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INFRARED INTENSITIES AS A QUANTITATIVE MEASURE OF INTRAMOLECULAR INTERACTIONS—XVI[1]

2-SUBSTITUTED THIOPHENES AND FURANS

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Abstract—IR intensities of ring stretching bands for 2-substituted furans and thiophenes can be correlated with the substituent σ_R^0 constants and provide evidence for the electronic interactions within these compounds. For carbonyl substituents the results are influenced by the conformation of the carbonyl group relative to the ring.

INTEGRATED intensities of IR ring-stretching bands have assisted understanding of intramolecular substituent-ring and substituent-substituent electronic interactions.[2] Empirical relations connecting these intensities with σ_R^0 values could be justified qualitatively by valence-bond methods[3] and the intensities could be calculated quantitatively by the CNDO/2 procedure.[4] This work has been extended to pyridines[5,6] and into the aliphatic series;[1,7] we are concerned in the present paper with thiophenes and furans.

Although the geometry and symmetry of the benzene ring is considerably altered by the substitution of O or S for .CH:CH. (more than, *e.g.*, by substitution of N for CH), there is considerable evidence of similarity in electronic effects of substituents with and through such modified rings.[8] The Hammett equation holds well for pK_a of substituted thiophene, furan, and pyrrole carboxylic acids,[9–12] and the electrophilic substitution of substituted thiophenes follows linear free energy relationships.[13] For furans, the proton chemical shifts have been related to σ_R and σ_I parameters,[14] and the γ(CH) deformation frequency near 700 cm^{-1} for thiophenes is a linear function of σ_R^0.[15] Most of the work just mentioned has been primarily concerned with ρ-constants for use in furan and thiophene systems. However, recently some attention has been turned to the problem of σ-constants appropriate to the replacement of .CH:CH. by S or O; σ^+ constants for thiophene are available,[16] for a general discussion, see ref. 17.

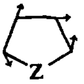
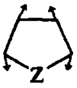
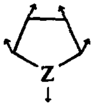
Frequency assignments for the infrared spectra of thiophenes, furans, and their 2-substituted derivatives are well understood[18] and good agreement is found with calculated thermodynamic functions in both the furan[19] and thiophene[20] series. Frequency assignments for 2-substituted thiophenes have recently been discussed in detail.[21] German[22,23] and especially, Russian[24] workers have investigated the ν(CH) intensities for furan and thiophene and their 2- and 3-substituted derivatives and found for the substituted compounds a monotonic dependence on substituent σ_I values. Previous semiquantitative intensities of the ring-stretching bands of

2-substituted furans[25] and of 2-[26] and 3-substituted thiophenes[27] had disclosed large variations which could be correlated with the nature of the substituent. We now report an investigation of the integrated intensities of the ring stretching bands of thiophene and furan and series of each of their 2-substituted derivatives. Some previous work along these lines has been reported by Andrieu and Mollier:[28] they have investigated a number of aryl 2-thienyl ketones and reached interesting conclusions regarding their conformation.

RESULTS AND DISCUSSION

Valence bond treatment of vibration ν_{15}. The forms of the vibrations, ranges of frequency and intensity found, and the notation* used are given in Table 1. During vibration ν_{15}, bonds C2—C3 and C4—C5 change in length out of phase, leading to distortions in the sense of **4** and **5** at the vibration extremes. In valence-bond notation, this implies varying importance of canonical forms, thus **6** and **7** contribute specifically to extreme **4** of the vibration and **8** and **9** to **5**. Thus vibration ν_{15} results in an oscillating dipole, changing in direction [**10** (for **4**) $\rightleftharpoons$ **11** (for **5**)] though not in scalar magnitude. This situation is similar to that found[4] for vibration ν_{16b} in monosubstituted benzenes. Hence vibration ν_{15} should be only weakly allowed in the infrared spectrum owing to the small contribution of the dipole change in direction β (of **12**). The observed intensity in thiophene is only A = 10 (*cf* Table 1). In furan the observed intensity

Table 1. Frequency and intensity ranges for ring stretching bands

		 **1** ν_{15}	 **2** ν_6	 **3** ν_5
Furan	ν (cm^{-1})	1586	1484	1378
	ε_A	10	50	20
	A	(380)	600	190
2-Subst. Furans	ν (cm^{-1})	1610–1558	1528–1470	1278–1396
	ε_A	7–540	35–310	10–140
	A	300–7260	460–4360	125–1945
Thiophene	ν (cm^{-1})	1504	1406	1358
	ε_A	0·7	35	vw
	A	10	390	—
2-Subst. Thiophenes	ν (cm^{-1})	1569–1504	1451–1404	1365–1335
	ε_A	7–250	20–340	5–150
	A	10–3430	510–3270	70–1390
3-Subst. Thiophenes	ν (cm^{-1})	1555–1481	1443–1392	1374–1355
	ε_A	90–240	65–135	5–45

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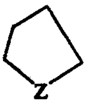
* Two notations have been used to describe the mode of furan and thiophene: the present paper uses that originally devised by R. C. Lord, Jr. and F. A. Miller, *J. Chem. Phys.* **10**, 328 (1942), and used later in refs 18, 25, 26, 27. The alternative notation of A. Hildago, *J. Phys. Rad.*, **16**, 366 (1955), has been used in ref 21. (ν_{14}, ν_5, ν_4 designate the three ring-stretching vibrations considered here).



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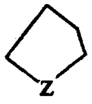

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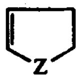

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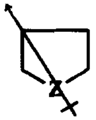

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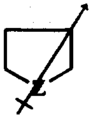

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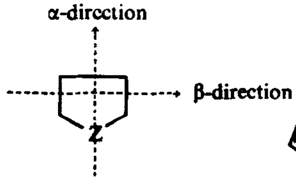

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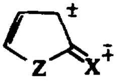

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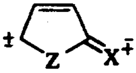

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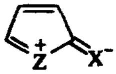

15

is 380 (at 1586 cm^{-1}) but most of this intensity probably arises from an overtone or combination band; thiophene[20] shows ν_R (903 cm^{-1}) + γCH (688 cm^{-1}) at 1586 cm^{-1} with A = 180, which also overlaps with 1556 cm^{-1} (867 + 688) (*cf.* ref 20) and for thiophene A (ν 1586 cm^{-1}) + A (ν 1556 cm^{-1}) = 250.

A 2-substituent will conjugate more effectively with the ring as distorted in sense **5** by virtue of increased contribution of canonical forms of type **13**, together with much smaller increases in contributions from **14** and **15** (the last for electron acceptor substituents only), compared with lessened influence of such canonical forms in the ring distortion as in **4**. The dipole change for orbital following induced by the substituent as a result of contributions from **13**, **14** and **15** will be approximately in the β-direction:* for an electron donor substituent it will be in the direction opposed to that of the oscillating dipole in unsubstituted thiophene. Hence an equation (1) analogous to that found for *para*-disubstituted benzenes,[40] should hold for 2-substituted furans and thiophenes, where "b" is a small *positive* value and λ is the correction needed for electron accepting substituents to account for contributions from **15**. For 2-substituted thiophenes, the overtone constant "c" will be small.

$$\underset{\text{2-furan}}{A_{\nu_{15}}} = a\,[b + \sigma_R^0 \;+\; \lambda]^2 + c \qquad (1)$$

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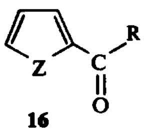
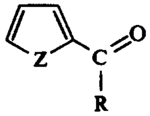
* It can be shown that. because of the small value of b in Eq. 1. errors arising from this assumption are not significant

Because of the large importance of variation in canonical forms **13**, and by analogy with α,β-unsaturated ketones,[7] variation in rotational populations **16**, and **17**, would be expected to have significant influence on the observed interaction for ν_{15}. The barriers to rotation in 2-formyl-furan[41] and -thiophen[42] are near 10 kcal mol^{-1}, so that essentially only the two near planar forms will be populated. However, for the t-butyl ketones, considerable twisting probably occurs in the ground states (*cf* ref 7).

The temperature invariability of the NMR spectrum of 4-bromo-2-formylthiophene[43] and 2-formylthiophene[44] indicates that they exist as single conformers: these are shown by the long-range coupling to be the s-*trans* conformations (**16**). Recent work on NMR solvent shifts[45] and NOE[45, 46] has confirmed these conclusions and further shown that 2-thienyl carbonyl compounds exist largely in the s-*trans* conformation (**16**); this is supported for 4-bromo-2-formyl-[43] and 2-acetyl-5-bromo-thiophene[47] by X-ray analysis. The s-*trans* conformations for 2-acetyl-, 2-benzoyl- and 2-formylthiophene are also supported by dipole moment studies.[48–50] However, at least for 2-benzoylthiophene there is probably rotation out of planarity[51] (*cf* also ref 28) although the phenyl group is rotated more than the thienyl group.[52] IR examination of the carbonyl band under high resolution is stated to show the presence in CCl_4 solution of a small proportion (20% at 25°) of the s-*cis* form for 2-thienylaldehyde,[53] although other authors[50] attribute the band splitting to Fermi resonance, a conclusion which has recently been supported by infrared investigation of ^{18}O- and ^{2}H-labelled species,[54a] and the solvent and temperature dependence of the band pattern.[54b]



(s-*trans*) **16**



(s-*cis*) **17**

The interpretation of rotational isomerism in the furan series has been far less clear-cut. Low temperature NMR shows two isomers for furfuraldehyde with $K = 6{\cdot}7$ at $-80°$: the more abundant form was assigned s-*cis* from the chemical shifts[41] and this assignment originally appeared to be supported by IR torsional frequency studies[55] and gas-phase microwave measurements.[56] However, the more recent interpretation of the shielding by CO-groups should reverse the assignment[57, 43] and the predominance of the s-*trans* form is confirmed by long range coupling constants,[58, 53] solvent effects on NMR shifts,[59] and by the X-ray determination of the s-*trans* form for 4-bromofurfural.[43] No clear-cut conclusion is possible from the dipole moments of furfural and substituted derivatives.[60, 50] Study of the IR $\nu_{C=O}$ band of furfural has shown that it appears split with relative intensities which depend on the solvent:[61] the temperature dependence has been studied,[61, 62] and the most recent results[53] indicate $K = 0{\cdot}40$ at 25°. By the low temperature NMR technique,[57] two isomers exist for 2-acetylfuran, with $K = 1{\cdot}0 \pm 0{\cdot}1$ at $-95°$. Dipole moments tentatively suggest[60] 70% s-*cis* for 2-methoxycarbonylfuran. Solvent effects on NMR shifts indicate comparable proportions of both rotamer forms for 2-acetyl- and 2-methoxycarbonylfuran.[59]

TABLE 2. 2-MONOSUBSTITUTED THIOPHENES

X	ν_{15}			ν_6			ν_5		
	ν[a] (cm^{-1})	ε_A (ε_{lit}[b])	A[c]	ν[a] (cm^{-1})	ε_A (ε_{lit}[b])	A[c]	ν[a] (cm^{-1})	ε_A (ε_{lit}[b])	A[c]
OMe	1538	250	3400	1424	80	1740	1355	20	—
OEt	1538	160	3430	1456†	—	—	1355	43	500
	1535*	135		1436					
OCOMe	1538	85	1100	1437	140	1660	—	—	—
F	1554	140	2055	1451	210	2120	1356	7	—
Cl	1518	50(30)	470	1414	120(115)	1150	1347	16(10)	—
Br	1510	30(20)	320	1404	120(95)	1050	1342	16(10)	70
I	1504	8·5	180	1396	80	880	1335	18	150
SMe	1506	7	70	1423	40	—	1337	10	110
				1433†					
				1406					
NCO	1576*	160	2100	1406	30	510	—	—	—
	1569								
Me	1537	5(3)	60	1448†	50(45)	670	1282†	—	—
				1440			1354		
Et	1533	5	50	1458†	25	—	1376†	—	—
				1446			1360		
Pr^n	1533	7	70	1460†	40	—	1380†	—	—
				1446			1360		
H	1504	(vw) 0·7	10	1406	35	390	1338	vw	—
CN	1510	5·4	55	1430*	170	965[f]	1349	16	10T
				1413					
Ph	1531	15(15)	110	1446†	20(20)	—	1351	7(5)	7T
				1430					
NO_2	1532	(220)	—	1402	140(130)	1390	1365	—	—
	1506†								
COOH	1526	250	3420	1430	300	6350	1358	50	390
CO_2Me	1527	150(110)	1260	1419	140(120)	1200	1362†	156(150)	—
	1524*						1356	60	
CO_2Et	1526	130(110)	1300	1420	225(220)	2610[d]	1357	70(75)	—
	1524*								
CHO	1518	50(50)	705	1420	280(190)	2480	1355	60(45)	340
	1518*								
COMe	1516	75(70)	1040	1416	340(350)[e]	1825	1367†	115(110)	—
	1513*			1427*			1356		
COEt	1517	90	1205	1418	340(315)[e]	3270[d]	1367†	77	—
	1514*	80					1356		
COPr^i	1517	80	1210	1415	330	2880[f]	—	—	—
	1511	70		1411*					
COBu^t	1515	40	840	1413	150	2000	1367†	—	—
	1502	30					1352		

[a] * Shoulder, † band from substituents generally CH_3, CH_2 or Ph or NO_2 deformation frequencies—when A values missing, overlap too important

[b] Values from ref 26

[c] Solution in chloroform, A in l. mol^{-1} cm^{-2}

[d] A value is double the value found for methyl derivative—may be caused by superimposition of the band with CH_2 frequencies

[e] From ref 21

[f] High value caused by the 1411 band

Added in Proof: Further work on the rotational isomerism of thiophene and furan carbonyl compounds for the most part substantiates the preceding conclusions. The Overhauser effect confirms that 4-bromo-2-formylthiophene and 2-acetyl-4, 5-dibromothiophene exist in the s-*trans* forms.[63] Coupling constants for a series of substituted 2-formylthiophenes indicate predominance of the s-*trans* form in all cases,[64] and liquid crystal NMR indicates this for 2, 5-diformylthiophene.[65] The F/H coupling constants in 5-fluoro-2-formyl- and 5-fluoro-2-acetylthiophene also show the s-*trans* configurations as predominant.[66] Infrared assignments for thiophene-2-carboxylic esters[67] and calculation[68, 69] of the relative stabilities of s-*cis* and s-*trans* forms of thiophene carbonyl compounds have been made.

Further evidence for the predominance of the s-*trans* form in 2-formylfurans comes from the Overhauser effect in the 4-bromo-derivative.[63] The same technique applied to 2-acetylfurans shows that for these compounds also the s-*trans* form is the more stable at low temperatures.[70] Further work on coupling constants in a series of 2-formylfurans agrees.[64] However, infrared evidence for reversing the assignments for 2-formylfurans has been presented[71] at least at room temperature, so that the matter is still not completely settled. Work has also appeared on the conformation of esters[67] and calculations.[69, 72]

2-Substituted thiophenes Intensity for v_{15}.

The observed intensities for donor and d-orbital acceptor substituents (Table 2) are fitted satisfactorily by Eq. 2 which is of the form of Eq. 1 as expected: the overtone constant c is negligible. For donor substituents (OMe, OEt, OAc, F, Me, Et, n-Pr, Ph, H), $\lambda = 0$. For d-orbital acceptor substituents (Cl, Br, I, SMe), λ is given by Eq. 3,[40] where K_x values for heavy halogens and SMe are taken from ref 40 and σ_R^0 (thioph) = 0·14 as is derived later in this paper (see discussion for ν_6 band). The correlation coefficient for Eq. 2 is 0·997 for the donor substituents only, from ref 40 and σ_R^0 (thioph) = 0·14 as is derived later in this paper (see discussion for and 0·997 for donor substituent and d-orbital acceptors. The relation is shown graphically in Fig 1..

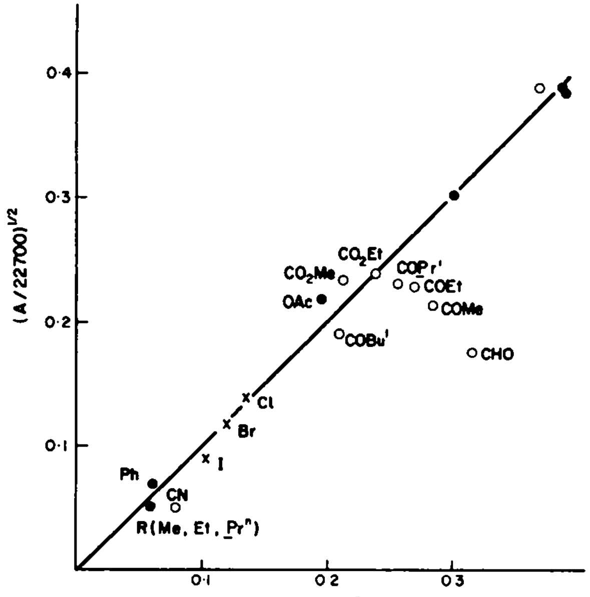


FIG 1. $[A_{obs}/22{,}700]^{\frac{1}{2}}$ plotted against $[0{\cdot}04 + \sigma_R^0 + \lambda]$ for ν_{15} for 2-substituted thiophenes: ● donor substituents; × d-orbital acceptors; ○ π-acceptors.

$$\underset{\text{2-thioph}}{A\nu_{15}} = 22{,}700[0{\cdot}04 + (\sigma_R^0 + \lambda)]^2 \tag{2}$$

$$\lambda = K_x.\ \sigma_R^0\ (\text{thioph}) \tag{3}$$

$$\lambda = 6{\cdot}5.\sigma_R^0\ (\text{A}).\ [\sigma_R^0\ (\text{thioph})]^2 \tag{4}$$

For π-acceptor substituents λ should be given by Eq. 4, one of two alternative methods given in ref. 40 for calculation of such interaction terms. The result is satisfactory for the linear substituent CN, but as follows for the carbonyl substituents:

Subst.	CHO	COMe	COEt	COPr^i	COBu^t	CO_2Me	CO_2Et	COOH
$(A_{obs}/22{,}700)^{\frac{1}{2}}$	0·18	0·21	0·23	0·23	0·19	0·23	0·24	0·39
$(0{\cdot}04 + \sigma_R^\circ + \lambda)$	0·31	0·29	0·27	0·26	0·21	0·22	0·24	0·37

The marked discrepancies (see also Fig 1) are ascribed to rotational isomerism. As discussed above, the s-*trans* form predominates for the 2-thienyl carbonyl compounds, and this, by analogy with the $CH_2{=}CH.COR$ compounds,[7] is expected to reduce the observed intensity greatly, especially for R = H or CH_3. For the larger groups, deviation from planarity reduces the importance of the rotational isomerism.[7]

$$\underset{\text{2-furan}}{A\nu_{15}} = 38{,}400\,(\sigma_R^0 + \lambda)^2 + 110 \tag{5}$$

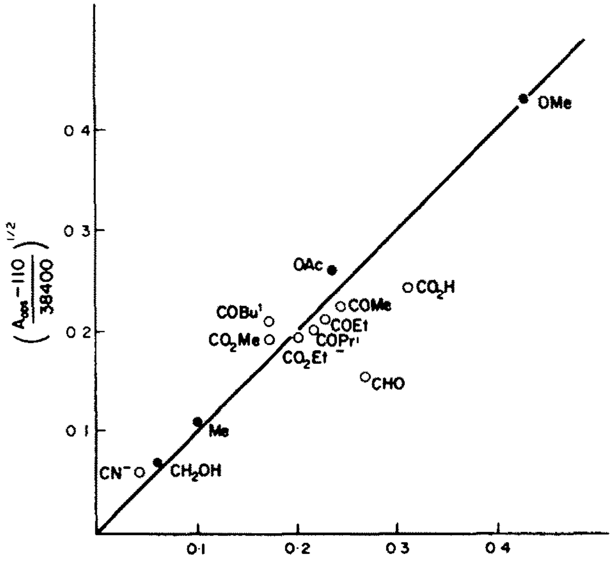


FIG 2. $[(A_{obs}\text{-}110)/38{,}400]^{\frac{1}{2}}$ plotted against $[\sigma_R^\circ + \lambda]$ for ν_{15} for 2-substituted furans: ● donor substituents: ○ π-acceptors.

2-Substituted furans Intensity for ν_{15}.

The observed intensities for the donor substituents (OMe, OAc, Me, CH_2OH) (Table 3) fit Eq. 5 (which is again of the expected form), with λ = 0 and a correla-

TABLE 3. 2-MONOSUBSTITUTED FURANS

	ν_{15}			ν_6			ν_5		
	ν^a (cm^{-1})	ε ($\varepsilon^b_{\text{liq}}$)	A^c	ν^a	ε ($\varepsilon^b_{\text{liq}}$)	A^c	ν^a	ε ($\varepsilon^b_{\text{liq}}$)	A^c
OMe	1606	540	7260	1520	165	1830	1392	138	1945
OCOMe	1610	150	2800	1510	120	1700	1390	—	—
	1596*						1370		
Me	1602	40(30)	590	1508	40(40)	710	1390	(15)	—
CH_2OH	1598	7(10)	300	1503	(35)	460	1381	(50)	—
CH_2SH	1597	15	350	1504	50	580	1381	3	30
H	1586^d	10	380^d	1484	50	600	1378	20	190
				1470*	10				
CN	1570*	7(5)	250	1474^e	(75)	1440	1380	(10)	125
	1586			1472					
COOH	1582	90	2330	1484	175	3860	—	—	—
	1571	150		1472^f	240				
CO_2Me	1582	120(100)	1550	1482^f	170(175)	3300	1395	(100)	940
	1570	60(60)		1470	130				
CO_2Et	1582	95(85)	1520	1482^f	157(155)	3230	1400	(95)	—
	1570	60(55)		1474	162		1388†		
CH=CH COMe	1558	190(135)	1210	1478	70	980	1392	(60)	—
CHO	1569	135(95)	1050	1472	100(180)	3390	1394	(115)	1130
				1465*	240				
COMe	1570	180(145)	1730	1470	310(290)	3050	1396	105(105)	870
COEt	1568	200	1810	1469	300	4230	—	—	—
COPr^i	1567	145	1620	1478^e	200	4360	—	—	—
				1473	200				
COBu^t	1560	170	1810	1478	170	—	—	—	—
				1460	350				

[a] * Shoulder; † band from substituents, generally CH_3 and CH_2 deformation frequencies

[b] From ref 25

[c] Solution in chloroform. A in l. mol^{-1} cm^{-2}

[d] Estimated value (band estimated graphically) overlap with ν (1572, 1566 and 1550)

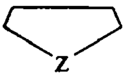
[e] Doublet of equal intensities

[f] Doublet

tion coefficient of $r = 0{\cdot}98$ (see Fig 2). In the derivation of Eq. 5. the intensities of the compound with the carbonyl substituents CO_2Me, CO_2Et, COMe and COPr^i and the linear π-acceptor CN were also used; for these λ was calculated using Eq. 4 and the value of σ^0_R (furan) $= 0{\cdot}13$ derived later. Eq. 5 predicts A = 110 for furan itself, but as already discussed most of the observed intensity probably derives from an overtone. For the carbonyl substituents, the discrepancies are generally much smaller than for the corresponding thiophenes, except for CHO:

Subst.	CHO	COMe	COEt	COPr^i	COBu^t	CO_2Me	CO_2Et	CO_2H
$[(A_{obs} - 110)/38{,}400]^{\frac{1}{2}}$	0·156	0·210	0·210	0·20	0·210	0·193	0·192	0·240
$(\sigma^0_R + \lambda)$	0·270	0·243	0·228	0·215	0·170	0·172	0·199	0·324

The effect of rotational isomerism is less important for the furans; for the CHO substituent in furfural the s-*trans* isomer predominates (see above) and a discrepancy is indeed found in the direction of a lower observed intensity (as expected[7]), but for the other compounds the populations of the s-*cis* and s-*trans* forms are comparable, and the discrepancies are much less, again as expected.



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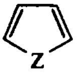

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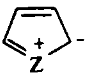

22

Valence bond treatment of vibration ν_6. In this vibration, bonds C2—C3 and C4—C5 change in phase leading to distortions in the sense of **18**, **19**: this implies increased contributions of **20** to extreme **18** and of **21** and **22** to extreme **19**. During vibration ν_6 there is clearly an oscillating dipole in the α-direction, which changes in magnitude, but not direction (and thus comparable to ν_{16a} in monosubstituted benzenes[4]). In the unsubstituted parent compounds, ν_6 is therefore strongly allowed: it is found with A = 390 for thiophene and A = 600 for furan (Table 1).

A 2-substituent will conjugate more effectively with the ring distorted in sense **19**, and now the canonical form involving the substituent that is particularly favoured will be **14** and also, for acceptor substituents only, **15**. The oscillating dipole thus induced by the substituent will be in the β-position to a close approximation, *i.e.* at right angles to the oscillating dipole due to the heteroatom for this vibration. Hence their contributions to the intensity should be additive and we expect equations of type 6. Further, because *variations* in the contribution of canonical form **13** are now of diminished importance, rotational isomerism in carbonyl compounds should not be of major significance, and it is expected that results for these compounds should be correlated together with those for other substituents.

$$\underset{\text{2-subst.}}{A\nu_6} = a\,(\sigma_R^0 + \lambda)^2 + \underset{\text{unsubst.}}{A\nu_6} \qquad (6)$$

2-*Substituted thiophenes Intensity for* ν_6.

The observed intensities (Table 2) are fitted by Eq. 7, which is of the expected form. In Eq. 7, $\lambda = 0$ for electron donor substituents (H, Me, OAc, F). For d-orbital acceptors (Cl, Br, I, SMe), λ is given by Eq. 3 with K_x taken from ref 40 and for π-acceptors (NO_2, CN, CHO, COMe, CO_2Me), λ is given by Eq. 4.

$$\underset{\text{2-thioph}}{A\nu_6} = 22{,}700[(\sigma_R^0 + \lambda)^2 + 0{\cdot}14^2] \qquad (7)$$

Band overlap interferes for COEt, CO_2Et, $COPr^i$ and $COBu^t$ (see Table). The value of $-0{\cdot}14$ is used for σ_R^0 (thioph), in Eq. 3 and Eq. 4 for the calculation of λ. As the last term in Eq. 7; this was found to give the best overall fit; Eq. 7 thus predicts A = 440 for thiophene itself compared with $A_{obs} = 390$, which is considered to be good agreement, especially as a change in substitution pattern often changes the constant "a" of equations of type 6. No previous experimental determination of σ_R^0 (thioph) has been made although a calculated value is available of $-0{\cdot}03$ or $-0{\cdot}14$ depending on the ring position.[17]

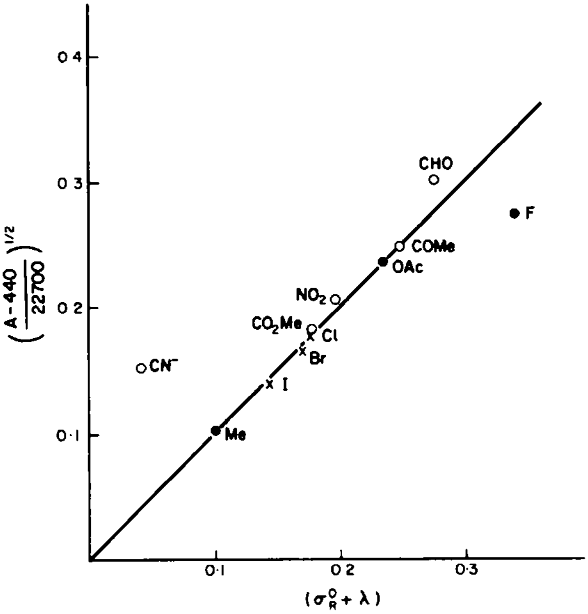

FIG 3. $[(A\text{-}440)/22{,}700]^{\frac{1}{2}}$ plotted against $[\sigma_R^0 + \lambda]$ for ν_6 for 2-substituted thiophenes: ● donor substituents: × d-orbital acceptors; ○ π-acceptors.

Eq. 7 is followed with $r = 0{\cdot}991$; the result is shown graphically in Fig 3 where the corresponding observed quantity is plotted against $(\sigma_R^0 + \lambda)$. Substituents of all classes lie satisfactorily on the line, including, as predicted, the carbonyl substituents indicating that the phenomenon of rotational isomerism does not upset the correlation. The only serious discrepancy is 2-methoxythiophene which has an intensity much lower than expected for reasons which are not clear: this behaviour is reflected in the corresponding furan (see below).

$$A\nu_6 \quad 23{,}200\,[(\sigma_R^0 + \lambda)^2 + 0{\cdot}13^2] \qquad (8)$$

2-furan

2-Substituted furans Intensity for ν_6.

Results for the furans are less complete, due to the non-availability of the halogeno-compounds, and the correlation is less satisfactory. The results for three donor substituents (OAc, CH_3, CH_2OH) fit Eq. 8; however, there are systematic deviations from Eq. 8 (Fig 4) in that it tends to predict lower than observed intensities

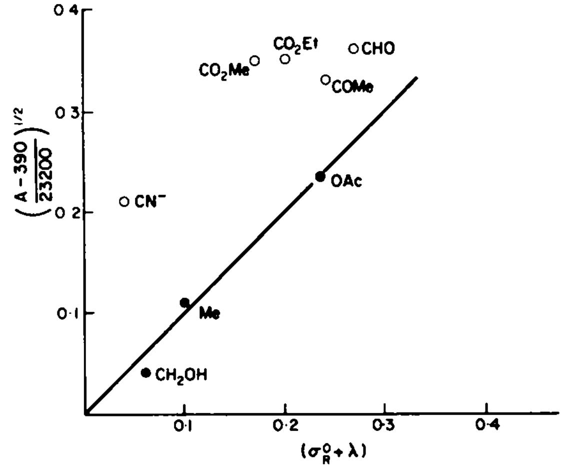

Fig 4. $[(A\text{-}390)/23{,}200]^{\frac{1}{2}}$ plotted against $[\sigma_R^0 + \lambda]$ for ν_6 for 2-substituted furans: ● donor substituents; ○ π-acceptor substituents.

for the compounds with acceptor substituents, and there is also a serious deviation for the 2-methoxy compound. This treatment implies σ_R^0 (furan) is − 0·13, and this value has been used in Eq. 5 (see above). Russian workers have calculated[17] the σ_R^0 for furan as − 0·07 or − 0·28 depending on the ring position.

$$\underset{\text{PhCOR}}{A^{t}_{C=O}} = \underset{\text{MeCOR}}{A^{t}_{C=O}} + 128\,(\sigma_R^0)_{tw} - 17 \tag{9}$$

$$\underset{\text{2TCOR}}{A^{t}_{C=O}} = \underset{\text{MeCOR}}{A^{t}_{C=O}} + 205\,(\sigma_R^0)_{tw} - 25 \quad (r = 0{\cdot}991) \tag{10}$$

$$\underset{\text{2FCOR}}{A^{t}_{C=O}} = \underset{\text{MeCOR}}{A^{t}_{C=O}} + 325\,(\sigma_R^0)_{tw} - 40 \quad (r = 0{\cdot}988) \tag{11}$$

Carbonyl intensities. We found[7] that relation 9 correlates the carbonyl intensities for analogous phenyl and methyl aldehydes and ketones; from the present results (Table 4), equations 10 and 11 may be deduced.

TABLE 4. CARBONYL INTENSITIES FOR 2-THIENYL AND 2-FURYL ALKYL KETONES AND ALDEHYDES

	2-Thienyl			2-Furyl		
R of COR	$\nu_{(C=O)}$ (cm^{-1})	ε_A	$A^{a}_{C=O}$	$\nu_{C=O}$ (cm^{-1})	ε_A	$A^{b}_{C=O}$
H	1688	285	11.100	1692	350	
	1678	510		1672	480	13.100
Me	1671	480	8540	1674	460	10.500
Et	1672	350	7880	1674	400	9900
Pr^i	1672	345	7720	1678	350	8940
	1664*					
Bu^t	1664	300	6580	1662	370	6500
	1656*					

* Shoulder

[a] Spectrum recorded in CCl_4

[b] Spectrum recorded in $CHCl_3$

In these equations $(\sigma_R^\circ)_{tw}$ implies the value appropriate to the twisted acyl group (see ref 7). These relations are at present empirical, but they give further evidence of the power of correlation of infrared intensities with σ_R° values.

General conclusions

The wide variations in the IR intensities of the two highest frequency ring-stretching modes of 2-monosubstituted furans and thiophenes, ν_{15} and ν_6, have been correlated with σ_R° substituent constants, using equations the form of which was deduced from a valence-bond treatment of the molecular distortions (intensity data for ν_5 is insufficient to allow similar treatment). This work further extends the area of application of σ_R°—IR intensity relations, to molecules of lower symmetry than hitherto studied.

EXPERIMENTAL

The compounds commercially available were purified by standard methods and checked by VPC or m.p. IR spectra were recorded using a model 125 Perkin–Elmer spectrophotometer; chloroform purified as before[3] was used as solvent. The 2399 cm^{-1} band of $CHCl_3$ was used to balance the spectrum. Intensity area A values are quoted as averages of two readings. Results are recorded in Tables 2 and 3.

The compounds were synthesized as follows and characterized by their NMR and IR spectra.

2-Monosubstituted thiophenes. 2-Methoxy, bp 60–62° (25 mm) [lit.[29] 74–75° (50 mm)]; 2-ethoxy, bp 68° (25 mm) [lit.[29] 56° (13 mm)]; 2-acetoxy, bp 71° (4 mm) [lit.[30] 96° (25 mm)]; 2-methylmercapto, bp 64° (6 mm) [lit.[31] 80–82° (22 mm)]; 2-isocyanato, bp 46° (6 mm) and 1580 (760 mm) [lit.[32] 158° (760 mm)]. The following 2-thienyl alkyl ketones were synthesized by the method previously described for 2-thienyl methyl ketone:[33] ethyl, bp 94° (5 mm) [lit.[34] 105° (13 mm)]; isopropyl, bp 92° (3·5 mm) [lit.[35] 115–117° (18 mm)]; t-butyl, bp 99–100° (5 mm) [lit.[35] 115–116° (16 mm)].

2-Monosubstituted furans. 2-Methoxy, bp 42° (30 mm) [lit.[36] 92–110° (760 mm)]; 2-acetoxy, bp 46° (11 mm) [lit.[37] 55–58° (10 mm)]. The following 2-furyl alkyl ketones were also made by the method of ref 33: methyl, bp 70° (15 mm) [lit.[38] 45–50° (5 mm)]; ethyl, bp 72° (8 mm) [lit.[39] 78–80° (17 mm)]; t-butyl, bp 56° (2 mm). 2-Isopropyl furyl ketone was made according to ref 39, bp 48° (0·3 mm) [lit.[39] 86–87 (18 mm)].

2-Fluorothiophene was kindly donated by Professor S. Gronowitz (Lund) and 2-phenyl- and 2-cyanothiophene by Professor H. Wynberg (Gröningen).

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