

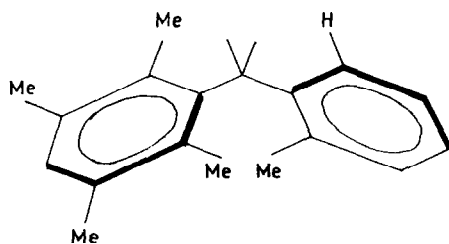
CONFORMATIONAL EQUILIBRIA IN MOLECULES CONTAINING  
SUBSTITUTED DIARYLMETHANE UNITS

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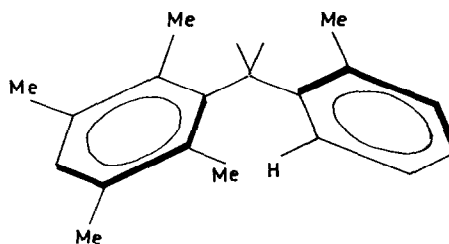
(Received in UK 19 January 1970; accepted for publication 29 January 1970)

We have observed that in molecules containing diarylmethane units (Table I), chemical shifts of methyl groups in ortho position to the methylene bridge vary markedly depending from the substitution pattern present in the adjacent aromatic ring, in contrast with the nearly constant chemical shifts of methyls in meta and para positions.

Considering that conformations where the two adjacent aromatic rings would lie in parallel planes are energetically disfavored because of repulsive interaction between non-bonded atoms (1,2), one could write two non-coplanar low-energy forms for these molecules, i.e.



Ia



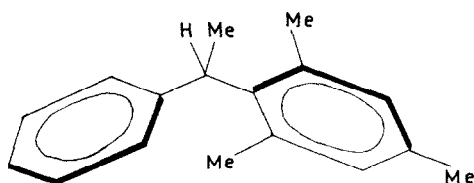
Ib

In the two rapidly interconverting conformers, ortho methyl groups will be shielded (Ia) or deshielded (Ib) by the ring current of the adjacent aromatic nucleus and the corresponding nmr signal should be seen in a field position reflecting the relative population of two forms (3).

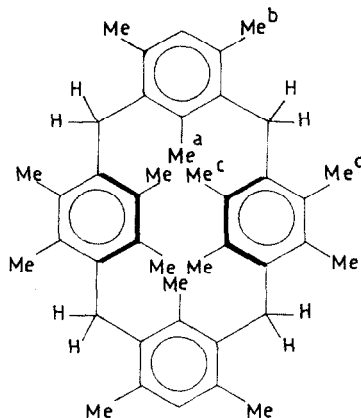
Moreover, when an ortho methyl and an ortho aromatic proton are attached to the same benzene ring then deshielding of the methyl group will be accompanied by shielding of the proton and vice versa (Ia - Ib).

Recently(4,5), compounds II and III have been reported to show restricted rotation of the mesityl and duryl groups, respectively. For compound II, 2- and 6-methyl signals were at 148 and 106 cps at  $-55^{\circ}\text{C}$ , in  $\text{d}_3$ -acetone, 60 MHz (4).

For compound III, in our conditions, we have measured  $b=160$ ;  $d=155$ ;  $c=96$  cps at  $-45^{\circ}\text{C}$ , in  $\text{CDCl}_3$ .



II



III

Chemical shifts of ortho methyl groups in Ia and Ib should have values close to those of pertinent methyls in compounds II and III, as indicated by molecular geometry considerations.

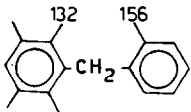
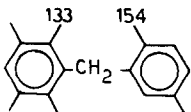
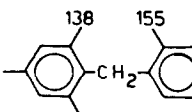
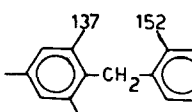
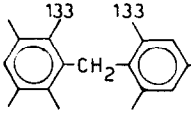
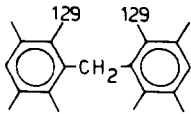
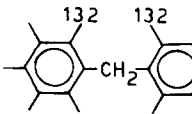
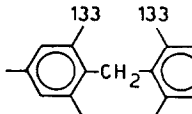
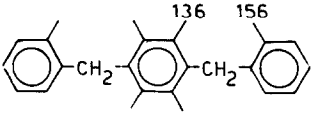
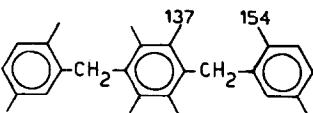
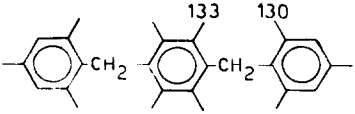
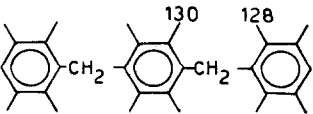
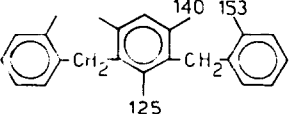
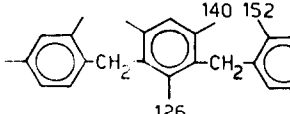
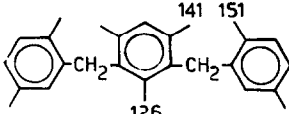
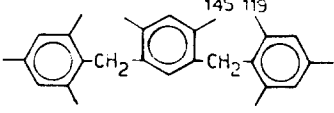
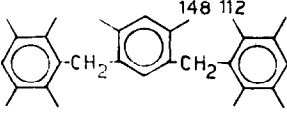
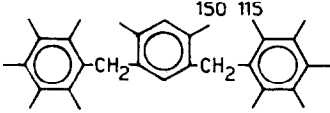
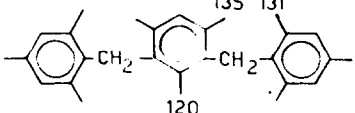
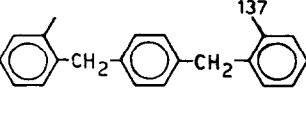
Data collected in Table I show that in all cases where, from the molecular structure, conformational equilibrium Ia - Ib might be expected to influence nmr ortho methyl signals, methyl chemical shifts indicate the preponderance (75-90%) of Ib forms.

On the contrary, in cases where such equilibria are not expected to have effects on nmr signals (i.e. didurylmethane), methyl chemical shifts appear at average field values.

At least three ortho positions, of the four available in diphenylmethane units, must be occupied by methyl groups in order to have appreciable effects. When only one or two ortho methyls are present, chemical shifts appear again at average field values (Table I).

Chemical shifts of ortho aromatic protons nicely confirm these observations. In fact, nuclear ortho hydrogens ( $\text{H}_o$ ) are found shifted 30-40 cps upfield with

Table I  
Chemical shifts<sup>a</sup> of ortho methyl groups ( / = CH<sub>3</sub> )

a) Chemical shifts measured in CHCl<sub>3</sub> at +38 °C, in cps downfield from TMS as internal standard, at 60 MHz

respect to other aromatic hydrogen signals ( $H_{m,p}$ ), (i.e., duryl-p-xylyl-methane:  $H_o$  374,  $H_{m,p}$  415 cps; mesityl-p-xylyl-methane:  $H_o$  376,  $H_{m,p}$  415 cps; duryl-o-tolyl-methane:  $H_o$  387,  $H_{m,p}$  421 cps; mesityl-o-tolyl-methane:  $H_o$  387,  $H_{m,p}$  420 cps; duryl-phenyl-methane:  $H_{o,m,p}$  424 cps).

Assignments reported in Table I were made correlating a large number of compounds and relying heavily on relative intensities of methyl peaks which are all sharp singlets.

Measurements were carried out at different temperatures (-45; +38; +80°C, in  $CDCl_3$  and  $CCl_4$ ) and the free energy difference between the two forms was calculated (3) at each temperature taking methyls b and c in compound III as standards.

$\Delta F$  values obtained for compounds shown in Table I were in the range of 1.0 - 1.5 Kcal/mole.

Details on the synthetic procedures will follow.

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