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CONFORMATIONAL ANALYSIS OF FURAN AND THIOPHEN CARBONYL DERIVATIVES

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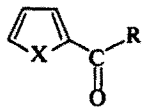
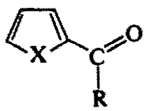
Abstract—The 220 MHz NMR spectra of furan and thiophen carbonyl compounds were measured, and further investigated by benzene solvent shifts, induced chemical shifts by the lanthanide shift reagent Eu(FOD)$_3$; and by the Nuclear Overhauser effect.

Two planar isomers of the furan derivatives exist in the ratio of *ca.* 1 : 1·05 ~ 1 : 1·18 (*cis/trans*), while the *cis* form of thiophen derivatives is favoured. Semi-empirical calculations (CNDO/2) are reported and the influence of sulfur 3d-orbitals are discussed.

INTRODUCTION

Conformational analysis of the rotational isomers of furan and thiophen carbonyl compounds has been recently studied by several authors, who have each employed different techniques to determine the conformations. The results obtained, however, are inconsistent with themselves and this problem has still some ambiguous points. For instance, it has been considered that 2-formyl and 2-acetyl furan have two planar isomers, o-cis and o-trans, since two separate carbonyl absorption bands appear in the IR spectrum.[1]


(X-cis)


(X-trans)

(I) X=O, R=H (III) X=S, R=H
(II) X=O, R=CH_3 (IV) X=S, R=CH_3

The results of X-ray analysis,[2] NMR solvent shifts[3] and NOE experiments[4] show that, at equilibrium, the amount of the o-cis form is larger than that of the o-trans form but the results of IR torsional frequency studies,[5] low temperature NMR chemical shifts[6] and gas-phase microwave measurements[7] demonstrate that the o-trans form is dominant. Thus there are still disagreements on the ratio of two conformers.

On the other hand, it was demonstrated from the NMR spectra of 4-bromo-2-formylthiophen and 2-formylthiophen that thiophen aldehyde derivatives did not exist as double conformers but as the s-cis form (according to the analysis of the long range coupling[2,8]), and that this s-cis form did not isomerise if the temperature was varied. This is also supported for these compounds by dipole moment measurements,[9] NOE,[2] liquid crystal NMR,[10] F/H coupling constants.[11] On the contrary, Chadwick *et al.*[12] pointed out that the IR carbonyl absorption band of thiophen-2-carbaldehyde showed the presence of 20% s-trans form.

In order to make these problems clearer, we employed NMR benzene solvent shifts and NMR measurements of lanthanide induced chemical shifts which are known to be quite effective for the conformational analysis of the organic compounds containing carbonyl groups. Furthermore, for the thiophen carbonyl derivatives, which have not been treated theoretically, we carried out a CNDO/2 calculation without and with sulfur 3d-orbitals, in order to evaluate the energy difference of isomers and internal rotational barrier. The NOE experiment was performed to confirm the result expected by calculation for 2-acethylthiophen.

RESULTS AND DISCUSSION

NMR solvent effect. There is an empirical law[13–15] for benzene solvent effects of organic compounds containing carbonyl groups. That is to say, considering the plane perpendicular to the C=O bond through the carbon atom of carbonyl group (Fig 1), the solvent shift $\Delta\tau_{CCl_4-C_6D_6}$ is negative (shifts to the lower field) for the protons on the left hand side from this plane, while positive (shifts to the higher field) for the protons on the opposite side. The

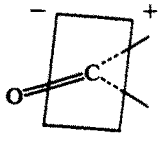


Fig 1.

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NMR solvent shift ($CDCl_3$-C_6D_6)* for the four kinds of carbonyl derivatives (I) to (IV) (at 298°K) listed in Table 1 show that (i) in the furan derivatives (I) and (II), H_B and H_c protons show larger shifts than other protons, while in the thiophen derivatives (III) and (IV), H_C protons show remarkably higher shifts than other protons, and (ii) the difference of H_A proton shift of (II) is smaller than that of (IV). According to the empirical law which means, in this case, that X-trans form makes H_A proton shift to lower field, it follows from these results that furan derivatives, (I) and (II) exist in both O-cis and O-trans forms, and while thophene derivatives, (III) and (IV) take the S-cis form predominantly. On the other hand, from the study of NMR benzene solvent shifts, Timmons[16] obtained the following results (Fig 2).†

Table 1. Chemical shifts in $CDCl_3$ and C_6D_6 (ppm), and $\Delta\tau_{CDCl_3-C_6D_6}$

Compound		$CDCl_3$	C_6D_6	$\Delta\tau_{CDCl_3-C_6D_6}$
I	H_A	7·19	6·50	0·69
	H_B	6·53	5·77	0·76
	H_C	7·63	6·84	0·79
	H(—CHO)	9·58	9·22	0·36
II	H_A	7·11	6·71	0·40
	H_B	6·45	5·83	0·62
	H_C	7·51	6·84	0·67
	$H(CH_3)$	2·45	2·05	0·40
III	H_A	7·67	6·97	0·70
	H_B	7·12	6·48	0·64
	H_C	7·69	6·87	0·82
	H(—CHO)	9·95	9·51	0·44
IV	H_A	7·56	7·00	0·56
	H_B	7·04	6·48	0·56
	H_C	7·64	6·85	0·79
	$H(CH_3)$	2·53	2·03	0·50

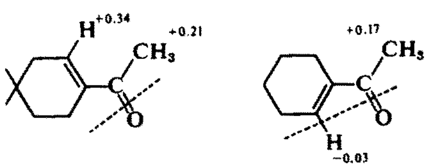
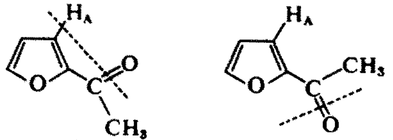


Fig 2. Benzene solvent shifts of organic compounds containing a carbonyl group ($\Delta\tau_{CCl_4-C_6H_6}$, ppm).

Provided that the solvent shifts of H_A and methyl proton in the two compounds in Fig 2 are the same for the two isomers of 2-acetylfuran, one obtains following relationship for the amount of the solvent shift:



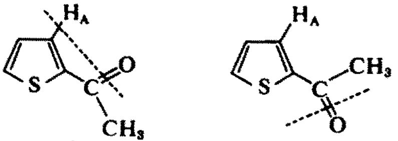
1 : α

$$\left.\begin{array}{lll} H_A: & -0{\cdot}03\times 1+0{\cdot}34\times\alpha=0{\cdot}40 & \alpha=1{\cdot}265 \\ CH_3: & 0{\cdot}17\times 1+0{\cdot}21\times\alpha=0{\cdot}40 & \alpha=1{\cdot}095 \end{array}\right\}\alpha=1{\cdot}18$$

(average)

where, α is the ratio of the amount of the O-cis form to that of the O-trans form. This ratio, 1 : 1·18, is in good agreement with previous results (1 : 1·1)[4b] obtained by NOE experiment.

By the same method as for the furan derivatives, we obtained the following results for thiophen derivatives:



1 : α

$$\left.\begin{array}{lll} H_A: & -0{\cdot}03\times 1+0{\cdot}34\times\alpha=0{\cdot}56 & \alpha=1{\cdot}735 \\ CH_3: & 0{\cdot}17\times 1+0{\cdot}21\times\alpha=0{\cdot}50 & \alpha=1{\cdot}571 \end{array}\right\}\alpha=1{\cdot}65$$

(average)

From these experimental results, it may be concluded that in furan derivatives (I) and (II), two planar isomers exist in about equal amounts with the O-cis form slightly predominating and that in the thiophen derivatives (III) and (IV), the same tendency in the benzene solvent shifts is observed, namely the ratio in equilibrium is not affected by the substituents, whether proton or methyl group. To confirm these results, we measured the induced chemical shifts by the lanthanide shift reagent.

NMR measurements of induced chemical shifts of lanthanide shift reagent $Eu(FOD)_3$. Lanthanide shift reagent is known to induce large paramagnetic shifts, so that it has been utilized to give coincident peaks from formally non-equivalent protons and non-analyzable spectra of organic compounds as well as assignments of proton signals or conformational analysis based on pseudocontact shifts.[18,19] The Eu^{3+} ion is a paramagnetic ion with low-lying Russell-Saunders states, giving a small separation of the highest and lowest occupied metal orbitals, and this has been found empirically to lead to inefficient nuclear spin-lattice relaxation.[20]

By the addition of lanthanide ion Eu^{3+} to samples of compounds (I)–(IV), we also tried to induce largely pseudocontact shifts dependent only on distance and geometry rather than contact shifts dependent on covalent bonding.[21,22] The results

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*In our experiments, there was no difference in proton chemical shifts between CCl_4 and $CDCl_3$ solutions.

†The experimental results obtained by Timmons are confirmed by other workers.[17]

obtained by adding 10 mg a time to these compounds are shown in Figs 3–6 as linear plots of induced proton shifts *vs.* the amounts of Eu(FOD)$_3$.

From calculations on the ratio of the gradient of these straight lines (see Table 2), we obtained the following characteristic features for each furan and thiophen derivatives. These compounds (I)–(IV) have not only carbonyl oxygen lone pair but oxygen or sulfur lone pairs in the heterocyclic ring, so that it is necessary to estimate the amounts due to the induced shifts of thiophen and furan themselves in the same conditions. Addition of the Eu(FOD)$_3$ shift reagent to these samples, however, caused no shifts of protons in comparison with the protons of compound (I)–(IV). This fact demonstrates that the shift reagent Eu(FOD)$_3$ is coordinated only to the carbonyl lone pair under the experimental conditions used. Although this fact is novel and interest-

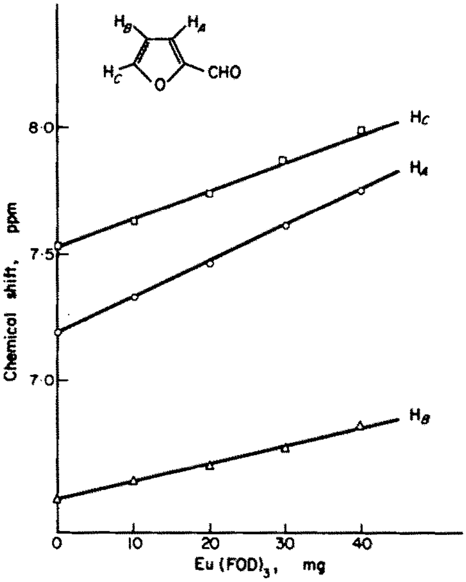

Fig 3. The variations of chemical shifts of ring protons after adding Eu(FOD)$_3$.

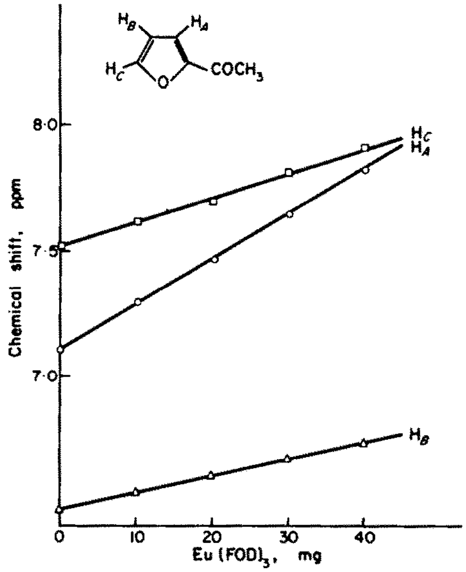

Fig 4. The variations of chemical shifts of ring protons after adding Eu(FOD)$_3$.

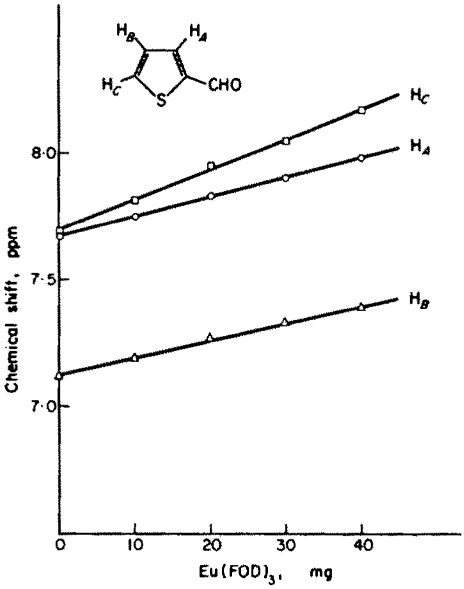

Fig 5. The variations of chemical shifts of ring protons after adding Eu(FOD)$_3$.

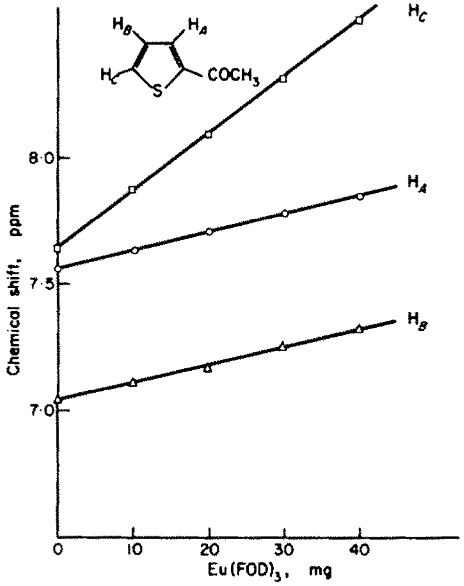

Fig 6. The variations of chemical shifts of ring protons after adding Eu(FOD)$_3$.

Table 2. The ratio of the gradient of linear plots

	I	II	III	IV
H_A	2	2·65	1·13	1
H_B	1	1	1	1
H_C	1·20	1·39	1·96	2·39

ing, we lay it aside to discuss the ring-proton shifts only. From Table 2, we find very large shifts of H_A protons in furan derivatives and H_C protons in thiophen derivatives, respectively. These results support the idea that two planar conformers exist in furan derivatives (I) and (II), and that the s-cis form is favoured relative to the s-trans form in thiophen derivatives (III) and (IV), in accord with the results obtained from benzene solvent shifts.

In order to discuss these experimental results quantitatively, we calculated the relative value of the psedocontact shift[23] (Eq. 1)

$$\frac{\Delta H_i}{\Delta H_P} = \frac{K(3\cos^2\phi_i - 1)}{R_i^3} \tag{1}$$

where K is a constant for any given molecule at a known temperature and ϕ_i is the angle between the i-th proton and principal axis and R_i is the distance from the i-th proton to the Eu^{3+} ion.

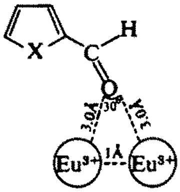

Fig 7. The two locations of the Eu^{3+} ion.

Following Hinckley's approximation for the position of the Eu^{3+} ion,[18] the location and distances between carbonyl oxygen atom and Eu^{3+} ion are estimated as in Fig 7 and the results of the shift ratio for H_A, H_B and H_C protons are presented in Table 3. Calculations were carried out in a given ratio on the assumed distance between Eu^{3+} ion and carbonyl oxygen atom, 3·0 Å, as usual, only for compounds, (I) and (III), since acetyl derivatives show the same tendency as formyl derivatives, respectively as shown by benzene solvent shifts.

Thus, it may be concluded from Table 3 that in compound (I) two isomers exist in the ratio of *ca.* 1:1·05 (o-trans to o-cis) in contrast to 1:1·18 deducted from NMR solvent shifts; while in compound (III) the ratio is 1:1·65, obtained from NMR solvent shifts, showing the nearest experimental value to that obtained by calculation. These results are in good agreement with the results of NMR solvent shifts and demonstrate that two isomers exist in about equal amounts in furan derivatives, while in thiophen derivatives it may show that the s-cis form is favoured relative to the s-trans form with little possibility of existing largely in the s-cis form.

Calculation by CNDO/2 *method.* For furan-2-carbaldehyde, the CNDO/2 calculation[24,25] accounted successfully for experimental results such as the existence of two isomers, the more stable conformer (o-cis), the height of barrier (8·5 Kcal/mol[25]), and other data.

In this section, we account for experimental results of thiophen derivatives which have not been treated theoretically elsewhere. As shown in the experimental section, one of the most interesting results in thiophen carbonyl derivatives may be the fact that the s-cis form is overwhelmingly predominant part relative to s-trans form, or it may be said to exist as a single conformer, contrasting with the existence conformer mixtures for furan derivatives. Particularly, it is interesting to estimate whether sulfur d-orbitals participate to determine the conformation. First, we studied thiophene-2-carbaldehyde by the CNDO/2 method without including sulfur 3d-orbitals and the results of the total energy and internal rotational barrier are given in Fig 8, which surprisingly shows that thiophene-2-carbaldehyde is rather stable when the plane of the aldehyde group is perpendicular to the ring plane in the s-trans form. We measured NOE experiment of 2-acetylthiophen to examine whether this result is reasonable. It is expected from this experiment that the irradiation of the methyl signal

Table 3. Calculated values for assumed ratio in equilibrium

	Compound (I)				Compound (III)			
ratio	o-cis only[a]	1:1·05[a]	1:1·18[a]	o-trans only[a]	s-cis only[b]	1:1·65[b]	1:1·30[b]	s-trans only[b]
H_A	2·33	2·98	3·09	4·77	1·21	2·00	2·62	4·11
H_B	1·01	1·00	1·00	1·00	1·00	1·00	1·00	1·00
H_C	1·00	1·21	1·22	1·49	4·43	3·02	2·81	1·03

[a] In compound (I), these values were calculated on the assumption that the Eu^{3-} ion exists on the line of carbonyl group.

[b] In compound (III), these values were calculated on the other position of Eu^{3+} ion (see Fig 7), since the other calculated values, on the line of carbonyl group, are extremely too much of H_A in comparison with experimental results.

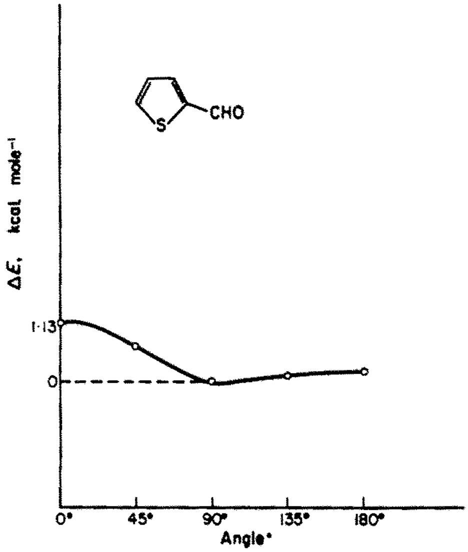

Fig 8. The energy difference in total energy of thiophen-2-carbaldehyde by sp basis set calculation.

*angle: between ring plane and aldehyde group
0°: s-cis form 180°: s-trans form

would result in enhancement of H_A proton signal only in the s-cis form, since the distance between the methyl and H_A proton is 2·00 Å in the s-cis form and 3·56 Å in the perpendicular form. The result obtained from the NOE experiment shows that only H_A proton signal is enhanced (NOE (%): 37·0%*), demonstrating that the s-cis form is preferable to the perpendicular form. This conclusion is also indicated from the long-range coupling by zigzag path.[2,8]

On the other hand, one cannot expect that the result obtained by CNDO/2 method will be so largely improved by using some more accurate methods, if excluding d-orbitals, because there is so much evidence that CNDO/2 method describes well the internal rotational barrier, since it succeeded in accounting for the case of furan derivatives.[24,25] Thus we again tried to calculate by CNDO/2 method including sulfur d-orbitals and obtained the results† shown in Fig 9, showing that the s-cis form is more stable by *ca.* 3·76 Kcal/mole than the s-trans form, and the barrier is about 10·58 Kcal/mole. This result explains the experimental results, that thiophen-2-carbaldehyde takes mainly the s-cis form and that its barrier is 10·3 ± 0·3 Kcal/mole according to the ultrasonic relaxation experiments,[28] and it also implies that the s-trans form may exist in equilibrium even if it is minor amount, as was pointed out by Chadwick *et al.*[11] from IR spectral evidence.

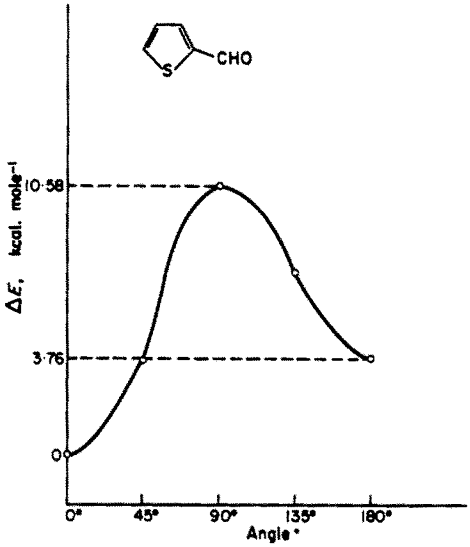

Fig 9. The energy difference in total energy of thiophen-2-carbaldehyde by spd' basis set calculation.

*angle: between ring plane and aldehyde group
0°: s-cis form 180°: s-trans form

Moreover, in order to elucidate the origin of the potential barrier (ΔE) and particularly the role of sulfur 3d-orbitals, we first divided ΔE into two parts: $\Delta E = \Delta E^{del.} + \Delta E^{th.}$‡ where the first term $\Delta E^{del.}$ is the delocalization energy along the π-system and then may be further divided into two parts: $\Delta E^{del.} = \Delta E(\pi - \pi) + \Delta E(d - \pi)$ corresponding to the delocalization energy $\Delta E(\pi - \pi)$ by π-conjugation and $\Delta E(d - \pi)$ by $d - \pi$ conjugation, respectively. The second term $\Delta E^{th.}$ represents through-space interactions which are considered to vary appreciably according to the rotation of aldehyde proton. All through-space interactions are presented in Tables 4 and 5, and the sum ($\Delta E^{th.}$) of these are shown in Fig 10. It follows from Fig 10 that in the case of only sp basis set for sulfur atom, $\Delta E^{th.}$ is the shallow-well type potential barrier, while in the case of spd' basis set a large stabilization energy for the s-cis form is obtained by the participation of 3d-orbitals of sulfur atom, as is shown in Fig 10.

Furthermore, it will be seen from Table 5 that the main factors to give rise to such a large stabilization are the through-space interactions ΔE

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*See the Ref. 4b or the experimental section with regard to the calculated value.

†In this calculation which includes 3d-orbitals in sulfur atomic orbital basis set, we obtained the energy difference of *ca.* 30 eV in total energy in comparison with the calculation excluding d-orbitals. Although the value seems to be somewhat large, the calculation may be valid to discuss the difference between conformations.

‡Here, we defined $\Delta E^{del.}$ as the energy of π-conjugation between neighboring atoms at Z-direction and $\Delta E^{th.}$ as the energy of through-space interaction between non-neighboring atoms.

Table 4. E_{AB} values (diatomic parts) for various geometries by sp basis set calculation

	0° (s-cis)	45°	90°	135°	180° (s-trans)
E_{S-O}	0·10626 (eV)	0·04949 (eV)	−0·03853 (eV)	−0·04003 (eV)	−0·01453 (eV)
E_{S-8H}*	−0·08076	−0·06313	−0·01548	0·04868	0·08139
E_{HA-O}	0·00060	0·00087	−0·00966	−0·00966	−0·01809
E_{HA-8H}	−0·00743	−0·00452	−0·00250	−0·00231	−0·00250
E_{3C-O}	−0·19276	−0·12647	−0·02985	−0·04283	−0·06830
E_{3C-8H}	0·06383	0·03785	−0·02985	−0·07001	−0·07545
E^{th}(total)	−0·11026	−0·10591	−0·11705	−0·11616	−0·09748

*8H is the proton of the aldehyde group.

Table 5. E_{AB} values (diatomic parts) for various geometries by spd′ basis set calculation

	0° (s-cis)	45°	90°	135°	180° (s-trans)
E_{S-O}	−2·18417 (eV)	−1·57606 (eV)	−0·52771 (eV)	0·09774(eV)	0·27896 (eV)
E_{S-8H}*	−0·19812	−0·24976	−0·49977	−0·98239	−1·28227
E_{HA-O}	−0·01461	−0·01701	−0·02435	−0·04071	−0·05292
E_{HA-8H}	−0·01510	−0·00925	−0·00313	0·00008	0·00128
E_{3C-O}	−0·27828	−0·22571	−0·14326	−0·16133	−0·18892
E_{3C-8H}	0·05711	0·03311	−0·03336	−0·06922	−0·06993
E^{th}(total)	−2·63317	−2·04468	−1·23158	−1·15583	−1·31380

*8H is the proton of the aldehyde group.

[S(3d)−A]* as shown in Fig 11, which clearly shows that the longer the distance between them, the smaller the interaction becomes. Therefore, the fact that the s-cis form is much more stable than the s-trans form may be attributed to the large participation of sulfur 3d-orbitals by through-space interactions.

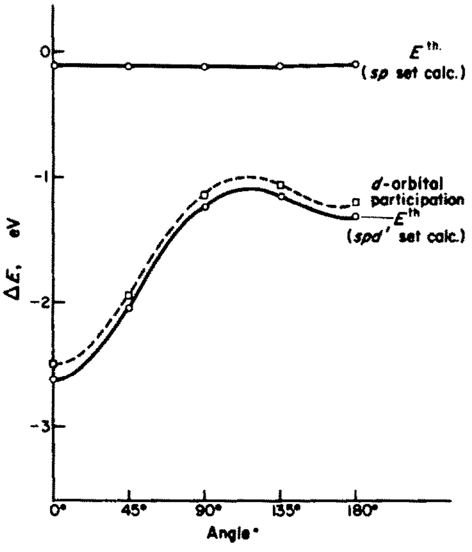

Fig 10. d-orbital participation; the difference of $\Delta E^{th.}$ between sp and spd′ basis set calculation.

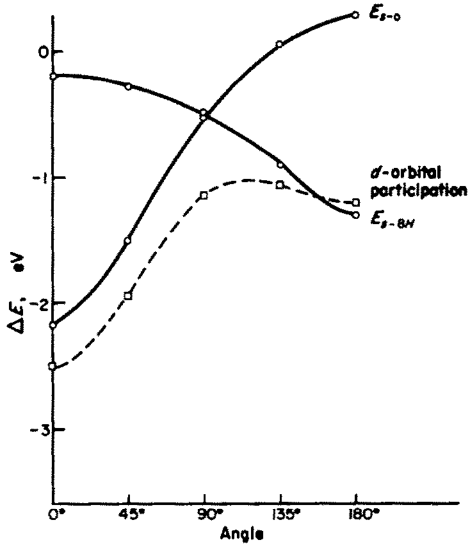

Fig 11. The main components of d-orbital participation.

Thus, it may be appropriate to represent the through-space interaction $\Delta E^{th.}$ as $\Delta E^{th.} = \Delta E[S(3p)-A] + \Delta E[S(3d)-A]$, where $\Delta E[S(3p)-A]$ is the through-space interaction energy between sulfur 3p-orbitals and the oxygen and hydrogen atoms in the aldehyde group, and then is considered

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*ΔE[S(3d)−A] is defined as the through-space interaction between sulfur 3d-orbitals and aldehyde proton or oxygen atom.

to be approximately equal to $\Delta E^{th.}$ in the case of the sp basis set of sulfur atom.

In the case of furan-2-carbaldehyde, ΔE is approximated by $\Delta E = \Delta E(\pi - \pi) + \Delta E[O(2p) - A]$ and the repulsive energy $\Delta E[O(2p) - A]$ is usually very small ($\leqq 0{\cdot}150\,eV$) so that, approximately $\Delta E \sim \Delta E(\pi - \pi)$ which means that the origin of the potential barrier of furan-2-carbaldehyde is mainly $\pi - \pi$ delocalization, as was discussed earlier.

On the other hand, in the case of thiophen derivatives, if 3d-orbitals are excluded, $\Delta E(\pi - \pi)$ and $\Delta E[S(3p) - A]$ cancel out and consequently the total energy difference ΔE shows such a curve as in Fig 8. In the calculation including sulfur 3d-orbitals in thiophen derivatives, however, $\Delta E(\pi - \pi)$ value is approximately equal to the internal rotational barrier of compounds with π-conjugation, for example 6·60 Kcal/mole for benzaldehyde and 4·39 Kcal/mole for acetophenone by *ab initio* calculations,[27] and $\Delta E(d - \pi)$ and $\Delta E[S(3d) - A]$ will cancel each other out. So it is reasonable that the total energy as is shown in Fig 9 consists from the summation of $\Delta E(\pi - \pi)$, $\Delta E(d - \pi)$ and $\Delta E[S(3d) - A]$ values.

These considerations lead us to the conclusion that the interaction between sulfur 3d-orbitals and the carbonyl oxygen lone pair is attractive and that this through-space interaction is the cause of the greater stability of the s-cis form relative to the s-trans form.

CONCLUSION

Conformational analysis of furan carbonyl derivatives by NMR has given further conclusive evidence for their existence in two planar isomers and at the same time has given more quantitative results (1; 1·18), in good agreement with experimental values, while in thiophen carbonyl derivatives the reason why the s-cis form is preferred is mainly due to sulfur 3d-orbital participation, which decreases as the interacting atoms are separated.

EXPERIMENTAL

The samples of thiophen- and furan-2-carbonyl compounds were of commercial quality (Tokyo Kasei Org. Chemicals) and distilled under vacuum before use. The NMR measurements were performed on a 10% soln with *ca.* 1% of tetramethylsilane, but NOE experiments were performed on a 20% soln. The solvents, deuterochloroform, hexadeuterobenzene and carbon disulfide (spectrograde) were also of commercial quality and used without further purification.

NMR measurements of induced proton shifts by Eu(FOD)$_3$

The 220 MHz NMR spectrum (Varian HR-220 spectrometer) was obtained at 297°K and the first concentration of these samples was 60–70 mmol/l. Eu(FOD)$_3$ was added 10 mg at a time into four sample tubes.

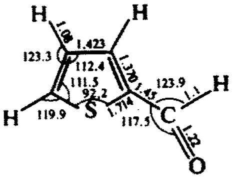
Nuclear Overhauser effect experiment

The 100 MHz NMR spectrum of 2-acetylthiophen was recorded at 298°K on 20% solution of carbon disulfide in sealed tubes. Before sealing, most of the oxygen was removed by freeze-pump-thaw cycles under high vacuum. The nuclear Overhauser enhancements were calculated from measurements of the quotient of the integrated intensities of the 3-proton absorptions with and without irradiation of the methyl proton signal.

Method of calculation

The calculation was carried out with CNDO/2 method of Pople *et al.*[28] which was expanded by Santry and Segal,[29] who considered three possible basis sets for second-row atom referred to as sp, spd, spd′. The sp set consists of 3s and 3p functions only and is analogous to the calculations on first-row atoms. The spd set also includes five 3d atomic orbitals with same radial part as the 3s and 3p functions, while spd′ has d functions which are more diffuse. So that, in this case, sp and spd′ set were used for the calculations.

The geometry used (shown below) is taken from the microwave data of thiophen, the crystal structure determination of C.C.CO$_2$H angle in 2-furoic acid and the known geometry of the aldehyde group.[30]



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