were as follows: $^1$H NMR (CDCl$_3$) $\delta$ 3.09 (s, 3 H), 7.24-7.53 (m, 4 H), 8.28-8.36 (m, 4 H); MS analysis 98.9 mol % d$_5$.

**9-Ethyl-10-anthracenecarboxaldehyde.** (9-Ethylanthracenyl)lithium, prepared from 2.86 g (10.0 mmol) of 10-ethyl-9-bromoanthracene and 6.5 mL (13.0 mmol, 1.3 equiv) of 2.0 M phenyllithium in 30 mL cyclohexane-ether, was allowed to react with 10.0 mL (0.13 mol) of dimethylformamide at room temperature for 30 min. Water (30 mL) was added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted with two 25-mL portions of ether, and the combined organic extracts were dried over Na$_2$SO$_4$. The concentrate was recrystallized from petroleum ether to yield 1.27 g (54%) of yellow needles: mp 96-97 °C [lit.[34] mp 96-96.5 °C]; $^1$H NMR (CDCl$_3$) $\delta$ 1.49 (t, 3 H), 3.70 (q, 2 H), 7.4-8.65 (m, 8 H), 11.47 (s, 1 H).

**9-(Hydroxymethyl)-10-ethylanthracene.[33]** 10-Ethyl-9-anthracenecarboxaldehyde (0.590 g, 2.50 mmol) in 25 mL of diethyl ether was treated with 0.12 g (3.1 mmol) LiAlH$_4$ and the mixture refluxed for 1 h. After treatment with 5 mL of ethyl acetate and 20 mL of H$_2$O the organic fraction was separated, chlorobenzene (25 mL) was added and ether was removed at reduced pressure. The product (0.33 g; 56% yield) crystallized from the hot chlorobenzene solution as pale yellow needles, mp 182-183 °C [lit.[35] mp 180-183 °C].

**9-Methylanthrone.[36]** 2-(1-Phenylethyl)benzoic acid, prepared by the reaction of 4.51 g (20.0 mmol) of o-benzoylbenzoic acid with 17 mL (51.0 mmol) of 3.0 M MeMgI in ethyl ether followed by reduction of the product with Zn and alcoholic NH$_3$ (yield 4.20 g; 93%), was stirred in

50 mL of concentrated H$_2$SO$_4$ for 30 min at room temperature. The mixture was poured on ice, and the solid was recrystallized from MeOH-H$_2$O to give 1.40 g (6.73 mmol) of 9-methylanthrone (38% yield) as light yellow needles: mp 63-64 °C [lit.[37] mp 65 °C]; $^1$H NMR (CDCl$_3$) $\delta$ 1.60 (d, 3 H), 4.33 (q, 1 H), 7.45-8.43 (m, 8 H); MS m/e (relative intensity) 208 (100), 207 (9.6), 192 (11.3), 180 (63.3), 152 (53.5), 151 (30.0), 150 (11.7), 76 (19.3), 75 (11.1), 42 (10.4).

**9-Ethylanthrone.[35]** The procedure of Heymann et al. was used. Recrystallization from MeOH-H$_2$O gave the pure anthrone in 31% yield: mp 50-52 °C (lit.[38] mp 50-52 °C); H$^1$ NMR (CDCl$_3$) $\delta$ 0.34 (t, 3 H), 1.96 (m, 2 H), 4.25 (t, 1 H), 7.2-8.5 (m, 8 H).

**9-(1-Hydroxyethyl)-10-methylanthracene.** 10-Methylanthracene-9-carboxaldehyde (2.20 g, 9.32 mmol) was allowed to react with 7.0 mL (0.02 mol) of 3.0 M MeMgI in ethyl ether. The product isolated by ether extraction was recrystallized from petroleum ether-methylene chloride: yield 1.7 g (73%); mp 107-109 °C [lit.[39] mp 108-110 °C]; $^1$H NMR (CCl$_4$) $\delta$ 1.92 (d, 3 H), 2.38 (s, 1 H), 3.13 (s, 3 H), 6.55 (q, 1 H), 7.34-7.67 (m, 4 H), 8.30-8.61 (m, 4 H).

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# High-Pressure $^{19}$F NMR Study of the Degenerate Isomerization of Hexafluoroacetone Anils. Evidence for the Existence of Two Different Inversion Transition States

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**Abstract:** Solvent, temperature, and pressure effects on the rate of the degenerate isomerization of hexafluoroacetone anils were studied by $^{19}$F NMR. The results unequivocally demonstrated that the mechanism is not rotation about the carbon-nitrogen bond even in the presence of a strongly electron-donating substituent in the para position of the phenyl group because the polarity of the reactant did not increase in the activation step. Combined with the substituent effects, the present results can be explained most reasonably by assuming two different conformations for the phenyl group in the inversion transition state, i.e., perpendicular and planar conformations for the electron-attracting and -donating substituents, respectively.

The mechanism of geometrical isomerization about the nitrogen-nitrogen,[3] carbon-nitrogen,[4] and carbon-carbon[5,6] double bond has been actively investigated in recent years in many laboratories. The argument was focused on whether the reaction proceeds by inversion at the nitrogen atom or by rotation about

the nitrogen-nitrogen or the carbon-nitrogen bond. For example, Perrin and Thoburn[7] studied the substituent effects on the E-Z and Z-E isomerization rates of N-arylformamidates (eq 1) and
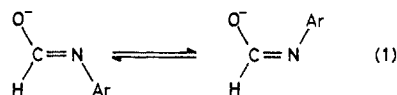


concluded that the reaction proceeds by nitrogen inversion. As can be seen in this recent example, it has been agreed that the inversion mechanism is more common than the rotation mechanism. A number of arguments have been adduced in support of

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this point of view, and they were summarized in a previous paper.[4] Since the average bond energy for C=N and N=N double bond is more than 280 kJ mol⁻¹ higher than that of the corresponding single bond, and all of the observed activation energies are lower than 100 kJ mol⁻¹, rotation following the homolytic $\pi$ bond scission (diradical transition state) is inconceivable. The observation[8-10] of preexponential factors as high as $10^{12}$–$10^{13}$ s⁻¹ precludes the intervention of triplet excited states also. Therefore, if the cleavage of the $\pi$ bond is involved, it is almost certainly heterolytic. In other words, if the mechanism is rotation, the transition state must be stabilized by the substituents via dipolar resonance structures, and we must observe a large solvent-polarity- and pressure-induced acceleration. However, if the mechanism is inversion, both of these effects will be marginal. These two extreme cases were found in the $Z$–$E$ isomerization of azobenzenes. The isomerization of ($Z$)-azobenzene was retarded a little by an increase in the solvent polarity[8] and was affected only slightly by an increase in the pressure.[11] On the other hand, the $Z$–$E$ isomerization of 4-(dimethylamino)-4'-nitroazobenzene, hereafter referred to as NMe₂-NO₂-AB, was greatly accelerated by an increase in the solvent polarity and in the pressure.[11,12] Competition between the dipolar rotational transition state 1 and the less polar inversion transition state 2 was proposed for this compound[11,13] and proved by the observation of nonlinear Arrhenius plots and an anomalous temperature dependence of the activation volume.[14] Shin and Whitten[3] also proved the dual mechanism by showing the existence of breaks in the plot of $\Delta G^{\ddagger}$ against Taft's $\pi^{*}$ values in a few push–pull substituted azobenzenes.
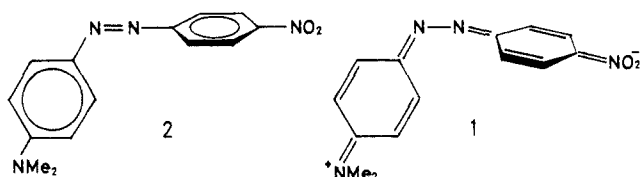


Considering the resemblance of the syn–anti type isomerization in carbon-nitrogen double bonds to the $Z$–$E$ isomerization of azobenzenes, it is reasonable to expect similar competition between the inversion and the rotation mechanisms. Two groups of compounds were examined in the previous papers.[4,15] They were pyrazolone azomethines 3 and benzylideneanilines 4. In 3, the



3a X = NEt₂
b X = NMe₂
c X = H
d X = NO₂

4a X = NMe₂, Y = NO₂
b X = NO₂, Y = NMe₂
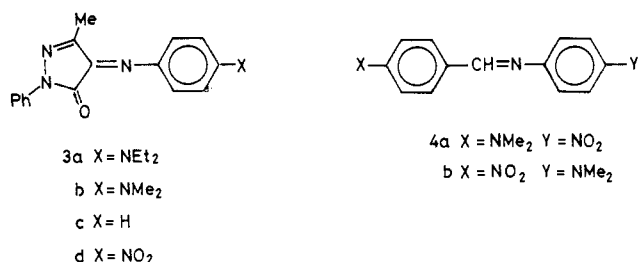
pyrazolone ring is electron-attracting. Therefore, 3a and 3b are considered to be push–pull substituted as in NMe₂-NO₂-AB, and the rotation mechanism is expected. In fact, Herkstroeter[16] observed a V-shaped Hammett-type correlation between the $E$–$Z$ isomerization rate of 3 and $\sigma^{+}$, and he concluded that 3a and 3b isomerized by rotation while 3d isomerized by inversion. However, both 3a and 3b failed to show the evidence for the polarity increase expected for rotation. The reaction was found to be slower in polar solvents, and the pressure effect was small and retarding in most

of the cases examined.[4,15] In 4a, the $Z$–$E$ isomerization was slightly accelerated both by pressure and solvent polarity, but the effects were much smaller than those found in NMe₂-NO₂-AB. The solvent effect study for 4b clearly demonstrated that the polarity of the transition state is slightly lower than that of the initial state as found for azobenzene.[15] The activation volumes were small and positive. From these results, it was concluded that the rotational mechanism could not be realized in carbon–nitrogen double bonds simply by introducing a strongly electron-donating substituent to the para position of the phenyl group connected to the imino nitrogen even if the imino carbon bears electron-attracting group(s).

If this conclusion was correct, we must observe a similar lack of polarity increase in the isomerization of other compounds which show a nonlinear Hammett plot as observed for 3. Although Prosyanik and his co-workers[17-19] reported such substituent effects for iminomalonates and acetone anils, the degenerate isomerization of hexafluoroacetone anils 5 seems to be the best choice for our purposes. Because of the existence of the six strongly electro-



5a R=H
b R=MeO
c R=NMe₂
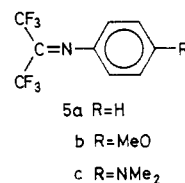
negative fluorine atoms, the intervention of the dipolar transition state 6 is highly probable when R is strongly electron-donating. In fact, Roberts[20] reported clear evidence for the change in the sign of the reaction constant $\rho$ of the Hammett-type correlation with the electronic nature of the para substituent; i.e., the reaction was accelerated by the $p$-nitro group as expected for the inversion mechanism, but the $p$-methoxy group also facilitated the reaction more than the $p$-nitro group. In this communication, the effects of temperature, pressure, and solvent on the rate of the degenerate isomerization of three different hexafluoroacetone anils will be reported, and the mechanism of the reaction will be discussed.

## Experimental Section

**Materials.** The boiling and melting points are uncorrected. *N*-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]benzeneamine, **5a**, 4-methoxy-*N*-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]benzeneamine, **5b**, and *N,N*-dimethyl-*N'*-[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]-1,4-benzenediamine, **5c**, were prepared from the corresponding aryl isocyanate (Aldrich) and hexafluoroacetone (Central Glass) in the presence of triphenylphosphine oxide[21] and purified by column chromatography (silica gel/hexane-benzene) and distillation. 4-(Dimethylamino)phenyl isocyanate was prepared as described.[22] **5a**: bp 57.5 °C/39 mmHg, $n^{25}$D 1.4132 (lit.[21] 72–73 °C/73 mmHg, $n^{22}$D 1.4152). Anal. (C₉H₅F₆N) C, H, N, F. **5b**: bp 100–101 °C/27 mmHg, $n^{25}$D 1.4566 (lit.[20] 79–80 °C/9.8 mmHg, $n^{25}$D 1.4575). Anal. (C₁₀H₇-F₆NO) C, H, N, F. **5c**: bp 57–57.5 °C/1 mmHg, mp 34 °C; IR (KBr) 2920, 2816, 1584, 1524, 1450, 1378, 1334, 1304, 1270, 1216, 1158, 1066, 978, 950, 822, 730, 710 cm⁻¹; ¹H NMR (CDCl₃) 3.30 (s, 6 H) 6.60 and 7.16 (AB q, $J$ = 9 Hz, 4 H); ¹³C NMR (CDCl₃) 40.1 (q), 111.6 (d), 125.8 (d), 131.9 (s), 151.4 (s); ¹⁹F NMR (CH₂Cl₂, 0 °C) -65.5, -70.6 from CFCl₃; EIMS ($m/z$) 284 (M⁺), 215, 146, 120. Anal. (C₁₁H₁₀-F₆N₂) C, H, N, F. Solvents: CD₃CN (Aldrich), DMSO-$d_6$ (MSD Isotopes), propylene carbonate (Aldrich Gold Label), CD₂Cl₂ (Aldrich Gold Label), and redistilled pyridine (Fisher Certified ACS grade) were dried over 4A molecular sieves prior to use.

**Kinetic Measurements.** Fluorine-19 NMR spectra of solutions of **5a** and **5b** at ambient pressure were obtained with a Varian XL-200 spectrometer at 188.19 MHz, with 8.9-μs pulses, acquisition time typically 4 s, and spectral width 2–8 kHz over 32k points. The signals were locked

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**Table I.** Temperature Dependence of Rate Constants $k$ for Fluorine Site Exchange in $p$-RC$_6$H$_4$N=C(CF$_3$)$_2$ in Various Solvents

| R | solvent | wt% solute | T, K | $k$, s$^{-1}$ |
|---|---|---|---|---|
| CH$_3$O | PC[a] | 4.8 | 289.8 | 62 ± 5 |
| | | | 299.7 | 137 ± 10 |
| | | | 310.0 | 307 ± 15 |
| | | | 320.5 | 650 ± 30 |
| | | | 331.1 | 1250 ± 40 |
| | | | 341.5 | 2500 ± 80 |
| | | | 352.1 | (4.5 ± 0.2) × 10$^3$ |
| | | | 362.7 | (8.8 ± 0.2) × 10$^3$ |
| | | | 373.2 | (16.0 ± 1.0) × 10$^3$ |
| | | | 383.7 | (27.3 ± 1.0) × 10$^3$ |
| | | | 393.9 | (47.0 ± 4.0) × 10$^3$ |
| | | | 404.2 | (78.0 ± 4.0) × 10$^3$ |
| | DMSO | 3.0 | 299.7 | 120 ± 7 |
| | | | 310.0 | 280 ± 15 |
| | | | 331.1 | 1250 ± 40 |
| | | | 378.4 | (20.0 ± 1.0) × 10$^3$ |
| | CD$_3$CN | 7.6 | 289.8 | 56 ± 5 |
| | | | 299.7 | 130 ± 7 |
| | | | 310.0 | 270 ± 15 |
| | | | 320.5 | 600 ± 30 |
| | | | 331.1 | 1200 ± 40 |
| | | | 341.5 | 2400 ± 80 |
| | | | 352.1 | (4.15 ± 0.1) × 10$^3$ |
| | | | 357.4 | (5.2 ± 0.2) × 10$^3$ |
| | C$_5$D$_5$N | 6.6 | 289.8 | 80 ± 7 |
| | | | 299.7 | 150 ± 7 |
| | | | 310.0 | 360 ± 15 |
| | | | 320.5 | 725 ± 25 |
| | | | 331.1 | 1430 ± 40 |
| | | | 341.5 | 2800 ± 75 |
| | | | 352.1 | (5.5 ± 0.2) × 10$^3$ |
| | | | 362.7 | (10.5 ± 0.2) × 10$^3$ |
| | | | 373.2 | (19.5 ± 1.0) × 10$^3$ |
| | | | 383.6 | (32.0 ± 2.0) × 10$^3$ |
| | | | 388.8 | (39.0 ± 2.0) × 10$^3$ |
| | CD$_2$Cl$_2$ | 2.8 | 294.8 | 95 ± 5 |
| | | | 304.8 | 215 ± 15 |
| | dioxane | 3.1 | 294.8 | 80 ± 7 |
| | | | 299.7 | 120 ± 7 |
| | | | 304.8 | 180 ± 10 |
| | | | 336.4 | 1600 ± 50 |
| | | | 346.8 | 2700 ± 80 |
| | | | 357.4 | (4.85 ± 0.1) × 10$^3$ |
| | | | 368.0 | (7.6 ± 0.3) × 10$^3$ |
| | | | 378.4 | (11.1 ± 0.4) × 10$^3$ |
| H | CD$_3$CN | 16.0 | 315.3 | 70 ± 7 |
| | | | 325.8 | 160 ± 10 |
| | | | 336.3 | 350 ± 15 |
| | | | 346.8 | 700 ± 50 |
| (CH$_3$)$_2$N | CD$_3$CN | 3.7 | 252.4 | 30 ± 2 |
| | | | 272.0 | 150 ± 7 |
| | | | 287.6 | 400 ± 20 |
| | | | 304.8 | 900 ± 40 |
| | | | 326.8 | (4.15 ± 0.2) × 10$^3$ |

[a] Propylene carbonate.

**Table II.** Activation Parameters and Rate Constants at 298 K for Fluorine Site Exchange in $p$-RC$_6$H$_4$N=C(CF$_3$)$_2$ in Solvents of Dielectric Constant $D$

| R | solvent | $D$ | $\Delta H^{\ddagger}$,[a] kJ mol$^{-1}$ | $\Delta S^{\ddagger}$,[a] J K$^{-1}$ mol$^{-1}$ | $k^{298}$, s$^{-1}$ |
|---|---|---|---|---|---|
| CH$_3$O | PC | 65.0 | 57.9 ± 0.5 | -11.4 ± 1.4 | 113 |
| | DMSO | 46.6 | 58.3 ± 0.3 | -10.4 ± 0.8 | 108 |
| | CD$_3$CN | 36.7 | 55.2 ± 0.8 | -20.3 ± 2.3 | 115 |
| | C$_5$D$_5$N | 12.3 | 57.8 ± 0.6 | -10.4 ± 1.8 | 133 |
| | CD$_2$Cl$_2$ | 9.1 | 58.7[b] | -8.0[b] | 124 |
| | dioxane | 2.2 | 52.0 ± 1.4 | -30.6 ± 4.1 | 122 |
| H | CD$_3$CN | 36.7 | 64.1 ± 0.9 | -6.8 ± 2.7 | 16.5 |
| (CH$_3$)$_2$N | CD$_3$CN | 36.7 | 41.7 ± 1.9 | -49.2 ± 6.6 | 770 |

[a] Uncertainties are standard deviation of the fit. [b] Two rate constants only.

**Table III.** Effect of Pressure $P$ on the Rate Constants for Fluorine Site Exchange in $p$-RC$_6$H$_4$N=C(CF$_3$)$_2$ in Acetonitrile-$d_3$

| R | wt% solute | T, K | P, MPa | $k$, s$^{-1}$ | $\Delta V^{\ddagger}$, cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|
| CH$_3$O | 23.9 | 298.0 | 0.1 | 120 ± 10 | 3.7 ± 0.7 |
| | | | 51.8 | 110 ± 5 | |
| | | | 103.6 | 95 ± 5 | |
| | | | 109.6 | 105 ± 10 | |
| | | | 148.4 | 90 ± 10 | |
| | | | 154.9 | 100 ± 5 | |
| | | | 199.3 | 85 ± 5 | |
| | | | 206.6 | 90 ± 5 | |
| (CH$_3$)$_2$N | 3.8 | 326.7 | 0.1 | 4000 ± 50 | 0.5 ± 0.1 |
| | | | 22.5 | 4000 ± 100 | |
| | | | 51.2 | 4000 ± 50 | |
| | | | 102.3 | 3950 ± 50 | |
| | | | 132.0 | 3950 ± 50 | |
| | | | 150.2 | 3900 ± 50 | |
| | | | 193.1 | 3850 ± 100 | |

on deuterium in the perdeuterated solvents (or in a DMSO-$d_6$ insert for solvents having normal hydrogen isotopic abundance). The temperature of the spinning samples, as measured by the sensor of the Varian flowing-nitrogen variable temperature unit, was calibrated by using the 200 MHz methylene and hydroxyl $^1$H resonances of ethylene glycol.[23] Spectra of **5c** were obtained at 84.68 MHz on a Bruker WH-90 spectrometer with quadrature detection in a similar fashion, except with 2.0-$\mu$s (45°) pulses and 2–10-kHz spectral widths over 8k points. Spectra of sweep width 2 kHz were best suited to dynamic analysis. Fluorine-19 NMR spectra at elevated pressures were obtained by using a pressurizable probehead, described previously,[24] which was originally built for proton NMR but which can be retuned for $^{19}$F. Temperature control was effected with circulating water from an external thermostat for the dynamic NMR measurements or with chilled nitrogen for the low-temperature (zero exchange) spectra.

## Results

The $^{19}$F spectra were similar to those reported by Roberts and co-workers;[20] a selection of spectra from a typical set of variable-temperature experiments is shown in Figure 1. Thus, in spectra recorded at 230–260 K at 188.19 MHz, two quartets with $^4J_{FF} \simeq 7.0$ Hz were seen with a center-to-center separation of about 1500 Hz for **5a** and 1300 Hz for **5b**, with only a slight dependence on solvent and temperature. As the temperature was increased, the quartet resolution was lost first, and then the two resulting peaks coalesced to a single resonance.

First-order rate constants $k$ for the isomerization reactions were obtained by matching the experimental $^{19}$F spectra with those calculated from the GNMR computer program[25] by using the eight-line spectra obtained at about 240 K as the zero-exchange basis set. These calculations extended over the complete temperature range, from the fully-resolved pair of quartets to the single peak in the fast-exchange limit, whereas Roberts and co-workers[20] were obliged to treat the collapse of the quartets separately from the coalescence of the two resulting peaks. For the relatively rapid isomerization of **5c**, the true base spectrum required a temperature at least 10 K lower than the minimum attainable with the high-pressure equipment (243 K), and the corrections were therefore applied in this case by using the line width of the standard compound, CFCl$_3$, measured in the high-pressure probehead.

Isomerization rate constants so obtained and the derived activation parameters are listed in Tables I–III. The data for **5b** in pyridine agree satisfactorily with the parameters reported by Roberts and co-workers[20] for the same system ($\Delta H^{\ddagger} = 56.5$ kJ mol$^{-1}$, $\Delta S^{\ddagger} = -12.1$ J K$^{-1}$ mol$^{-1}$, $k^{298} = 183$ s$^{-1}$).

The most striking feature of the results in Table II is the near-constancy of the interpolated rate constants at 298.2 K for **5b**, despite an enormous variation in the chemical nature and the dielectric constant of the solvents. Similarly, the enthalpies and entropies of activation show only a small variation, of which at

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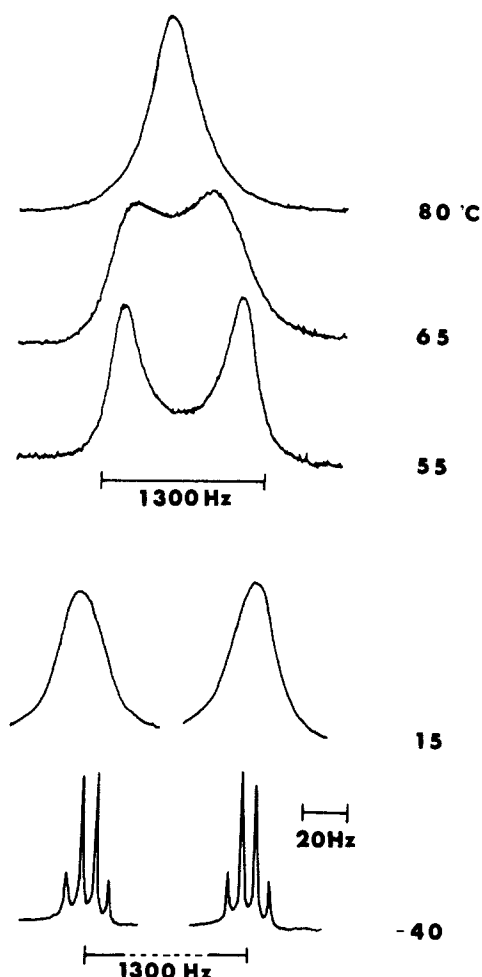
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**Figure 1.** Temperature dependence of $^{19}F$ NMR spectra of **5b** in $CD_3$-CN. Note that the frequency scale of the spectra at 15 and -40 °C has been expanded 16.6-fold and is interrupted. Vertical scales are normalized for clarity.

least part probably originates in mutually compensatory errors in these parameters. The kinetic parameters for isomerization of **5a** in acetonitrile are also not very different from those of **5b**, as might be anticipated from the results of Roberts.[20] For **5c** in acetonitrile, $k$ is some 6-fold greater and $\Delta H^{\ddagger}$ is distinctly lower than for **5b**, but the small, slightly positive values of the activation volume (Table III) are sufficiently close to indicate that further measurements of this quantity for other compounds of the series or for different solvents would simply produce more values of about this magnitude, and no more of these technically demanding high-pressure experiments were therefore carried out.

**Discussion**

**Isomerization Mechanism.** As discussed in the introduction, if the isomerization studied here proceeds via rotation about the carbon–nitrogen bond, the $\pi$ bond must be cleaved heterolytically, and there must be a large increase in the polarity during activation. This polarity increase, in turn, has to be detected as a strong pressure and solvent-polarity dependence of the rate constant as shown in push–pull substituted azobenzenes. The results for **5a** and **5b** show clearly that the *p*-methoxy group accelerates the reaction as observed by Roberts.[20] However, failure to observe any systematic solvent effect clearly denies the possibility of the polarity increase during the activation in **5b**. The small retarding effect of increasing pressure in acetonitrile also supports this conclusion. Obviously, this compound isomerizes by inversion.

However, the rotation mechanism might be realized by introducing a para substituent which has much higher electron-donating ability than the methoxy group. In order to examine this possibility, the effect of the *p*-dimethylamino group was studied, but the result was disappointing. Although the compound **5c** isom-

erized faster than the other anils and a fairly large negative activation entropy was obtained in acetonitrile, the pressure effect unequivocally demonstrated the absence of the expected polarity increase. Furthermore, the acceleration by this substituent was, by no means, greater than that expected from log $k - \sigma^+$ correlation. It must be concluded that the reaction mechanism is inversion for all of the anils studied here.

This conclusion presents another problem, however. What is the reason for the acceleration of the reaction by the electron-donating substituents? According to the ab initio STO-3G calculations by Hofmann and his co-workers,[26] the energy differences between the initial state and the inversion transition state in formaldimine $CH_2$=NH and *N*-phenylformaldimine $CH_2$=NPh are 171.5 and 121.8 kJ $mol^{-1}$, respectively. This large difference seems to come mainly from the conjugation of the 2p orbital of the sp-hybridized nitrogen atom with the phenyl group because the activation energy in benzaldimine PhCH=NH, where no such conjugation exists, is almost as high as formaldimine (170.2 kJ $mol^{-1}$). Furthermore, in *N*-phenylformaldimine, the perpendicular conformation **7** is favored by 21.8 kJ $mol^{-1}$ compared with the



**6**          **7**
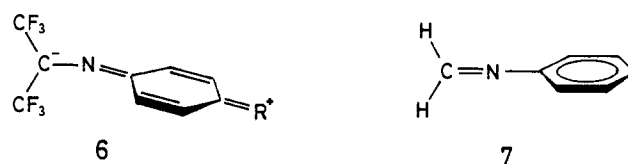
planar arrangement **8**. The calculation on *N*-(4-nitrophenyl)-formaldimine shows that the energy difference in the initial state and the inversion state is 113.5 kJ $mol^{-1}$ which is about 8 kJ $mol^{-1}$ lower than *N*-phenylformaldimine, and the conformation in the transition state is perpendicular. From these results, it may be safely concluded that the acceleration by the nitro group[20] is the result of the contribution of a resonance structure **9**.



**8**          **9**
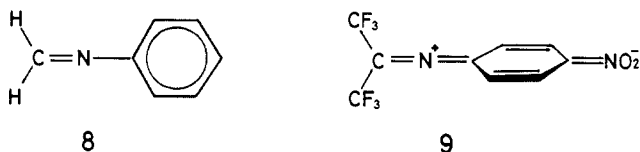
However, there is no way to explain the stabilization of the inversion transition state by the electron-donating substituents in this conformation. Hofmann's calculation shows that the activation of *N*-(4-hydroxyphenyl)formaldimine to the perpendicular inversion state requires 5.8 kJ $mol^{-1}$ more than *N*-phenylform-aldimine. Therefore, we must consider another conformation in order to rationalize the effect of the electron-donating groups. If the 2p orbitals of the carbon and nitrogen atoms in the C=N bond and the carbons of the phenyl group are arranged parallel to each other, it is possible to draw a resonance structure such as **10**.



**10**
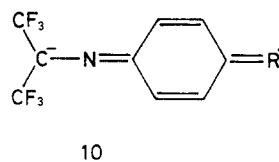
Although this planar conformation has not been proposed for the inversion activated complex on the basis of the experimental results, considering this conformation has some theoretical basis. According to Hofmann,[27] the energy difference between the perpendicular and the planar inversion states decreases with the increasing electron-donating tendency of the para substituent in *N*-phenylformaldimine, i.e., 34.2 for *p*-$NO_2$, 21.8 for H, and 12.8 kJ $mol^{-1}$ for *p*-OH, respectively. Therefore, it may be expected that the planar conformation may become lower in energy when the imino carbon has electron-attracting groups as in the present anils. Consideration of these two perpendicular and planar

(26) Hofmann, H.-J.; Cimiraglia, R.; Tomasi, J. *J. Mol. Struct.* **1987**, *152*, 19.

(27) Hofmann, H.-J. Private communication.

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transition states in inversion seems to be the only reasonable way to explain the observed acceleration of the isomerization both by electron-attracting and -donating substituents reported for **5** and other various types of imines. Judging from the results of the solvent effect study for **5b** and the small pressure effect for **5c**, the charge separation cannot be extensive, and, therefore, the contribution of **10** must be small. This is in accordance with the relatively small acceleration by the dimethylamino and the methoxy groups in the present anil. The introduction of a di-methylamino group to the other para position in 4-nitroazobenzene results in a highly polar transition state, but the acceleration is far greater than in the present system. In methanol at 25 °C, the rate constants were $6.3 \times 10^{-5}$ s$^{-1}$ for 4-nitroazobenzene[12] and 47.03 s$^{-1}$ for NMe$_2$-NO$_2$-AB.[14] In **5**, the rate ratio $k_{5c}/k_{5a}$ was only 47.

Although the activation entropy for **5c** is more negative than those for **5a** and **5b**, it is not clear whether it has any mechanistic importance. Since Roberts[20] failed to observe any correlation between the electronic nature of the substituent and the activation entropy in solvent pyridine, we need further information to draw any conclusions on this matter.

**Differences in C=N and N=N Bonds.** The results in the present paper clearly demonstrate a surprising difficulty to bring about rotational isomerization in a carbon–nitrogen double bond. In azobenzene, the heterolytic cleavage of the bond was brought about easily by introducing 4-dialkylamino and 4'-nitro groups. It was also demonstrated[13] that the presence of the nitro group is not essential. Thus the *Z–E* isomerization of 4-[[4-(di-methylamino)phenyl]azo]benzenesulfonate ion (methyl orange) was ca. 1400 times faster in water than in methanol, and the activation volumes were $-17$–$18$ cm$^3$ mol$^{-1}$ in both of the solvents. Since the sulfonate group is expected to be only slightly elec-tron-attracting ($\sigma_p = 0.09$), the crucial role in changing the mechanism from inversion to rotation is played by the amino group. However, the same substituent could not induce the ro-tation mechanism in benzylideneanilines, pyrazolone azomethines, and even in hexafluoroacetone anils. The main reason for this difference in N=N and C=N bonds almost certainly exists in the stability of the inversion transition states. The activation energies for the *Z–E* isomerization are ca. 95 kJ mol$^{-1}$ for azo-benzene[8] and 60–70 kJ mol$^{-1}$ for benzylideneaniline.[9,28] The half-lives at room temperature are a few hundred hours and milliseconds, respectively.

This large energy difference was also confirmed in Hofmann's calculation.[26] The inversion energies for diimide HN=NH and formaldimine were 241.7 and 171.5 kJ mol$^{-1}$, respectively. A similar difference was found between phenyldiimide (195.7 kJ

mol$^{-1}$) and *N*-phenylformaldimine (121.8 kJ mol$^{-1}$). Therefore, the facility of the rotation in azobenzene is almost certainly the result of the energetic difficulty of inversion in the azo linkage. The reason for this higher inversion barrier in azo compounds is not clear, but, if a speculation is allowed, the repulsion between the lone pairs in sp$^2$ and 2p orbitals (see **11**) might be responsible.[29]
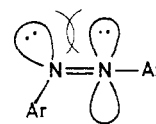


11

This electron repulsion can be seen already in the *Z* configuration of phenyldiimide, i.e., (*Z*)-phenyldiimide is 24.3 kJ mol$^{-1}$ less stable than its *E* isomer, while in benzaldimine the configurational energy amounts only to 4.1 kJ mol$^{-1}$.[26] This lone pair repulsion will increase in the rehybridization step because the two lone pairs are brought somewhat closer in the process.

The higher energy of the inversion transition state of azobenzene does not preclude the possibility of the planar conformation, however. As a matter of fact, Talaty and Fargo[30] observed slight accelerations of the *Z–E* isomerization by para alkyl and methoxy groups as expected for the intervention of the planar inversion transition state in these monosubstituted azobenzenes.

**Conclusions**

In the geometrical isomerization about a carbon–nitrogen double bond, not a single example of polarity increase during activation has been discovered, and it must be concluded that the reaction proceeds by nitrogen inversion despite the electronic nature of the substituents. The acceleration of the reaction both by electron-donating and -attracting substituents in the para position of the *N*-phenyl group can be rationalized by assuming perpendicular and planar phenyl group conformations in the transition state for electron-attracting and -donating substituents, respectively. The reason for the difficulty in realizing a rotation mechanism in the C=N bond is the lower energy increase in the inversion compared with that in the N=N bond.

Registry No, **5a**, 2002-95-1; **5b**, 34025-21-3; **5c**, 125172-69-2.

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(29) We are grateful to Professors Kobayashi and Sonoda of Kyushu University for this suggestion.

(30) Talaty, E. R.; Fargo, J. C. *J. Chem. Soc., Chem. Commun.* **1967**, 65.