A CORRELATION BETWEEN PMR COUPLING CONSTANTS

AND REPE IN NITROGEN HETEROCYCLES

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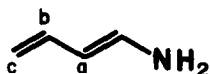
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The success of the calculation of resonance energies of cyclic systems

using the Hückel method is now well documented.[1]   However, we have usually

been limited to making only qualitative comparisons between calculated reson-

ance energy per π-electron (REPE) and experimental results.   Ideally one would

like to have thermochemical data with which to compare REPE,[2] but these are

not available for an extensive range of compounds.

There has been much discussion about a correlation between aromaticity

and nmr.   It generally has been concluded that there is not necessarily to be

expected a connection between delocalization and chemical shifts.[3]   On the

other hand vicinal coupling constants have been used with some success in un-

derstanding the degree of delocalization in cyclic systems.   Bertelli, using

proton-proton coupling constants, has found that tropone contains little de-

localization beyond that expected in a typical acyclic polyenone.[4]   This is in

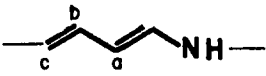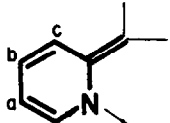agreement with our finding that it has quite a small REPE (0.007β).[1]
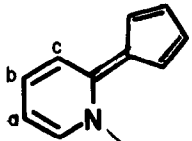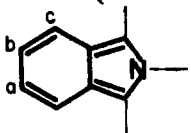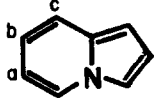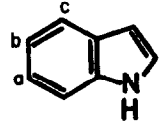
More recently Crews has suggested a correlation between a ratio of two

coupling constants and electron delocalization in a series of nitrogen heter-

ocycles.[5]   The ratio which he compared was that between coupling constants

across two adjacent carbon-carbon bonds, for example:

     $J_{ratio} = J_{ab}/J_{bc}$

He found that this ratio varied from 0.55 in an acyclic conjugated system to 1.00 in pyridine and benzene, and that it appeared to correlate qualitatively with what was known about the delocalization of these systems.   In the Table are listed a series of compounds and their J_{ratio} and REPE.

Table. J_{ratio} and REPE of Nitrogen Heterocycles

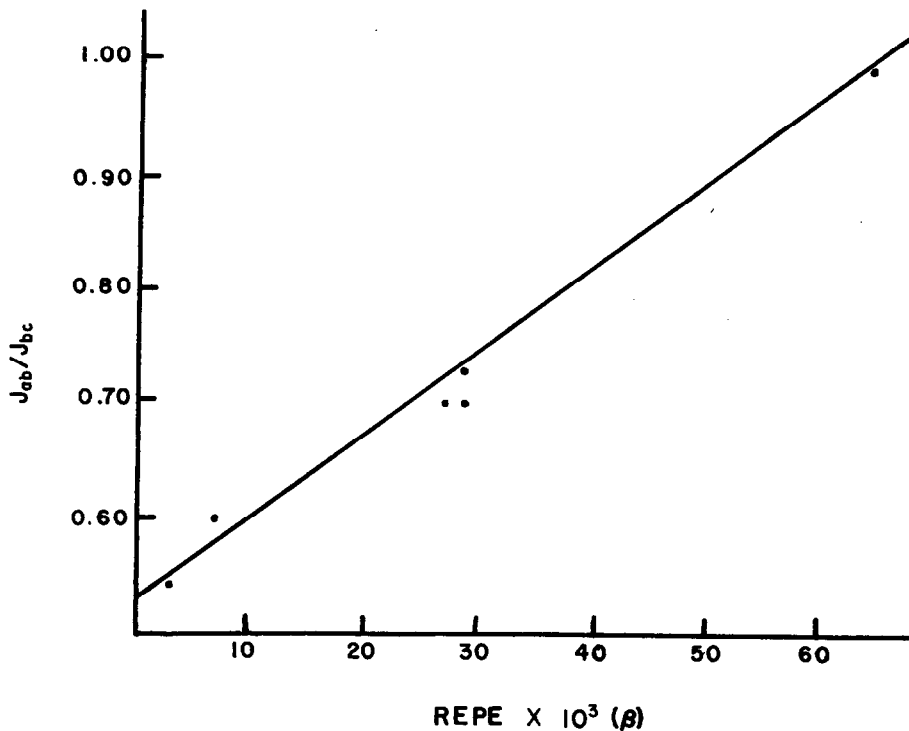| Conjugated system	J_{ab}/J_{bc}	REPE(β)
	$0.55^{a,b}$	0.003
	$0.61^{a,b}$	0.007
	$0.71^{a,b}$	0.027
	$0.74^{a,b}$	0.029
	0.71^{a}	0.029
	0.91^{c}	0.047

[a] ref. 5
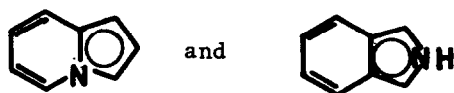[b] value obtained from a substituted derivative
[c] ref. 6

It is obvious from the Table that REPE increases as J_{ratio} does. These data

are plotted along with REPE (0.065β) of benzene and its J_{ratio} (1.00) in the Figure, from which it is seen that there is in fact an excellent linear relation between the two quantities. This gives strong support to the idea that pmr coupling constants when used properly can give an indication of electron delocalization.

$$REPE \times 10^3 \ (\beta)$$

Of particular interest in this series are indolizine and isoindole. It may be argued that any resonance stabilization in these compounds is due merely to the presence of the pyrrole ring and therefore that one might consider their structures best represented by

However, our finding that their respective total resonance energies, 0.27β and 0.29β, are both larger than the total RE of pyrrole (0.23β) suggests that this may not be the case, $i.$ $e.$, the two double bonds in the six-membered rings as written above are not butadiene-like but also participate in the overall delocalization. The measurements of J_{ratio} were made on this ring and therefore are also indicative (since the ratio is considerably higher than that found in the aminobutadiene) that there is delocalization throughout both rings of these two compounds.

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