November, 1988] *Bull. Chem. Soc. Jpn.,* ***61,*** *4057—4065 (1988)*

# Multinuclear NMR and the Rotational Barriers about the C-N Bonds of Several, *N,N*-Disubstituted Arenecarboxamides

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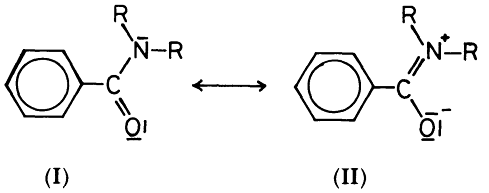
The $^{15}$N, $^{17}$O, and $^{13}$C NMR spectra of substituted *N,N*-dimethyl- and *N,N*-dibenzylbenzamides and *N,N*-dimethylnaphthamides were measured and correlated with the height of their rotational barriers. The $^{15}$N and $^{17}$O chemical shifts of the amides were shown to be controlled predominantly by the extent of the contribution of the polar mesomeric structure (**II**) and, especially in the case of $^{15}$N, could be used to estimate the rotational barrier.

In recent decades, dynamic nuclear magnetic resonance spectroscopy has supplied much useful information on the exchange and the dynamic behaviors of molecules. Amides and related nitrogen compounds were investigated most extensively by this method partly because their NMR spectra show the coalescence phenomena at temperatures near ambient.[1–7]

Rotational barrier about the C–N bond of the amide is directly related to the partial double bond character of the bond and often used to examine the electronic properties of amides, such as the effect of conjugation, the effect of the electronegativity of the substituent on the acyl carbon, etc. For instance, the rotational barriers about the C–N bond of unsaturated and aromatic amides have been shown to be affected very sensitively by the conjugative properties of their hydrocarbon moieties with the carbonyl group. The fact is reflected in the rotational barriers of *N,N*-dimethylacrylamide (69.8 kJ mol$^{-1}$)[1] and *N,N*-dimethylbenzamide (64.9 kJ mol$^{-1}$)[2] which are considerably lower than that of *N,N*-dimethylformamide (87.4 kJ mol$^{-1}$).[3] The partial double bond character of the C–N bond is usually assumed to be originated from the polar mesomeric structure (**II**) bearing a positive charge on the nitrogen and a negative charge on the carbonyl oxygen; the higher C–N bond order should be expected when the contribution of the canonical structure **II** becomes more predominant. Hence, the pi-electron densities on the nitrogen and the oxygen atoms should be correlated with the height of the rotational barrier.

Very extensive studies on the $^1$H and $^{13}$C chemical shifts of aromatic compounds revealed the fact that the chemical shift could be correlated linearly with the electron density of the carbon atom derived from MO calculations for the series of aromatic compounds having closely related structures.[8–10] It has thus become a well-known fact that the electron density should be correlated linearly with the chemical shift of the respective nucleus in a manner to induce a shift towards a higher field by the increase in the electron density. As to $^{15}$N chemical shifts, this fact was substantiated by Mason.[11] Carbonyl $^{17}$O chemical shifts of many acyl derivatives were also measured and correlated with the electron densities by Delseth and coworkers.[12]



(I) (II)

For this reason, the increase in the rotational barrier should cause the down-field shift of $^{15}$N signal and the up-field shift of $^{17}$O signal. From this point of view, the $^{13}$C, $^{15}$N, and $^{17}$O chemical shifts were measured with several arenecarboxamides and correlated with their rotational barriers, or their activation free energies of internal rotation, about the C–N bonds.

## Results and Discussion

Carbonyl and *N*-methyl carbons, amide nitrogen, and carbonyl oxygen are expected to be affected most significantly by the change in the partial double bond character of the amide moiety. Hence, the NMR spectra were reported only with the nuclei concerned (viz., $^{13}$C of carbonyl and *N*-methyl, $^{15}$N of amide, and $^{17}$O of carbonyl) in several solvents; the chemical shifts are given in Table 1. The table also includes the rotational barriers of the amides reported previously by the present authors.[13,14] In order to examine the correlation with the rotational barrier, the chemical shifts were plotted as ordinate and the rotational barriers as abscissa; the results are given in Figs. 1 and 2 for the $^{15}$N chemical shift and in Fig. 3 for the $^{17}$O chemical shift. Throughout this paper chemical shifts were expressed by the conventional $\delta$-scale, which assigns a positive value to the region more deshielded than the standard. Here the chemical shifts ($\delta$/ppm) were correlated linearly with the height of the rotational barrier ($\Delta G^{\neq}$/kJ mol$^{-1}$) by the following equation:

Table 1. $^{15}$N, $^{17}$O, and $^{13}$C NMR Chemical Shifts of *N,N*-Dialkyl Aromatic Amides

| No. | X | Solvent | $\delta_{^{15}N}$ | $\delta_{^{17}O}$ | $\delta_{^{13}C(CO)}$ | $\delta_{^{13}C(Me)}$ | $\Delta G^{\neq}$13,14) |
|---|---|---|---|---|---|---|---|
| | | | ppm | | | | $\mathrm{kJ\ mol^{-1}}$ |
| (a) *N,N*-Dimethylbenzamides $XC_6H_4CONMe_2$ | | | | | | | |
| 1 | H | $CDCl_3$ | 101.4 | 341 | 171.0 | 39.0, 34.7 | 65.5 |
| | | $C_5D_5N$ | 101.6 | 342 | 171.4 | 39.6, 34.5 | 63.2 |
| | | $CD_3SOCD_3$ | 105.2 | 332 | 170.0 | 38.6, 34.5 | — |
| | | $CD_3OD$ | 108.3 | 326 | 173.2 | 39.9, 35.6 | 67.8 |
| 2 | 4-Cl | $CDCl_3$ | 101.3 | — | 170.0 | 39.1, 35.0 | 64.6 |
| | | $C_5D_5N$ | 99.0 | — | 169.9 | 39.1, 35.1 | 63.3 |
| | | $CD_3SOCD_3$ | 105.9 | — | 169.0 | 38.9, 34.3 | 65.1 |
| | | $CD_3OD$ | 108.8 | — | 171.1 | 39.8, 35.7 | 67.2 |
| 3 | 4-$CH_3O$ | $CDCl_3$ | 100.0 | 368 | 170.4 | 38.5, 35.2 | 61.4 |
| | | $C_5D_5N$ | 99.5 | 370 | 171.2 | 37.7* | 58.8 |
| | | $CD_3SOCD_3$ | 103.9 | 342 | 170.0 | 35.9* | — |
| | | $CD_3OD$ | 107.4 | — | 172.5 | 38.2* | 63.3 |
| 4 | 4-$CH_3$ | $CDCl_3$ | 99.6 | 345 | 171.2 | 39.0, 35.1 | 64.0 |
| | | $C_5D_5N$ | 98.7 | 338 | 171.0 | 37.7* | 62.0 |
| | | $CD_3SOCD_3$ | 104.8 | 320 | 170.3 | 38.6, 34.8 | — |
| | | $CD_3OD$ | 107.7 | 320 | 173.3 | 39.9, 35.7 | 66.5 |
| 5 | 2-Cl | $CDCl_3$ | 105.1 | 328 | 167.6 | 37.3, 33.9 | — |
| | | $C_5D_5N$ | 104.7 | 331 | 168.0 | 37.8, 34.5 | 78.5 |
| | | $CD_3SOCD_3$ | 108.8 | — | 166.9 | 37.3, 33.9 | 80.4 |
| | | $CD_3OD$ | 111.6 | 310 | 170.0 | 38.5, 34.9 | — |
| 6 | 2-$CH_3O$ | $CDCl_3$ | 104.5 | 330 | 168.2 | 37.1, 33.5 | — |
| | | $C_5D_5N$ | 103.7 | 344 | 168.9 | 37.5, 34.2 | 75.7 |
| | | $CD_3SOCD_3$ | 108.0 | 315 | 170.9 | 37.3, 33.9 | 77.5 |
| | | $CD_3OD$ | 111.3 | 312 | 167.9 | 38.4, 34.8 | — |
| 7 | 2-$CH_3$ | $CDCl_3$ | 104.3 | 335 | 170.6 | 37.6, 33.8 | 74.1 |
| | | $C_5D_5N$ | 102.9 | 339 | 171.0 | 38.0, 34.3 | 72.6 |
| | | $CD_3SOCD_3$ | 107.9 | 315 | 169.8 | 37.6, 33.7 | 74.6 |
| | | $CD_3OD$ | 111.5 | 311 | 172.6 | 38.7, 34.8 | — |
| 8 | 2-OH | $CDCl_3$ | 103.1 | — | 172.1 | 38.5* | 51.1 |
| | | $C_5D_5N$ | 103.4 | 328 | 169.8 | 38.9, 34.8 | 57.1 |
| | | $CD_3SOCD_3$ | 108.6 | 342 | 168.8 | 35.3* | — |
| | | $CD_3OD$ | — | — | — | — | 59.6 |
| 9 | 2-OH | $CDCl_3$ | 103.7 | — | 170.6 | 38.5* | 51.3 |
| | 5-Cl | $C_5D_5N$ | 103.4 | — | 168.2 | 36.0* | 59.2 |
| | | $CD_3SOCD_3$ | 108.2 | — | 167.1 | 35.4* | 63.1 |
| | | $CD_3OD$ | — | — | 170.8 | 36.8* | 61.1 |
| 10 | 2-OH | $CDCl_3$ | — | — | — | — | 51.6 |
| | 5-$NO_2$ | $C_5D_5N$ | 104.3 | — | 167.5 | 36.4* | 61.0 |
| | | $CD_3SOCD_3$ | 109.2 | — | 167.1 | 36.0* | 64.1 |
| | | $CD_3OD$ | — | — | — | — | 61.6 |
| 11 | 2-OH | $CDCl_3$ | 106.7 | 284 | 170.5 | 37.0* | 51.3 |
| | 5-$CH_3O$ | $C_5D_5N$ | 103.4 | 358 | 169.6 | 36.1* | 56.8 |
| | | $CD_3SOCD_3$ | 108.3 | 340 | 168.4 | 35.9* | — |
| | | $CD_3OD$ | 112.6 | 348 | 172.0 | 36.9* | 59.7 |
| 12 | 2-OH | $CDCl_3$ | 104.2 | 283 | 171.5 | 37.8* | 50.9 |
| | 5-$CH_3$ | $C_5D_5N$ | 103.0 | 369 | 170.1 | 36.2* | 57.0 |
| | | $CD_3SOCD_3$ | 108.7 | 330 | 169.1 | 36.1* | — |
| | | $CD_3OD$ | 111.4 | 345 | 172.5 | 37.4* | 59.9 |
| 13 | 2-OH | $CDCl_3$ | 103.0 | 288 | 171.9 | 37.8* | 50.9 |
| | 3,5-$(CH_3)_2$ | $C_5D_5N$ | 103.6 | — | 171.9 | 37.4* | 53.6 |
| | | $CD_3SOCD_3$ | 108.3 | — | 169.6 | 36.4* | — |
| | | $CD_3OD$ | 112.2 | — | 172.7 | 37.5* | 55.4 |

Table 1. (Continued)

| No. | X | Solvent | $\delta_{^{15}N}$ | $\delta_{^{17}O}$ | $\delta_{^{13}C(CO)}$ | $\delta_{^{13}C(Me)}$ | $\Delta G^{\neq}$13,14) |
|---|---|---|---|---|---|---|---|
| | | | ppm | | | | kJ mol$^{-1}$ |
| (b) *N*,*N*-Dibenzylbenzamides $XC_6H_4CON(CH_2Ph)_2$ (b benzyl $CH_2$) | | | | | | | |
| 14 | H | $CDCl_3$ | 125.7 | 360 | 171.8 | 51.2, 46.7b) | 64.3 |
| | | $C_5D_5N$ | 124.6 | — | 172.0 | 51.8, 47.5b) | 62.6 |
| | | $CD_3SOCD_3$ | 128.8 | — | 171.1 | 51.6, 46.7b) | 63.5 |
| | | $CD_3OD$ | — | — | — | — | 65.0 |
| 15 | 4-Cl | $CDCl_3$ | 125.9 | — | 170.9 | 51.4, 47.1b) | 63.1 |
| | | $C_5D_5N$ | 124.3 | — | 171.0 | 51.6, 47.8b) | 62.8 |
| | | $CD_3SOCD_3$ | 129.0 | — | 170.2 | — | 63.6 |
| | | $CD_3OD$ | — | — | — | — | 63.3 |
| 16 | 4-$CH_3O$ | $CDCl_3$ | 123.9 | 384 | 171.7 | 49.8*b) | 60.3 |
| | | $C_5D_5N$ | 124.2 | 396 | 171.9 | 49.2*b) | 59.0 |
| | | $CD_3SOCD_3$ | 127.5a) | 354 | 170.9 | 49.3*b) | — |
| | | $CD_3OD$ | 131.6a) | — | 174.5 | — | 59.9 |
| 17 | 4-$CH_3$ | $CDCl_3$ | 124.9 | — | 171.8 | 51.2, 46.9b) | 63.3 |
| | | $C_5D_5N$ | 123.6 | — | 172.1 | 49.7*b) | 62.0 |
| | | $CD_3SOCD_3$ | 127.9 | — | 171.3 | 51.0, 47.8b) | — |
| | | $CD_3OD$ | 131.9a) | — | 174.5 | 49.0*b) | 63.8 |
| 18 | 2-OH | $CDCl_3$ | 126.6 | 305 | 172.3 | 50.1*b) | 54.5 |
| | | $C_5D_5N$ | 123.8 | — | 172.0 | 51.8, 47.4b) | 61.8 |
| | | $CD_3SOCD_3$ | 130.6 | — | 169.5 | 50.9, 46.1b) | 65.9 |
| | | $CD_3OD$ | — | — | — | — | 62.1 |
| 19 | 2-Cl | $CDCl_3$ | 130.0 | — | 168.9 | 50.7, 46.5b) | 68.3 |
| | | $C_5D_5N$ | 128.4 | — | 168.7 | 51.1, 46.8b) | 67.0 |
| | | $CD_3SOCD_3$ | 132.5 | — | 167.9 | 50.7, 46.5b) | — |
| | | $CD_3OD$ | 136.1a) | — | 171.0 | 52.4, 48.2b) | — |
| 20 | 2-$OCH_3$ | $CDCl_3$ | 129.3 | 350 | 169.6 | 50.8, 46.0b) | 67.0 |
| | | $C_5D_5N$ | 128.0 | 363 | 170.3 | 51.7, 47.0b) | 67.7 |
| | | $CD_3SOCD_3$ | 131.3 | 327 | 168.9 | 50.8, 46.1b) | 68.4 |
| | | $CD_3OD$ | 131.5 | — | 172.3 | 52.5, 47.8b) | 68.2 |
| (c) *N*,*N*-Dimethylnaphthamides $XC_{10}H_6CONMe_2$ | | | | | | | |
| 21 | 1-$CONMe_2$ | $CDCl_3$ | 105.8 | 331 | 170.2 | 38.1, 34.4 | — |
| | | $C_5D_5N$ | 103.8 | 335 | 170.9 | 38.7, 35.0 | 74.6 |
| | | $CD_3SOCD_3$ | 109.8 | 304 | 169.3 | 38.0, 34.1 | 76.4 |
| | | $CD_3OD$ | 113.4 | — | 173.0 | 39.2, 35.1 | — |
| | | $C_6D_6$ | 102.7 | — | 169.9 | 37.9, 34.2 | 71.4 |
| 22 | 2-$CONMe_2$ | $CDCl_3$ | 101.9 | 352 | 170.9 | 38.9, 34.7 | 65.9 |
| | | $C_5D_5N$ | 99.7 | 360 | 171.7 | 39.7, 35.5 | 64.2 |
| | | $CD_3SOCD_3$ | 105.6 | 315 | 170.1 | 38.8, 34.8 | — |
| | | $CD_3OD$ | 108.7 | — | 173.3 | 39.9, 35.6 | 68.6 |
| | | $C_6D_6$ | 97.9 | — | 170.7 | 36.4* | <64 |
| 23 | 1-$CONMe_2$<br>2-OH | $CDCl_3$ | 107.5 | 290 | 170.8 | 37.3* | 55.9 |
| | | $C_5D_5N$ | 106.3 | 364 | 169.3 | 37.5, 34.5 | 65.4 |
| | | $CD_3SOCD_3$ | 111.6 | — | 167.7 | 37.1, 33.9 | 69.0 |
| | | $CD_3OD$ | 115.4 | — | 171.3 | 36.8* | 66.9 |
| 24 | 2-$CONMe_2$<br>1-OH | $CDCl_3$ | 101.9 | 296 | 172.7 | 38.1* | 49.0 |
| | | $C_5D_5N$ | 104.4 | — | 172.1 | 37.7* | — |
| | | $CD_3SOCD_3$ | 109.2 | — | 169.9 | 36.7* | — |
| | | $CD_3OD$ | 112.9a) | — | 173.1 | 37.7* | 52.0 |
| 25 | 2-$CONMe_2$<br>3-OH | $CDCl_3$ | 103.6 | 292 | 171.1 | 38.0* | 55.6 |
| | | $C_5D_5N$ | 104.0 | 337 | 169.8 | 36.0* | 63.6 |
| | | $CD_3SOCD_3$ | 109.2 | 345 | 168.6 | 36.7, 34.3 | 67.4 |
| | | $CD_3OD$ | 110.8a) | 352 | 172.0 | 38.7, 35.3 | 66.3 |
| 26 | 1-$CONMe_2$<br>2-$OCH_3$ | $CDCl_3$ | 107.7 | 309 | 168.7 | 37.7, 34.5, | — |
| | | $C_5D_5N$ | 105.6 | 302 | 168.2 | 37.3, 34.3 | 90.5 |

Table 1. (Continued)

| No. | X | Solvent | $\delta_{^{15}N}$ | $\delta_{^{17}O}$ | $\delta_{^{13}C(CO)}$ | $\delta_{^{13}C(Me)}$ | $\Delta G^{*13,14)}$ |
|---|---|---|---|---|---|---|---|
| | | | ppm | | | | kJ mol$^{-1}$ |
| 26 | | $CD_3SOCD_3$ | 111.1 | 281 | 167.2 | 37.0, 33.8 | 91.9 |
| | | $CD_3OD$ | 115.4 | — | 170.6 | 38.1, 34.8 | — |
| | | $C_6D_6$ | 104.0 | — | 167.9 | 37.0, 34.1 | — |
| 27 | 2-CONMe$_2$ | $CDCl_3$ | 105.7 | 340 | 169.0 | 37.8, 34.5 | — |
| | 1-OCH$_3$ | $C_5D_5N$ | 103.8 | 336 | 169.2 | 38.0, 34.4 | 78.2 |
| | | $CD_3SOCD_3$ | 109.4 | 309 | 168.2 | 37.7, 34.1 | 79.8 |
| | | $CD_3OD$ | 113.4 | — | 171.9 | 39.0, 35.2 | — |
| 28 | 2-CONMe$_2$ | $CDCl_3$ | 104.9 | 336 | 167.8 | 37.0, 33.5 | — |
| | 3-OCH$_3$ | $C_5D_5N$ | 102.7 | 335 | 168.5 | 37.7, 34.4 | 78.9 |
| | | $CD_3SOCD_3$ | 108.6 | 329 | 167.6 | 37.5, 34.0 | 81.7 |
| | | $CD_3OD$ | 112.7 | — | 172.2 | 38.7, 35.0 | — |
| | | $C_6D_6$ | 101.4 | — | 168.2 | 37.5, 34.3 | 75.0 |

a) Measured at 55 °C. b) $CH_2$ signals of benzyl group. * denotes a coalesced peak.

Table 2. Chemical Shift vs. Rotational Barrier Correlations[a)]

(a) $^{15}N$ chemical shift vs. rotational barrier correlation with the amides lacking *o*-hydroxyl group.

| Amide[c)] | Solvent[c)] | *n* | *k* | *m* | *r* |
|---|---|---|---|---|---|
| a,c | C | 6 | 0.362 | 77.58 | 0.94 |
| a,c | P | 12 | 0.230 | 85.60 | 0.91 |
| a,c | D | 8 | 0.182 | 94.41 | 0.89 |
| a,c | M | 5 | 0.250 | 91.48 | 0.83 |
| a,c | C,P | 18 | 0.229 | 85.92 | 0.90 |
| a | C,P | 12 | 0.300 | 81.28 | 0.92 |
| c | C,P | 6 | 0.188 | 88.76 | 0.90 |
| b | C,P | 12 | 0.697 | 81.49 | 0.92 |

(b) $^{17}O$ chemical shift vs. rotational barrier correlation with the amides lacking *o*-hydroxyl group.

| Amide[b)] | Solvent | *n* | *k* | *m* | *r* |
|---|---|---|---|---|---|
| a,c | C | 5 | −2.07 | 485.40 | 0.78 |
| a,c | P | 11 | −1.47 | 447.60 | 0.80 |
| a,c | C,P | 16 | −1.48 | 447.73 | 0.80 |
| a,c | D,M | 7 | −1.62 | 433.57 | 0.93 |
| a,b,c | C | 8 | −3.05 | 553.40 | 0.81 |
| a,b,c | P | 13 | −1.92 | 483.01 | 0.82 |
| a,b,c | C,P | 21 | −1.95 | 483.97 | 0.81 |

(c) $^{15}N$ chemical shift vs. rotational barrier correlation with the *o*-hydroxyl amides.

| Amide[b)] | Solvent | *n* | *k* | *m* | *r* |
|---|---|---|---|---|---|
| a*,c* | C | 8 | 0.447 | 80.95 | 0.57 |
| a*,c* | P | 8 | 0.204 | 91.83 | 0.77 |
| a*,c* | D | 4 | 0.446 | 80.13 | 0.86 |
| a*,c* | M | 6 | 0.116 | 105.90 | 0.51 |

a) *n*; number of plotted data, *k*; slope of the regression line, *m*; intercept of the regression line, *r*; correlation coefficient. b) The amides are classified as follows: a; **1—7**, b; **14—17**, **19**, and **20**, c; **21**, **22**, and **26—28**, a*; **8—13**, c*; **23—25**. a* and c* are *o*-hydroxylated amides. c) C; $CDCl_3$, P; $C_5D_5N$, D; $CD_3SOCD_3$, M; $CD_3OD$.

$$\delta = k\Delta G^{*} + m$$

The best fit slope (*k*) and the intercept (*m*) values for the plot were calculated by the least squares calculations and given in Table 2. In order to show the limit of reliability of the plot explicitly, the correlation coefficient (*r*) was given in the same table.

The plotted data of *o*-hydroxy derivatives constitute a group clearly distinguishable from those of other amides lacking *o*-hydroxyl group in the chemical shift vs. rotational barrier diagram of both $^{15}N$ and $^{17}O$ series. Besides the presence of the *o*-hydroxyl group, the important factors affecting the chemical shifts are (i) the polar and the conjugative properties of the substituents and (ii) the nature of the solvent. However, the influence induced by these factors were sometimes obscured because the rotational barriers are also perturbed by the similar factors in a manner proportional to the effect on the chemical shift.

In order to make the discussion more straightfor-

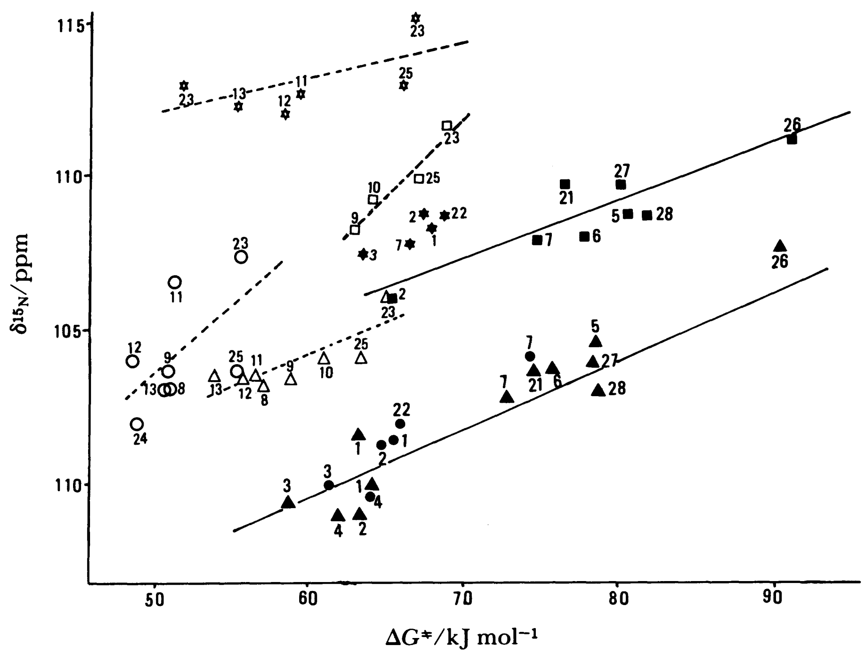


Fig. 1. The $^{15}N$ chemical shift ($\delta_{^{15}N}$) vs. the height of the rotational barrier[14] ($\Delta G^{*}$) plots of *N*,*N*-dimethylbenzamides (a) and *N*,*N*-dimethylnaphthamides (c) in various solvents [chloroform-*d* (●), pyridine-$d_5$ (▲), dimethyl-$d_6$ sulfoxide (■), and methanol-$d_4$ (★)]. The amides bearing *o*-hydroxyl group are shown by open marks; those without *o*-hydroxyl group shown by filled marks.

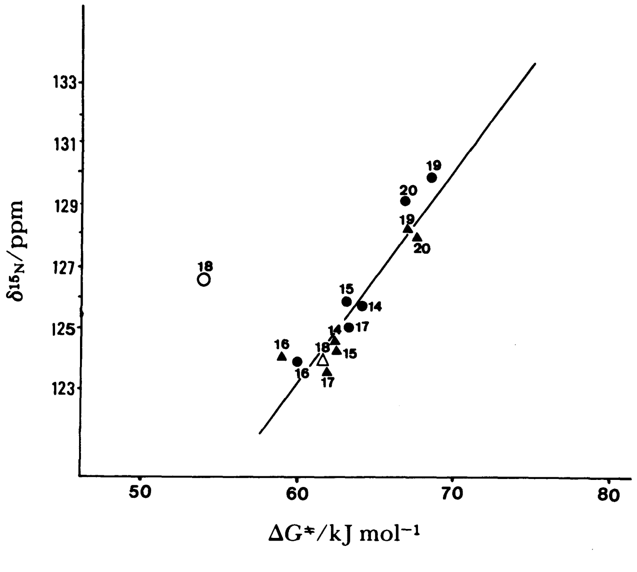


Fig. 2. The $^{15}N$ chemical shift ($\delta_{^{15}N}$) vs. the height of the rotational barrier[14] ($\Delta G^{*}$) plots of *N*,*N*-dibenzylbenzamides (b) in various solvents. The points have the same meaning as in Fig. 1.

ward, the amides employed in this work were classified on the basis of their structural feature into three groups; namely, (a) *N*,*N*-dimethylbenzamides **1**—**13**, (b) *N*,*N*-dibenzylbenzamides **14**—**20**, and (c) *N*,*N*-dimethylnaphthamides **21**—**28**. As the chemical shift was perturbed considerably by the solvent, the chemical shift data in each solvent were correlated individually with the rotational barriers in the same solvent; the difference in the solvent was also discussed. In several cases, the plots in several different solvents were combined in the statistical treatment. Except for the *o*-hydroxy derivatives, good to excellent correlations were obtained. Since these factors affect each nucleus of the atoms comprising the $CONR_2$ moiety in a different way, their chemical shift vs. rotational barrier correlations will be discussed individually.

**The Correlation of $^{15}N$ Chemical Shifts with the Rotational Barriers.** As expected, the $^{15}N$ chemical shift vs. rotational barrier plots in various solvents were shown to have positive slopes, which means that the chemical shift moves towards down-field as the height of the rotational barrier increases. The trend is in line with the rotational barrier vs. $^{15}N$ chemical shift plots for a series of *m*- and *p*-substituted benzamides reported by Randall and coworkers.[15] Since the $^{15}N$ chemical shifts were perturbed most predominantly by the nature of the substituent on the nitrogen atom, the *N*,*N*-dibenzyl derivatives (b) resonate at far lower fields than the *N*,*N*-dimethyl derivatives (a) and (c), constituting a group of plotted points in the upper half of Fig. 1. The down-field shift might be caused by either or both of the electronic and the magnetic anisotropy effects.

The effects on the $^{15}N$ chemical shift of the

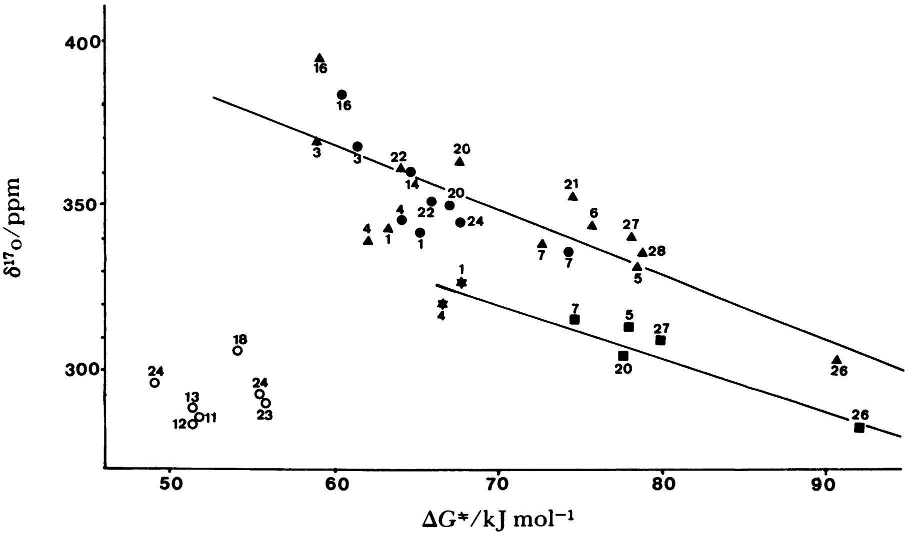


Fig. 3. The $^{17}O$ chemical shift ($\delta_{^{17}O}$) vs. the height of the rotational barrier[14] ($\Delta G^*$) plots of the three series of the *N,N*-dialkylarenecarboxamides (a, b, and c) in various solvents. The points have the same meaning as in Fig. 1.

structural changes and of the substituent(s) in the aromatic part of the molecule do not seem to cause apparently observable deviation from the combined regression lines for the series of *N,N*-dimethylbenzamide (a) and -naphthamide (c) except for *o*-hydroxy derivatives (Fig. 1). This implies that the direct through-space effects, such as anisotropy and steric effects, due to the structural change far apart from the $^{15}N$ nucleus do not induce a serious deviation of the $^{15}N$ chemical shifts of these amides.

If we assume (i) that the chemical shift should be controlled exclusively by the electron density on the nitrogen atom throughout these two series of *N,N*-dimethyl derivatives [(a) and (c)], and (ii) that the solvent effect is merely electrostatic,[16] both the increase in the rotational barrier and the down-field shift should be originated by the increase in the contribution of the polar mesomeric structure (**II**), which causes the descreening of the nitrogen nucleus. Therefore, the chemical shift vs. rotational barrier plot should merge into a single regression line irrespective of the solvent used. This situation may be realized approximately when the solvent is less polar as in the cases of chloroform and pyridine solutions. Thus, the plots in these two solvents constitute a group, giving a regression line with $r$=0.90. However, the correlation is better with the regression lines drawn by use of the data in the two solvent independently ($r$=0.94 for the $CDCl_3$ solutions and $r$=0.914 for the $C_5D_5N$ solutions). The solvent effect becomes more evident in dimethyl sulfoxide and methanol.

In cases of the *o*-hydroxy derivatives (**8**—**13**, **18**, and **23**—**25**), the plots deviate strikingly from those for the amides lacking *o*-hydroxyl group. However, the chemical shift vs. rotational barrier plots still hold positive slopes analogous to the other series of amides investigated; the plots showed clearly that the $^{15}N$ chemical shift is controlled by the contribution of polar mesomeric structure (**II**) even in this series of amides. The regression lines separately drawn for the plot of the *o*-hydroxy amides occupy considerably upward positions in Fig. 1 in comparison with the corresponding lines for the amides lacking *o*-hydroxyl group; which means that the nitrogen is more deshielded than estimated by the screening of the nucleus probably due to the strong neighbor anisotropy effect of the hydrogen-bonded chelate ring.

**The Correlation of $^{17}O$ Chemical Shifts with the Rotational Barriers.** The $^{17}O$ chemical shift vs. rotational barrier plots are given in Fig. 3. As rationalized by the increased contribution of the polar mesomeric structure **II** which increases the negative charge on the oxygen, the regression lines for the plots have negative slopes (negative $k$ values). In sharp contrast to the large separation between the plots of $^{15}N$ chemical shifts, the plotted points of $^{17}O$ chemical shifts for the *N,N*-dimethyl amides [(a) and (c)] and those for the *N,N*-dibenzyl amides (b) constitute a rather scattered but single group in Fig. 3. The fact suggest that the effect of *N*-substituent is attenuated significantly on the carbonyl oxygen.

The direct through-space effect caused by the *o*-substituent (and peri-substituent) becomes more important in the $^{17}O$ chemical shift, which may cause irregular fluctuation of the chemical shift and decreased the reliability of the correlation (lowering of $r$ value).

The chelate ring formation by intramolecular

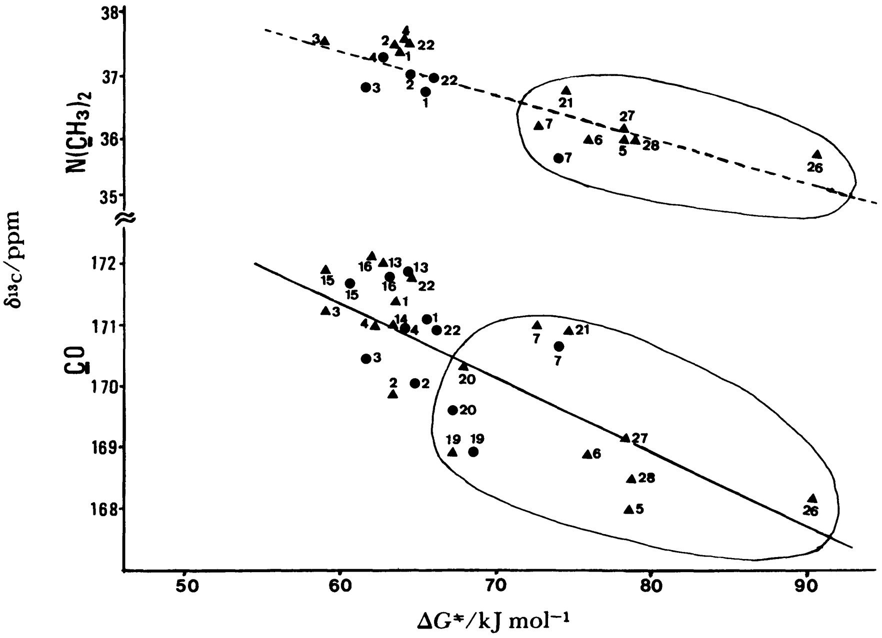


Fig. 4. The $^{13}$C chemical shift ($\delta_{^{13}C}$) vs. the height of the rotational barrier[14)] ($\Delta G^{*}$) plots of the three series of the *N*,*N*-dialkylarenecarboxamides (a, b, and c) in chloroform-*d* and pyridine-$d_5$. The points have the same meaning as in Fig. 1.

hydrogen bonding with the *o*-hydroxyl group causes a considerable up-field shift of carbonyl $^{17}$O chemical shift. This tendency is in accord with the reported chemical shifts of salicylaldehyde and methyl salicylate.[17)]

**The Correlation of $^{13}$C Chemical Shifts with the Rotational Barrier.** The $^{13}$C chemical shifts of the *N*-methyl and the carbonyl carbons were also measured and given together in Table 1 and correlated with the rotational barriers in Fig. 4. It is remarkable that the $^{13}$C chemical shift of the *N*-methyl carbon would move apparently towards high field as the rotational barrier increases, since this trend is just opposite to the direction of the shift observed with $^{15}$N which moves down-field during the similar change. The methyl $^{13}$C chemical shift can be expected to move in the same direction as the $^{15}$N if the inductive effect which decreases the carbon electron density alone is assumed to operate. Thus we need an explanation for this apparently contradictory behavior of the carbon chemical shift.

The *N*-methyl $^{13}$C chemical shift is generally rather insensitive to the structural modification of the aromatic part and also to the nature of the solvent; populating in a narrow range of the chemical shift. The range became far narrower when the amides were classified in reference to the presence of the ortho substituent. Thus, the *o*-unsubstituted amides resonate within the range 36.8—37.6 ppm and most of the *o*-substituted amides (but void of *o*-hydroxyl group) in the range 35.7—36.2 ppm.

If we adopt the geometries estimated by Baumstark and co-workers,[18)] one of the *N*-methyl groups of *N*,*N*-dimethyl-1-naphthamide (**21**) should be subjected to the strong diamagnetic anisotropy effect from the aromatic ring. If we assume that the *o*-substituted amide takes a conformation similar to **21** due to the steric hindrance caused by the ortho-substituent, this conclusion is effective to all ortho-substituted amides. In contrast, the methyl group does not seem to be exposed to diamagnetic magnetic field induced by the aromatic ring in the cases of the *o*-unsubstituted amides. When we examined the $^{13}$C chemical shift vs. rotational barrier plot closely, superficial negative slope is suspected to arise from the fact that the plotted points for the *o*-substituted amides (encircled points in Fig. 4) lie in the right bottom part of the diagram. This comes, of course, from the anisotropy effect just described. The explanation could be extended to the *o*-hydroxy amides whose methyl carbons resonate at lower fields and which are assumed to become more planar due to chelate ring formation.

The $^{13}$C chemical shifts of *p*-substituted *N*,*N*-dimethylbenzamides were correlated with $\sigma_p$ and also with Dewar's F constants by Jones and Wilkins.[19)] Analogously, the carbonyl $^{13}$C chemical shifts of **5**—**13** could be interpreted by the somewhat exaggerated electronic effect caused by the ortho-substituent, or by the combined substituent effect in the cases of polysubstituted derivatives, operating in a through-bond manner.

**Solvent Effect on the $^{15}$N and $^{17}$O Chemical**

Table 3. Solvent Effect on the $^{15}N$ and $^{17}O$ Chemical Shifts[a)]

| Compd No. | $\Delta\delta_{^{15}N}$ ($\Delta\delta_{^{17}O}$)/ppm | | | |
|---|---|---|---|---|
| | $C_5D_5N$ | $(CD_3)_2SO$ | $CD_3OD$ | $C_6D_6$ |
| (a) *N*,*N*-Dimethylbenzamides | | | | |
| **1** | 0.2 ( 1) | 3.8 ( −9) | 6.9 (−15) | |
| **2** | −1.3 ( 2) | 4.6 (−26) | 7.5 | |
| **3** | −0.5 | 3.9 | 7.4 | |
| **4** | −0.9 ( 7) | 5.2 (−25) | 8.1 (−25) | |
| **5** | −0.4 ( 3) | 3.7 | 6.5 (−18) | |
| **6** | −0.8 ( 14) | 3.5 (−15) | 6.8 (−18) | |
| **7** | −1.4 ( 4) | 3.6 (−20) | 7.2 (−24) | |
| **8** | 0.3 | 7.5 | — | |
| **9** | −0.4 | 4.5 | — | |
| **10** | — | — | — | |
| **11** | −3.4 ( 74) | 1.6 ( 56) | 5.9 ( 64) | |
| **12** | −1.2 ( 86) | 4.5 ( 47) | 7.2 ( 62) | |
| **13** | 0.6 | 2.3 | 9.2 | |
| (b) *N*,*N*-Dibenzylbenzamides | | | | |
| **14** | −1.1 | 3.1 | — | |
| **15** | −1.6 | 3.1 | — | |
| **16** | −0.3 ( 12) | 3.6 (−30) | 7.5 | |
| **17** | −1.3 | 3.0 | 7.0 | |
| **18** | −2.8 | 4.0 | — | |
| **19** | −1.6 | 2.5 | 6.1 | |
| **20** | −1.3 ( 13) | 2.0 (−23) | 2.2 | |
| (c) *N*,*N*-Dimethylnaphthamides | | | | |
| **21** | −2.0 ( 18) | 4.0 (−27) | 7.6 | −3.1 |
| **22** | −2.2 ( 8) | 3.7 (−37) | 6.8 | −4.0 |
| **23** | −1.2 ( 74) | 4.1 | 7.9 | — |
| **24** | 2.3 | 7.3 | 11.0 | — |
| **25** | 0.4 ( 45) | 5.6 ( 53) | 7.2 ( 60) | — |
| **26** | −2.1 (−7) | 3.4 (−28) | 7.7 | −3.7 |
| **27** | −1.9 (−4) | 3.7 (−31) | 7.7 | — |
| **28** | −2.1 (−1) | 3.7 ( −7) | 7.8 | −3.5 |

a) $\Delta\delta=\delta_{solv}-\delta_{CDCl_3}$.

**Shifts.** The solvent induced shifts with reference to the chemical shifts in chloroform-*d* solutions are given in Table 3. At a glance of the whole data, they seemed to be in line with a very simple and straightforward interpretation that the polarity of the solvent favors the contribution of the dipolar mesomeric structure **II**.

However, the whole of the solvent induced shift could not be attributed merely to the dielectric nature of the solvents, since the rotational barrier vs. chemical shift plots were solvent dependent giving a different regression line for each solvent. Moreover, the down-field shift of the $^{15}N$ chemical shift and the up-field shift of the $^{17}O$ chemical shift becomes more predominant in the following order of the solvent: benzene<pyridine<chloroform<DMSO<methanol. Pyridine is exceptional when the solvent effect is compared in reference to the dielectric nature of the solvent, inducing an up-field shift of $^{15}N$ signal and a down-field shift of $^{17}O$ signal. Similar irregularity was observed with the rotational barrier of the same amides reported in our previous paper.[14)] This trend of the solvent effect is in accord with the order of the hydrogen-donating ability[20)] (in forming hydrogen bonds) of the C–H or OH group in the solvent molecule. Association by forming hydrogen bonds is a specific solvent–solute interaction which requires the access of the solvent molecule with an appropriate orientation from a specified direction. In this situation, the solvent molecule, usually anisotropic, should induce an anisotropic field around the amide molecule. Thus the observed solvent dependency of the regression lines is explicable by the hydrogen-bond-like interaction between the solvent and the solute molecules.

In conclusion, both the rotational barrier and the $^{15}N$ and $^{17}O$ chemical shifts can be assumed to be controlled by the same origin, the extent of the mesomeric contribution of the canonical structure **II**, or the C–N bond order and the electron densities on the nitrogen and oxygen atoms, when their measurements were carried out in the same solvent. The correlation is excellent with the rotational barrier vs. $^{15}N$ chemical shift plot for the dimethylamides lacking *o*-hydroxyl group. Consequently, $^{15}N$ chemical shifts of the amides should be a probe of the heights of their rotational barriers.

## Experimental

*N*,*N*-Dimethyl- and *N*,*N*-dibenzylarenecarboxamides were prepared as usual by the reaction of the corresponding aroyl chlorides with dimethyl- and dibenzylamines, respectively.

$^{15}N$, $^{17}O$, and $^{13}C$ NMR spectra were recorded on a JEOL FX-90Q spectrometer using 10-mm probe. In order to obtain strong signals from $^{15}N$ and $^{17}O$ nuclei of natural abundance, the samples for the measurements were prepared by dissolving as concentrated as possible, ca. 500 mg of the amide in ca. 1.5 ml of the solvent. Chloroform-*d*, methanol-$d_4$, pyridine-$d_5$, dimethyl-$d_6$ sulfoxide (DMSO-$d_6$), and benzene-$d_6$ were used as solvents throughout this work. The multi-nuclear measurements were carried out under the following conditions:

| Nucleus | $^{15}N$ | $^{17}O$ | $^{13}C$ |
|---|---|---|---|
| Resonance frequency (MHz) | 9.04 | 12.10 | 22.50 |
| Pulse length (μs) | 18(45°) | 20(90°) | 12(45°) |
| Delay | 3 s | 100 ms | 2 s |
| Number of data points | 8K | 1K | 8K |
| Spectral width (Hz) | 3000 | 10000 | 5000 |
| Accuracy (Hz) | 0.7 (0.08 ppm) | 10 (0.8 ppm) | 1.2 (0.05 ppm) |
| Number of scans | ca. 10000 | ca. 100000 | ca. 500 |
| Reference | liq. $NH_3$ external | $H_2O$ external | TMS internal |

The authors wish to express their hearty thanks to Professor Masatsune Kainosho, Tokyo Metropolitan University, for his valuable advice throughout this work. The $^{15}$N experiments were set forth by his suggestion to which we are especially grateful. This research is partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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