

Ring Currents and Chemical Shifts in Furan, Thiophen and Pyrrole

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INTEREST has recently been shown in the ring currents obtained from proton shielding¹ and deshielding effects^{1,2,3} in furan and thiophen, and from the de-shielding effect³ in pyrrole. It has been suggested by different authors that the ring currents are less in the heterocyclic compounds than in benzene,^{1,3} and that they are about the same.² The object of this communication is to report the results of some calculations of these ring currents.

Calculations of ring currents in heterocyclic compounds have been made by two methods^{4,5} based on self-consistent molecular orbital theory. For pyridine the two methods give similar results. In one method⁵ the perturbing effect of the magnetic field on the orbital coefficients is taken into account, whereas in the other method⁴ this effect is assumed to be negligible. This assumption enables calculations of ring currents to be made from the results of unperturbed self-consistent molecular orbital calculations by finding the eigenvalues of one matrix. Such unperturbed calculations are available for furan,⁶ thiophen,⁷ and pyrrole,⁸ and they were used for the calculations of the ring currents. The necessary eigenvalues were obtained on the TR 4 computer at the Rekencentrum of this University. A similar calculation for benzene had been made previously,⁴

and relative values of the ring current susceptibilities for benzene, thiophen, pyrrole, and furan were thus found to be 1:0.55:0.53:0.49, respectively. With the ring areas used in the calculations the ratios of the ring currents are 1:0.72:0.80:0.76. These may be compared with the values given by Elvidge,³ based on different ring areas, of 1:0.75:0.59:0.46. With the areas used here, Elvidge's values become 1:0.90:0.67:0.52.

The relative values of the calculated ring currents depend on the parameters used for the oxygen, sulphur, and nitrogen atoms, and further work is necessary on these. It is clear, however, that the ring currents are less in the heterocyclic compounds than in benzene. Comparison with the chemical shift values is also made difficult by the possible intrusion of factors other than the ring current. Thus Pople⁹ has pointed out the influence of local anisotropic effects on the difference in proton chemical shifts between ethylene and benzene. The calculations do, however, support the interpretation of the chemical shifts that leads to lower ring currents in the heterocyclic compounds than in benzene.

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