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HINDERED ROTATION AROUND THE ARYL-TO-NITROGEN BOND OF N-ACETYL, N-ETHOXYCARBONYLMETHYL-2-AMINO, 5-NITROTHIOPHEN

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Abstract—Two stereoisomers of the title compound are observed by H NMR at 10°. Their spectra coalesce at higher temperature (10°–90°). The equilibrium and rate constants K and k, strongly dependent on the solvent used (1,4-dioxane, tetrahydrofuran, acetone, chloroform); typical values for these parameters and the related thermodynamic functions are: $K(25°) = 0.170$; $k(25°) = 23.2\ s^{-1}$; ΔH_R and $\Delta H^+ = 4.94$ and 17.9 kcal.mol.$^{-1}$; ΔS_R and $\Delta S^+ = 13.1$ and 7.7 e.u, in a 0.2 molar solution in 1,4-dioxane. The two isomers are shown to result from a hindered rotation around the aryl-to-nitrogen bond, presumably due to a direct resonance effect between the amide and nitro groups. The more abundant isomer was assigned a planar molecular structure in which the O atom of the amide group is close to the S atom of the thiophen ring, presumably on account of an electrostatic interaction between these two atoms which bear partial electrical charges of opposite sign.

In the course of a study of a series of 2-aminothiophens, our attention was drawn to the pecularities of the NMR spectrum of N-acetyl, N-ethoxycarbonylmethyl, 2-amino, 5-nitrothiophen (**1**). The entire spectrum can be resolved into two independent sets of lines x and y with the same intensity ratio all along the frequency range, thus showing the presence of two stereoisomers. The two sets of lines coalesce into a single spectrum on raising the temperature, thus showing a fast conversion on the NMR time-scale of each isomer into the other (Fig. 1).

The presence of two stereoisomers in amido-thiophens seems to have been described in one case,[1] namely in 3-thiophenformamide (**2**). Their existence was accounted for by a hindered rotation (R_A) about the amide bond.[2] It was shown however by the same authors that N-acetyl, N-ethoxycarbonylmethyl 2-aminothiophen (**3**) displays only one set of signals. Comparison of **1** and **3** then allows to conclude that the addition of a 5-nitro substituent to 3 is responsible for the existence of a second isomer in **1**. This suggests a hindered rotation (R_N) around the aryl-to-nitrogen bond[2] as a result of electron delocalisation from the lone pair of the amide N atom to the nitro group through the aromatic ring. Electron-donation from this N atom is therefore feasible in either of two ways, either to the CO or to the NO_2 group. The molecular structure of **1** can thus be imagined to be planar, even if some steric hindrance may prevent a perfect coplanarity of the thiophen ring with the amide group.

The problem then is to elucidate which rotational process, either R_A or R_N, actually intervenes in the mutual interchange of the two isomers. In fact, it is possible to write down up to four stereoisomers: α, β, γ, δ (Fig. 2) deriving from each other by either process R_A or R_N. Two of them only are observed which are characterised by their spectra, x and y. (In the following, we shall mark the subspectra and the corresponding unknown isomers by the same letters, x and y, where y is chosen to denominate the most abundant isomer).

The assignment of subspectra x and y to isomers α to δ, and the determination of the height of the rotational barrier is the purpose of this paper.

EXPERIMENTAL

Materials. Deuterated solvents ($CDCl_3$, CD_3COCD_3–THF-d_6, 1,4-dioxane-d_8) were obtained from the Commissariat à l'Energie Atomique (CEA) and were checked for purity before use. The N-acetyl, N-ethoxycarbonylmethyl 2-amino, 5-nitrothiophen (**1**) was synthesised by reacting ethylbromoacetate with 2-acetamido-5-nitrothiophen[3] (**4**) according to a procedure described in a previous publication.[4] The yellow solid compound (F = 129°) was purified by recrystallisation from EtOH and $CHCl_3$.

Preparation of the solutions. Compound **1** was dissolved at concentrations sufficiently high to have a good sensitivity in the NMR spectra, and however as low as possible both to avoid the precipitation of the solid at low temps (up to −90° in acetone) and to prevent any intermolecular amide–amide associations.[5] An optimum concentration of 0.2 mol.dm^{-3} was found which satisfied approximately all these requirements. The solvents were chosen so as to obtain a good solubility of **1** and to cover a wide range of polarities.

NMR spectroscopy. Proton spectra were taken either on a Jeol C60-HL spectrometer operating at 60 MHz with TMS as an internal reference, or on a Cameca superconducting spectrometer at 250 MHz. Operations at 60 MHz were in fact necessary to bring the exchange to the NMR timescale at temperature below the b.p. of the solvents. "*Static*" *spectra*, i.e. without any line-broadening due to exchange phenomena, were performed at temps below 10° and at 250 MHz for the opposite reasons. High frequencies were also necessary to disentangle lines which were overlapping at 60 MHz. The use of Fourier Transformation was necessary in soln where the molar ratio of isomer x is very small (1000 scans of 8K points over a frequency range of 2 kHz using the deuterium signal of the solvent as an internal lock). The temp was periodically checked with a thermometer immersed in the sample tube and was found constant within ±0.5°. The spectra were taken at several temps up to a critical value (*ca* 10°) above which lineshapes are modified by exchange phenomena. Chemical shifts were measured over this temp range. They are found independent of temp and concentration (≤0.2 mol dm^{-3}) within experimental errors (±0.1 to ±0.5 Hz), and strongly dependent on the solvent (Table 1). Intensity measurements allow to com-

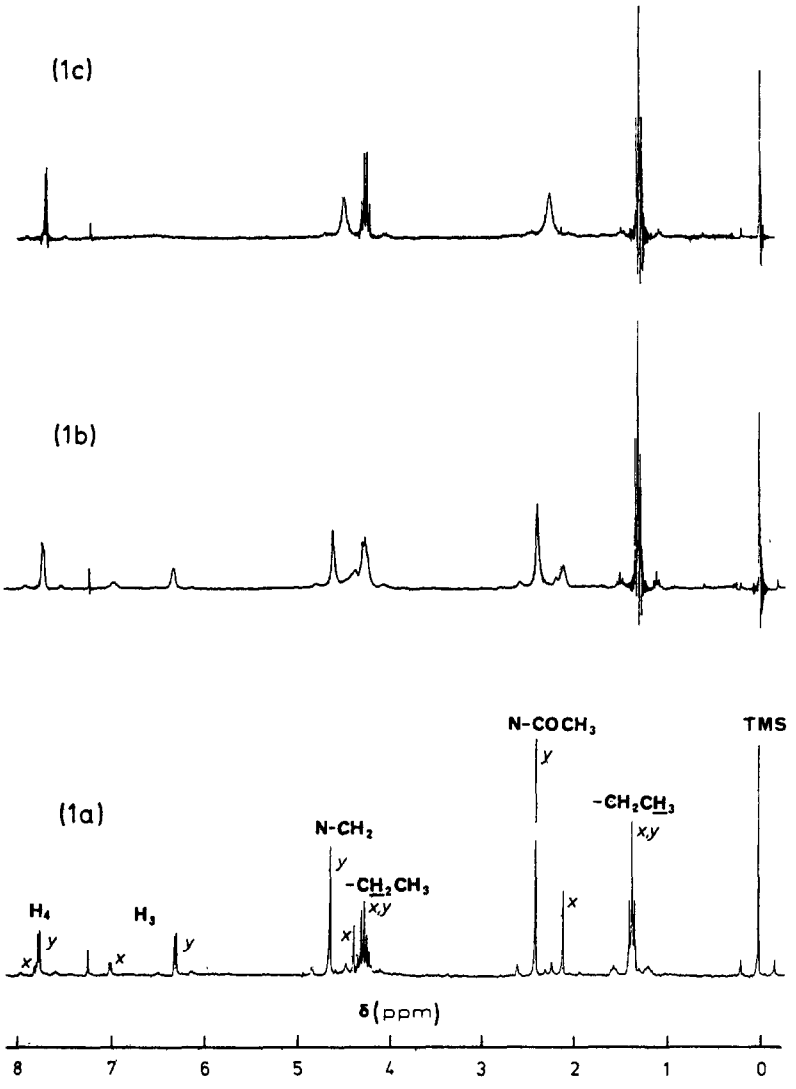


Fig. 1. The spectrum of compound (1) at −10°C (1a), 25°C (1b) and 55°C (1c) at 250 MHz in $CDCl_3$.

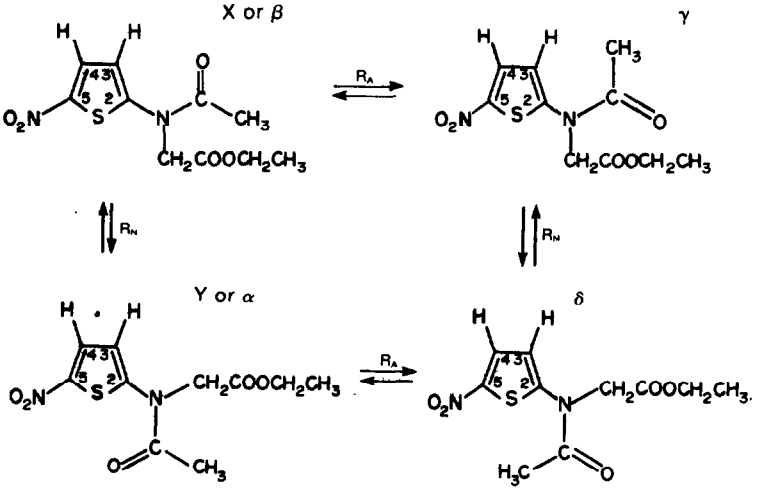


Fig. 2. The four possible stereoisomers of (1).

Table 1. The proton chemical shifts δ (ppm from TMS) of compound (1) at 10°C in four solvents

δ	1,4-dioxane d_8	Tetrahydrofuran-d_8	Acetone-d_6	Chroroform-d
H_{4x}	7.85	7.93	8.02	7.82
H_{4y}	7.79	7.83	7.92	7.79
H_{3x}	7.05	7.16	7.28	7.03
H_{3y}	6.44	6.58	6.73	6.37
$N\text{-}CH_{2x}$	4.36	4.40	4.44	4.39
$N\text{-}CH_{2y}$	4.73	4.88	5.02	4.64
$-\underline{CH_2}\text{-}CH_{3x,y}$	4.21	4.23	4.26	4.31
$N\text{-}CO\text{-}CH_{3x}$	2.02	2.04	2.17	2.13
$N\text{-}CO\text{-}CH_{3y}$	2.30	2.35	2.46	2.42
$-CH_2\text{-}\underline{CH_{3x,y}}$	1.23	1.26	1.27	1.32

pute the molar fractions p_x, p_y of the two isomers, the equilibrium constant $K = p_x/p_y$, and the related thermodynamic functions $\Delta G_R = -RT \log K$, $\Delta H_R = -RT^2 \, d \log K/d(1/T)$ and $\Delta S_R = (\Delta H_R - \Delta G_R)/T$ (Tables 2 and 3). Graphs of log K as a function of 1/T (Fig. 3) show a reasonable scattering of experimental points around the least squares straight line. In fact, a more complex procedure is used to obtain the final values of these parameters as explained below.

Line-shape measurements. Two types of exchange are examined in this paper: the exchange (I) of the methylic (and/or methylenic) protons of the amide group between two unequal singlets; the exchange (II) of the AB type quadruplet of the ring protons H_3, H_4 (J = 4.41 Hz) of isomer x with the corresponding AB type quadruplet (J = 4.78 Hz) of isomer y (Fig. 4). Theoretical line-shapes are computed using a matrix formulation due to Anderson *et al.* and the program ECHGN[7] for exchange (I), and the density matrix formalism[8] in the second case (program EXCH 14[9]). All calculations were performed using a Texas Instruments 980A minicomputer equipped with a digital plotter, Hewlett-Packard 7210A. These computations required introducing two parameters: the relative populations of the exchanging sites (i.e. the equilibrium constants K) and the rate constant k_x (or $k_y = k_x K$) for the forward (or reverse) process $x \rightarrow y$ (assuming constant chemical shift separation between exchanging lines). These parameters were adjusted by trial and error so as to obtain the best fit between experimental and theoretical curves (Table 2). This was achieved by the following iterative procedure. The first trial value K_0 of K was extrapolated from low-temp equilibrium measurements (see above) and k was adjusted to give the best fit for exchange (II). The value k_0 of k thus obtained was kept constant in a second step while K_0 was adjusted to a new value K_1 so as to obtain the best fit for exchange (I). A second iteration then began using K_1 instead of K_0 as the initial K value. These iterations were repeated until a good fit is obtained for both exchanges (I) and (II). New values of K can then be reported on graphs (Fig. 3), thus considerably improving the accuracy upon the equilibrium enthalpy ΔH_R by increasing the temperature range examined. Satisfactory Arrhenius plots (Fig. 5) are obtained for rate constants k, from which a least squares analysis yields the activation parameters ΔH^+ and ΔS^+, and, in turn, the smoothed value of k at 25° (and the corresponding free energy ΔG^+, using Eyring's equations) (Table 3). The accuracy is difficult to estimate, but uncertainties should not be larger than ±5% over K and k, 0.5 to 1.0 kcal mol^{-1} over ΔH_R and ΔH^+, and 1.5 to 3.0 e.u over ΔS_R and ΔS^+.

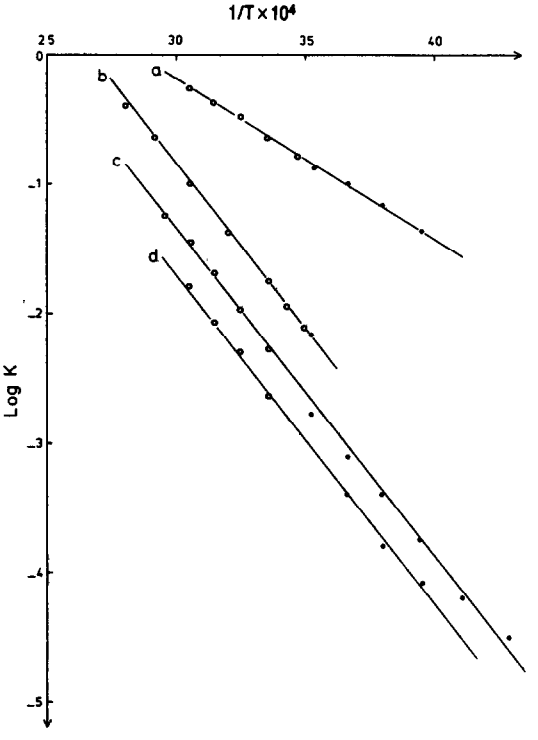


Fig. 3. Plots of the logarithm of the equilibrium constants K versus the reciprocal of temperature (1/T), in chloroform (a), 1,4-dioxane (b), tetrahydrofuran (c), acetone (d) by measurement of line intensities in the absence of exchange (●) or from the coalesced spectra (○).

Table 2. The equilibrium constants $K = p_x/p_y = [\beta]/[\alpha]$ and rate constants k_α, $k_\beta(s^{-1})$ as a function of temp for a 0.2 molar solution of compound (1) in tetrahydrofuran-d_8

Temperature	-40	-30	-20	-10	0	10	25	35	45	55	64
$Kx10^3$	11.0	14.7	23.6	33.1	43.8	62.1	103.1	138.9	181.8	232.5	285
k_y(or k_α)				0.26	0.87	3.10	18.56	62.50	181.8	465.0	100
k_x(or k_β)				8	20	50	180	450	1000	2000	350

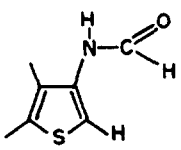
Table 3. Equilibrium and rate constants (s^{-1}) at 25°C and the related thermodynamic functions ΔG_R, ΔH_R (kcal mol^{-1}), ΔS_R (cal mol^{-1} K^{-1} or e.u) (for equilibrium), and $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ (for the exchange process; the subscript α and β refers to exchanges $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$, respectively)

Solvent	1,4-dioxane-d_8	Tetrahydrofuran-d_8	Acetone-d_6	Chloroform-d
K	0.170	0.104	0.074	0.528
ΔG_R	1.04	1.34	1.54	0.38
ΔH_R	4.94	4.99	5.11	2.45
ΔS_R	13.05	12.26	11.95	6.95
k_α	23.18	20.69	14.12	23.50
$\Delta G^{\ddagger}_\alpha$	15.59	15.66	15.88	15.58
$\Delta H^{\ddagger}_\alpha$	17.88	19.12	18.92	18.96
$\Delta S^{\ddagger}_\alpha$	7.70	11.61	10.23	11.35
k_β	136.08	198.83	191.53	44.48
$\Delta G^{\ddagger}_\beta$	14.54	14.32	14.34	15.20
$\Delta H^{\ddagger}_\beta$	12.94	14.12	13.81	16.51
$\Delta S^{\ddagger}_\beta$	-5.35	-0.65	-1.77	+4.40

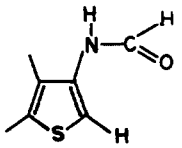
Identification of the two isomers

Two majors points are emerging from the chemical shift data reported in Table 1.

(i) The proton H_3 in isomer x is strongly deshielded, by about 0.6 ppm, with respect to proton H_3 in isomer y, whatever the solvent may be. This indicates that H_3 is quite close to the N-carbonyl group in the molecular plane of isomer x. The deshielding effect of amide groups has been the matter of some controversy in literature, but it is now certain that the amide magnetic field is deshielding over the amine plane.[2a] Clear evidence for the validity of this conclusion in the case of amidothiophens is furnished by the spectrum of **2**: a 0.7 ppm downfield shift of proton 2 is indeed observed in the *trans* (*Z*) isomer with respect ot the corresponding *cis*



E



Z

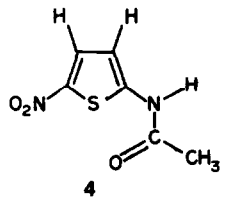
(*E*) isomer (each of which can be unambiguously identified on the basis of the magnitude of the coupling constant between the carbonyl and amide protons, 11.5 and 2.0 Hz respectively). Coming back to **1**, it can be observed that a close vicinity of H_3 to the amide substituent is obtained in one only of the four possible conformations represented in Fig. 2. This allows to assign spectrum x to molecular structure β.

(ii) Selectively irradiating the carbonyl Me protons of the most abundant isomer y is accompanied by a 7% enhancement of the intensity of the corresponding N-methylenic protons. The intramolecular Overhauser effect thus obtained reveals a *cis* configuration of these methylene and methyl groups. This allows to assign spectrum y to rotamer α.

Further pieces of evidence supporting these assignments arise from the following observations.

(iii) The intensity of H_3 lines remains unaltered in the above NOE experiment, suggesting the absence of dipolar interaction between H_3 and the carbonyl Me of isomer y (and x, as well), and thus excluding the γ rotamer.

(iv) Compound **4**, which differs from the examined **1** by the absence of the N-ethoxycarbonylmethyl substituent, presumably exists predominantly as the *trans*



4

(*Z*) isomer, as it is the case for all N-monosubstituted amides.[2a] A single set of lines is effectively observed and the chemical shift of proton H_3 in **4** is quite similar to the one observed in isomer α (6.53 and 6.58 ppm, respectively, in THF-d_6), as expected from analogous configurations of proton H_3 (with respect to the amide group) in both compounds.

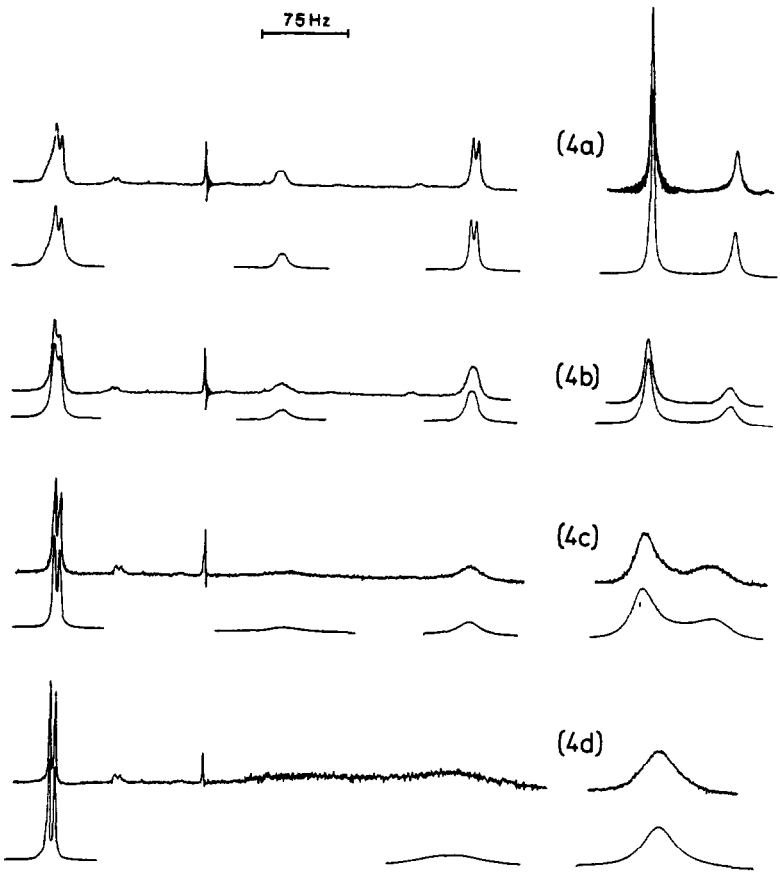


Fig. 4. Experimental and theoretical curves (above and below respectively) for the exchange of the methylic protons of the amide group (right) and the ring protons H_3, H_4 (left) as a function of the temperature: 15°C (4a), 25°C (4b) 35°C (4c), 45°C (4d).

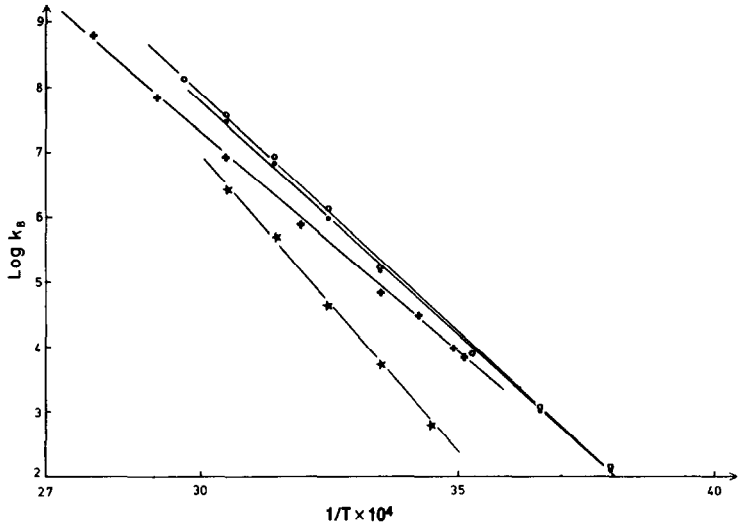


Fig. 5. Arrhenius plots of rate constants k_β (or k_α) in the four solvents used: chloroform (★), 1,4-dioxane (+), tetrahydrofuran (○), and acetone (●).

The equilibrium constant and the related thermodynamic functions

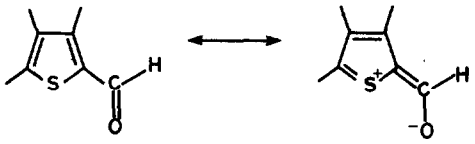
Influence of the solvent. The molar ratio $K = [\beta]:[\alpha]$ of the two isomers strongly depends on temp (Table 2), and its variations allow to derive the enthalpy and entropy change, ΔH_R and ΔS_R, in the equilibrium reaction (Table 2)

$$\alpha \rightleftarrows \beta.$$

The equilibrium constant K is found to be smaller than unity in any medium, with however a strong dependence

of its magnitude upon the solvent used. If we schematically plot chemical shifts as a function of the solvent (Fig. 6), we observe roughly parallel curves for each group of protons in both isomers. This is particularly striking for protons H_3 in isomers α and β (say $H_{3\alpha}$ and $H_{3\beta}$), when using the series of aprotic solvents: 1,4-dioxane (D), tetrahydrofuran (THF) and acetone (A), displayed in the order of increasing dipolar moment $\mu = 0.45$, 1.63 and 2.69 Debyes, respectively. This presumably shows that the solvent has similar effects on electron delocalisation in the aromatic ring of both isomers, but that the gap between curves for $H_{3\alpha}$ and $H_{3\beta}$ is due to the two orientations of the magnetic anisotropy tensor of the amide groups. In orher words, electron delocalisation may account for a rotational barrier between isomers α and β-characterised by the kinetic and activation parameters k, ΔG^+, ΔH^+ and ΔS^+—but not for the equilibrium free energy ΔG_R and the related parameters K, ΔH_R and ΔS_R.

If we take into consideration the close contact of the S atom of thiophen and the O atom of carbonyl in the most abundant isomer α, we are led to assume that the driving force that stabilizes isomer α is an electrostatic interaction between the negatively charged O and the positively charged S atoms. The sign and magnitude of the electrical charge on the S atom of unsubstituted thiophen is in fact the matter of some controversy in literature, depending on whether the participation of S 3d orbitals is neglected or not.[10] The most recent computations using a linear combination of Gaussian orbitals (LGCO) result in a slightly positive net charge (+0.018).[11] Anyway this charge should be greatly shifted towards positive values by the presence of a powerful electron-withdrawing 5-nitro substituent. Analogous assumptions had already been used by Roques *et al.*[12] to account for a 100% predominance of the *cis* configuration in 2-formyl-



thiophen. The assumption of a S–O electrostatic interaction is supported in the present case by four additional observations.

(a) *The influence of the solvent.* A striking feature from the data of Table 3 is the large increase of K with

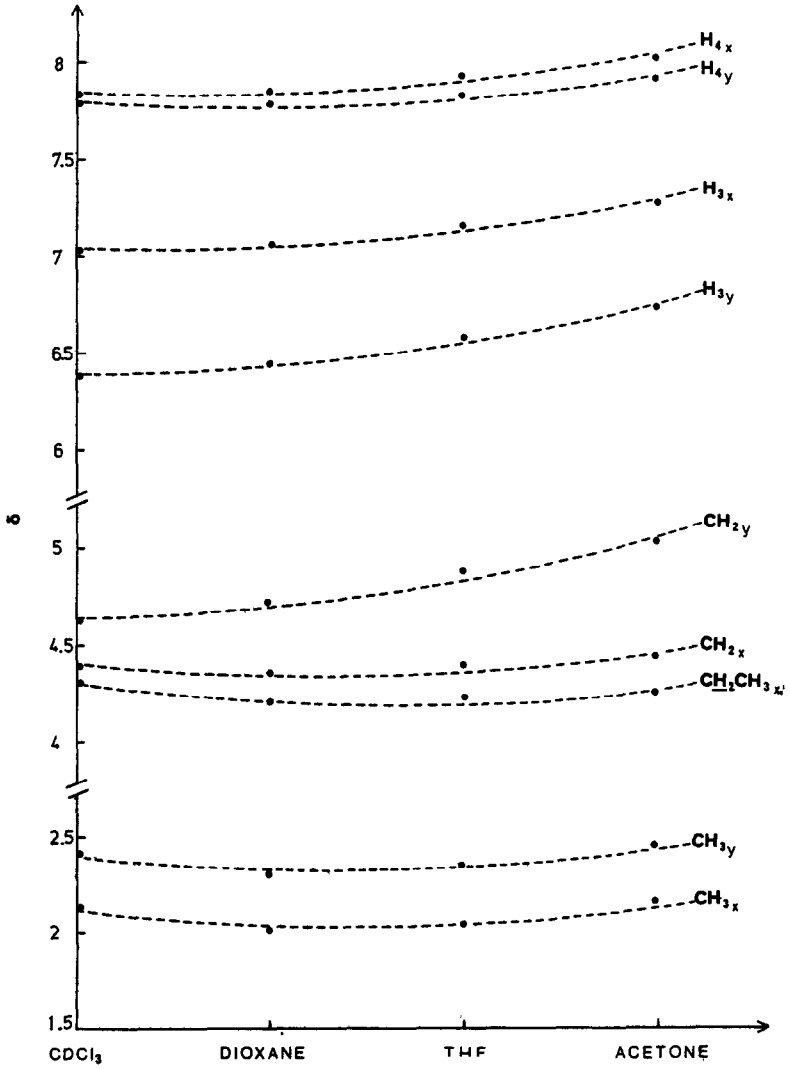
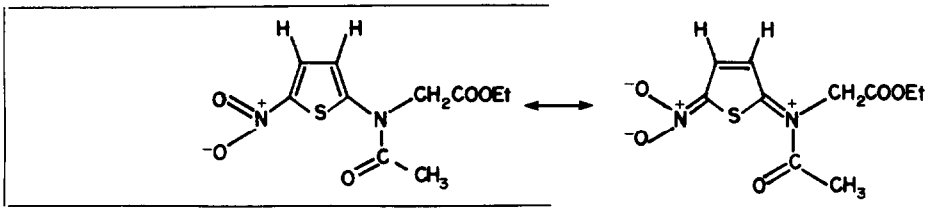


Fig. 6. Graph of chemical shifts (in ppm from TMS) for the protons of compound (1) as a function of the solvent.

the polarity of the three solvents mentioned above (D, THF and A) and its large decrease when using $CDCl_3$, a H-bond donor solvent. The polarity of the solvent is classically assumed to enhance the C–N partial double bond of the amide[2a] and nitro groups, thus increasing the negative and positive charges on the O and S atoms respectively. The increase of the S–O electrostatic interaction therefore accounts for an increasing abundance of isomer α in the more polar solvents. The case of chloroform is exceptional in this respect, because H-bonding of $CDCl_3$ to the amide oxygen[5,13] tends to break the internal O–S interaction, on account of both a neutralisation of the negative charge on O and an increased steric hindrance around the carbonyl extremity.



(b) *The positive sign of the equilibrium enthalpy* ΔH_r. An increased proportion of isomer β on raising the temperature reveals an endothermic process $\alpha \rightarrow \beta$ as expected for the rupture of an internal interaction. The energy necessary to do so is weak in the three aprotic solvents (~ 5 kcal mol^{-1}) and is decreased by half in $CDCl_3$ for the reasons mentioned above.

(c) *The sign and magnitude of the equilibrium entropy* ΔS_R. A large and positive value of ΔS_R (12–13 e.u) in all solvents but $CDCl_3$ (6.95 e.u) reflects the loss of internal strain on going from isomer α to β.

(d) *The downfield shifts of the* N-*methylenic and* C-*methylic protons of the amide group in isomer* α. The electric field arising from the positive charge of S is able to induce an electron shift all along the bonds in the amide group towards the O extremity, which may account for the deshielding of the methylenic and methylic protons in isomer α (0.58 and 0.29 ppm in acetone, respectively).

The rotational barrier

Rate constants k, activation free energies, enthalpies and entropies, ΔG^+, ΔH^+ and ΔS^+ are subscribed with letters α and β depending on whether they refer to either of the two opposed processes: $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$, respectively. These two sets of parameters are related to each other by the well-known relationships

$$k_\alpha[\alpha] = k_\beta[\beta]$$

$$\Delta G_\alpha^\ddagger = \Delta G_\beta^\ddagger + \Delta G_R$$

$$\Delta H_\alpha^\ddagger = \Delta H_\beta^\ddagger + \Delta H_R \text{ and } \Delta S_\alpha^\ddagger = \Delta S_\beta^\ddagger + \Delta S_R$$

The activation enthalpy is clearly larger than the equilibrium enthalpy, e.g. $\Delta H_R = 5.1$ and $\Delta H_\alpha^\ddagger = 18.9$ kcal mol^{-1} in acetone. The activation energy is therefore much larger than the energy required to break the O–S interaction mentioned in the previous paragraph (which is presumably quite close to ΔH_R). The difference between $\Delta H_\alpha^\ddagger$ and ΔH_R, namely $\Delta H_\beta^\ddagger$, thus represents the energy barrier for the aryl-to-nitrogen rotation R_N which was introduced to account for the presence of isomers α and β. This barrier is indeed lower ($\Delta H_\beta^\ddagger = 13$ to 16 kcal mol^{-1}) than the one expected for a hindered rotation R_A about an amide bond, e.g. $\Delta H^+ = 17$–20 and 21–22 kcal mol^{-1} for dimethylacetamide and dimethylformamide.[5] This barrier indicates the creation of a partial double bond between the aryl C2 and the amide N in isomers α and β. This barrier is surprisingly high if we remember that an amide substituent is known to be neither an electron donor nor an electron acceptor towards the aromatic ring, e.g. the Hammett σ (para) constant is zero for the N-acetyl substituent in benzene.[14] Electron delocalisation observed in **1** should then be traced to a direct resonance effect (as in the nitrophenoxide ion[15]) of the type

The activation entropy ΔS^+ for rotation R_N is not significantly different from zero as it is observed for other rotational interconversions, e.g. for rotation R_A of N,N'-dimethylacetamide[5] (in dilute solution). On the whole, the activation free energies are thus smaller by a few kilocalories than those observed for hindered rotation in amides,[2a] and the coalescence temperatures are consequently lower (10–30° instead of 100–150°).

CONCLUSIONS

Slow rotation around the aryl-to-nitrogen bonds had been previously observed in analogous systems, namely in anilides,[2a] but only in the case when rotation was hindered by the presence of *ortho* substituents. It seems to be the first time where such a rotation is hindered by the creation of a partial aryl-to-nitrogen double bond, presumably on account of a direct resonance effect with the nitro substituent. The predominance of isomer α over isomer β, in spite of an energetically unfavourable arrangement of the dipoles of the two substituents (amido and nitro), requires the existence of another interaction of weaker amplitude,[16] which is tentatively assigned to an electrostatic attraction between the positive S atom of the thiophene ring and the negative O atom of the amide substituent.

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