Ring Currents in Furan and Thiophen

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RECENTLY Elvidge and Jackman[1] suggested a new definition of an aromatic compound as one that will sustain an induced ring current. To test this hypothesis, and further to see whether the magnitude of the ring current is a measure of the degree of aromaticity of the molecule, we have measured the ring currents in furan and thiophen and compared them with benzene. These were measured by the comparison of the chemical shifts of the protons in the molecule with those of similarly constituted protons in molecules in which no ring current can occur (see Table).[2]

Proton chemical Shifts of aromatic against dihydro-aromatic compounds

Compound	H_2	H_3	Me	ΔH_2	ΔH_3	ΔMe	$\Delta H/\Delta H$ (Benzene) H_2	H_3	Me
Benzene	2·66	2·66	—	1·48	1·48	—	1·00	1·00	—
Cyclohexa-1,3-diene	4·14	4·14	—						
Toluene			7·66			0·62			1·00
2-Methylcyclohexa-1,3-diene			8·28						
Furan	2·54	3·59	—	1·15	1·46	—	0·78	0·99	—
4,5-Dihydrofuran	3·69	5·05	—						
2-Methylfuran	—	4·02	7·70	—	1·41	0·51	—	0·95	0·82
4,5-Dihydro-2-methylfuran		5·43	8·21						
Thiophen	2·65	2·87	—	1·18	1·50	—	0·80	1·03	—
4,5-Dihydrothiophen	3·83	4·37	—						
2-Methylthiophen	—	3·28	7·52	—	1·47	0·54	—	1·00	0·87
4,5-Dihydro-2-methylthiophen	—	4·75	8·06						

The 2-H* and 2-methyl shifts can be used to obtain the ratios of the ring currents in furan and thiophen compared to benzene as follows. On the equivalent dipole approximation, the ratio of the ring currents in furan (i_B) and benzene (i_F) is given by

$$\frac{i_F}{i_B} = \frac{\Delta_F A_B}{\Delta_B \cdot B_F} \cdot \left(\frac{R_F}{R_B}\right)^3 \quad \cdots \quad \cdots \quad (1)$$

where Δ_F and Δ_B are the observed chemical shift differences for furan and benzene, A_F and A_B the areas of the rings, and R_F and R_B the distances of the protons from the centre of the ring.

Using values for A and R calculated from the known dimensions of the molecules,[4] and the observed ΔH's, the approximate equation 1 gives values of the ring currents in furan and thiophen of *ca.* 90% that in benzene. Using the more accurate calculation of the magnetic field of the two loops of current of the π orbitals tabulated by Johnson and Bovey[2] gives calculated shifts in furan and thiophen, the ring current being assumed to be as in benzene, of 1·16 and 0·47 p.p.m. for the 2-H and 2-methyl protons of furan and 1·14 and 0·50 p.p.m. for thiophen. Comparison with the Table shows that these are in very good agreement with the observed shifts.

We conclude that the aromatic ring currents in furan and thiophen do not differ significantly from that in benzene. As the aromaticity estimated by either the reactivity or resonance energy of thiophen and especially furan, is very different from that of benzene, we also conclude that the magnitude of the ring current is independent of the degree of aromaticity of these compounds as judged by the above criteria. This result emphasises the discrepancy for these molecules between the Elvidge and Jackman definition of an aromatic

* The 3-H shifts cannot be used, because the increased contribution of the mesomeric form $-\overset{+}{X}=CH-\overset{-}{C}H-$ (X = O, S) in the hydroaromatic series leads to anomalous resonance positions.[3]

[1] Elvidge and Jackman, *J.*, 1961, 856.

[2] Johnson and Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

[3] Bohlmann, Arndt, and Starnick, *Tetrahedron Letters*, 1963, 1605.

[4] "Tables of Interatomic Distances," The Chemical Society, London, 1958.

compound and the accustomed definition in terms of chemical reactivity and resonance energy. This discrepancy is further emphasised by the recent measurement[5] of a large ring current in the Hückel hydrocarbon [18]-annulene but not in the non-Hückel [24]-annulene, although both compounds show the typical reactions of poly-olefins.[5]

Finally, it is noteworthy that magnetic susceptibility measurements have been used to measure aromaticity by comparing the observed magnetic susceptibility with that calculated from Pascals constants.[6] However this difference is also proportional to iA. Thus a large part of the observed variation is due to the variation in the size of the aromatic ring. This has not been considered previously.

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[5] See discussion by Raphael, *Proc. Chem. Soc.*, 1962, 97.

[6] Craig, Ch. I in "Non-benzenoid Aromatic Compounds," ed. Ginsburg, Interscience Publ., Inc., New York, 1959.