Experimental Section

The ^{13}C NMR spectra for CCl_4, $CDCl_3$, TFA, and sulfuric acid solutions were obtained in 8-mm tubes at 30 °C on a 20-MHz Varian CFT-20 spectrometer. Tetramethylsilane was used as an internal reference for CCl_4 and $CDCl_3$ solutions. For TFA and sulfuric acid solutions the reference was tetramethylsilane in the form of a 50% solution in acetone-d_6 placed in a coaxial 5-mm tube. A coaxial tube containing neat acetone-d_6 was employed for lock purposes when CCl_4 was the solvent. Protons were noise decoupled and the spectra are Fourier transform of the sums of 1000–2000 free induction decays obtained under the following conditions: 45° pulse angle, 4K data points, 4000 Hz spectrum width, and a pulse delay of 0.5–1.0 s.

Measurements for ethanol, Me_2SO, and HFP solutions were made in 10-mm tubes at 30 °C on a 63.1-MHz superconducting solenoid spectrometer.[26] Tetramethylsilane was used as an internal reference and the fluorine signals of C_6F_6 or HFP were employed as lock. Protons were noise decoupled and the spectra are Fourier transforms of the sums of 1000–2000 free induction decays obtained under the following conditions: 30° pulse angle, 8K data points, 11 000 Hz spectrum width. All coupling constants and line width measurements were done on this spectrometer with 30° pulse angle, 8K data points, 4000 Hz spectrum width, and an exponential broadening function corresponding to 1–2 Hz.

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(27) **Note Added in Proof.** Recent INDO calculations indicate that the Fermi contact term makes a dominant contribution to $^1J_{NC}$ in I and IV, and that the low value of $^2J_{NC}$ in pyridine is caused by a cancellation effect because of the presence of the lone pair of electrons on nitrogen [J. M. Schulman and T. Venanzi, *J. Am. Chem. Soc.*, **98**, 4701 (1976); see also T. Bundgaard and H. J. Jakobsen, *Tetrahedron Lett.*, 1621 (1976)].

Nuclear Magnetic Resonance Determination of Rotational Barriers in Five-Membered Heterocycles

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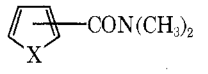
Dynamic NMR has been used to obtain the values of the rotational barriers in furan, pyrrole, and thiophene-2- and -3-*N*,*N*-dimethylcarboxamides.

There is continuing interest in the electronic structure of five-membered heterocycles, and recent reports have described the calculation of σ^+ substituent constants from reaction rate[1,2] or quantitative infrared spectroscopic data.[3] An alternative approach is the use of NMR data to determine rotational barriers in suitable *N*,*N*-dimethylamides, since Jackman and his co-workers[4] have shown that a correlation exists between σ^+ values and the magnitude of such barriers in substituted *N*,*N*-dimethylbenzamides. More recently Riddell and Williams[5] have extended Jackman's results to a pyridyl-substituted dimethylamide. In this journal[6] it was recently reported that $\Delta G^{\ddagger}_{298.2}$ for the rotational barrier in *N*,*N*-dimethyl-2-furanamide was 16.8 kcal/mol, a value that seems anomalously high. It implies that furan, relative to benzene ($\Delta G^{\ddagger} = 15.8$ kcal/mol),[6] is an electron *acceptor* at its 2 position, a result contrary to chemical experience.

We have prepared all six possible amides I (X = NH, O, S), and determined the rates of internal rotation about the N–C(O) bond in these amides at temperature intervals of 5–10 °C, using computer-simulated band-shape analysis of the exchange-broadened NMR signals of the dimethylamino protons.



I

The free energy of activation, $\Delta G^{\ddagger}_{298.2}$, was obtained through use of Eyring plots of these rates. These $\Delta G^{\ddagger}$ values, and other NMR parameters, are given in Table I. For 3-thiophenamide the small value of $\Delta\nu$, and the low T_c, precluded meaningful calculation of $\Delta G^{\ddagger}_{298.2}$.

The partial double bond character of the C(O)–N bond in the amide group, and hence the barrier to rotation about that bond, arise from resonance interaction between the lone pair of electrons on the N atom and the electronegative oxygen of the carbonyl group. An electron donor attached to this car-

Table I. Chemical Shifts and Chemical Shift Differences, $\Delta\nu$, of the *N*-Methyl Protons of Five-Membered Heteroaromatic *N,N*-Dimethylcarboxamides, Their Coalescence Temperatures (T_c), and Their Rotational Barriers ($\Delta G^{\ddagger}$)[f]

Registry no.	Compd	ν_{AB},[a] Hz	ν_1,[d] Hz	ν_2,[d] Hz	$\Delta\nu$,[d] Hz	T_c, °C	$\Delta G^{\ddagger}_{298.2}$ kcal/mol
13156-75-7	2-Furan-	185.4	183.0	194.6	11.6	16	15.1 ± 0.1
14757-80-3	3-Furan-	181.8	183.0	188.9	5.9	13	15.2 ± 0.1
30717-57-8	2-Thiophene-	184.7	184.3	193.8	9.5	1	14.5 ± 0.2
59906-37-5	3-Thiophene-[b]	177.5[c]	177.1	179.9	2.8	−51	*e*
7126-47-8	2-Pyrrole-	187.6	185.9	197.9	12.0	5	14.4 ± 0.1
60031-39-2	3-Pyrrole-	183.0	181.2	190.4	9.2	6	14.6 ± 0.1
611-74-5	Dimethylbenzamide	177.0	176.1	183.9	7.8	28	15.9 ± 0.1

[a] Average chemical shift at the ambient probe temperature, 53 °C. [b] Data in vinyl chloride solution ($\Delta\nu = 0$ in $CDCl_3$). [c] Corresponding value in deuteriochloroform: 182.0 Hz. [d] At 40 °C below T_c, except for 3-thiophenamide, in which it is 20 °C below T_c. [e] $\Delta\nu$ too small, and T_c too far from 298.2 °C, to allow meaningful calculations. [f] Measured in $CDCl_3$ unless indicated otherwise.

bonyl reduces this interaction and so lowers the rotational barrier. Our $\Delta G^{\ddagger}$ values show, as expected, that the order of electron donation of the heteroatoms is N > S > O and that the 2 position is a better donor than the 3 position. All are electron donating relative to benzene.

The values of $\Delta G^{\ddagger}$ correlate fairly well with σ^+ substituent constants such as those obtained by Morgan and his coworkers.[1]

Experimental Section

A computer program DNMR3, originally written by Binsch and Kleier,[7] was used for the computation of NMR band shapes.

Samples were 0.5 M in deuteriochloroform, with 1% Me_4Si, except for the 3-thiophenamide where signal isochrony necessitated the use of vinyl chloride. Samples were degassed by the pump and thaw technique and sealed under vacuum in precision-drawn thin-walled NMR tubes. The ^1H NMR spectra of the *N,N*-dimethyl protons were recorded over a range of temperatures using a Varian Associates A-60D analytical spectrometer equipped with a V-6040 variable temperature controller.

The general techniques and precautions given in Jackman's book[8] were followed.

The *N,N*-dimethylamides employed in this study were prepared by treatment of the corresponding acid chlorides with ice-cold ethereal or aqueous dimethylamine solution, followed by extraction with ether, etc. Purity was checked by TLC in each case.

***N,N*-Dimethyl-2-thiophenecarboxamide** formed colorless crystals, mp 44–45 °C, bp 156–157 °C (12 mm) [lit.[9] bp 145–148 °C (12–13 mm)]. Anal. Calcd for C_7H_9NOS: C, 54.2; H, 5.8; N, 9.0. Found: C, 53.9; H, 5.7; N, 9.0.

***N,N*-Dimethyl-3-thiophenecarboxamide** also formed colorless crystals, mp 45–46 °C, bp 107–108 °C (0.8 mm). Anal. Calcd for C_7H_9NOS: C, 54.2; H, 5.8; N, 9.0. Found: C, 54.5; H, 5.9; N, 9.1.

***N,N*-Dimethyl-3-pyrrolecarboxamide** was obtained as colorless crystals from chloroform–light petroleum, mp 128–129 °C. Anal. Calcd for $C_7H_{10}N_2O$: C, 60.8; H, 7.3; N, 20.3. Found: C, 60.6; H, 7.1; N, 19.9.

Other amides were prepared as described in the literature,[10–13] and their properties agreed closely with those reported.

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Registry No.—2-Thiophenecarboxylic acid chloride, 5271-67-0; 3-thiophenecarboxylic acid chloride, 41507-35-1; 3-pyrrolecarboxylic acid chloride, 50405-33-9; dimethylamine, 124-40-3.

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