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# CONFORMATIONAL PREFERENCES AND ELECTRONIC EFFECTS IN SELENOPHENE AND TELLUROPHENE CARBONYL DERIVATIVES INVESTIGATED BY LANTHANIDE INDUCED SHIFTS

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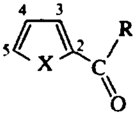
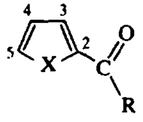
**Abstract**—Computer simulation of the lanthanide induced shifts has been applied to study of the conformational preferences in the 2-formyl and 2-acetyl derivatives of furan, thiophene, selenophene and tellurophene. The results assign a nearly equipopulated mixture of *s-cis* and *s-trans* conformers to the furan, and a preponderance of the *s-trans* form to the thiophene, selenophene and tellurophene derivatives. This difference is interpreted as due to the interaction between the heteroatom and carbonyl oxygen lone pairs. The 2-N,N-dimethylcarboxyamide derivatives of furan, thiophene and selenophene are found to exist mainly in a *quasi*-planar *s-cis* form. The barriers to the rotation about the amide bond in these amides have been measured and related to the electronegativity of the heteroatom.

## INTRODUCTION

Conformational analysis of the rotational isomers of furan and thiophene 2-carbonyl compounds has been recently reported by several authors[1-17] using various techniques, and the results indicate that, in solution, 2-formyl and 2-acetyl-thiophene exist largely in the *s-trans* form[1-5,11-13], whilst 2-formyl- and 2-acetyl- furan exist as mixtures of the *s-cis* and *s-trans* forms[6-10,12,14] and furan and thiophene 2-N,N-dimethyl carboxyamides exist mainly in the *s-cis* form.[15,16]



s-*trans*



s-*cis*

The isomer distributions in 2-formyl-selenophene, 2-formyl and 2-acetyl-tellurophene, obtained from dipole moments in benzene, have been recently reported.[18,19]

The congener 2-carbonyl derivatives of furan, thiophene, selenophene and tellurophene are an interesting class of compounds since they enable a study of the influence of geometrical and electronic parameters on the population of the rotational isomers to be made. It is known[17,18] that the isomer distribution in these compounds is strongly dependent on the solvent used, and therefore homogeneous data are highly desirable in comparative studies.

We report here pertinent data on the 2-formyl, 2-acetyl and 2-N,N-dimethylcarboxyamides of the four heterocycles.

In the present study we have applied the $^1$H-NMR lanthanide induced shifts (LIS) technique, using a previously described[15,16] computer method to simulate the observed LIS in $\alpha,\beta$-unsaturated carbonyl compounds. We could detect no measurable alteration of the conformational equilibria in these systems caused by the presence of lanthanide shift reagents, as shown by the general agreement between our results and the findings of other authors using different techniques.[15,16]

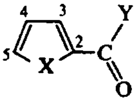
## EXPERIMENTAL

*Synthetic*. All the compounds investigated are collected and numbered in Table 1.

2-Formyl and 2-acetyl derivatives of selenophene and tellurophene were prepared as reported in literature.[20,21] 2-N,N dimethylcarboxyamide derivatives were prepared using a general procedure.[22]

*Tellurophene*-2-N,N-*dimethylcarboxyamide* (**12**). A mixture of 2-tellurophenecarboxylic acid[20] (6 g) and hexamethylphosphoramide (1·5 g) was heated at 180° for 3 h. After cooling at room temp the mixture was repeatedly extracted with benzene and the extracts washed several times with a NaHCO$_3$aq, dried (Na$_2$SO$_4$) and evaporated *in vacuo*.

Table 1. Chemical shifts, coupling constants, measured and simulated LIS, preferred conformations for compounds of general formula



| No | X, Y | H-3[a] | H-4[a] | H-5[a] | Y[a] | $^3J_{34}$ | $^3J_{45}$ | $^4J_{35}$ | $^5J_{CHO\text{-}5}$ | K<br>$\varphi$<br>$\omega$ | A.F. | % *s-cis* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | O, H | 7·17 | 6·55 | 7·60 | 9·53 | 3·61 | 1·65 | 0·78 | 0·74 | 531 | 0·075 | 56 |
| | | 4·43 | 2·03 | 2·55 | 8·99 | | | | | 155 | 0·276[b] | |
| | | 4·39 | 1·78 | 1·83 | 9·20 | | | | | 180 | | |
| **2** | O, $CH_3$ | 7·21 | 6·55 | 7·63 | 2·45 | 3·55 | 1·73 | 0·78 | — | 758 | 0·016 | 47 |
| | | 5·70 | 2·10 | 1·90 | 8·10 | | | | | 175 | 0·502[b] | |
| | | 5·67 | 2·00 | 2·02 | 8·12 | | | | | 100 | | |
| **3** | O, $N(CH_3)_2$ | 6·92 | 6·40 | 7·43 | 3·15 | 3·50 | 1·76 | 0·83 | — | 1246 | 0·049 | 95 |
| | | 11·20 | 2·37 | 3·22 | 7·18 | | | | | 110 | 0·342[b] | |
| | | 11·11 | 3·01 | 2·98 | 7·15 | | | | | 120 | | |
| **4** | S, H | 7·63 | 7·13 | 7·71 | 9·80 | 3·76[c] | 4·90[c] | 1·23[c] | 1·24[c] | 788 | 0·025 | 1 |
| | | 4·53 | 2·40 | 2·86 | 14·19 | | | | | 145 | 0·182[b] | |
| | | 4·51 | 2·45 | 2·50 | 14·26 | | | | | 180 | | |
| **5** | S, $CH_3$ | 7·63 | 7·05 | 7·46 | 2·50 | 3·64 | 4·96 | 1·25 | — | 1617 | 0·044 | 21 |
| | | 5·44 | 1·83 | 2·79 | 9·66 | | | | | 90 | 0·242[b] | |
| | | 5·44 | 1·56 | 2·37 | 9·80 | | | | | 120 | | |
| **6** | S, $N(CH_3)_2$ | 7·38 | 6·97 | 7·27 | 3·13 | 3·67 | 4·86 | 1.20 | — | 699 | 0·004 | 98 |
| | | 6·00 | 1·09 | 1·32 | 6·30 | | | | | 165 | 0·403[b] | |
| | | 5·99 | 1·11 | 1·33 | 6·30 | | | | | 170 | | |
| **7** | Se, H | 7·98 | 7·50 | 8·48 | 9·79 | 3·90 | 5·36 | 1·16 | 1·13 | 411 | 0·012 | 2 |
| | | 2·35 | 1·24 | 1·36 | 7·64 | | | | | 140 | 0·191[b] | |
| | | 2·35 | 1·27 | 1·27 | 7·66 | | | | | 180 | | |
| **8** | Se, $CH_3$ | 7·88 | 7·36 | 8·34 | 2·54 | 3·87 | 5·38 | 1·10 | — | 593 | 0·006 | 13 |
| | | 3·41 | 1·45 | 1·31 | 6·18 | | | | | 125 | 0·413[b] | |
| | | 3·41 | 1·44 | 1·36 | 6·17 | | | | | 120 | | |
| **9** | Se, $N(CH_3)_2$ | 7·50 | 7·30 | 8·15 | 3·15 | 3·83 | 5·40 | 1·14 | — | 560 | 0·016 | 95 |
| | | 4·45 | 0·97 | 1·35 | 4·56 | | | | | 130 | 0·448[b] | |
| | | 4·46 | 1·02 | 1·25 | 4·57 | | | | | 110 | | |
| **10**[d] | Te, H | 8·50 | 8·00 | 9·43 | 9·50 | 4·02 | 6·48 | 1·28 | 0·90 | 424 | 0·027 | 4 |
| | | 2·48 | 1·35 | 1·51 | 8·10 | | | | | 135 | 0·081[b] | |
| | | 2·47 | 1·41 | 1·28 | 8·13 | | | | | 180 | | |
| **11** | Te, $CH_3$ | 8·31 | 7·96 | 9·32 | 2·55 | 4·13 | 6·60 | 1·21 | — | 588 | 0·002 | 10 |
| | | 3·08 | 1·39 | 1·21 | 5·83 | | | | | 115 | 0·420[b] | |
| | | 3·08 | 1·38 | 1·21 | 5·83 | | | | | 120 | | |
| **12** | Te, $N(CH_3)_2$ | 7·84 | 7·84 | 9·05 | 3·15 | 4·10[e] | 6·69[e] | 1·24[e] | — | | | |
| | | 2·69 | 0·58 | 0·69 | 3·68 | | | | | | | |

[a] Figures in the first row indicate chemical shifts ($\delta$) of undoped spectra; figures in the second row indicate observed molar induced shifts; figures in the third row indicate calculated molar induced shifts.

[b] A.F. obtained by permutating the observed LIS of protons 3 and 5.

[c] In presence of a molar ratio L/S = 0·09.

[d] $|J_{CHO\text{-}3}|$ = 0·40.

[e] In presence of a molar ratio L/S = 0·05.

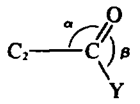
The residue was distilled at 0·05 mmHg (114–116°) and then crystallized from ligroin to give 2 g of **12** with m.p. 69–70°, pure on TLC and GLC analysis; $\nu_{C=O}$(CCl$_4$) 1627 cm$^{-1}$; (Found C, 33·62; H, 3·72; N, 5·48, $C_7H_9ONTe$ requires: C, 33·52; H, 3·61; N, 5·58%).

*Selenophene*-2-N,N-*dimethylcarboxyamide* (**9**). From 2-selenophene carboxylic acid (5 g) pure **9** (2·2 g) was obtained using the above reported procedure, b.p. 96–97° at 0·05 mmHg; m.p. 48–49° from light petroleum (lit[23] m.p. 48–49°); $\nu_{C=O}$(CCl$_4$) 1627 cm$^{-1}$; (Found C, 41·59; H, 4·49; N, 6·76. $C_7H_9ONSe$ requires: C, 41·59; H, 4·48; N, 6·90%).

*LIS*. Lanthanide induced shifts measurements were performed with Eu(fod)$_3$. Spectra of approximately 5% CDCl$_3$ solns (TMS as internal reference), containing 0–0·15 mole of ligand (L) per mole of substrate (S), were obtained at 60 MHz using a Varian A 60–D analytical spectrometer. The lanthanide shift reagent was added stepwise from a stock solution 0·40 M, with the help of a 50 $\mu$l microsyringe. Each signal was followed in the spectra and the LIS were found to be directly proportional to the [L]/[S] molar ratio present.

A least squares fit of the experimental points was used

Table 2. Structural parameters of the carbonyl moiety



| | Y = H | Y = C[a] | Y = N[b] |
|---|---|---|---|
| C–O (Å) | 1·22 | 1·22 | 1·22 |
| C–Y (Å) | 1·08 | 1·54 | 1·32 |
| α (°) | 117 | 120 | 120 |
| β (°) | 124 | 122 | 121 |

[a] Averaged methyl proton coordinates were taken: $H_{av}$–Y = 0·35 Å, colinear with the C–Y bond.

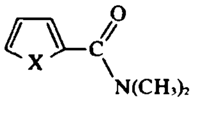
[b] Averaged proton of the methyls were taken: $H_{av}$–Y = 0·91 Å, colinear with the C–Y bond.

to obtain the observed LIS. Calculations relating to the simulation of the experimental LIS data were performed on an CDC-6600 digital computer.

*DNMR*. Temp measurements were based on the chemical shift separation of the protons of a MeOH sample, and utilized the temp-shift correlation of Van Geet.[24] $T_c$ in Table 3 represent the average of several measurements. The Gutowsky–Holm[25] approximation was used in order to calculate the rate constants for the site exchange; these rates were employed to derive the free energies of activation ($\Delta G^{\neq}$) from the Eyring equation, at the coalescence temp. The estimated error in the $\Delta G^{\neq}$ values reported is ±0·2 Kcal/mole and is due almost exclusively to uncertainties in $T_c$.

*Coupling constants*. The coupling constants are calculated directly from the spectra using a scale expansion of 2 Hz/cm, and the values in Table 1 represent the average of several measurements. The accuracy is ±0·05 Hz.

Table 3. Barrier heights to site exchange measured in the presence or absence of Eu(fod)$_3$ in N,N-dimethylamides of general formula.



| No. | X | molar ratio of Eu(fod)$_3$ to amide | Δν Hz | $\Delta G^{\neq a}$ Kcal mol$^{-1}$ | $T_c$ °C |
|---|---|---|---|---|---|
| **3** | O | 0·00 | *b* | — | — |
| | | 0·13 | 42·5 | 16·8 | 26 |
| **6** | S | 0·00 | *b* | — | — |
| | | 0·15 | 41·5 | 14·1 | 12 |
| **9** | Se | 0·00 | 8·0 | 14·2 | −4·8 |
| | | 0·08 | 46·6 | 14·0 | 11 |
| **12** | Te | 0·00 | 8·0 | 13·8 | −11 |
| | | 0·17 | 98·8 | 13·7 | 13·8 |

[a] $\Delta G^{\neq}$ measured at $T_c$.

[b] Accidental isochronous signals, in the experimental conditions (see experimental section).

### *Proton assignments and coupling constants*

The three heterocyclic protons corresponding to each compound in Table 1 yield in most cases well resolved ABX spectra from which proton assignments and coupling constants values can be deduced. However, for compounds **4**, **5** and **12** two signals are almost accidentally isochronous in the undoped $CDCl_3$ spectra, so that complete assignments and coupling constants values cannot be obtained. The addition of LSR removes the signal isochrony (Fig 1), and complete analysis can be achieved in these cases, enabling us to correct some wrong assignments in the literature.[1,3] The doped spectrum of compound **4** permits us to assign unequivocally the $J_{CHO\text{-}5}$ long range coupling constant. This obeys the zig-zag rule and thus suggests *s-trans* conformation.

Compound **10** shows an interestingly high $J_{CHO\text{-}3}$ which can suggest a *s-trans* conformation, in analogy to that reported for other 2-formylheterocycles.[26]

From previous observations, made both by ourselves and other workers,[27–33] coupling constant values are not subject to change when measured in presence of *small* quantities of LSR. Similarly in the present case, coupling constants extracted from the doped spectra are coincident, within the experimental error, with the values which may be deduced from the undoped spectra.

Finally, in analogy to other systems[34–37], an excellent linear relationship exist between the value of the $J_{45}$ (cis olefinic) coupling constant and the Pauling electronegativity of the corresponding heteroatom, for the three classes of carbonyl compounds studied here.

### *LIS simulation*

Computer simulation of the experimental LIS were performed according to methods previously described,[15,16] and the results are collected in Table 1. Symbols have the usual meaning: K is the scale factor in the McConnell and Robertson equation, φ and ω identify the location of the lanthanide ion in the space around the coordination site and the agreement factor (AF) is a measure of the error in the LIS simulation.

The structural model and the internal coordinate system are shown in Fig 2.

Geometries of the hetero-rings, including the $C_2$–C(O) bond, were taken from the X-ray data of the 2-carboxylic acids;[38–40] the interatomic distances and angles in the carbonyl moiety are listed in Table 2. These structural parameters were used to calculate the atomic coordinates of each proton.

Great care is necessary in order to ensure reliability of the results of the LIS simulation process. In our method, all the possible lanthanide spatial locations in the lanthanide-substrate complex are explored, the equilibrium molar fraction of the isomers is a variable in the optimisation process, so that the lanthanide location corresponding to the best LIS simulation (minimum AF) identifies the most likely population ratio between the *s-cis* and *s-trans* isomers. Furthermore, since uncertainties in signal assignments may lead to serious errors in the resulting optimal geometry of the complex, we have systematically exchanged the signals corresponding to protons 3 and 5 in compounds in Table 1. Higher AF have been invariably obtained in the case of the assignments alternative to those reported in Table 1.

In our opinion, some recent[1] LIS simulation data on compounds **1**, **2**, **4** and **5** (Table 1) cannot be considered reliable. In fact, only one lanthanide spatial position (arbitrarily assumed) was considered, and exchanged LIS values for protons 3 and 5 (Table 1) were used for compounds **4** and **5**.

According to structural data,[38-42] the carbonyl group and the heterocyclic ring can be regarded as always coplanar in the case of the 2-formyl and 2-acetyl derivatives in Table 1.

Planar *s-cis* and *s-trans* forms were therefore taken for all these compounds in the calculations of population ratio ($\vartheta = 0°$ and $180°$, respectively, in the model in Fig 2). However, in the case of the four 2-N,N-dimethylamides derivatives in Table 1 (compounds **3**, **6**, **9** and **12**) it is likely that steric hindrance causes deviations from planarity.[16,43] Plots of the minimum AF corresponding to each torsional angle (Fig 2), obtained as previously described,[16] show that a *quasi-planar* ($\vartheta = 40°$) *s-cis* form is the most populated in the cases of amides **3**, **6**, and **9** (Table 1). In this case the atomic coordinates of the "twisted" *s-cis* ($\vartheta = 40°$) and *s-trans* ($\vartheta = 160°$) forms were entered in the simulation process to obtain the population ratio.

In one instance, the tellurophene amide **12**, LIS simulations do not provide a reliable estimate of the relative populations. This is due to artefacts[16] appearing in the above mentioned plot of minimum AF vs the torsional angle $\vartheta$.

### *Barriers to site exchange in N,N-dimethylcarboxyamides*

The influence of the heteroatom on the barrier to rotation about the amide C(O)–N bond in compounds **3**, **6**, **9** and **12** can be deduced from the inspection of the data in Table 3. The highest barrier being observed with the furan-2-N,N-dimethylcarboxyamide. $\Delta G^{\neq}$ were measured at the coalescence temperature in presence and/or ab-

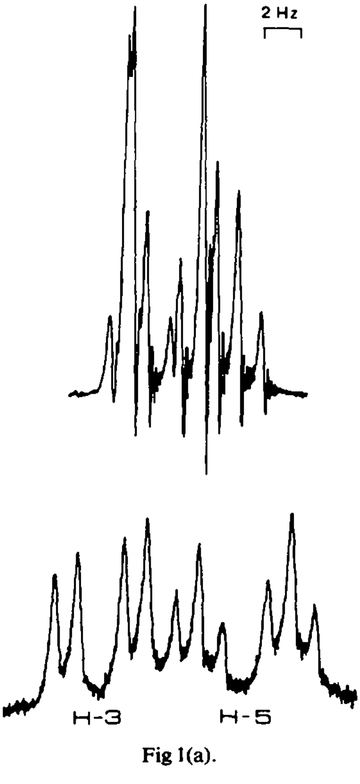


Fig 1(a).

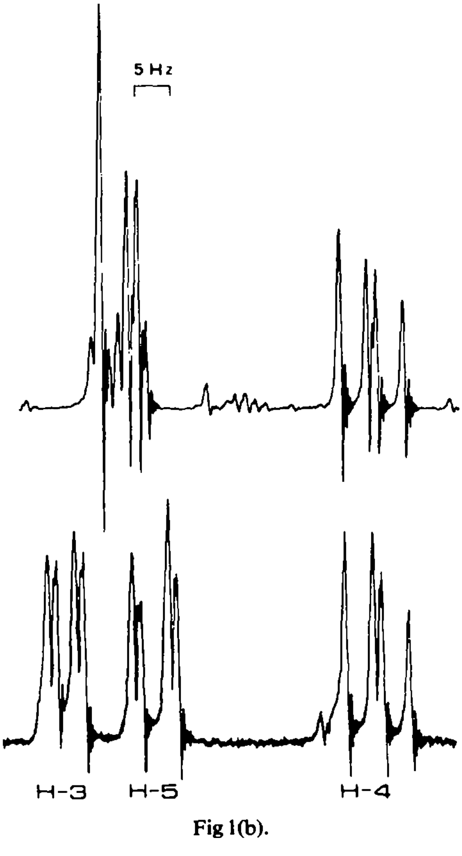


Fig 1(b).

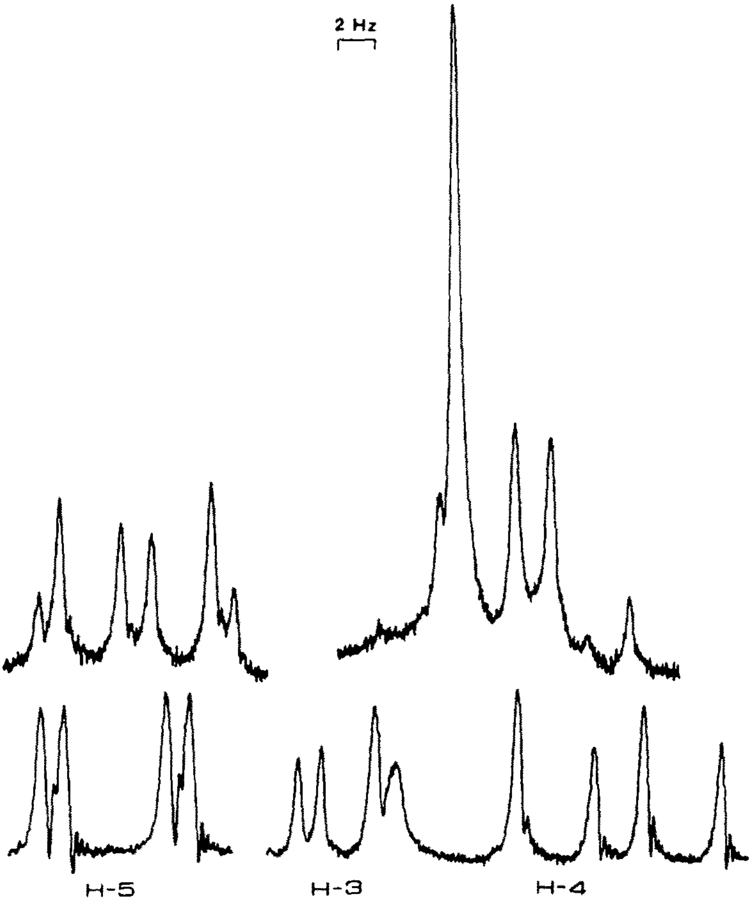


Fig 1(c).

Fig 1. Spectra in absence (upper) and presence (lower) of Eu(fod)$_3$: (a) 2-formylthiophene, (b) 2-acetylthiophene, (c) tellurophene-2-N,N-dimethylcarboxyamide.

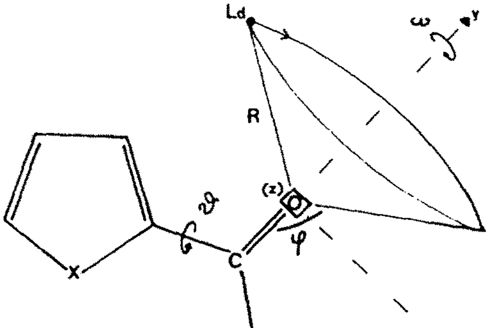


Fig 2. Structural model of the complex carbonyl compound/Eu(fod)$_3$. R represents the Eu–O distance (3 Å); $\varphi$ is the Eu–O–C internuclear angle; the dihedral angle Eu–O–C–C, $\omega$, is zero for the configuration indicated in Figure. Varying R, $\varphi$ and $\omega$ all the Ld spatial locations can be explored. The internal coordinate systems is also shown.

sence of low concentrations of LSR. The addition of LSR allows us to measure the $\Delta G^{\neq}$ of compounds **3** and **6** despite the accidental isochronous methyl signals exhibited in the undoped spectra. Two well resolved signals for the diastereotopic N-methyls are obtained in presence of the LSR.

The reliability of the $\Delta G^{\neq}$ figures obtained in presence of LSR (low molar ratio L/S) is shown by the agreement with the corresponding values obtained in absence of LSR (Table 3). Further evidence showing the reliability of this technique is available in the recent literature.[44–46]

## DISCUSSION

A comparison of the conformational preferences in 2-formyl and 2-acetyl derivatives of furan, thiophene, selenophene and tellurophene can be made on the basis of the LIS simulation results in Table 1. Our data show a nearly equipopulated mixture of *s-cis* and *s-trans* isomers for the furan derivatives, and a preponderance of the *s-trans* form for the thiophene, selenophene and tellurophene compounds.

At present two hypotheses have been advanced to explain the conformational preference of formyl and acetyl derivatives of furan and thiophene. In the first one,[3,4] the existence of a partial negative charge on furan oxygen creates a repulsive interaction with the carbonyl oxygen, so that the otherwise more stable *s-trans* form becomes destabilized in the furan derivatives. A partial positive charge is thought to be present on thiophene sulfur atom[47] creating an attractive interaction which stabilizes the *s-trans* form in thiophene derivatives.

In the second hypothesis,[1] a through-space attractive interaction between sulfur orbitals is invoked to explain the stability of the *s-trans* conformer.

Recent[48] CNDO/2 calculations on selenophene and tellurophene assign a slightly negative charge distribution on selenium (−0·0408) and tellurium (−0·0409) atoms and, consequently, the hypothesis based on the simple electrostatic interaction between the hetero-atom and the carbonyl oxygen does not appear consistent.

On the other hand, going from furan to tellurophene the ring becomes more elongated and the atomic orbitals of hetero-atom become larger, so that a partial overlap between the hetero-atom and carbonyl oxygen lone pairs may become progressively more important.

In the furan derivatives, the above overlap is less significant, and the electrostatic interaction plays a major role.[17,49]

The conformational preferences of $\alpha,\beta$-unsaturated N,N-dimethylcarboxyamides derivatives are strongly determined by steric hindrance factors which shift the conformational equilibrium towards the *s-cis* form,[15,16] and this is true also in the case of amides **3**, **6** and **9** (LIS simulation results in Table 1).

The influence of electronic factors can be inferred also in this case from the respective $\Delta G^{\neq}$ data in Table 3. Structural effects on the barrier to the rotation about the amide bond have been acknowledged in the recent literature on amides.[50]

Our results (Table 3) can be explained considering that the measured torsional barriers about the amide C–N bond reflect the different electronegativity character of the four hetero-atoms. Therefore, the barrier height loss from the value of N,N-dimethylalkylamides ($\Delta G^{\neq}$ about 18·5 Kcal/mole)[50] in our case can be directly related to the inductive electron-actracting ability of the hetero-atom, and the present results are in agreement with the behaviour of these heterocycles in reactions where the inductive effect of the hetero-atom is predominant.[51]

## REFERENCES

[1] S. Nagata, T. Yamabe, K. Yoshikawa and H. Kato, *Tetrahedron* **29**, 2545 (1973)

[2] S. Combrisson, B. Roques, P. Rigny and J. J. Basselier, *Can. J. Chem.* **49**, 904 (1971)

[3] B. Roques and M. C. Fournie-Zaluski, *Org. Magn. Resonance* **3**, 305 (1971)

[4] B. Roques, S. Combrisson, C. Riche and C. Pascard-Billy, *Tetrahedron* **26**, 3555 (1970)

[5] J. M. Angelelli, A. R. Katritzky, R. F. Pinzelli and D. R. Topsom, *Ibid.* **28**, 2037 (1972)

[6] B. R. Larsen, F. Nicolaisen and J. J. Nielsen, *Acta Chem. Scand.* **26**, 1736 (1972)

[7] K. I. Dahlqvist and A. B. Hornfeldt, *Tetrahedron Letters* 3837 (1971)

[8] D. J. Chadwick, J. Chambers, G. D. Meakins and R. L. Snowden, *Chem. Commun.* 624 (1971)

[9] M. L. Martin, J. Roze, G. J. Martin and P. Fournari, *Tetrahedron Letters*, 3407 (1970)

[10] L. Arlinger, K. I. Dahlqvist and S. Forsén, *Acta Chem. Scand.* **24**, 662 (1970)

[11] L. Kaper and Th. J. De Boer, *Recl. Trav. Chim., Pays-Bas* **89**, 825 (1970)

[12] H. Lumbroso, D. M. Bertin and P. Cagniant, *Bull. Soc. Chim. Fr.* 1720 (1970)

[13] M. L. Martin, C. Andrieu and G. J. Martin, *Ibid.* 698 (1968)

[14] F. Mönnig, H. Dreizler and H. D. Rudolph, *Z. Naturforsch.* A, **20**, 1323 (1965)

[15] G. Montaudo, V. Librando, S. Caccamese and P. Maravigna, *J. Am. Chem. Soc.* **95**, 6365 (1973)

[16] G. Montaudo, S. Caccamese, V. Librando and P. Maravigna, *Tetrahedron* **29**, 3915 (1973)

[17] R. J. Abraham and J. M. Siverns, *Ibid.* **28**, 3015 (1972)

[18] H. Lumbroso, D. L. Bertin, J. Morel and C. Paulmer, *Bull. Soc. Chim. Fr.* 1924 (1973)

[19] H. Lumbroso, D. L. Bertin, F. Fringuelli and A. Taticchi, *C.R. Acad. Sc. Paris*, Ser. C, 203 (1973)

[20] F. Fringuelli and A. Taticchi, *J.C.S. Perkin I*, 199 (1972)

[21] J. M. Morel, C. Paulmer, M. Garreau and G. Martin, *Bull. Soc. Chim. Fr.* 4497 (1971)

[22] J. Kopecky and J. Smejkal, *Chem. Ind.* 1529 (1966)

[23] L. Chierici and G. Pappalardo, *Gazz. Chim. Ital.* **88**, 453 (1958)

[24] A. L. Van Geet, *Anal. Chem.* **42**, 679 (1970); **40**, 2227 (1968)

[25] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* **25**, 1228 (1956)

[26] B. P. Roques and S. Combrisson, *Can. J. Chem.* **51**, 573 (1973)

[27] K. T. Liu, *Tetrahedron Letters*, 2747 (1973)

[28] A. F. Bramwell and R. D. Wells, *Tetrahedron* **28**, 4155 (1972)

[29] B. L. Shapiro, M. D. Johnston, Jr. and R. L. R. Towns, *J. Am. Chem. Soc.* **94**, 4381 (1972)

[30] A. F. Bramwell, G. Riezebos and R. D. Wells, *Tetrahedron Letters* 2488 (1971)

[31] J. K. M. Sanders and D. H. Williams, *Chem. Commun.* 422 (1970)

[32] I. Armitage and L. D. Hall, *Chem. Ind.* 1537 (1970)

[33] J. Briggs, F. A. Hart and G. P. Moss, *Chem. Commun.* 1506 (1970)

[34] F. Fringuelli and A. Taticchi, *Gazz. Chim. Ital.* **103**, 453 (1973)

[35] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.* **39**, 905 (1961)

[36] P. Faller and J. Weber, *Bull. Soc. Chim. Fr.* 3193 (1972)
[37] T. Schaefer, *Can. J. Chem.* **40**, 1 (1962)
[38] L. Fanfani, A. Nunzi, P. F. Zanazzi, A. R. Zanzari, M. A. Pellinghelli, *Cryst. Struct. Commun.* **1**, 273 (1972)
[39] P. Hudson, *Acta Cryst.* **15**, 919 (1962)
[40] M. Nardelli, G. Fava and G. Girardi, *Ibid.* **15**, 737 (1962)
[41] C. Riche, *Ibid.* **B29**, 756 (1973)
[42] H. J. Streurman and H. Schenk, *Recl. Trav. Chim. Pays-Bas* **89**, 392 (1970)
[43] M. A. M. Meester and H. Schenk, *Ibid.* **90**, 508 (1971)
[44] G. Montaudo, P. Maravigna, S. Caccamese and V. Librando, *J. Org. Chem.* in press
[45] H. N. Cheng and H. S. Gutowsky, *J. Am. Chem. Soc.* **94**, 5505 (1972)
[46] S. R. Tanny, M. Pickering and C. S. Springer, *Ibid.* **95**, 6227 (1973)
[47] D. J. Clark, *Tetrahedron* **24**, 2663, 3285 (1968)
[48] V. Galasso, Private communication
[49] L. Lunazzi and C. A. Veracini, *J.C.S. Perkin II*, 1739 (1973)
[50] W. E. Stewart and T. H. Siddall, III, *Chem. Rev.* **70**, 517 (1970)
[51] F. Fringuelli, G. Marino and A. Taticchi, *J.C.S. Perkin II*, 1738 (1972)