The Question of Ring Current in the Heteronins

By A. G. Anastassiou* and H. Yamamoto

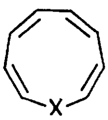
(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

Summary Three key heteronins and cyclononatetraene are compared in terms of their ring anisotropy as determined by n.m.r. spectroscopy.

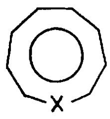
Of the many criteria of aromatic character, ring diamagnetism is perhaps the least equivocal. A convenient procedure was recently devised[1] for a comparative measure of this property, whereby the ring anisotropy of a given solvent is estimated in terms of its effect on the chemical shift of a standard solute (MeCN). We describe here our results with this technique when applied to three heteronins (**1b**, **2a**, and **2b**) and to cyclononatetraene (**1a**).†

Cyclononatraene, (**1a**), [*S*(0°) − 0·05]. The slightly negative *S* term characterizing this substance may indicate weak ring paramagnetism. This is consistent with the 8π-electron frame of (**1a**) and further confirms its π similarity to cyclo-octatetraene[1] [*S*(0°) −0·19] which had been suggested previously[2] on the basis of u.v. data. Also, the *S* value of (**1a**) is weakly temperature dependent in a direction indicative of enhanced paramagnetism and/or more effective solvent–solute association at lower temperatures, *e.g.*, *S*(−19°) −0·06, *S*(−31°) −0·07.

Oxonin, (**1b**), [*S*(0°) − 0·07]. In spite of its 10π aromatic potential this molecule emerges as mildly antiaromatic under the present criterion. This is not surprising when viewed in light of the fact that oxonin is known to be thermally less stable than its 8π analogue, (**1a**). Both molecules are believed to possess heavily distorted frames.[3] Oxonin further resembles (**1a**) in that its *S* term becomes increasingly negative with decreasing temperature, *e.g.*, *S*(−16°) −0·09, *S*(−40°) −0·11.



(1) a; $X=CH_2$
b; X=O



(2) a; X=NH
b; X=NMe

On contrasting oxonin with its 6π homologue, furan, which possesses ring diamagnetism [*S*(+33°) + 0·42][1] we conclude that the latter behaves as a (4*n* + 2)π system simply because it is forced into planarity by its relatively small size. Further, judging from the overall behaviour of

---

† In the present study all determinations were carried out with solutions containing 1·6 vol. % MeCN and 1·6 vol. % C_6H_{12} in the solvent of choice. In the case of (**2a**) and (**2b**) all runs were conducted in vacuum-sealed n.m.r. tubes owing to the sensitivity of these substances to air.

oxonin it appears that given a choice an oxygen atom of a π-excessive heterocycle will strongly resist its contribution into the π system.

1H-*Azonine*, (**2a**), [$S(0°) + 1{\cdot}35$]. In sharp contrast to both oxonin and (**1a**), (**2a**) is associated with an S value that is both large and positive, *i.e.*, one which indicates strong ring diamagnetism. In fact, the S value of 1*H*-azonine is considerably larger than that of pyrrole,[1] [$S(0°) + 0{\cdot}90$] and appears to reflect its 10π-electron structure.‡ The behaviour of (**2a**) as a $(4n + 2)\pi$ system under the present criterion is fully consistent with our earlier classification[3,4] of this substance as aromatic on the basis of its pronounced thermal stability, and spectral characteristics. The S value of 1*H*-azonine is quite sensitive to temperature variations, *e.g.*, $S(+8°)$ $+1{\cdot}29$, $S(+37°)$ $+1{\cdot}13$.

N-*Methylazonine*, (**2b**), [$S(0°) + 0{\cdot}34$]. This azonine is interesting in view of the fact that while its thermal stability and u.v. characteristics suggest a skeleton which is more distorted than that of 1*H*-azonine (**2a**) but considerably less so than that of oxonin (**1b**), its n.m.r. spectrum is not immediately indicative of ring diamagnetism.[3] Earlier, we tentatively interpreted the n.m.r. spectrum of this substance in terms of a weak diamagnetic ring current within a mildly puckered frame.[3] The slightly positive S value associated with this substance is, we believe, consistent with this interpretation.

Most likely, the less developed aromaticity of this substance (**2b**) compared to its 1H parent (**2a**) is due to its inability to assume an entirely planar geometry without developing a sterically unfavourable situation between the methyl substituent and each of the α-protons.[5] Finally, we note that the S value of (**2b**) is temperature dependent in the manner of (**2a**), *e.g.*, $S(+37°)$ $+0{\cdot}29$, $S(-32°)$ $+0{\cdot}42$.

We acknowledge support from the National Science Foundation.

(*Received*, 29*th December* 1971; *Com.* 2203.)

---

‡ It is interesting to note in this connection that the S value of 1*H*-azonine is larger than that of benzene ($S + 1{\cdot}0$)[1] but comparable to that of the 10π naphthalene skeleton ($S + 1{\cdot}35$).[1]

[1] F. A. L. Anet and G. E. Schenck, *J. Amer. Chem. Soc.*, 1971, **93**, 556. Solvent anisotropy is measured in terms of an S value defined by the ratio $\sigma(X) - \sigma(C_6H_{12})/60$ where $\sigma(X)$ is the difference in chemical shift between cyclohexane and acetonitrile in solvent X and $\sigma(C_6H_{12})$ is the analogous difference in cyclohexane solvent.

[2] G. Boche, H. Bohme, and D. Martens, *Angew. Chem.*, 1969, **81**, 565; A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Letters*, 1969, 4491.

[3] A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Comm.*, 1970, **1133**, and references therein.

[4] A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Letters*, 1970, **925**.

[5] For a description of the effect of ring size on the magnitude of H–H repulsions see: H. E. Simmons and J. K. Williams, *J. Amer. Chem. Soc.*, 1964, **86**, 3222.