,[5] and photon mode information storage.[6,7] It is well known that a normal fluoroalkyl group forms a hard and straight chain, but the interaction between the groups is very weak. The formation of the condenced films of azobenzene compounds populating small area per molecule was expected by introducing a fluorocarbon chain into azobenzene derivatives. Therefore, the fluoroalkyl groups in the azobenzene compounds would also have a property of weak interaction. It is interested to investigate the photoisomerism of the films because fluorocarbon chain may have higher mobility, although a difficulty of condenced monomolecular film formation of amphipathic compounds having fluorocarbon chain has been reported in the literature.[8]

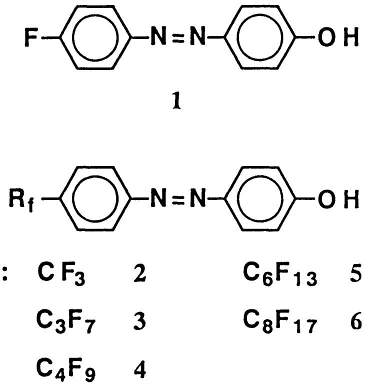

Fig. 1. Molecular formula of compounds **1**—**6**.

In this paper, we report the syntheses of azobenzene compounds with fluoroalkyl group of various chain length, and their monomolecular film formations at the air/water interface by surface pressure measurements. To prepare the new series of azobenzene derivatives having fluorocarbon chain, we prepared 4-(perfluoroalkyl)anilines having comparatively long fluorocarbon chain by using the methods of Kobayashi[9] and McLoughlin.[10] The compounds shown in Fig. 1 were used for monomolecular film formation study.

Experimental

Materials. Nonafluorobutyl iodide, C_4F_9I (bp 67 °C), tridecafluorohexyl iodide, $C_6F_{13}I$ (bp 119 °C), and heptadecafluorooctyl iodide, $C_8F_{17}I$ (bp 95 °C/13700 Pa) were purchased from Japan Halon Co., Ltd. and purified by distillation. Phenol (bp 181 °C), 4-fluoroaniline (bp 43 °C/400 Pa) and 4-(trifluoromethyl)aniline (bp 57.5 °C/400 Pa) were commercially available (Tokyo Kasei Kogyo Co., Ltd) and purified by distillation. They were checked by GLC not to show detectable impurities. 4-(Heptafluoropropyl)acetanilide (mp 126 °C) was donated from Nippon Oil & Fats Co., Ltd. This was prepared by the reaction of bis(heptafluorobutanoyl) peroxide, $(C_3F_7COO)_2$, with acetanilide, and isolated by column chromatography on silica gel. 4-Iodoaniline, sodium nitrite (Tokyo Kasei Kogyo Co., Ltd) and copper bronze (Aldrich Chemical Co., Inc.) were used without further purification. The solvents (dimethyl sulfoxide (DMSO) and diethyl ether) were purified by the usual methods.

Measurements and Instruments. FT-IR spectra were measured in a liquid film or by a KBr method with a JEOL JIR-5300 spectrophotometer. Each spectrum was recorded at a resolution of 4 cm^{-1} with a total of 30 scans. UV spectra were taken on a Hitachi U-3210 spectrophotometer. Pulsed Fourier Transform 100-MHz ^{1}H NMR was run in acetone-d_6 with TMS as an internal standard using a JEOL JNR-PX-100 spectrometer at room temperature. The FT mode 90-MHz ^{19}F NMR was recorded at 27 °C on a JEOL JNM-FX-90Q in acetone-d_6 with fluorobenzene (−113.6 ppm[11] from $CFCl_3$ in $CDCl_3$) as an external standard. The ^{19}F NMR spectra were assigned by the aid of the data book.[11] Gas chromatography (GLC) was performed with a Hitachi 663-30 (G-100 40 m column, film thickness 2.0×10^{-6} m, I.D. 1.2 mm, FID) and the intensities were measured with a Hitachi D-2500 chromato integrator. Mass spectra were measured (70 eV) with a Hitachi M-80A GC-MS spectrometer and the data were with a Hitachi M-003 data processing system. Surface pressures of monomolecular films of azobenzene compounds at the air/water interface were measured by a Wilhelmy type surface pressure meter (HBM-A type of Kyowa Interface Science Co., Ltd.) with a glass plate. The spreading solvent for surface pressure measurements was benzene (>99% pure, Wako Pure Chemical Industries Co., Ltd.). Water used in this experiment was twice distilled and deionized by an ion-exchange instrument (NANO pure D-1791 of Barnstead Co., Ltd.); its resistivity was about 18.0 MΩ cm and its pH was 6.7.

Syntheses of 4-(Perfluoroalkyl)anilines. Synthesis of 4-(Nonafluorobutyl)aniline: The dispersions of nonafluorobutyl iodide (52.7 g, 152.2 mmol), 4-iodoaniline (30.0 g, 137.0 mmol), and copper bronze (29.0 g, 456.4 mmol) in 150 cm^3 DMSO were heated with stirring for 10 h at 120 °C in a two-necked 500-ml flask connected with a reflux condenser and a three-way stop cock. The produced copper(I) iodide and excess copper bronze were removed by filtration. To the filtrate was added 100 cm^3 water and 100 cm^3 diethyl ether. After the mixture was stirred for 5 min, the ether layer was separated. The ether layer was washed five times with 100 cm^3 water to remove DMSO and nonafluorobutyl iodide, and evaporated under reduced pressure. 4-(Nonafluorobutyl)aniline (41.1 g, yield 96.6%, bp 74—76 °C/200 Pa) was obtained as a colorless liquid by distillation. IR 3496w, 3406m, 3226w, 3051w, 1630s, 1610s, 1524s, 1352s, 1300s, 1273s, 1238vs, 1132s, 1088s, 1001m, 870s, 847s, 833s, 802s, 742s, 690s, 652m, 590m, 532m, and 517m cm^{-1}; MS *m/z* (rel intensity) 311 (14; M$^+$), 292 (4; M$^+$−F), 173 (4; M$^+$−C_3F_5, −F), and 142(100; M$^+$−C_3F_7); ^{1}H NMR δ=3.83 (2H, s, NH_2), 6.64 (2H, d, J=8.4 Hz, *o*-protons from NH_2), and 7.43 (2H, d, J=8.4 Hz, *m*-protons from NH_2); ^{19}F NMR δ=−12.87 (2F, m, b), −10.00 (2F, m, c), 3.37 (2F, t, J=11.9 Hz, d), and 31.31 (3F, t, J=9.2 Hz, a) for $C\overset{a}{F_3}C\overset{b}{F_2}C\overset{c}{F_2}C\overset{d}{F_2}(C_6H_4)NH_2$.

Syntheses of 4-(Tridecafluorohexyl)aniline and 4-(Heptadecafluorooctyl)aniline: The procedures and purification techniques were almost the same as those for the preparation of 4-(nonafluorobutyl)aniline.

4-(Tridecafluorohexyl)aniline was a colorless liquid (yield 98.5%, bp 76—78 °C/200 Pa, mp 23.5—24.5 °C): IR 3496w, 3408m, 3226w, 3051w, 1630s, 1610s, 1524m, 1441w, 1363m, 1292m, 1240vs, 1203vs, 1146vs, 1120s, 1088m, 827m, 802m, 787m, 744m, 692m, and 513m cm^{-1}; MS *m/z* 411 (10; M$^+$), 392 (45; M$^+$−F), 173 (3; M$^+$−C_4F_9, −F), and 142 (100; M$^+$−C_5F_{11}); ^{1}H NMR δ=3.88 (2H, s, NH_2), 6.70 (2H, d, J=9.0 Hz, *o*-protons from NH_2), and 7.40 (2H, d, J=9.0 Hz, *m*-protons from NH_2); ^{19}F NMR δ=−13.22 (2F, m, b), −9.76(2F, m, c), −8.99 (4F, m, d and e), 3.67 (2F, t, J=13.8 Hz, f), and 31.89 (3F, t, J=9.2 Hz, a) for $C\overset{a}{F_3}C\overset{b}{F_2}C\overset{c}{F_2}C\overset{d}{F_2}C\overset{e}{F_2}C\overset{f}{F_2}(C_6H_4)$-$NH_2$.

4-(Heptadecafluorooctyl)aniline was a colorless solid (yield 90.0%, bp 86—88 °C/200 Pa, mp 42—43 °C): IR 3489m, 3390m, 1624s, 1522m, 1439w, 1371m, 1298s, 1211vs, 1149vs, 1117vs, 1090m, 847m, 843m, 802m, 661m, 563m, 561m, 559m, and 515m cm^{-1}; MS *m/z* 511 (52; M$^+$), 492 (35; M$^+$−F), 173 (16; M$^+$−C_6F_{13}, −F), and 142 (100; M$^+$−C_7F_{15}); ^{1}H NMR δ=3.83 (2H, s, NH_2), 6.63 (2H, d, J=8.4 Hz, *o*-protons from NH_2), and 7.31 (2H, d, J=8.4 Hz, *m*-protons from NH_2); ^{19}F NMR δ=−12.65 (2F, m, b), −9.15 (2F, m, c), −8.35 (8F, m, d-g), 4.15 (2F, t, J=13.8 Hz, h), and 32.59 (3F, t, J=9.2 Hz, a) for $C\overset{a}{F_3}C\overset{b}{F_2}C\overset{c}{F_2}C\overset{d}{F_2}C\overset{e}{F_2}C\overset{f}{F_2}C\overset{g}{F_2}C\overset{h}{F_2}(C_6H_4)NH_2$.

Syntheses of Azobenzene Compounds. Synthesis of 4-(4-Fluorophenylazo)phenol (1): To an ice-cooled solution of 4-fluoroaniline (3.82 g, 34.4 mmol) in 50 cm^3 2 M (M=1 mol dm^{-3}) hydrochloric acid, an aqueous solution of sodium nitrite (2.61 g, 37.8 mmol in 10 cm^3 water) was added with stirring. The solution changed to a white emulsion. The coupling reaction was accomplished by slowly adding an aqueous solution of sodium phenoxide (phenol (3.56 g, 37.8 mmol) in 50 cm^3 1 M aqueous solution of sodium hydroxide). The color of the emulsion changed to yellow. After the reaction mixture was neutralized with an aqueous solution of sodium hydrogencarbonate, the crude product was obtained by filtration. The pure product (6.82 g, yield 91.7%) was obtained by recrystallization from water-methanol solution (water : methanol=1 : 1). IR 3456w, 3240m, 3232m, 3197m, 3034w, 2972w, 1591vs, 1504m, 1477m, 1444m, 1325vs, 1252s, 1142vs, 1103s, 1065vs, 856s, 852s, and 544m cm^{-1}; UV λ_{max} (MeOH) 347 nm; MS *m/z* 216 (55; M$^+$), 123(21; M$^+$−$(C_6H_4)OH$), 121 (35; M$^+$−$(C_6H_4)F$), 95 (94; M$^+$−N=N-$(C_6H_4)OH$), and 93 (100; M$^+$−N=N$(C_6H_4)F$); ^{1}H NMR δ=6.51 (1H, b, OH), 6.96 (2H, d, J=9.0 Hz, *o*-protons from OH), and 7.73—7.88 (6H, another phenylene protons); ^{19}F NMR δ=0.54 (m).

Syntheses of 4-(4-Perfluoroalkylphenylazo)phenols. The procedures and purification techniques were almost the same as those for the preparation of 4-(4-fluorophenylazo)phenol.

4-(4-Trifluoromethylphenylazo)phenol (2): From the reaction of 4-(trifluoromethyl)aniline (3.40 g, 21.1 mmol), sodium nitrite (1.60 g, 23.2 mmol) and phenol (2.19 g, 23.3 mmol), the compound **2** was obtained as a yellow powder (5.26 g, yield 93.6%). IR 3304m, 2966w, 2927w, 1591m, 1502m, 1329vs, 1169m, 1142m, 1122m, 1066s, 850m, and 597w cm^{-1}; UV λ_{max} (MeOH) 348 nm; MS *m/z* 266 (26; M$^+$), 247 (6; M$^+$−F), 145 (34; M$^+$−N=N$(C_6H_4)OH$), 121 (35; M$^+$−$(C_6H_4)CF_3$), and 93 (100; M$^+$−N=N$(C_6H_4)CF_3$); ^{1}H NMR δ=5.87 (1H, b, OH), 7.07 (2H, d, J=9.0 Hz, *o*-protons from OH), and 7.82—8.16 (6H, another phenylene protons); ^{19}F NMR δ=49.92 (m).

4-(4-Heptafluoropropylphenylazo)phenol (3): Only for this case, 4-(heptafluoropropyl)acetanilide was used as the starting material. From the reaction of 4-(heptafluoropropyl)aniline hydrochloride (prepared from 4-(heptafluoropropyl)acetanilide (2.70 g, 8.91 mmol) with hydrochloric acid (2M, 50 cm^3) at 90 °C for 5 h, it was not isolated), sodium nitrite (0.68 g, 9.86 mmol) and phenol (0.92 g, 9.78 mmol), the compound **3** was obtained as a yellow powder (2.66 g, yield 81.5%). IR 3433s, 2927w, 1597s, 1502m, 1359w, 1223vs, 1173m, 1138s, 1076m, 1043w, 904w, 872w, 746w, and 546 cm^{-1}; UV λ_{max} (MeOH) 351 nm; MS *m/z* 366 (15; M$^+$), 347 (3; M$^+$−F), 261 (27; M$^+$−CF_3, −F, −OH), 245(13; M$^+$−N=N$(C_6H_4)OH$), 121 (47; $\mathrm{M^+{-}(C_6H_4)C_3F_7}$), and 93 (100; $\mathrm{M^+{-}N{=}N(C_6H_4)C_3F_7}$; ^{1}H NMR δ=9.30 (1H, s,OH), 7.04 (2H, d, J=9.3 Hz, *o*-protons from OH), and 7.86—8.40 (6H, another phenylene protons); ^{19}F NMR δ=−3.41 (2F, m, c), 0.04 (2F, m, b), and 30.37 (3F, m, a) for $\mathrm{CF_3^aCF_2^bCF_2^c(C_6H_4)N{=}N(C_6H_4)OH}$.

4-(4-Nonafluorobutylphenylazo)phenol (4): From the reaction of 4-(nonafluorobutyl)aniline (5.10 g, 16.4 mmol) with sodium nitrite (1.16 g, 16.8 mmol) and phenol (1.58 g, 16.8 mmol), the compound **4** was obtained as a yellow powder (5.52 g, yield 80.9 %). IR 3421m, 1593m, 1560m, 1354m, 1269s, 1230vs, 1203s, 1198s, 1136vs, 1101m, 1093m, 864m, 841m, 816m, 748m, 692m, 675w, and 584w cm^{-1}; UV $\lambda_{\max}$ (MeOH) 356 nm; MS *m*/*z* 416 (17; M$^+$), 397 (4; M$^+$−F), 295 (4; $\mathrm{M^+{-}N{=}N(C_6H_4)OH}$), 176 (5; $\mathrm{M^+{-}(C_6H_4)N{=}N(C_6H_4)OH, {-}C_2F_5}$), 121 (44; $\mathrm{M^+ {-}(C_6H_4)C_4F_9}$), and 93 (100; $\mathrm{M^+ {-}N{=}N\text{-}(C_6H_4)C_4F_9}$); ^{1}H NMR δ=9.18 (1H, s, OH), 6.95 (2H, d, J=9.3 Hz, *o*-protons from OH), and 7.65—8.10 (6H, another phenylene protons); ^{19}F NMR δ=−13.39 (2F, m, b), −10.44 (2F, m, c), 1.83 (2F, t, J=12.8 Hz, d), and 30.87 (3F, t, J=9.17 Hz, a) for $\mathrm{CF_3^aCF_2^bCF_2^cCF_2^d(C_6H_4)N{=}N(C_6H_4)OH}$.

4-(4-Tridecafluorohexylphenylazo)phenol (5): From the reaction of 4-(tridecafluorohexyl)aniline (3.04 g, 7.40 mmol) with sodium nitrite (0.59 g, 8.60 mmol) and phenol (0.79 g, 8.44 mmol), the compound **5** was obtained as a yellowish brown powder (3.73 g, yield 97.5 %). IR 3433m, 3253w, 1595m, 1506w, 1481m, 1446m, 1365m, 1288m, 1236s, 1198s, 1144vs, 1122m, 1092m, 847m, and 652w cm^{-1}; UV $\lambda_{\max}$ (MeOH) 350 nm; MS *m*/*z* 516 (9; M$^+$), 497 (3; M$^+$−F), 395 (3; $\mathrm{M^+{-}N{=}N(C_6H_4)OH}$), 176(7; $\mathrm{M^+{-}N{=}N(C_6H_4)OH,{-}C_4F_9}$), 126 (7; $\mathrm{M^+{-}N{=}N(C_6H_4)OH,{-}C_5F_{11}}$), 121 (54; $\mathrm{M^+{-}(C_6H_4)\text{-}C_6F_{13}}$), and 93 (100; $\mathrm{M^+{-}N{=}N(C_6H_4)C_6F_{13}}$); ^{1}H NMR δ=9.30 (1H, s, OH), 7.05 (2H, d, J=9.3 Hz, *o*-protons from OH), and 7.70—8.20 (6H, another phenylene protons); ^{19}F NMR δ=−13.87 (2F, m, b), −10.46 (2F, m, c), −9.29(4F, m, e and d), 2.15 (2F, t, J=14.7 Hz, f), and 31.13 (3F, t, J=9.2 Hz, a) for $\mathrm{CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^f(C_6H_4)N{=}N(C_6H_4)OH}$.

4-(4-Heptadecafluorooctylphenylazo)phenol (6): From the reaction of 4-(heptadecafluorooctyl)aniline (3.77 g, 7.38 mmol) with sodium nitrite (0.58 g, 8.45 mmol) and phenol (0.80 g, 8.48 mmol), the compound **6** was obtained as a yellowish brown powder (4.19 g, yield 92.2 %). IR 3421m, 3267sh, 1597m, 1506m, 1371m, 1300m, 1201vs, 1147vs, 1117m, 856m, 854m, 656m, and 561w cm^{-1}; UV $\lambda_{\max}$ (MeOH) 355 nm; MS *m*/*z* 616 (6; M$^+$), 597 (2; M$^+$−F), 495 (2; $\mathrm{M^+{-}N{=}N\text{-}(C_6H_4)OH}$), 176 (4; $\mathrm{M^+{-}N{=}N(C_6H_4)OH,{-}C_6F_{13}}$), 121 (62; $\mathrm{M^+{-}(C_6H_4)C_8F_{17}}$), and 93 (100; $\mathrm{M^+{-}N{=}N(C_6H_4)C_8F_{17}}$); ^{1}H NMR δ=9.24 (1H, s, OH), 7.02 (2H, d, J=9.3 Hz, *o*-protons from OH), and 7.65—8.35 (6H, another phenylene protons); ^{19}F NMR δ=−13.89 (2F, m, b), −10.46 (2F, m, c), −9.29 (8F, m, d, e, f and g), 2.33 (2F, t, J=14.7 Hz, h), and 31.13 (3F, t, J=9.2 Hz, a) for $\mathrm{CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^h\text{-}(C_6H_4)N{=}N(C_6H_4)OH}$.

Measurement of Surface Pressure. The samples were dissolved in benzene at concentrations of about 1.5×10^{-3} M. After spreading the benzene solution on the water using a microsyringe, avoiding surface disturbance, the system was allowed to stand for 10 min. Compression was carried out at a constant rate of 20 mm min^{-1}, compatible with the absorption equilibrium of samples at the air/water interface. It was found that the compounds **3**—**6** formed monomolecular films at the air/water interface, but the compounds **1** and **2** did not form them. Surface pressure (π) is defined by the following equation.

$$\pi=\gamma_{\mathrm{w}}-\gamma_0,$$

where γ_{w} is the surface tension of pure water and γ_0 is the surface tension of solution.

Results and Discussion

Syntheses of Azobenzene Compounds. The diazotization products were obtained in high yield as a yellow to yellowish brown powder, and all of these azobenzene compounds were found to be trans isomer by the UV spectra measurements.

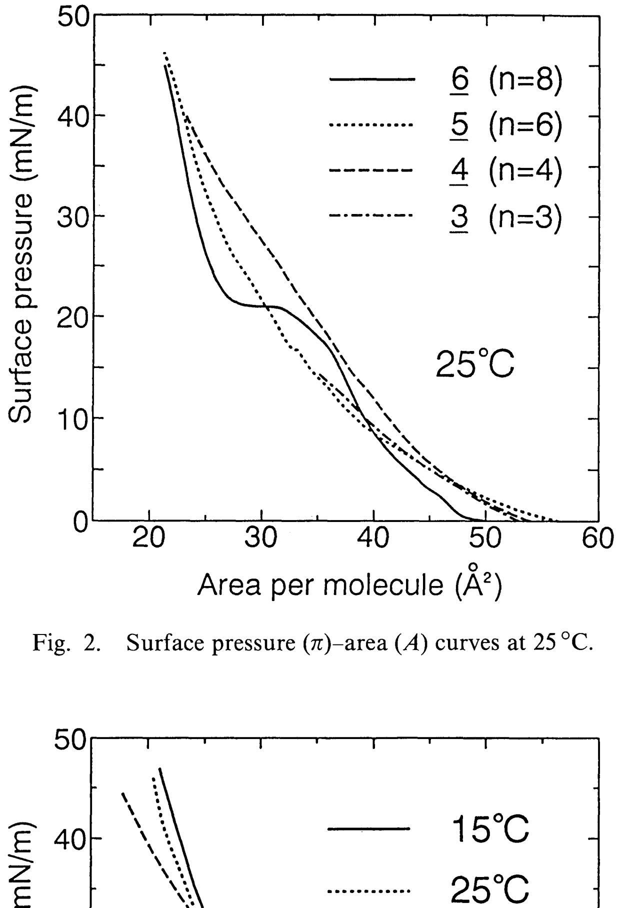

Fig. 2. Surface pressure (π)-area (A) curves at 25 °C.

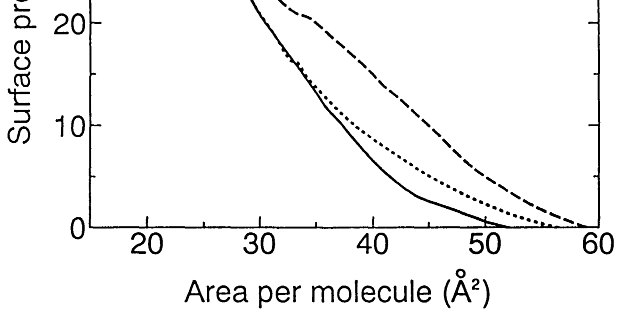

Fig. 3. Temperature dependence of π-A curves for 4-(4-tridecafluorohexylphenylazo)phenol (compounds **5**).

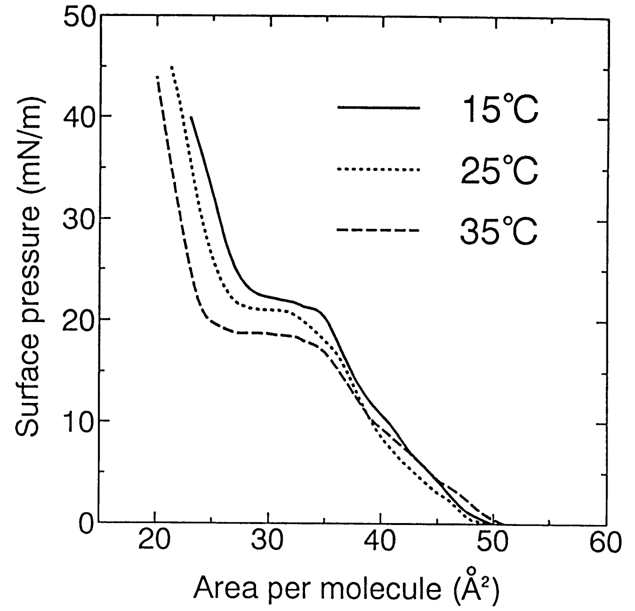

Fig. 4. Temperature dependence of π–A curves for 4-(4-heptadecafluorooctylphenylazo)phenol (compound **6**).

The Monomolecular Films at the Air/Water Interface. Figure 2 shows surface pressure (π)-area (A) curves of azobenzene compounds containing fluoroalkyl chain at 25 °C. As seen in Fig. 2, the compounds **3** (fluoroalkyl chain length n=3), **4** (n=4), **5** (n=6), and **6** (n=8) form monomolecular films at the air/water interface. The compounds **3** and **4** form only expanded films. But the slopes of their π–A curves are constant even in the range of low surface pressure (around 10 mN m^{-1}). Therefore, in the case of the compounds **3** and **4**, they form the monomolecular films at the air/water interface on developing such samples, but when surface pressure increases, the molecules which constitute the monomolecular films are dissolved in water. On the other hand, the compounds **5** and **6** form an expanded film in a lower surface pressure region, and a condensed film in a higher surface pressure region. The transition point for the compound **5** between the two states is indicated to be in the vicinity of 15 mN m^{-1}. In the case of compound **6**, it is clearly recognized at around 20 mN m^{-1}, much more distinctly than in the case of the compound **5**. It is inferred that the compounds **5** and **6** form stable monomolecular films at the air/water interface.

Figures 3 (compound **5**) and 4 (compound **6**) show π–A curves at various temperatures (15, 25, and 35 °C). Although the compound **5** forms an expanded film and a condensed film at 25 and 35 °C, respectively, it forms only a condensed film at 15 °C.

It has been found that the nature of monomolecular films formed by azo-type surfactants (azobenzene compounds) having fluoroalkyl chain at the air/water interface are dependent on the fluoroalkyl chain length acting as a hydrophobic group.

Studies on the photoisomerism of the films are now in progress.

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