Tetrahedron Letters,Vol.22,No.51,pp 5139-5140,1981 0040-4039/81/515139-02$02.00/0
Printed in Great Britain

THE SYNTHESIS OF AN UNUSUAL DIHYDROPYRENE CONTAINING ONE AROMATIC π-CLOUD WITHIN AND PERPENDICULAR TO A SECOND.[1]

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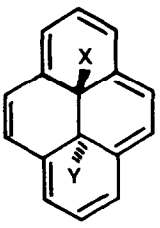
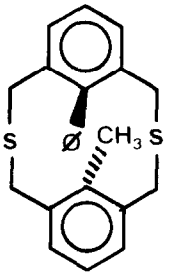
Summary: *trans*-10b-methyl-10c-phenyl-10b,10c-dihydropyrene is prepared. Its ^{1}Hmr spectrum shows the internal aryl protons are the most highly shielded aryl protons yet reported.

Few annulenes are as well suited to study effects associated with ring currents as Boekelheide's[2] *trans*-15,16-dimethyldihydropyrene[3], **1** . Since this annulene is stable, has a planar[4] 14π-electron periphery and has its internal bridges and substituents close to the "center of the ring current," effects caused by the ring current are easily seen. For example, the internal methyl protons of **1** appear in its ^{1}Hmr spectrum highly shielded at δ -4.25. Boekelheide and DuVernet[5] have studied both ^{1}H and ^{13}Cmr spectra for a number of alkylated derivatives of **1** and have shown that the ring current effects on such groups generally follow Bovey and Johnson's calculations[6].



1 X=Y=CH_3

2 X=ϕ; Y=CH_3



3

Unfortunately thus far it has not proved possible to introduce a functional group directly as X or Y, though more recently Boekelheide has reported[7] the preparation of more remote functionalisation, i.e. X= $-CH_2CH_2OCH_3$ and $-CH_2CH_2CH=CH_2$.

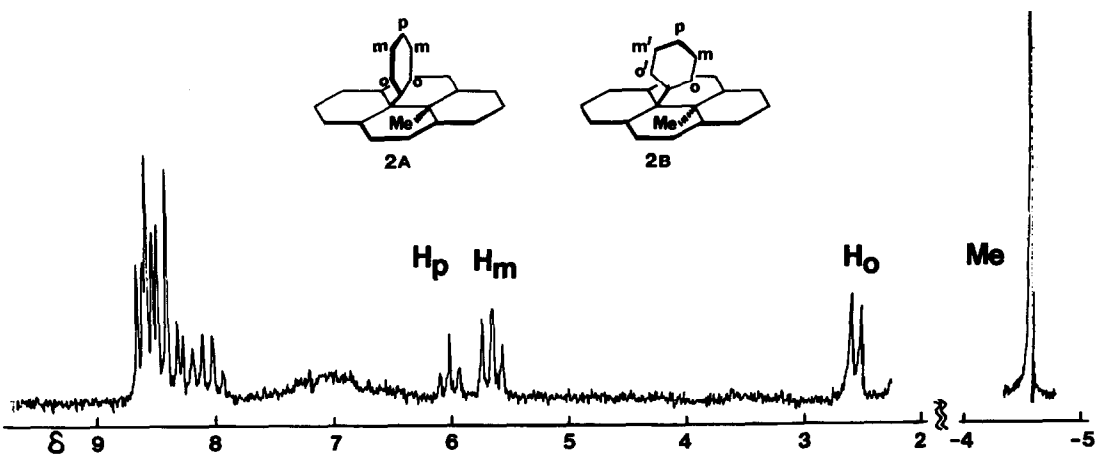
In order to map the magnetic field due to the ring current more fully[8], it is desirable to have more rigid internal groups than alkyl, and also in order to study substituent effects, groups that are easier to functionalise are preferable. One such group would be an internal phenyl substituent, especially since a novel molecule containing one π-cloud within and perpendicular to a second is produced. We now report such a molecule, *trans*-10b-methyl-10c-phenyl-10b,10c-dihydropyrene, **2** .

Wittig rearrangement[9] of the *anti*-methylphenylthiacyclophane **3** , described in the preceding accompanying paper[10], followed by a Hofmann elimination[11] using potassium t-butoxide-THF at reflux temperature gave a 40% yield of **2** , obtained as green crystals mp 159-160°C. Its structure

was confirmed by elemental analysis and its mass spectrum $M^{+\cdot}$ at *m/e* 294 (16%) with peaks at 279 ($M-CH_3$, 30%), 217($M-C_6H_5$, 27%) and 202($M-CH_3$, C_6H_5; 100%). The ^{1}Hmr spectrum of **2** is quite outstanding and is shown in figure 1. The internal methyl protons (in CS_2) appear at δ -4.45, indicating a normal dihydropyrene ring current to be present, and probably that little interaction takes place between the two π-systems (this is also indicated by its u.v. spectrum, which is almost identical to that[2,11] of **1** . Of major interest is the appearance of the *ortho*-aromatic protons at δ2.55, now, the most shielded aryl protons known[12]. Their 4.8ppm shielding with respect to normal aryl protons, is somewhat less than the 5.4ppm that the internal methyl groups are shielded, probably because the latter are closer to the axis of the molecule. The spectrum is invariant over the temperature range +100°C to -100°C and thus at this stage we are not able to state whether the phenyl group is rotating or fixed as in **2A** (note **2B** would require different chemical shifts for each *ortho* and *meta* proton). Even the *meta*-protons (δ5.6) and *para*-protons (δ6.0) show strong residual shieldings of 1.7 and 1.3ppm respectively, even though these protons must be at least 4-6A° above the plane of the ring. When an X-ray structure, together with a more detailed knowledge of the conformation preference in solution of **2** , is known, these results should allow us to comment on the magnetic field above annulenes in more detail. We also hope to further study the interaction between the two π-clouds by esr.

We thank the Natural Sciences and Engineering Research Council of Canada and University of Victoria for financial support.

Figure 1: ^{1}Hmr Spectrum (90MHz, CS_2, +20°C) of **2**



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(Received in USA 18 August 1981)