Tetrahedron Letters, Vol.31, No.37, pp 5281-5284, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

AN EXPERIMENTAL NMR METHOD TO ESTIMATE RESONANCE ENERGIES OF 4N+2 π-ELECTRON SYSTEMS RELATIVE TO THAT OF BENZENE.[1]

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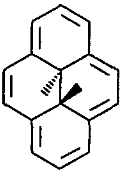
Summary: The change in chemical shift ($\Delta\delta$) of the internal methyl protons of **1** on annelation with various aromatics, is proportional to RE*, the resonance energy of the annelating aromatic less any resonance energy of a residual aromatic ring in the Kekulé structure(s) which has the 14π ring of **1** delocalized. This correlation is linear between RE* values of 0 and 1.5 times the resonance energy of benzene, and hence, can be used to predict resonance energies of other aromatics relative to benzene, simply by measurement of chemical shift.

Both Haddon[2] and Aihara[3,4] have shown that theoretically there is an exact relationship between the resonance energy (RE) and ring current (RC) in an aromatic annulene. Except for Verbruggen's[5] incorporation of ring area into the results of Hess, Schaad and Nakagawa,[6] no quantitative use has been made of these results. However, they have been used qualitatively to indicate whether or not a molecule is aromatic. It occurred to us that with a suitable probe molecule, ring currents might be used to give a simply determined experimental estimation of resonance energies. Dimethyldihydropyrene, **1**, is such a probe, because the internal methyl protons are strongly shielded (by about 5.2 ppm) by the RC of the 14π ring. Moreover, this shielding is not affected much (<10%) by either electron donating or withdrawing substituents (including phenyl) around the ring,[7] and is, therefore, not subject to strong local anisotropy effects. We have also shown[8] that this shielding correlates well with bond delocalization in the 14π ring.

Consider the benzannelated annulene **2**: it may be thought of as having two main contributing structures, **2A** and **2B**, which share a common Kekulé structure. Only in the annulene structure, **2A**, is there a significant



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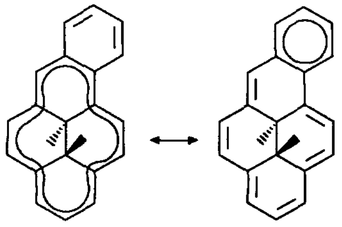
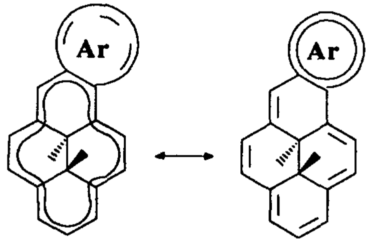
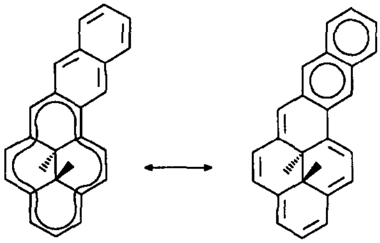


2A **2B**

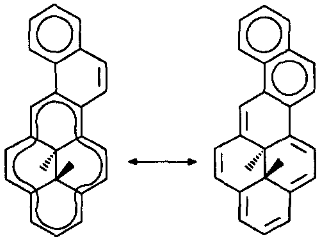


3A **3B**

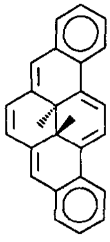
contribution to the shielding of the internal methyl protons by the RC, since the benzene structure, **2B**, if anything, would deshield (<0.2 ppm)[9,10] these protons. The relative contributions of **2A** and **2B** will depend upon the RE's of the 14π (**A**) and 6π (**B**) systems.[11,12] Since the chemical shift observed for the methyl protons in **2** depends mostly on the RC in the 14π ring (**2A**), the RC shielding observed for such protons will depend inversely on the RE of the annelating ring, which in this case is a benzene ring. Now, consider the more general annelated annulene, **3**, which has the contributors **3A** and **3B**. The larger the RE of the annelating ring (**B**), the less will be the contribution of **3A** and the smaller will be the chemical shift shielding of the methyl protons observed; conversely, the smaller the RE of **B**, the greater will be the contribution of **3A** and the greater the chemical shift shielding observed. Thus, by comparing the reduction in RC's on annelating the parent **1** with benzene, **2**, or annulene, **3**, i.e., comparing δ(1) - δ(2) with δ(1) - δ(3), a comparison of the resonance energies of benzene and the annelating ring of **3** should be possible. In order to do this with polycyclic annelating rings, e.g., naphthalene, the position of fusion must be considered. In the naphthannulene **4**, all the RE of the naphthalene is lost in contributor **4A**, while for the isomeric naphthannulene **5**, it is the difference between the RE of naphthalene and the residual benzene (which is present both in **5A** and **5B**), which we call RE^*; thus we define RE^* = RE [annelated rings - residual aromatic annelated rings] (in benzene units).



4A **4B**



5A **5B**



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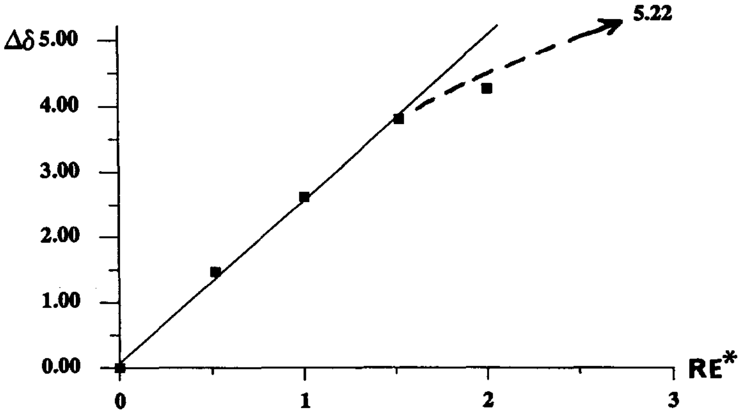
It was now possible to test this idea using data reported in the accompanying preceding communication[13] and from previous compounds,[8] and is given in Table 1. Plotting the change in chemical shift of the methyl protons of **1** on annelation (Δδ) against RE^* of the annelating ring gave Figure 1.

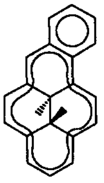
TABLE 1

Compound	Dewar[14] RE of annelating group		RE^*(B)	δ	Δδ
	(eV)	(ϕH units)	(ϕH units)	(ref. 8,13)	
1	0.000	0	0	-4.25	0.00
2	0.869	1	1	-1.62	2.63
4	1.323	1.52	1.52	-0.44	3.81
5	1.323	1.52	0.52	-2.78	1.47
6	1.738	2	2	+0.02	4.27

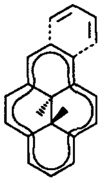
Figure 1: Plot of $\Delta\delta$ (ppm) vs RE* (benzene units) for compounds **1** - **6**. The solid line follows: $\Delta\delta = 2.50\mathrm{RE}^* + 0.08$; beyond RE* = 1.5 benzene units, the plot should curve towards $\Delta\delta = 5.22$ (----).



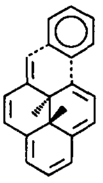
Clearly, a correlation exists. For RE* values up to about twice that of benzene, the plot is approximately linear; in the region RE* = 0.5 to 1.5 benzene RE units, $\rho = 0.9998$. When RE* is very large, $\Delta\delta$ must approach 5.22 ppm, i.e. almost no RC exists in the 14π ring. When RE* is very small, $\Delta\delta$ must approach zero, i.e. the 14π RC is not reduced significantly at all. This correlation can be understood from a theoretical standpoint by considering the real annelated annulene **AB** to be represented by the partial structures **A** (the annulene fragment) and **B** (the benzene or annelating ring fragment), by setting the coefficients of the wave equation to be proportional to chemical shift and $\Delta\delta = kb^2 = k(1-a^2)$.



AB



A



B

Thus, $\Psi_{AB} = a\Psi_A + b\Psi_B$ (where $b^2 = 1 - a^2$, taking the overlap between A and B to be zero),

and taking $E_x = (E_A + E_B)/2 - [((E_A - E_B)/2)^2 + H_{AB}^2]^{1/2}$

Then the coefficients a and b can be represented in terms of E_A, E_B and H_{AB} if we let $E_A - E_B = \mathrm{RE(A)} - \mathrm{RE^*(B)}$ then,

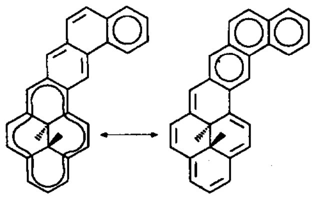
$$\Delta\delta = k/2\left[1 + \frac{[\mathrm{RE^*(B)} - \mathrm{RE(A)}]}{\{[\mathrm{RE^*(B)} - \mathrm{RE(A)}]^2 + 4H_{AB}^2\}^{1/2}}\right]$$

If H_{AB} is approximately constant, when RE*(B) is large (i.e., b→1), $\Delta\delta$ approaches k (5.22 ppm), and when RE*(B) is small (i.e., a→1), $\Delta\delta$ approaches zero. Such a curve is approximately linear in its central portion.

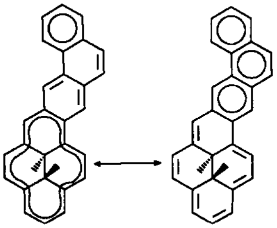
We thus believe that a reasonable experimental estimate of resonance energy, relative to that of benzene, can now be made for any aromatic by synthesis of the appropriate annelated annulene **3**, and measurement of the change in chemical shift from **1** of the internal methyl protons (Δδ), and then use of the equation:

$$\Delta\delta = 2.50\mathrm{RE}^{*} + 0.08$$

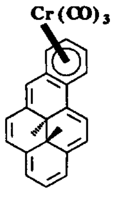
A test of this equation is possible using the data obtained[13] for **7** and **8**. The chemical shifts of the internal methyl protons of **7** and **8** appear at -0.90 and -0.88 respectively, despite the very different geometries. Thus for these phenanthrene annelated dihydropyrenes, Δδ = 3.37, giving RE* = 1.32. Since both **7A** and **7B** or **8A** and **8B** contain one benzene ring, the experimental RE for phenanthrene is 1 + 1.32 = 2.32 times that of benzene, in excellent agreement with the Dewar[14] theoretical value of 2.22 times that of benzene.
We have recently synthesised[15] the complexed benzannulene **9**. In this case Δδ = 3.28, indicating the RE for a tricarbonylchromium-complexed benzene ring to be about 1.3 times that of benzene itself. We are currently synthesising examples of **3** which will permit us to compare experimental resonance energies of several heterocycles, azulene, cyclopentadienide and metal complexed aromatics. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support.



7A **7B**



8A **8B**



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(Received in USA 30 May 1990)