Approximate π-Electron ' Ring Current ' Intensities in Some Sulphur-Heterocyclic Analogues of Fluoranthene

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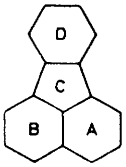
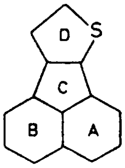
Approximate MO calculations are reported on the π-electron 'ring current' properties of two sulphur-heterocyclic isosteres of fluoranthene (I) [acenaphtho[1,2-*b*]thiophen (II) and acenaphtho[1,2-*c*]thiophen (III)]. On the basis of recently published ^{1}H n.m.r. experimental measurements, order-of-magnitude estimates have been made of the relative π-electron ' ring current ' intensities in the various rings of these polycyclic molecules. Comparison is therefore made here between the calculated values of relative ' ring current ' intensities being reported, and those derived from experiment. The experimentally deduced values are qualitatively confirmed by these approximate calculations in that the computed ' ring current ' intensities in the ' naphthalenic ' parts of (II) and (III) (rings A and B), and in the central five-membered rings (rings C), are very similar to the intensities previously evaluated for the analogous homocyclic rings in fluoranthene itself, whilst the heterocyclic rings (rings D) in (II) and (III) appear to bear a smaller π-electron ' ring current ' intensity than does the corresponding *benzenoid* ring D, in (I). This reduction in the ' ring current ' intensity associated with ring D, on going from the hydrocarbon (I), to the heterocycles (II) and (III), is attributed almost entirely to the assumed *smaller area* of the thiophenoid rings.

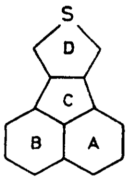
RECENT, approximate, semi-empirical calculations [1] suggest that the five-membered ring (C) of fluoranthene (I) has associated with it only a small π-electron ' ring current ' [2,3] intensity (*ca.* 5% that of benzene), when these hydrocarbons are in the presence of an external magnetic field having a similar component perpendicular to their respective molecular planes. Prompted by this theoretical observation, Bartle *et al.*[4] have reported an experimental ^{1}H n.m.r. study of two sulphur-heterocyclic isosteres [acenaphtho[1,2-*b*]thiophen (II) and acenaphtho[1,2-*c*]thiophen (III)] of fluoranthene (I). From their experimental measurements, they inferred [4] that the ' ring current ' intensities in the thiophenoid rings (D) of (II) and (III) are smaller than that in the corresponding benzenoid ring (D) of (I); and that the ' ring current ' intensity in the central rings (C) of (II) and (III) is apparently negligible—as is predicted theoretically [1] for the case of the analogous five-membered ring (C) in fluoranthene itself.



(I)



(II)



(III)

It is, however, very difficult to distinguish and resolve the various different contributions to the relative proton chemical shifts in molecules such as (II) and (III) which are not only heterocyclic, but which, furthermore, are related to hydrocarbons having a basic ' sigma-bond ' topology which is ' non-alternant ' (in the sense of the Coulson–Rushbrooke Theorem [5]); and, although the ' ring current ' theory alone gives a good account of the relative proton chemical shifts of the non-hindered protons in alternant, benzenoid hydrocarbons (*e.g.* see refs 6—8), when proton shifts in non-alternant [1,9,10] and in heterocyclic [11-16] molecules are considered, this is certainly not generally the case.[1,8-16]

Accordingly, it was considered to be of interest to investigate to what extent the qualitative conclusions concerning the apparent relative magnitudes of the π-electron ' ring current ' intensities in (II) and (III) as deduced from experimental measurements *via* the kinds of arguments outlined by Bartle *et al.*,[4] are confirmed by even a very simple empirical MO calculation. Here, therefore, approximate calculations are presented of the relative ' ring current ' intensities in the sulphur heterocyclic isosteres (II) and (III) of fluoranthene (I), in an attempt to effect such an assessment of the empirically-deduced values.

CALCULATIONS

The calculations were performed using Veillard's adaptation [11] of the standard London–McWeeny [2,3] Linear Combination of ' Gauge Invariant ' Atomic Orbitals method; the HMO parameters used were those of Streitwieser [17]—the same, in fact, as the ones favoured by Bartle *et al.*[4] on the basis of fitting calculated to experimental u.v. spectra (see ref. 4, p. 2094 for discussion). The simplest assumptions

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about molecular geometry were made—*i.e.* that all carbon–carbon bond lengths could be taken as the standard benzene value of *ca.* 1·39 Å (see ref. 6 for a justification of this), and that the areas of six-membered and five-membered rings were in the ratio $6 \cot (\pi/6) : 5 \cot (\pi/5)$ (*i.e. ca.* 1·0 : 0·66). The calculations were performed on the Oxford University KDF 9 computer, by use of a modified version of the program NPRC (see refs. 6 and 18).

As a check, the calculations on molecules (II) and (III) were performed three times, and, on each occasion, they were based on a *different* initial ‘ open chain.’ In two of these three sets of calculations on each molecule, one ‘ circuit-completing bond ’ involved orbitals centred on the sulphur atom, whilst in the third, all ‘ circuit-completing bonds ’ were carbon–carbon bonds (see ref. 3 on pp. 317—318 for an explanation of the terms ‘ open chain ’ and ‘ circuit-completing bond ’). As pointed out by McWeeny [3] for the case of hydrocarbons, the final result is, and must be, independent of the original ‘ open chain ’ selected as a basis for the calculation; and the same is, of course, true for the more-general case of the heterocycles. For molecule (II), the results arising from the three sets of calculations, each based on one of the three arbitrarily-chosen ‘ open-chains,’ were in exact agreement, to the number of decimal places quoted in the Table—as also were the three sets of results for molecule (III).

Calculated π-electron ‘ ring current ’ intensities (expressed as a ratio to the calculated ‘ ring current ’ intensity in benzene) by the McWeeny–Veillard [3,11] method, in the various rings of the polycyclic molecules (I)—(III)

Molecule	Calculated ‘ ring current ’ intensity (as a ratio to the calculated ‘ ring current ’ intensity in benzene) in rings			
	A	B	C	D
Fluoranthene (I) *	0·987	0·987	0·050	0·860
Acenaphtho[1,2-*b*]thiophen (II)	0·977	0·967	0·055	0·503
Acenaphtho[1,2-*c*]thiophen (III)	0·991	0·991	0·032	0·511

* Calculated ‘ ring current ’ intensity values for fluoranthene (I) are taken from ref. 1.

RESULTS AND DISCUSSION

The calculated ‘ ring current ’ intensities are shown in the Table; of course, because of the very approximate nature of the calculations just described, only orders-of-magnitude and trends will be discussed. Orders-of-magnitude are, in any case, all the data that are available from the experimental evidence,[4] on which to base the discussion.

It can be seen immediately that two aspects of the experimental results of Bartle *et al.*[4] are borne out by these calculations, in that (*a*) the ‘ ring current ’ intensities in the ‘ naphthalenic ’ parts of (II) and (III) (that is, rings A and B), are much the same as those calculated for the corresponding rings of fluoranthene (I) itself, and that (*b*) the central five-membered rings (C) in (I), (II), and (III) all appear to support an almost negligible diamagnetic ‘ ring current.’

However, as anticipated, the heterocyclic rings in (II) and (III) are the most interesting. It was inferred from the experimental results [4] that the diamagnetic ‘ ring current ’ intensity in these rings (D) was smaller than that of benzene, and, indeed, smaller than that of the analogous (but homocyclic) ring D in (I). This is qualitatively confirmed here, for the calculation predicts a value for rings D in (II) and (III) of about half that calculated for benzene, whilst in fluoranthene itself, the ‘ ring current ’ intensity in the corresponding ring, D, is (from previous computation [1]) *ca.* 0·86 of the benzene value.

It is of interest to consider, in some detail, those factors in the calculation which reduce the ‘ ring current ’ intensity in ring D by *ca.* 30% on passing from fluoranthene (I), to the heterocyclic molecules (II) and (III). That there should be the greatest change in the ‘ ring current ’ intensity in the heterocyclic ring is, perhaps, not surprising, for the thiophenoid ring is the one most greatly ‘ perturbed ’ from the situation which obtains in fluoranthene. However, contrary to initial intuition, the details of the calculation show that this reduction in ‘ ring current ’ in rings D, between (I), and (II) and (III), is *not* due to any very significant changes in the MO quantities—bond-orders and imaginary bond–bond polarisabilities [3]—which are used in the calculation; for, in the Streitwieser model which has been used here (see ref. 17 on p. 127 for discussion) the HMO secular determinant for (II) and (III) differs from that for fluoranthene (I) *only* in that *two* off-diagonal elements are 0·8 instead of 1·0. Consequently, almost the whole of the apparent 30% change in the ‘ ring current ’ intensity in the rings D, on passing from (I), to (II) and (III), can, on the approximations made in *this* calculation, be attributed to the *smaller area* of the thiophenoid rings, D, in (II) and (III), compared with the area of the homocyclic, benzenoid ring D in (I). On the assumptions made about molecular geometry (see CALCULATIONS), the areas of these rings are approximately in the ratio 0·66 : 1·0—and, to first order, this is about the ratio of the intensity of the ‘ ring current ’ in rings D of (II) and (III), to that in ring D of (I).

This importance of ring area in ‘ ring current ’ effects has been emphasised before,[1-3,6,19-22] and it can be rationalised physically by the fact that the external field manifests itself through *ring fluxes*, so that the smaller the area of a given ring, the smaller will be the magnetic flux through that ring (and, hence, the smaller the total flux through the molecule as a whole) when there is, perpendicular to the molecular plane, a component of the external magnetic field; it is, of course, this component which is inducing the current distribution in the molecule, *via* these ring fluxes.

CONCLUSIONS

Before the conclusions from this work are considered, the following two important points must be borne in

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mind. (i) The procedure of attempting to identify and to resolve the various different contributions to the relative proton chemical shifts in non-alternant and heterocyclic molecules, and, especially, of trying experimentally to isolate the ' ring current ' contribution to such shifts, is beset with difficulties. ' Experimentally-deduced ' values of ' ring current ' intensities obtained in this way [4] are, therefore, at best, to be considered only as qualitative—and, indeed, Bartle *et al.*[4] have not claimed otherwise.

(ii) The calculations presented here are also very approximate, being based on the simple Hückel–McWeeny scheme.[2,3] Some *apologia* would, in fact, seem necessary for using such an approximation for the calculation of relative ' ring current ' intensities as distinct from the computation merely of the *total combined effect* on proton chemical shifts arising from all the ' non-local contributions from the π-electrons ' [23,24] in a given molecule (for which more elaborate formalisms have been considered appropriate [12-16]). The reasons for our adopting here the simplest possible semi-empirical scheme, instead of more sophisticated approaches,[10,12-16,24] are that (1) use of the HMO approximations does avoid some of the conceptual difficulties about the definition of ' ring currents ' in a polycyclic molecule, which might otherwise arise (these difficulties will be discussed elsewhere [25]) ; (2) we are interested here only in *relative* ' ring current ' intensities (expressed as a *ratio* to the benzene ' ring current ') for the calculation of which the simplest approximations appear to be surprisingly adequate, when numerical results obtained from them [11] are compared with those arising from more realistic (but still semi-empirical) approximations;[10,16] (3) use of the simple London–McWeeny approach is pedagogically convenient in that it does enable clear and unambiguous identification of the various contributory factors to ' ring current ' sizes (see Results and Discussion) ; (4) we are here attempting to rationalise only very qualitative experimental trends [see (i), above].

In spite of these two reservations, however, both the experimental measurements of Bartle *et al.*,[4] and the approximate calculations reported here, appear to support the conclusions that, in (II) and (III), (*a*) the ' ring current ' intensities in rings A and B are very similar in magnitude to those in the corresponding rings of fluoranthene (I) itself, (*b*) the ' ring current ' intensity in the thiophenoid rings D is smaller than the benzene value, and smaller, also, than the ' ring current ' intensity in the analogous benzenoid ring D in fluoranthene, (*c*) the central five-membered rings C in (I), (II), and (III) all bear an almost negligible diamagnetic, π-electron ' ring current.'

Thus, although they are approximate, these calculations do lend support to that tentative interpretation [4] of proton chemical shifts which leads to the qualitative pattern of ' ring current ' intensities in (II) and (III) suggested by Bartle *et al.*[4]

I thank Dr. K. D. Bartle and Dr. D. W. Jones for kindly communicating results to me in advance of their publication. I thank also Professor C. A. Coulson, F.R.S., for hospitality at the Oxford University Mathematical Institute, the S.R.C. for the award of a Research Fellowship, and the Governing Body of Christ Church, Oxford, for my tenure of a Research Lectureship of the House.

[2/2034 *Received*, 30*th August*, 1972]

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