of *cyclo*hexylmagnesium bromide, accounting for the formation of *cyclo*hexane. This mechanism is consistent with additional experiments which show that (a) reduction of Ph_3SiCl to Ph_3SiH is not a part of the coupling reaction, and (b) the coupling reaction proceeds by a polar, rather than a free-radical, mechanism. Further studies of the limitations and uses of the coupling reaction are in progress.

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Asymmetric annellation effects

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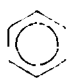
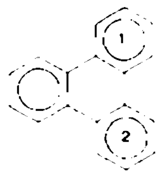
Successive connexion of two diphenylene systems (rings 1, 2 and 3, 4 respectively) to benzene forming triphenylene II and tetrabenzanthracene III respectively causes very different spectral shifts.

$$\lambda_\beta = 1819 \xrightarrow{+751} 2570 \xrightarrow{+355} 2925\ \text{Å}$$

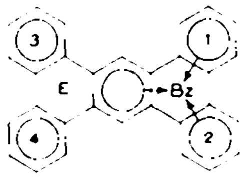
$$\sqrt{\lambda_\beta} = 42{\cdot}65 \xrightarrow{+8{\cdot}05} 50{\cdot}70 \xrightarrow{+3{\cdot}40} 54{\cdot}10\ \sqrt{\text{Å}}$$



I



II



III

This is in striking contrast to the constant shifts in the acene and phene series (linearly and angularly condensed benzene rings respectively)[1] and it is incompatible with the resonance theories about aromatic character which would require a symmetric annellation effect.

The above shifts for the β-bands are recorded in wavelength (Å) and in $\sqrt{\text{Å}}$, the latter being a scale for reciprocal nuclear charges. The nature of this electronic asymmetry becomes obvious if the second shift is deducted from the β-band of triphenylene II. This means the elimination of the influence of the two angular rings (1 and 2) in II. The result is a β-band at 2237 Å which is almost identical with β-band found in the absorption spectrum of naphthalene which is at 2210 Å for alcoholic solution. It is obvious that the first annellation with rings 1 and 2 produces an induced benzenoid ring in "Bz" and extends the aromatic system of the central benzene ring to a naphthalene system, whilst the second annellation with ring 3 and 4 does not extend it to an anthracene system but forms an empty ring "E".

It appears that the formation of an induced π-electron sextet in the ring "Bz" has preference over a symmetric distribution of π-electrons as required by the resonance theory. It is also a new manifestation of the Robinson aromatic sextet in its original definition. Since no aromatic sextet is formed in ring "E" it must be concluded that each inherent benzenoid ring (as marked by the circles) can transfer two π-electrons only to the induced benzenoid ring (Bz).

This asymmetric annellation effect can also be observed in higher tetrabenzacenes, dibenzacenes and in the perylene series.

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[1] P. Lambert and R. H. Martin, *Bull. Soc. Chim. Belg* 61, 124 (1952).

[2] E. Clar, *Aromatische Kohlenwasserstoffe* p. 26. Springer-Verlag (1952).