A Comparative Study of the Aromatic Character of Furan, Thiophen, Selenophen, and Tellurophen [1]

By **Francesco Fringuelli, Gianlorenzo Marino,*** and **Aldo Taticchi,** Istituto di Chimica Organica, Università di Perugia, Via Elce di Sotto, 10, 06100 Perugia, Italy
Giuliano Grandolini, Istituto di Chimica Farmaceutica, Via del Liceo, Università di Perugia, Perugia, Italy

The ground state aromaticities of furan, thiophen, selenophen, and tellurophen have been compared using seven different criteria: the n.m.r. dilution shift, the difference in chemical shifts of the β- and α-protons, the effect of a 2-methyl substituent on the ring proton chemical shifts, the diamagnetic susceptibility exaltation, the sum of the bond orders, the Julg parameter, and the mesomeric dipole moment. The agreement among the results obtained using the various approaches is remarkably good. The following order of decreasing aromaticity has been established: benzene > thiophen > selenophen > tellurophen > furan.

FURAN, thiophen, selenophen, and tellurophen form a very interesting series of four stable 'aromatic' rings, which differ only in the nature of the heteroatom which all belong to Group VI.

Although some authors think that the term 'aromaticity' is ambiguous and should be eliminated from the scientific vocabulary,[2] nevertheless we believe that it is still a very useful concept, which summarizes the whole

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[1] Preliminary account, F. Fringuelli, G. Marino, and A. Taticchi, *Gazzetta*, 1973, in the press.

[2] See for instance J. F. Labarre in 'Aromaticity, Pseudo-aromaticity, Anti-aromaticity,' eds. E. D. Bergmann and B. Pullman, Israel Academy of Sciences and Humanities (Academic Press), Jerusalem, 1971, p. 55.

of those chemical and physical properties typical of benzene, the ' aromatic ' molecule *par excellence*.

From the ' chemical ' viewpoint it is well known that furan, thiophen, and selenophen tend to react by substitution rather than addition. Recently it has also been shown that tellurophen exhibits similar behaviour with most electrophiles.[3] Quantitatively, the reactivity order observed in all the electrophilic substitutions examined[4] is furan > tellurophen > selenophen > thiophen > benzene.

From the ' physical ' viewpoint, many quantitative, semiquantitative, and qualitative estimations of the ' ground state aromaticities ' are available for the first two members of the series, furan and thiophen. All available information[5] indicates that thiophen is more aromatic than furan and that both are less aromatic than benzene.

TABLE 1

Aromaticities (A) of furan, thiophen, selenophen, and tellurophen determined by the dilution shift method

	$-\delta_1$ [a]								
	Pure liquid		Infinite dilution		$\Delta\delta_1$ [b]				
Compound	α	β	α	β	α	β	Average	V_m [c]	A [d]
Furan	5·686	4·625	6·126	5·067	0·440	0·442	0·441	72·6	7·67
Thiophen	5·321	5·219	6·024	5·803	0·673	0·584	0·628	78·9	11·56
Selenophen	6·119	5·550	6·708	6·038	0·589	0·488	0·538	85·2	10·44
Tellurophen	7·100	6·143	7·623	6·507	0·523	0·364	0·443	84·3	8·50
Benzene							0·70 [e]	88·8	13·93

[a] The chemical shifts are in p.p.m. for CCl_4 solutions relative to cyclohexane as external standard and are corrected for bulk diamagnetic susceptibility. [b] Dilution chemical shift in p.p.m. [c] Molecular volume (cm^3 mol^{-1}). Densities are taken from ref. 3. [d] $A = \Delta\delta_1 V_m^{2/3}$. [e] Ref. 39.

An examination of the spectroscopic properties of selenophen[6] lead to the conclusion that its aromaticity is not very different from that of thiophen. A recent study[7] on the magnetic anisotropy of this molecule confirms this qualitative conclusion. Finally, it has been reported that tellurophen on the basis of its n.m.r. spectrum ' must have marked aromaticity '.[8]

In this paper, we compare some typical aromatic ground state properties of all four congeners under homogeneous conditions, and try to put the comparison, where possible, upon a quantitative basis.

The procedures used include the ' dilution shift method ', the difference in chemical shifts of β- and α-protons, the effect of a 2-methyl group on ring proton chemical shifts, the diamagnetic susceptibility exaltation, the comparison of the bond orders, the determination of the Julg's parameter, and the mesomeric dipole moment.

N.m.r. Dilution Shift.—It has been suggested[9,10] that the aromaticity of a compound can be estimated from the quantity $\Delta\delta_1 V_m$, where $\Delta\delta_1$ is the difference between the chemical shifts of aromatic protons in a pure liquid and in an infinitely dilute solution in a non-polar solvent and V_m is the molar volume of the compound. Using this procedure, Kanekar *et al.*[10] have determined the percentage aromaticity of furan and thiophen.

Recently Pasdeloup and Laurent[11] have critisized the approximation that the distribution factor is inversely proportional to the molar volume and proposed, on the basis of theoretical considerations, equation (1) for the dependence of aromaticity (A) on molar volume.

$$A = \Delta\delta_1 V_m^{2/3} \qquad (1)$$

We have used this approach to estimate the aromaticity of selenophen and tellurophen. In order to allow a homogeneous comparison, the measurements have been repeated for furan and thiophen under the same conditions.

The chemical shifts (δ_1) of the α- and β-protons in the pure liquid and in an infinitely dilute solution of carbon tetrachloride relative to cyclohexane as external standard, the dilution shifts $\Delta\delta_1$, and the aromaticity parameters A are summarized in Table 1. The chemical shifts were corrected for bulk diamagnetic susceptibility (see Experimental section) and the dilution shifts used for the calculation of A according to equation (1) were averages of values obtained for the α- and β-protons.[10]

Using this approach, selenophen appears to be slightly less aromatic than thiophen and tellurophen a little more aromatic than furan.

The A values for benzene, thiophen, and furan give an excellent linear correlation (r 0·9999) with the resonance energies determined by Pauling.[12]

Similarly, Bertelli and Golino[13] have found that the shift of the ^1H n.m.r. signal of solvents owing to aromatic solutes (a parameter substantially similar to our parameter A) is linearly correlated with many accepted

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

[4] F. Fringuelli, G. Marino, G. Savelli, and A. Taticchi, *Chem. Comm.*, 1971, 1441.

[5] For summaries of the available information see G. Marino, *Adv. Heterocyclic Chem.*, 1971, **13**, 235; M. J. Cook, A. R. Katritzky, and P. Linda, *ibid.*, in the press.

[6] N. N. Magdesieva, *Adv. Heterocyclic Chem.*, 1970, **12**, 1.

[7] W. Czieslik, D. Sutter, H. Dreizler, C. L. Norris, S. L. Rock, and W. H. Flygare, *Z. Naturforsch*, 1972, **27a**, 1961.

[8] W. Mack, *Angew. Chem. Internat. Edn.*, 1966, **5**, 896.

[9] S. S. Dharmatti, G. Govil, C. N. Kanekar, C. L. Khetrapal, and Y. P. Virmani, *Proc. Indian Acad. Sci.*, 1962, **56**, 71.

[10] C. R. Kanekar, G. Govil, C. L. Khetrapal, and M. M. Dhingra, *Proc. Indian Acad. Sci.*, 1966, **64**, 315.

[11] M. Pasdeloup and J. P. Laurent, *Bull. Soc. chim. France*, 1972, 1022.

[12] L. Pauling, ' The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 3rd edn., 1945.

[13] D. J. Bertelli and C. Golino, *J. Org. Chem.*, 1965, **30**, 368.

parameters for π electron delocalization, including empirical resonance energy. This fact and the other linear relationships reported below, give confidence to the *linear correlation* observed which otherwise could be criticized for being based on only three points. From the plot empirical resonance energies for selenophen (29 kcal mol^{-1}) and tellurophen (25 kcal mol^{-1}) can be estimated.

netic susceptibility exaltation (Λ) defined as the difference between the molar susceptibility (χ_M) found experimentally for a given compound and that estimated (χ'_M) for the identical but not electron-delocalized structure, has been proposed as a useful criterion for assessing aromaticity.[15] The theoretical basis of this proposal and the experimental evidence in support of it have recently been surveyed.[16]

TABLE 2

Aromaticity index *B* determined through the effect of methyl substitution on ring proton shifts of furan, thiophen, selenophen, and tellurophen

	$\Delta\delta_2$ [a]			$\Delta\Delta\delta_2$			
Compound	3-H	4-H	5-H	$(\Delta\delta_2)_{3\text{-H}} - (\Delta\delta_2)_{4\text{-H}}$	$(\Delta\delta_2)_{3\text{-H}} - (\Delta\delta_2)_{5\text{-H}}$	$(\Delta\delta_2)_{4\text{-H}} - (\Delta\delta_2)_{5\text{-H}}$	*B* [b]
Furan [c]	0·43	0·14	0·18	0·29	0·25	0·04	1·72
Thiophen [c]	0·37	0·24	0·28	0·13	0·09	0·04	3·85
Selenophen [d]	0·37	0·20	0·21	0·17	0·16	0·01	2·94
Telluorphen [e]	0·58	0·32	0·31	0·26	0·27	0·01	1·85
Benzene [f]	0·20	0·12	0·22	0·08	0·02	0·10	5·00

[a] $\Delta\delta_2$ = ring proton chemical shifts (in p.p.m.) of the 2-methyl derivative relative to the chemical shifts of corresponding hydrogen atoms in the unsubstituted ring. [b] $B = 1/\Sigma|\Delta\Delta\delta_2|$. [c] S. Gronowitz, G. Sörlin, B. Gestblom, and R. A. Hoffman, *Arkiv. Kem.*, 1962, **34**, 483. [d] This work. For ^{1}H n.m.r. data for selenophen see J. Morel, C. Paulmer, M. Garreau, and G. Martin, *Bull. Soc. chim. France*, 1971, 4497. [e] This work. For ^{1}H n.m.r. data of tellurophen see ref. 3. [f] K. Hayamizur and O. Yamamoto, *J. Mol. Spectroscopy*, 1969, **29**, 183. The $\Delta\delta$ values refer to protons *ortho* (3-H), *meta* (4-H), and *para* (5-H) to the Me group of toluene referred to the chemical shift of benzene.

Other Methods based on N.m.r. Spectra.—The difference in chemical shifts of the β- and α-protons may be taken as a criterion of aromaticity:[6] the more aromatic the ring, the closer the difference approaches zero. When we applied this criterion to the shifts of the pure liquids (see Table 1) we again found the following order of decreasing aromaticity: thiophen (0·132) > selenophen (0·569) > tellurophen (0·957) > furan (1·061).

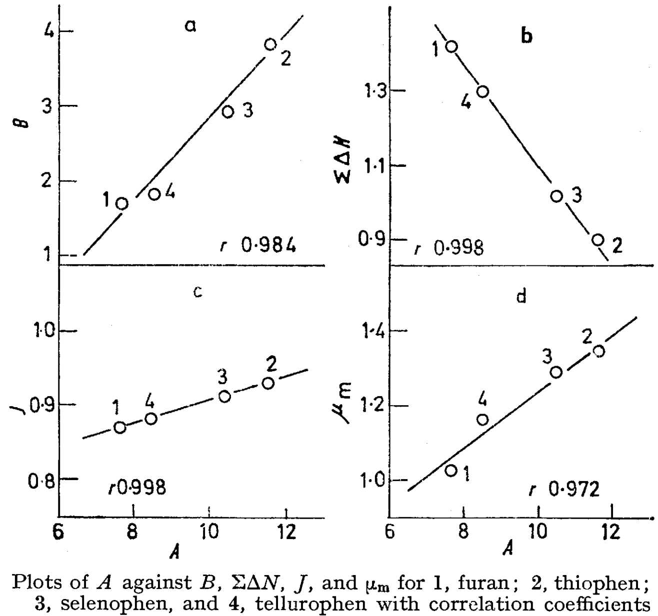
Additional information on the relative aromaticities of heteroaromatic rings may be derived by a comparison of the effects produced by a 2-methyl substituent upon the ring proton shifts. It has been noted[14] that the more aromatic the ring, the more uniform is the effect of the 2-methyl group on the shifts of the various nuclear protons. We have attempted to put this qualitative observation into quantitative form by introducing the parameter *B* [equation (2) where $\Delta\delta_2$

$$B = 1/\Sigma_{i,j}|(\Delta\delta_2)_i - (\Delta\delta_2)_j| \qquad (2)$$

is the difference between the ring proton chemical shifts of the 2-methyl derivative and the corresponding unsubstituted heterocycle and the indices *i* and *j* refer to all the non-equivalent protons (3-H, 4-H, and 5-H)]. The *B* values (which are the greater the more uniform the effect of the methyl groups) are summarized in Table 2. Good agreement exists between the ' chemical shift difference ' and the ' dilution shift ' parameters, as evidenced by the linearity of the plot of *B* against *A* (Figure a).

Diamagnetic Susceptibility Exaltation.—The diamagnetic susceptibility exaltation (Λ) defined as the difference between the molar susceptibility (χ_M) found experimentally for a given compound and that estimated (χ'_M) for the identical but not electron-delocalized structure, has been proposed as a useful criterion for assessing aromaticity.[15] The theoretical basis of this proposal and the experimental evidence in support of it have recently been surveyed.[16]

The experimental susceptibilities χ_M of furan, thiophen, and selenophen are available.[17] The value for tellurophen ($-74{\cdot}2 \times 10^{-6}$ cm^3 mol^{-1}) has been determined using the Gouy technique.[18]



Plots of *A* against *B*, $\Sigma\Delta N$, *J*, and μ_m for 1, furan; 2, thiophen; 3, selenophen, and 4, tellurophen with correlation coefficients (*r*)

The estimation of χ'_M values can be made by using one of two alternative methods which are substantially equivalent: the Pascal system of atomic constants[19] or the Haberditzl ' semiempirical increment system '.[20]

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[14] G. S. Reddy and J. H. Goldstein, *J. Amer. Chem. Soc.*, 1961, **83**, 5020.

[15] H. J. Dauben, J. D. Wilson, and J. L. Laity, *J. Amer. Chem. Soc.*, 1968, **90**, 812; 1969, **91**. 1991.

[16] H. J. Dauben, J. D. Wilson, and J. L. Laity, in ' Non-benzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1971, vol. II, p. 187.

[17] ' Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, 51st edn., 1970—1971, p. E-132.

[18] P. W. Selwood, ' Magnetochemistry,' Interscience, New York, 1964, 2nd edn., p. 3.

[19] P. Pascal, *Ann. Chim. Phys.*, 1910 [8] **19**, 5.

[20] W. Haberditzl, *Angew. Chem. Internat. Edn.*, 1966, **5**, 288.

The latter system, which assigns susceptibility increments to each type of bond and electron grouping is perhaps somewhat more accurate.[17] However, since the increment value for the carbon–tellurium bond is not available, we were forced to use the Pascal system.

The models for the calculation of χ'_M are somewhat inadequate in the case of heteroaromatic compounds and the results are not always reliable.[16] Anyhow, we have calculated the χ'_M values by the procedure described by Hutchison [equation (3)],[21] using the constants reported by Pascal *et al.*[22] The values of χ_M, χ'_M, and Λ

$$\chi'_M = 4\chi_C + 4\chi_H + 1\chi_X + 1\lambda(\text{-C=C-C=C-}) \quad (3)$$

for the four five-membered rings and benzene are summarized in Table 3. The Λ values for benzene, furan, and thiophen are a little different from the literature values,[16] calculated by using the Haberditzl procedure but the relative values are very similar.

TABLE 3

Diamagnetic molar susceptibilities and diamagnetic susceptibility exaltations (Λ) of furan, thiophen, selenophen, and tellurophen [a]

	$-10^6\chi_M$	$-10^6\chi'_M$	$-10^6\Lambda$
Furan	43·09	29·73	13·32
Thiophen	57·38	40·12	17·26
Selenophen	66·82	48·12	18·70
Tellurophen	74·20	62·42	11·78
Benzene	54·84	37·10	17·74

[a] Values in cm^3 mol^{-1}.

Applying this criterion of aromaticity, tellurophen appears to be less aromatic than furan and selenophen even more aromatic than benzene. These results are in sharp contrast with the conclusions derived from the application of all the other approaches and are clearly not credible.

TABLE 4

Bond orders and the aromaticity index $\Sigma\Delta N$ for furan, thiophen, selenophen, and tellurophen

	Bond orders [a]			Bond order differences (ΔN)			
Compound	N_a	N_b	N_c	$N_b - N_a$	$N_b - N_c$	$N_c - N_a$	$\Sigma\Delta N$
Furan	1·25	1·96	1·61	0·71	0·35	0·36	1·42
Thiophen	1·46	1·91	1·65	0·45	0·26	0·19	0·90
Selenophen	1·34	1·85	1·60	0·51	0·25	0·26	1·02
Tellurophen	1·27	1·92	1·58	0·65	0·34	0·31	1·30

[a] Bond orders calculated according to the Gordy formula (4)[29] (see text). N_a, N_b, and N_c refer to X–C(2), C(2)–C(3), and C(3)–C(4) bonds, respectively.

Evidently the method needs to be improved in order to give satisfactory results with heterocyclic rings; moreover the Pascal constants for selenium and tellurium atoms are probably inaccurate.

Bond Lengths and Bond Orders.—Completely different approaches to aromaticity are those based on structural criteria. As a consequence of π electron delocalization, the bond lengths of an aromatic ring tend to be intermediate between those typical of pure single and pure double bonds. Thus, an estimation of the aromaticity of a given system may be deduced by an examination of the bond orders of the various bonds.

Reliable, recently determined, values for bond lengths and angles of furan,[23] thiophen,[24] and selenophen [25] are available in the literature. For tellurophen, the parameters have been determined by three different approaches, microwave spectroscopy,[26] n.m.r. spectroscopy,[27] and *X*-ray diffraction of the 2-carboxylic acid.[28] Since each approach is subject to criticism,* we have preferred to adopt the average values for the three procedures [Te–C(2) = 2·053; C(2)–C(3) = 1·368; and C(3)–C(4) = 1·438 Å].

The bond orders N have been calculated by applying the Gordy [29] equation (4) where R is the bond length

$$N = aR^{-2} + b \quad (4)$$

and a and b are constants characteristic of any given pair of atoms and may be easily calculated when the bond lengths of pure single and double bonds are known.

Since experimental values for pure single and pure double carbon–selenium and carbon–tellurium bonds are not available, they have been calculated from the covalent radii [12] and the electronegativity [12] values, using the Shomaker–Stevenson rule.[30] The values so obtained are: C–Se 1·93, C=Se 1·73, C–Te 2·11, and C=Te 1·92 Å. The constants a and b calculated therefrom were 15·24 (a) and −3·09 (b) for carbon–selenium, and 21·41 (a) and −3·81 (b) for carbon–tellurium.

The bond orders N calculated according to this procedure are summarized in Table 4. The N values

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* The values determined from microwave spectra should be, in principle, preferable. However, they suffer from a serious drawback: the C(3)–C(4) bond length has been *assumed* equal to that of selenophen. Thus, we believe that the mean values approach the true values more than those obtained by each technique individually.

[21] C. A. Hutchinson, jun., in 'Determination of Organic Structures by Physical Methods,' eds. E. A. Braude and F. C. Nachod, Academic Press, New York, 1955, vol. I.

[22] P. J. Wheatley, 'The Determination of Molecular Structure,' Oxford Univ. Press, 1968, 2nd edn., p. 224.

[23] B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup-Andersen, and M. Schottlander, *J. Mol. Spectroscopy*, 1962, **9**, 124.

[24] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1961, **7**, 58.

[25] N. M. Pozdeev, O. B. Akulinin, A. A. Shapkin, and N. N. Magdesieva, *Doklady Akad. Nauk. S.S.S.R.*, 1969, **185**, 384. See also ref. 6.

[26] R. D. Brown and J. G. Croft, *Chem. Phys.*, 1973, **1**, 217.

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

[28] L. Fanfani, A. Nunzi, P. F. Zanassi, and A. R. Zanzari, *Cryst. Struct. Comm.*, 1972, **1**, 273.

[29] W. Gordy, *J. Chem. Phys.*, 1947, **15**, 305.

[30] V. Shomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

for furan and thiophen are slightly different from those of Gordy [29] since we have used more recently determined bond lengths,[23,24] based on microwave spectra.

The sum of the differences ΔN of the bond orders of a ring (Table 4) can be taken as a measure of its aromaticity, in the sense that it should be smaller the more aromatic the system (for benzene, obviously, $\Sigma\Delta N = 0$). Again, we found the same order of aromaticity: (benzene) > thiophen > selenophen > tellurophen > furan.

Good linear plots are observed when the values of $\Sigma\Delta N$ for the four congeners are plotted against other aromaticity parameters (Figure b).

The Julg Parameter.—Julg and his co-workers [31] have suggested that the degree of ring aromaticity can be estimated by equation (5) * where n is the number

$$J = 1 - \frac{225}{n} \Sigma_{rs} (1 - d_{rs}/\bar{d})^2 \qquad (5)$$

of peripheral bonds rs, d_{rs} their lengths, and $\bar{d}$ their mean length. The method has been applied by these authors to furan and thiophen, taking into account only the three C–C bonds.

Subsequently, the approach has been refined to account for resistance to π electron circulation.[32] Unfortunately, the charge gradient values necessary to calculate the term for resistance to electron circulation are not available for selenophen and tellurophen; accordingly, we calculated the cruder aromaticity index defined in equation (5). Using this criterion, the aromaticity order obtained is again: benzene ($J = 1{\cdot}00$) > thiophen ($J = 0{\cdot}93$) > selenophen ($J = 0{\cdot}91$) > tellurophen ($J = 0{\cdot}88$) > furan ($J = 0{\cdot}87$).† A plot of J against A is linear (Figure c) with a good correlation coefficient (r 0·998).

Mesomeric Dipole Moment.—The large dipole moment observed in many hydrocarbons has been taken as a criterion of aromaticity.[33] Although this approach has been criticized by Dewar,[34,35] it has without doubt a certain validity in that it is a direct consequence of the π electron delocalization.

For heteroaromatic rings, the mesomeric dipole moment (μ_m) determined by comparison of the experimental moments of the heteroaromatic rings and those of the corresponding non-aromatic models (the tetrahydro-derivatives) must be considered. The mesomeric dipole moments have been recently determined [36] for furan (1·03), thiophen (1·35), selenophen (1·29), and tellurophen (1·17 D). The μ_m values for the four rings correlate linearly with the other aromaticity indices A, B, $\Sigma\Delta N$, and J. (The correlation with A is shown in Figure d.)

Conclusions.—The aromaticities of furan, thiophen, selenophen, and tellurophen have been estimated by seven independent approaches. The results are summarized in Table 5.

TABLE 5

Summary of aromaticity indices for furan, thiophen, selenophen, and tellurophen

Compound [a]	A [b]	B [c]	$\beta - \alpha$ [d]	$\Sigma\Delta N$ [e]	J [f]	μ_m [g]
Furan	7·67	1·72	1·061	1·42	0·87	1·03
Tellurophen	8·50	1·85	0·957	1·30	0·88	1·17
Selenophen	10·44	2·94	0·569	1·02	0·91	1·29
Thiophen	11·56	3·85	0·132	0·90	0·93	1·35
Benzene	13·93	5·00	0	0	1·00	

[a] Listed in order of increasing aromaticity. [b] The dilution shift parameter $A = \Delta\delta_1 V_m^{2/3}$. [c] From the n.m.r. spectra of the 2-methyl derivatives; $B = 1/\Sigma|\Delta\Delta\delta_2|$ (see text). [d] Difference in chemical shifts of β- and α-protons. [e] Sum of the differences in bond orders of the three non-equivalent bonds. [f] The Julg parameter (see text). [g] The mesomeric dipole moment (in D).

Although all the criteria used have limited validity from a theoretical point of view and some experimental data are not very accurate, nevertheless the agreement among the results obtained is remarkably good. Six different criteria agree in establishing the order of decreasing ground state aromaticity as benzene > thiophen > selenophen > tellurophen > furan. The seventh criterion (the diamagnetic susceptibility exaltation) leads to a different aromaticity order, but we have already noted the reasons why this method is not very accurate.

The agreement among the different empirical aromaticity parameters is not only qualitative but also quantitative, as shown by the linear correlations in the Figure. In our opinion, the linearity observed in Figures b and c, in which aromaticity indices based on structural criteria are plotted against a parameter based on a magnetic property, is particularly significant.

To account for the observed order of ground state aromaticities, two properties of the heteroatoms must be taken into consideration: the electronegativity and the covalent radius. The degree to which the conjugation between O, S, Se, and Te and the adjacent carbon atoms occurs, obviously depends on the electronegativity of the heteroatom.[37] The more electronegative the heteroatom, the more contracted is the p orbital, and the less efficient is conjugation. In terms of the valence bond description, structures in which a positive charge is localized on the heteroatom are less important when the electronegativity is greater. According to this criterion the ability of conjugation should be in the order Te > Se > S > O.

However, the degree of overlap between the filled outer p orbitals of the heteroatom X and the $2p$ orbitals

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* These authors used the symbol A_1; we use the symbol J in order to avoid confusion with other aromaticity parameters used in this paper.

† The values reported by Julg and his co-workers for furan and thiophen using equation (5) are slightly different from ours since they used other literature values for the bond lengths of these molecules.

[31] A. Julg and P. Francois, *Theor. Chim. Acta*, 1967, **8**, 249.

[32] A. Julg, ref. 2, p. 383.

[33] E. D. Bergman and I. Agranat, ref. 2, p. 15.

[34] M. J. S. Dewar, in 'Aromaticity, Special Publication No. 21.' The Chemical Society, London, 1967, p. 177.

[35] M. J. S. Dewar, 'Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969, p. 181.

[36] H. Lumbroso, D. M. Bertin, F. Fringuelli, and A. Taticchi, *J.C.S. Chem. Comm.*, 1973, 342.

[37] A. D. Walsh, *Quart. Rev.*, 1948, **2**, 84.

of the aromatic ring carbon atoms also depends upon the C–X bond length and the disparity between the sizes of the carbon and the heteroatom *p* orbitals. Since the C–O bond is the shortest of the four and the *p* orbitals of oxygen are the most similar to those of carbon, overlap should be at a maximum in the case of oxygen * and the ability of conjugation should decrease in the order O > S > Se > Te.

The interplay of these opposing factors leads to the observed order of aromaticity with the maximum for the thiophen ring.

EXPERIMENTAL

Materials.—Furan and thiophen were commercial products. Selenophen was prepared from selenium and acetylene at 500 °C and purified by fractional distillation.[38] Tellurophen was prepared from sodium telluride and buta-1,3-diyne at 25° in methanol.[3]

2-Methyltellurophen was synthesized as previously reported [3] and purified by fractional distillation, b.p. 80° at 70 mmHg, δ (100 MHz; $CDCl_3$, Me_4Si internal standard) 2·58 (3H, d, $J_{Me\text{-}3}$ 1·0 Hz, Me), 7·20 (1H, m, 3-H), 7·46 (1H, q, $J_{4.3}$ 4·01, $J_{4.5}$ 7·0 Hz, 4-H), and 8·56 (1H, q, $J_{5.4}$ 7·0, $J_{5.3}$ 1·2 Hz, 5-H). 2-Methylselenophen was prepared using the procedure for 2-methyltellurophen,[3] b.p. 133° at 760 mmHg, δ (100 MHz; $CDCl_3$; Me_4Si internal standard) 2·57 (3H, d, $J_{Me\text{-}3}$ 1·0 Hz, Me), 6·90 (1H, m, 3-H), 7·07 (1H, q, $J_{4.3}$ 3·7, $J_{4.5}$ 5·6 Hz, 4-H), and 7·71 (1H, q, $J_{5.4}$ 5·6, $J_{5.3}$ 1·2 Hz, 5-H).

Dilution Chemical Shifts.—Furan, thiophen, selenophen, and tellurophen were separately dissolved in reagent grade carbon tetrachloride. For each compound five solutions at different concentrations (*ca.* 1·5, 0·75, 0·375, 0·185, and 0·095M) were prepared and the ^1H chemical shifts were measured relative to cyclohexane as external standard on a Varian 100 MHz spectrometer. The coaxial cylindrical tubes technique, with the reference in the inner tube and the sample in the surrounding region, was used. The measured chemical shifts (δ_{obs}) were corrected for bulk diamagnetic susceptibility using the Bothner-By–Glick equation (6).[39] χ_v, solution was calculated according

$$\delta_{corr} = \delta_{obs} - 2{\cdot}6\,(\chi_v,\ \text{solution} - \chi_v,\ \text{reference}) \qquad (6)$$

to equation (7) [40] where χ_{v1} and χ_{v2} are the volume sus-

$$\chi_v,\ \text{solution} = \phi_1\chi_{v1} + \phi_2\chi_{v2} \qquad (7)$$

ceptibilities of the two components and ϕ_1 and ϕ_2 the corresponding volume fractions.

The volume susceptibilities of furan ($-0{\cdot}598 \times 10^{-6}$), thiophen ($-0{\cdot}726 \times 10^{-6}$), and selenophen ($-0{\cdot}778 \times 10^{-6}$) were available;[17] the volume susceptibility of tellurophen ($-0{\cdot}879 \times 10^{-6}$) was determined experimentally (see below). The densities of the compounds were taken from ref. 3.

The corrected chemical shifts (δ_{corr}) were then plotted against the mole fraction and extrapolated to infinite dilution. The experimental error is ±0·002 p.p.m. The chemical shifts of pure compounds (i) were measured in a similar way and corrected for bulk diamagnetic susceptibility using equation (6) with $\chi_{v,(i)}$ instead of χ_v, solution.

The difference between the mean chemical shifts of α- and β-protons in the pure liquid and at infinite dilution gave the dilution shift $\Delta\delta_1$.

Magnetic Data.—The molar susceptibility of tellurophen ($-74{\cdot}2 \times 10^{-6}$ cm^3 mol^{-1}) was determined by the Gouy [18] technique using distilled water as the reference.

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* In this simplified exposition the possibility of participation by the *d* electrons of sulphur, selenium, and tellurium has not been taken into account; however, the conclusions should not be very different.

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