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(24) Neither adduct nor $BrC{\equiv}CBr$ were observed.

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(33) At 275 °C in a sealed tube containing cyclohexene in 24–48 h 25% adduct **13**, 50% 2-butyne, and 25% $(CH_3)_2C{=}CH[OSi(CH_3)_3]$ were observed. The 2-butyne and the adduct comprising 75% of the products are carbene derived, via deoxysilylation[34] of **25**.

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A Linear Relation between Nuclear Magnetic Resonance Chemical Shifts of Tetra-*tert*-butyldehydro[*n*]annulenes and Resonance Energies per π Electron

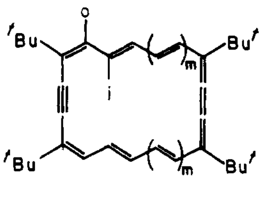
Summary: A linear correlation has been found between the Hückel resonance energies per π electron of 4*N* and 4*N* + 2 systems and the differences between chemical shifts of the inner and outer protons in tetra-*tert*-butyldehydro[*n*]annulenes.

Sir: The question of the aromaticity of the annulenes has been of interest for several decades, and in recent years there has been considerable progress in the synthesis of these compounds. Sondheimer among others has prepared many of the parent systems as well as dehydroannulenes.[1] Vogel,[2] Boekelheide,[3] and Sondheimer[4] have also prepared successfully a number of bridged annulenes. In most cases the two criteria reported for the aromaticity of these annulenes were their observed NMR chemical shifts and stabilities. However, fair agreement has been reached that there is not necessarily any basis for a relationship between NMR chemical shifts and aromatic character or resonance stabilization.[5] On the other hand, in recent papers one of the present authors (M.N.) has determined that there is a decrease in the difference in chemical shifts of the inner and outer protons of both dehydro[4*N* + 2]- (I)[6] and -[4*N*]annulenes (II)[7] as the ring size is increased from 14 to 30 carbons. He suggested that this might be an indication of the decreasing aromaticity and antiaromaticity within this series in possible agreement with theoretical predictions.[8]

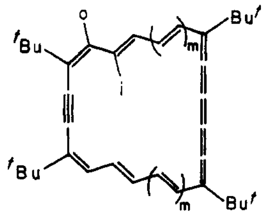
Table I. Chemical Shifts, Their Differences, and REPE of Dehydro[*n*]annulenes

[*n*]	τ_o	τ_i	$\tau_o - \tau_i$	REPE
14	0.68	14.44	−13.76	0.0161
16	5.92	−7.17	13.09	−0.0111
18	0.62	13.42	−12.80	0.0118
20	5.48[a]	−3.78[a]	9.26	−0.0052
22	1.28	10.83[a]	−9.55	0.0096
24	5.00	−1.79[a]	6.79	−0.0020
26	2.07	8.05	−5.98	0.0084
30	2.50[a]	6.50[a]	−4.00	0.0076

[a] Center of band.



I



II

In order to test this hypothesis quantitatively we decided to examine these chemical shift differences in both the 4*N* and 4*N* + 2 dehydroannulenes and to compare them with the calculated resonance energies per π electron (REPE) of Hess and Schaad.[8e] The calculated REPEs of the annulenes indicate there should be strong alternation between aromatic and antiaromatic character in the smaller annulenes with this alternation becoming less intense as the annulenes increase in size.[9] The two series of annulenes I and II are a particularly good set of compounds for making this comparison as they are all similar in structure and relatively planar. Furthermore, chemical shift data are available for a number of compounds in both series (4*N* + 2 and 4*N*) which represent the [*n*]annulenes where *n* is 14,[10] 16,[11] 18,[12] 20,[13] 22,[14] 24,[7] 26,[15] and 30.[16]

Since the overall environment of a proton affects its chemical shift we chose to take the difference ($\tau_o - \tau_i$) as the difference between the outer proton o in I and II and the inner proton i on the adjacent carbon. In most cases the assignments of protons o and i had been made. However, in several compounds the inner and outer proton absorption bands were not well enough resolved to make individual assignments. In these cases the center of the inner or outer proton absorption bands was used. Where this was done the proton patterns were narrow and any error introduced by this would be quite small relative to $\tau_o - \tau_i$.

In Table I are listed the chemical shifts of the inner and outer protons o and i, their differences, and REPE of the corresponding annulenes. A plot of $\tau_o - \tau_i$ vs. REPE (Figure 1) shows a definite linear correlation between these two quantities. This is the first example of a correlation between NMR chemical shifts and calculated resonance energies and

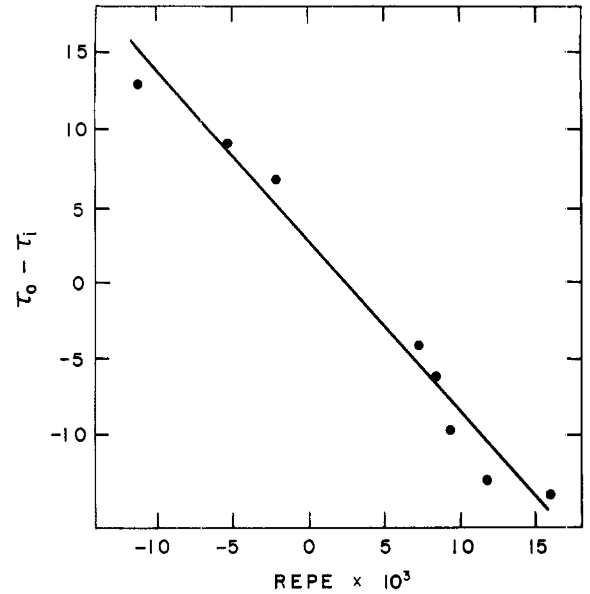


Figure 1. A plot of $\tau_0 - \tau_i$ of dehydro[*n*]annulenes vs. REPE (β) of the annulenes.

suggests that, if one treats chemical shift data in this way, one can obtain some quantitative measure of the aromaticity of the annulenes. We have also compared $\tau_0 - \tau_i$ with the graph theoretical resonance energies of Aihara[17] and Trinajstić[18] and found a similarly good linear correlation.

Finally we mention that this is now the second correlation that has been found between an experimental property of the annulenes and REPE. We have recently reported[19] a linear correlation between the log of the rate of annulene formation by a Diels–Alder reaction[20] and REPE.

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