A Comparative Study of Electric Dipole Moments of 2-Substituted Derivatives of Furan, Thiophen, Selenophen, and Tellurophen

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The electric dipole moments of tellurophen and some of its derivatives (tetrahydrotellurophen, nine 2-substituted and two 2,5-disubstituted) have been measured in benzene and compared with those of the corresponding derivatives of furan, thiophen, and selenophen, some of which (2-methylthio-furan and -selenophen, 2-acetylfuran, 2-methoxycarbonyl-furan and -selenophen and 2-*NN*-dimethylcarbamoyl derivatives) were not known. The mesomeric moments of the unsubstituted heteroaromatic congeners follow the ground state aromaticity order: thiophen > selenophen > tellurophen > furan. The mesomeric moments due to conjugation of the halogens with the heteroaromatic radical in the congener series are all greater than the benzene ones. The conformational problems of 2-methylthio-, 2-formyl, 2-acetyl, and 2-*NN*-dimethylcarbamoyl derivatives of tellurophen and its congeners have also been examined.

FIVE-MEMBERED heteroaromatic compounds containing group 6A elements, oxygen, sulphur, selenium, and tellurium, constitute an excellent series for investigating the influence of the heteroatom on molecular electronic properties. Although comparative studies of the geometry,[1] the reactivity,[2] the 'ground-state aromaticity',[3]

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[1] F. Fringuelli and A. Taticchi, *Gazzetta*, 1973, **103**, 453.

[2] S. Clementi, F. Fringuelli, P. Linda, G. Marino, G. Savelli, and A. Taticchi, *J.C.S. Perkin II*, 1973, 2097.

[3] F. Fringuelli, G. Marino, A. Taticchi, and G. Grandolini, *J.C.S. Perkin II*, 1974, 332.

the spectral properties,[4] and ring sensitivity to substituent effect [5] of the heterocycles furan, thiophen, selenophen, and tellurophen have been published there has been no comparative study of their dipole moments. And again although the electric dipole moments of furans,[6-10] thiophens, [6-9] and selenophens [6-8,11-13] have been studied, there have been only two preliminary papers on the dipole moments of tellurophens.[14]

In the present work we have measured in benzene solution at, or near 25 °C, the dipole moments of the compounds listed in Table 1.

TABLE 1

Physical data from dipole moment determination

Compounds	$t°$	w_{max}	α_0	$-\beta$	$P_{2\infty}$	R_D	μ(D)
Tetrahydrotellurophen	25.0	0.020	1.75	0.615	91.1	34.8	1.63
Tellurophen	25.0	0.030	0.31	0.662	36.3	32.0	0.46
2-Methylselenophen	31.2	0.040	0.32	0.467	38.9	32.6	0.56
2-Methyltellurophen	25.0	0.021	0.36	0.593	45.0	36.5	0.64
2-Chlorotellurophen	27.4	0.031	1.25	0.711	78.4	36.9	1.43
2-Bromotellurophen	27.4	0.033	1.05	0.730	81.1	38.6	1.44
2-Methylthiofuran	31.0	0.036	2.41	0.237	83.2	32.0	1.60
2-Methylthiothiophen	31.0	0.048	1.94	0.295	81.0	38.0	1.47 [a]
2-Methylthioselenophen	31.0	0.070	1.36	0.518	79.2	41.6	1.37
2-Methylthiotellurophen	31.0	0.034	1.06	0.632	80.3	45.5	1.30
2-Acetylfuran	25.0	0.098	10.26	0.238	242.0	29.6	3.23
2-Formyltellurophen	25.0	0.021	5.51	0.654	245.5	38.5	3.18
2-Acetyltellurophen	25.0	0.017	4.55	0.625	224.5	43.8	2.97
2-Methoxycarbonylselenophen	27.4	0.018	2.50	0.520	133.4	42.0	2.12
2-Methoxycarbonyltellurophen	25.0	0.020	1.95	0.637	123.5	44.0	1.95
2-Acetyl-5-methoxycarbonyltellurophen	25.0	0.010	2.56	0.635	177.3	55.3	2.44
2,5-Bis(methoxycarbonyl)tellurophen	25.0	0.018	2.20	0.607	171.6	54.5	2.42
NN-Dimethylbenzamide	27.4	0.024	10.8	0.230	344.7	45.1	3.84 [b]
p-Chloro-*NN*-dimethylbenzamide	27.4	0.037	8.83	0.330	350.6	50.0	3.85
Furan-2-*NN*-dimethylcarboxamide	27.4	0.030	10.0	0.288	297.5	37.1	3.58
Thiophen-2-*NN*-dimethylcarboxamide	27.4	0.029	11.0	0.327	360.3	43.3	3.95
Selenophen-2-*NN*-dimethylcarboxamide	27.3	0.028	7.8	0.512	335.9	46.9	3.77
Tellurophen-2-*NN*-dimethylcarboxamide	27.4	0.015	5.80	0.617	314.0	50.8	3.60
2-Hydroxymethyltellurophen	25.0	0.019	1.79	0.660	101.0	38.5	1.75

[a] Lit.[9] $\mu = 1.50$ D. [b] Other values quoted in literature [8] $\mu = 3.80$ and 3.85 D in benzene; 3.70 D in *p*-xylene; the recent value in benzene (3.15 D) is probably erroneous (S. L. Sparsov, V. S. Dimitrov, and I. Kantschovska, *Org. Magnetic Resonance*, 1974, **6**, 20).

EXPERIMENTAL

Synthetic.—Tetrahydrotellurophen ($n_D^{28} = 1.632\ 4$),[15] tellurophen ($d_4^{25} = 2.13$),[4a] 2-methyltellurophen,[4a] 2-chloro- and 2-bromo-tellurophens,[16] 2-formyl-, 2-acetyl-, and 2-methoxycarbonyl-tellurophens,[4a] 2-acetyl-5-methoxycarbonyltellurophen,[4a] 2,5-bis(methoxycarbonyl)tellurophen,[5] 2-methoxycarbonylselenophen,[17] and *NN*-dimethylbenzamide and *p*-chloro-*NN*-dimethylbenzamide [18] were prepared by literature methods.

2-*Methylthio-derivatives.*—A solution of freshly distilled dimethyl sulphide (5×10^{-2} mol) in dry ether (40 ml) was added dropwise, under nitrogen and at room temperature, to an ethereal solution of the appropriate 2-lithium derivative [from unsubstituted compound 5×10^{-2} mol) in dry ether (60 ml) and n-butyl-lithium (5.3×10^{-2} mol) in n-hexane]. The mixture was set aside for 4 h with stirring after which ice–water was added to it and the mixture extracted with ether. The extracts were washed with 2M-NaOH and then worked up to give a residue which was distilled at 14 mmHg; yields 50—55%; 2-methylthiofuran, b.p. 41—42 °C (lit.,[19] 43 °C at 16 mmHg); 2-methylthiothiophen, b.p. 67—68 °C (lit.,[20] 80 °C at 22 mmHg); 2-methylthioselenophen, b.p. 86—87 °C (lit.,[21] 58 °C at 1.5 mmHg); 2-methylthiotellurophen, b.p. 116—118 °C. All the compounds give n.m.r. spectra and elemental analyses consistent with the expected structures.

2-*Methylselenophen.*—Freshly distilled dimethyl sulphate (10.5 g) in dry ether (30 ml) was added dropwise to an ethereal solution of selenophen-2-yl-lithium [from selenophen (10 g) in dry ether (80 ml) and a 20% solution of n-butyl-lithium (38 ml)] cooled at −10 °C, well stirred and

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kept under nitrogen. The stirring was continued for 15 h at room temperature after which dilute NaOH was then added and the mixture extracted with ether. The extracts were washed (H_2O), dried (Na_2SO_4), and evaporated at 100 mmHg to give a residue which was chromatographed on a column (Al_2O_3); elution with n-pentane eliminated the dimethyl sulphate residue. The product was freed from unchanged selenophen (*ca.* 5—7%) by fractional distillation at 60 mmHg (b.p. 78—79 °C). The n.m.r. data and elemental analysis were in agreement with those expected.

2-Hydroxymethyltellurophen.—The compound was prepared from 2-carboxymethyltellurophen by $LiAlH_4$ reduction in dry ether by the standard procedure, b.p. 88—89 °C at 0.05 mmHg. The n.m.r. data and elemental analysis were in agreement with the expected ones.

Dipole Moments.—The dipole moments were measured in benzene solution at the temperature reported in Table 1. The total polarization of the solute ($P_{2\infty}$), extrapolated to infinite dilution, was calculated [22] from the ratios reported below, where w is the weight fraction of the solute, ε and v

$$\alpha_0 = \lim_{(w=0)} \frac{(\varepsilon - \varepsilon_1)}{w} \quad \beta = \frac{\Sigma(v - v_1)}{\Sigma w}$$

are, respectively, the dielectric constant and specific volume of the solutions; subscript one refers to the pure solvent as used, *i.e.* prepared in the *same* way as the solutions. The α_0 value has been determined by least-squares analysis of the $\varepsilon(w)$ polynomial function (linear or, in some cases, quadratic). A Sartorius microbalance was used. The distortion polarization $P_E + P_A$ was assumed to be equal to the molecular refraction (R_D) of the solute. Differences between the refraction indices of solutions and solvent were measured by using a Bellingham-Stanley differential refractometer, whilst the refraction indices of pure liquids were determined with a Féry refractometer. The technique for the measurement of dielectric constants has been described elsewhere.[9,23] For each solute examined, $w_{\text{max.}}$ (reported with only three decimal points), α_0, β, $P_{2\infty}$, R_D, and μ (in Debye units) are given in Table 1.

Both better thermostatting, and a gain in time to attain thermal equilibrium in the determination of dielectric constants were achieved by operating some degrees above the room temperature. This accounts for the different temperatures at which the measurements were made. However, differences in the temperature are so small (*ca.* 5 °C) that the dipole moments may still be compared. For furan-2-carbaldehyde two measurements in benzene at 25 and 50 °C gave 3.54 and 3.51 D,[8] respectively. Even in favourable cases, when a variation of the dipole moment with temperature can be expected to be the cause of relatively large differences between the dipole moments of conformers, the thermal effect is still small: [24] for 1-methylpyrrole-2-carbaldehyde in benzene, μ (8°) = 2.69 D, μ (56°) = 2.82 D, and for 3-acetyl-1-methylpyrrole in the same solvent, μ (7°) = 4.84 D, μ (56°) = 4.81 D.

RESULTS AND DISCUSSION

Table 2 lists the dipole moments (in benzene) found for the heterocycles and their various derivatives. The figures for tetrahydrofuran,[6-8] tetrahydrothiophen,[6-8] tetrahydroselenophen,[6-8] and tetrahydrotellurophen in the same solvent are 1.75, 1.09, 1.89, and 1.63 D, respectively.

TABLE 2

Dipole moments (Debye units) of 2-substituted derivatives of furan, thiophen, selenophen, and tellurophen in benzene ($\mathrm{R{\cdot}\overline{CH{:}CH{\cdot}CH{:}CH{\cdot}X}}$)

R	X = O	X = S	X = Se	X = Te
H	0.72 [a]	0.54 [b]	0.52 [c]	0.46
Cl	1.60 [a]	1.48 [a]		1.43
Br	1.46 [a]	1.35 [a]	1.37 [c]	1.44
I	1.14 [a]	1.18 [a]		
Me	0.72 [a]	0.67 [a]	0.56	0.64
SMe	1.60	1.47 [f]	1.37	1.30
CHO	3.54 [d]	3.48 [b]	3.25 [c]	3.18
Ac	3.23	3.37 [a]	3.18 [e]	2.97
CO_2Me	2.24	1.91 [g]	2.12	1.95
$CONMe_2$	3.58	3.95	3.77	3.60
CH_2OH	1.99 [a]			1.75

[a] From ref. 6—8. [b-e] See references 9, 12, 10, 11, respectively. [f] μ = 1.50 D[9]. [g] For the ethoxycarbonyl derivative.[6-8]

A comparative examination of the data allows us to make the observations reported below.

Mesomeric Moments of the Unsubstituted Heterocycles.—The dipole moments of furan, thiophen, selenophen, and tellurophen and their tetrahydro-derivatives(C_4H_8X) are all directed from the ring towards the heteroatom X,[14,25] but the aromatic heterocycles exhibit dipole moments much lower than the corresponding saturated ones.

As the C(2)–X–C(5) angles differ little in furan [26] and tetrahydrofuran [27] (106° 33′ and 106° 12′), thiophen [28] and tetrahydrothiophen [29] (92° 10′ and 93° 24′), selenophen [13] and tetrahydroselenophen [30](87° 46′ and 89° 6′), and tellurophen [31] and tetrahydrotellurophen [82° 32′ and 85° (assumed)], the difference μ (C_4H_4X)—μ (C_4H_8X) may serve as a measure of the C_4H_4X mesomeric moment and can represent a good criterion in establishing the ground-state aromaticity order of the congeners, in the sense that the greater the mesomeric moment, the more aromatic is the heterocycle C_4H_4X.

Change in the carbon atom hybridization state in going from C_4H_8X to C_4H_4X heterocycles probably leads to somewhat less polar C–X bonds but to slightly more polar H–C bonds, since trigonal carbon atoms are more electronegative than tetrahedral ones by, say,[32] 0.1 unit. This cannot, therefore, change the deduced ground-state aromaticity order.

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The mesomeric moments of furan, thiophen, selenophen, and tellurophen (1.03, 1.35, 1.29, and 1.17 D, respectively) are in harmony with other aromaticity indices based on structural and magnetic properties,[3] allowing the following ground-state aromaticity order: thiophen > selenophen > tellurophen > furan, to be firmly established.[3]

Electric Dipole Moments of 2-Halogeno and 2-Methyl Derivatives.—For R-substituted heterocycles RC_4H_3X we can define a mesomeric moment (m) due to conjugation of R with the heteroaromatic radical. The mesomeric moment (m_2) for axially 2-substituted heterocycles nearly coincides with the C(2)–R bond axis, and it can be calculated by solving the vectorial equations (1) and (2) where the vector M_2 is merely an element of

$$\mu\ (R\text{-}C_4H_3X) = \mu\ (C_4H_4X) + M_2 \qquad (1)$$

$$m_2 = M_2 - \mu\ (C_2H_5R) \qquad (2)$$

construction of the dipole moment, assumed to be along the C(2)–R bond.[12]

The m_2 mesomeric moments for 2-halogeno-substituted chalcogen heterocycles are directed from the halogen to C(2) atom and are readily derived under the condition * that X–C(2)–halogen angles are equal to X–C(2)–H ones in the unsubstituted heterocycles. For 2-halogeno-furan, -thiophen, -selenophen, and -tellurophen the angles between M_2 and the heterocycle dipole moments were taken equal to 62° 39′, 73° 46′, 77° 51′, and 83° 20′, respectively.

The pertinent m_2 figures (' halogen conjugation moments ') are given in Table 3, together with the data for halogenobenzenes. For all RC_4H_3X (R = Cl, Br, and I) derivatives the m_2 term decreases in going from furan to tellurophen and is always markedly higher than the corresponding halogenobenzene mesomeric moment.

TABLE 3

Halogen conjugation moments[a] (m_2) in 2-halogeno-congener five-membered heterocycles $R\text{–}C_4H_3X$ and halogenobenzenes (Debye units)

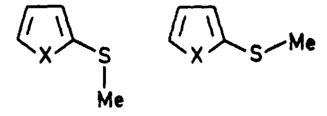
R	RC_4H_3O	RC_4H_3S	RC_4H_3Se	RC_4H_3Te	RPh[b]
Cl	0.87	0.76		0.70	0.41
Br	0.92	0.80	0.74	0.59	0.34
I	1.08	0.79			0.34

[a] As referred to $\mu(C_2H_5R)$ = 2.00, 1.90, and 1.70 D for R = Cl, Br, and I,[6–8] respectively. [b] μ(PhR) = 1.59, 1.56, and 1.36 D for Cl, Br, and I respectively.[6–8]

The greater m_2 mesomeric moments in 2-halogeno-substituted furans and thiophens, with respect to the m figures in the corresponding halogenobenzenes, probably reflect the higher conjugation ability (relative to phenyl) of 2-furyl [35] and 2-thienyl [36] (see also ref. 37). As expected by analogy with 2-furyl and 2-thienyl, selenophen-2-yl and tellurophen-2-yl appear to have a conjugation power superior to that of phenyl.

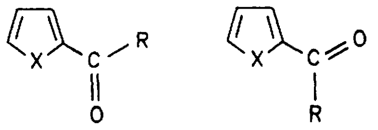
For 2-methyl derivatives the additional vector M_2 and methyl conjugation moment m_2 are certainly directed, as is the dipole moment of toluene,[6–8] from the methyl group towards the ring. On the basis of the above findings an m_2 value markedly higher than the mesomeric moment of toluene (0.4 D) is to be expected. Despite some uncertainty in the M_2 direction it is possible to derive an m_2 value of 0.5—0.6 D for 2-methyl-furan, -thiophen, -selenophen, and -tellurophen.

Rotational Isomerism in Various Chalcogen-heterocycle derivatives.—2-Substituted-furans, -thiophens, -selenophens, and -tellurophens with angular groups, such as methylthio, acyl (acyl = formyl, acetyl, and methoxycarbonyl), and *NN*-dimethylcarbamoyl, can exist as *cis* and *trans* rotational isomers (see Figure), having their methyl group or carbonyl oxygen atom close to, or away from, the X heteroatom. Several techniques have been used to study this kind of conformational isomerism. Our data (in benzene at nearly the same temperature), since all obtained by the same technique, are internally consistent and directly comparable.



(I) (II)

(A) (X,Me)-*cis* (I) and (X,Me)-*trans* (II) planar conformers for 2-methylthio-furan, -thiophen, -selenophen, and -tellurophen



(III) (IV)

(B) (X,O)-*cis* (III) and (X,O)-*trans* (IV) planar conformers for 2-acyl-furan, -thiophen, -selenophen, and -tellurophen (R = H, Me, or MeO: IIIa—c and IVa—c) and furan-, thiophen-, selenophen- and -tellurophen-2-*NN*-dimethylcarboxamides (R = NMe_2: IIId and IVd)

2-*Methylthio-derivatives*. Except for 2-methylthiothiophen,[9] the conformational problem of 2-methylthio-chalcogen-heterocycles has not until now been studied.

The conjugation energy of thiophenol is known to be very small,[38,39] certainly less than 0.6 kcal mol^{-1}, and

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* This is supported by the following: (i) the SCCl and SCBr angles in 2-chlorothiophen and 2-bromothiophen [33] are close to the corresponding SC(2)H angle in thiophen; (ii) the values of the X–C(2)–CO angles [34] in furan, thiophen, selenophen, and tellurophen-2-carboxylic acids are practically equal to the X–C(2)–H ones in unsubstituted heterocycles.

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that of thioanisole is also probably weak.[40,41] Consequently, 2-methylthio conjugation energies in the chalcogen-heterocyclic series, although somewhat higher, are likely to be also very weak. As a result, no rigid structures can be retained for both conformers (I) and (II) shown in the Figure.

The dipole moments of both conformers, *assumed* to be planar and rigid, have been calculated by using the vectorial equation (3), where the dipole moment of thioanisole [42] (1.34 D) is a vector acting at 77.5° to the Ph–S bond axis.* On these assumptions the results in Table 4 are obtained. Owing to the very low barriers to methylthio-rotation around the C(2)–S bond axis, models in which the methylthio-group almost freely rotates are to be preferred. Calculated free-rotation moments are 1.58, 1.47, 1.46, and 1.43 D for 2-methylthio-furan, -thiophen, -selenophen, and -tellurophen, respectively. Only for the first two derivatives can methylthio rotation be regarded as nearly free.

$$M\ (cis \text{ or } trans) = \mu\ (C_4H_4X) + \mu\ (PhSMe) \quad (3)$$

2-*Formyl*, 2-*acetyl*, *and* 2-*methoxycarbonyl derivatives*. The conformational problem of 2-formyl- and 2-acetyl-furan, -thiophen and -selenophen have been studied by quite different techniques.[6-12,37,44-47] Conflicting results are most often due to specific solvent effects.[48] Recently the preferred conformations of 2-acyl-furan, -thiophen, -selenophen, and -tellurophen (acyl = formyl and acetyl) have been determined by lanthanide-induced shift technique.[44] 2-Methoxycarbonyl-furan and -thiophen have also been examined.[49]

Because of the high-energy barriers to 2-acyl rotation around the C–CO bond axis,[50] planar and rigid models can be retained for both conformers (III) and (IV) of 2-acyl-furan, -thiophen, -selenophen, and -tellurophen [Figure, (IIIa—c) and (IVa—c)].

The dipole moments of conformers (III) and (IV) have been calculated by the vectorial equation (4) where μ (PhCHO) = 2.99 D and μ (PhCOMe) = 2.92 D act at 34° or 49° to the Ph–COR bond axis [51] and μ (PhCO$_2$Me) = 1.93 D [52] is at an angle of 63° to the Ph–CO$_2$Me link.[53] For 2-methoxycarbonyl derivatives it has been assumed that the methoxycarbonyl group adopts the less hindered (Me,O)-*cis* conformation.[54] The assumptions contained in equation (4) are supported by the following. (i) The electric moments of 2-cyanoselenophen [12] and 2-cyanopyrrole [55] (4.21 and 3.76 D) are practically additive, from selenophen (0.52 D), or pyrrole (1.84 D), and benzonitrile (4.05 D) dipole moments. (ii) Also additive are the dipole moments of 4,5,6,7-tetrahydrobenzo[*b*]thiophen-7-one [9] and 4,5,6,7-tetrahydroindolizin-4-one [56] (4.03 and 4.51 D) starting from those of thiophen (0.54 D), or n-butyl-pyrrole (2.03 D), acetophenone and adding the difference between the dipole moments of cyclohexanone and acetone (3.03—2.74).[9,57] (iii) The moments for (X,O)-*cis* conformers of 2-formylfuran and 2-formylpyrrole, as calculated by a sophisticated method (namely VESCF) [35], are close to the resultants of the heterocycle and benzaldehyde π-moments.[10,55,57]

$$M\ (cis \text{ or } trans) = \mu(C_4H_4X) + \mu(PhCOR) \qquad (4)$$

The results are given in Table 4. They are in agreement with most data reported in literature (see references 37, 44, and 45 for bibliography), especially in solvents of low dielectric permittivity. (X,O)-*cis*-conformer populations obtained (in CDCl$_3$) by the lanthanide-induced shift technique [44] are, respectively, 44, 99, 98, and 96% for 2-formyl-furan, -thiophen, -selenophen, and -tellurophen and 53, 79, 87, and 90% for 2-acetyl derivatives.

2-NN-*dimethylcarbamoyl derivatives*. Recently,[47] it has been shown that furan-, thiophen-, selenophen-, and tellurophen-2-*NN*-dimethylcarboxamides mainly exist in an (X,O)-*trans*-conformation (IVd), in which the dihedral angle (φ) between the planar amidic group and ring is *ca.* 40°.† It was also found that the barriers to

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* This angle derives from the dipole moment of 1,4-dimethylthiobenzene [43] (1.85 D), by solving the equation $\mu = \mu(\text{PhSMe}) \cdot \sin\theta \cdot \sqrt{2}$. From the known dipole moments of *p*-chlorothioanisole and *p*-bromothioanisole [43] (both equal to 1.83 D) one calculates θ = 77° and 78°, respectively, using μ(PhSMe) = 1.34 D,[42] μ(PhCl) = 1.59 D, and μ(PbBr) = 1.56 D.[6-8]

† The true conformation of *NN*-dimethylbenzamide is not known. A planar model is to be discarded since less hindered benzamides are characterised by a finite rotation angle (ϕ *ca.* 30°) around the Ph–CO bond axis,[58,59] and *NN*-dimethyl-*p*-bromobenzamide [60] is characterized by rotational angles about the C$_{ar}$–CO and C(sp^2)–N bonds of 45° 30′ and 9° 18′, respectively.

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rotation around the N–CO bond in the series (*ca.* 15 kcal mol^{-1}) are of the same order of magnitude to those for *NN*-dimethylamides[61] (*ca.* 20 kcal mol^{-1}) and *NN*-dimethylbenzamide[62] (16 kcal mol^{-1}). Since they are much higher than the barriers to phenyl rotation in benzaldehydes[63] (*ca.* 6—8 kcal mol^{-1}); aryl rotation is more likely to occur than *NN*-dimethylamino rotation).

TABLE 4

Calculated dipole moments (*M*, Debye units) for (X,O)-*cis*- and (X,O)-*trans*-conformers and content of (X,O)-*cis*-form [a]

	M(*cis*)	*M*(*trans*)	% cis
2-Methylthiofuran	0.91	2.04	48
2-Methylthiothiophen	0.91	1.88	51
2-Methylthioselenophen	0.89	1.86	59
2-Methylthiotellurophen	0.92	1.80	65
2-Formylfuran	3.64	3.00	83
2-Formylthiophen	3.42	2.88	100
2-Formylselenophen	3.38	2.84	80
2-Formyltellurophen	3.31	2.81	72
2-Acetylfuran	3.63	2.74	51
2-Acetylthiophen	3.42	2.68	92
2-Acetylselenophen	3.39	2.64	70 [b]
2-Acetyltellurophen	3.31	2.63	47
2-Methoxycarbonylfuran	2.65	1.60	55
2-Methoxycarbonylthiophen	2.46	1.57	33 [b]
2-Ethoxycarbonylselenophen	2.43	1.57	59
2-Methoxycarbonyltellurophen	2.37	1.57	42
Furan-2-*NN*-dimethylcarboxamide [c]	4.42	3.46	11
Thiophen-2-*NN*-dimethylcarboxamide [c]	4.27	3.50	56
Selenophen-2-*NN*-dimethylcarboxamide [c]	4.26	3.50	33
Tellurophen-2-*NN*-dimethylcarboxamide [c]	4.20	3.52	11

[a] It has been assumed that the methoxycarbonyl group adopts the (Me,O)-*cis* conformation.[54] [b] From μ = 3.18 D[11] and 1.91,[6–8] respectively. [c] Assuming the rotation angle of the amidic group to be 40° in both conformers (see text).

On these bases [no rotation around the N–CO bond and rotation of 40° about the C(2)–C link] the dipole moments for twisted (X,O)-*cis*- and (X,O)-*trans*-conformers of *NN*-dimethylcarbamoyl derivatives can be calculated by means of the vectorial equation (5) where the dipole moment of *NN*-dimethylbenzamide

$$M\ (cis \text{ and } trans) = \mu\ (C_4H_4X) + \mu\ (PhCONMe_2) \quad (5)$$

(3.84 D) makes an angle of 78.5° [as derived from the dipole moment of *NN*-dimethyl-*p*-chlorobenzamide (3.84 D)] with the Ph–CO bond axis.

The results in Table 4 do not seriously depend on the angle,ϕ, which may have a different value in $PhCONMe_2$ and in the chalcogen-heterocycle relatives.* Except for thiophen-2-*NN*-dimethylcarboxamide, they compare well with those derived by lanthanide-induced shift technique,[44] giving (X,O)-*cis*-conformer abundances of 5, 2, and 5% for furan-, thiophen-, and selenophen-2-*NN*-dimethylcarboxamides, respectively.

2-*NN*-dimethylcarbamoyl-chalcogen-heterocycles are principally in a twisted (X,O)-*trans*-conformation, probably because of steric hindrance in the (nearly) planar (X,O)-*cis*-conformations.

The conformational preferences shown in Table 4 for 2-formyl, 2-acetyl, 2-methoxycarbonyl, and 2-*NN*-dimethylcarbamoyl-chalcogen-heterocycles are in the main in agreement with the ones derived from other techniques. Some discrepancies arise because of the different experimental conditions (especially the medium).

To account for the observed conformational ratios of the derivatives listed in Table 4, a number of factors have to be considered, such as the electrostatic interaction between the heteroatom and acyl-oxygen atom,[44] steric hindrance in both conformers,[44] greater stability of the s-*trans* form for not too hindered αβ-unsaturated aldehydes and ketones.[12,24] The solvent effect is also of importance when comparing the conformational ratios for a given solute in various media.[48]

2-Acetyl-5-methoxycarbonyltellurophen and 2,5-bis-(methoxycarbonyl)tellurophen. These two disubstituted tellurophens exhibit dipole moments of 2.44 and 2.42 D, respectively. Assuming that the methoxycarbonyl group is (Me,O)-*cis*,[54] four planar conformers [(Te,O)-*cis-cis*, -*cis-trans*, -*trans-cis*, and -*trans-trans*] are possible, having the calculated dipole moments given in Table 5.

TABLE 5

Calculated dipole moments (Debye units) for (Te,O)-*cis-cis*, -*cis-trans*, -*trans-cis*, and -*trans-trans* conformers of tellurophen 2,5-diacyl derivatives

	2-Acetyl-5-methoxycarbonyltellurophen	2,5-Bis(methoxycarbonyl)tellurophen
μ(exp.)	2.44	2.42
M(2c,5c) [a]	4.78	4.08
M(2c,5t)	1.39	0.77
M(2t,5c)	1.51	0.77
M(2t,5t)	3.30	2.75

[a] Symbols 2 and 5 stand for 2-acetyl (or 2-methoxycarbonyl) and 5-methoxycarbonyl groups, respectively.

With the assumption that the energy differences between the conformers do not depend on the electrostatic interaction between the angular groups [*i.e.* they only depend on the factors that determine the actual

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* The Ph–CO conjugation has little effect on the dipole moment of *NN*-dimethylbenzamide, as shown by what follows: the dipole moments of *NN*-dimethylbenzamide (3.84 D) ana *NN*-dimethylformamide and *NN*-dimethylacetamide[6–8] (3.86 and 3.81 D) are close in magnitude and also direction, since the angles between $\mu(PhCONMe_2)$ and Ph–C, $\mu(HCONMe_2)$ and H–C, $\mu(MeCONMe_2)$ and Me–C, are 78.5, 74, and 72°, respectively. Angles concerning the dipole moments of aliphatic amides were obtained by solving the vectorial equation:[64] $\mu(RCONMe_2) = \mu(RCHO) + m(N{-}C{=}O)$. This simple method when applied to formamide $[\mu(HCONH_2) = \mu(H_2CO) + \mu(H_2N) - \mu(Me_2N) + m = (2.34)\cdot u + (0.4)\cdot v + m)]$ leads to a (μ, N–C) angle in accord with that found by microwave spectroscopy:[65] 42° instead of 39.6°

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conformational ratios for 2-acyl-tellurophens (acyl = acetyl or methoxycarbonyl)], it is easy to show:[66]

$$(2c,5c) = (2c) \times (5c),\ (2c,5t) = (2c) \times (5t);$$
$$(2t,5c) = (2t) \times (5c),\ (2t,5t) = (2t) \times (5t)$$

where (2c), (5c), (2t), and (5t), are the populations of (Te,O)-*cis* and (Te,O)-*trans* conformers for the monosubstituted derivatives reported in Table 4.

The observed dipole moment for 2-acetyl-5-methoxycarbonyltellurophen is 0.54 D less than that calculated taking (2c,5c) = (0.47 × 0.42), (2c,5t) = (0.47 × 0.58), (2t,5c) = (0.53 × 0.42), and (2t,5t) = (0.53 × 0.58), whereas the one found for 2,5-bis(methoxycarbonyl)-tellurophen is in accord with that (2.40 D) calculated from (2c,5c) = (0.47 × 0.47), (2c,5t) = (2t,5c) = (0.47 × 0.53), and (2t,5t) = (0.53 × 0.53).

2-Hydroxymethyltellurophen. This molecule has two axes of rotation [C(2)–CH_2 and CH_2–O] and can, therefore, exist in a number of conformations. In the stable conformations of 3-methylfuran[67] and 3-methylselenophen[13b] one of the methyl H–C bonds eclipses the C(2)=C(3) bond, and we may infer that the same situation occurs for 2-hydroxymethylfuran and 2-hydroxymethyltellurophen. If so, the hydroxyl oxygen atom is near the heteroatom, and this makes the formation of an O–H ··· X hydrogen bond possible.

Now the difference (0.24 D) in the dipole moments of 2-hydroxymethylfuran and 2-hydroxymethyltellurophen is close to that (0.26 D) between the electric dipole moments of furan and tellurophen. This strongly suggests that the two hydroxymethyl derivatives adopt the same conformation. By analogy with 2-hydroxymethylfuran, which principally exists in a chelated form with an O–H ··· O bridge,[68-70] a similar model may be retained for 2-hydroxymethyltellurophen. Although O–H ··· Te hydrogen bonds are doubtless much weaker than O–H ··· O ones, they are likely to exist. Indeed hydrogen-bonded complexes have been detected between indole, or phenol, and the four diethyl chalcogenides[71] $(C_2H_5)_2X$ (with X = O, S, Se, or Te).

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