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# APPLICATIONS OF INTERNAL NUCLEAR OVERHAUSER EFFECTS (NOE) IN ORGANIC CHEMISTRY :

## 1,2,3,4-TETRAMETHYLPHENANTHRENE 1)

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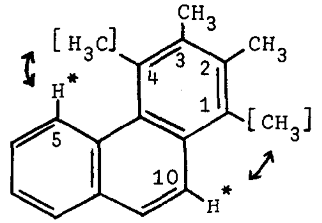
Internal nuclear Overhauser effects have been used to assign the methyl signals in the NMR spectrum of 1,2,3,4-tetramethylphenanthrene.

In 1965, Anet and Bourn 2) pointed out that "*studies of NOE's (Nuclear Overhauser Effects) can be of considerable stereochemical and conformational interest in organic chemistry*". However, relatively few applications of this technique have so far been published 3).

To our knowledge, no case involving an aromatic proton has yet been disclosed. We now wish to report such a case.

In 1,2,3,4-tetramethylphenanthrene 4), saturation of the *overcrowded* methyl group [ $CH_3(4)$ ] should give a NOE for H(5), whereas saturation of the other $CH_3$'s should have no effect on this particular proton. On the other hand, saturation of $CH_3(1)$ could have a small effect on the *peri* proton H(10).

Table 1.



60 Mc. spectrum ($CDCl_3$).

[ $CH_3(2)$ + $CH_3(3)$] quasi singlet (6 protons) at 146 c/s (partially resolved at 100 Mc; $\Delta\delta_{obs.}$ = 2 c/s), $CH_3(1)$ singlet at 158 c/s, $CH_3(4)$ singlet at 173 c/s, H(10) doublet centered at 476 c/s, H(5) multiplet centered at 511 c/s.

For NOE experiments, 12.5% $CDCl_3$ solutions of freshly sublimed 1,2,3,4-tetramethylphenanthrene were thoroughly degazed under high vacuum and sealed under helium. These solutions were studied, at 60 Mc, by a frequency sweept method, using TMS as an internal field frequency lock. The results are summarized in Table 1 and 2.

Saturation of $CH_3(4)$ results in an enhancement of 33 ± 3% of the integrated area of the multiplet of H(5), leaving the other parts of the spectrum unaltered, whereas saturation of $[CH_3(2) + CH_3(3)]$ has no effect on the signals of the aromatic protons.

Irradiation at the $CH_3(1)$ frequency gives a small (11 ± 3%) but apparently significant increase of the integrated area of the H(10) signals.

The assignments of the $CH_3$'s signals made on the basis of *internal nuclear Overhauser effects* are fully substantiated by the study of the chemical shifts, with reference to the monomethylphenanthrenes 5,6).

Table 2.

| Irradiation | Area of the signals in arbitrary units | | | Enhancement in % (± 3) |
|---|---|---|---|---|
| | H(5)* | H(10)* | H(6) + H(7) +H(8) + H(9) | |
| None | 21.5 | 30.0 | 100 | - |
| at $CH_3$ (1) | 21.5** | 33.3 | 100 | 11 H(10) |
| at $CH_3(2)+CH_3(3)$ | 21.9 | 30.9 | 100 | 0 |
| at $CH_3$ (4) | 28.7 | 30.3 | 100 | 33.5 H(5) |

* Average of 3 runs with H(6) + H(7) + H(8) + H(9) = 100.

** Value corrected for a small beating effect.

It is clear, from these results, that NOE experiments can yield valuable informations in the field of *Overcrowded Aromatic Hydrocarbons.*

Further work is in progress.

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