

A Tetra-adduct of 3,3'-Bi-indenyl and Dimethyl Acetylenedicarboxylate

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ALTHOUGH an earlier report¹ states that 3,3'-bi-indenyl does not take part in a Diels-Alder reaction with dimethyl acetylenedicarboxylate, we had found that the tetramethylbi-indenyl (I) reacts to give the diadduct (II),² and consequently we repeated the reaction between 3,3'-bi-indenyl and dimethyl acetylenedicarboxylate and obtained the tetra-adduct (III).

3,3'-Bi-indenyl (5 g.) was dissolved in dimethyl acetylenedicarboxylate (60 ml.) and heated at 70° for 20 days. Excess of ester was removed *in vacuo* and the residue, recrystallised from ethanol, had m.p. 210°, ν_{\max} (KBr) 1712 cm^{-1} .

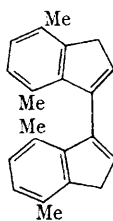
The n.m.r. spectrum of the tetra-adduct confirms the structure (III): in this, the protons can be divided into three groups.

The first group consists of the protons a, a', b, and c: these form an ABMX system as follows: τ 3.3—3.5 (4 protons, a and a', not distinguished; multiplet); τ 4.77 (2 protons, b, quartet: the corresponding tertiary protons in the adduct from anthracene and dimethyl acetylenedicarboxylate occur at τ 4.47); τ 5.51 (2 protons, c, quartet). Observed couplings are: $J_{a'b} = J_{ac} = 5.3$ c./sec. $J_{a'c} = J_{ab} = 2.3$ c./sec. $J_{aa'}$ unknown. J_{bc} insignificantly small.

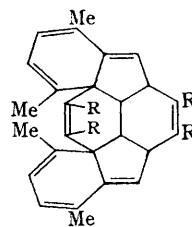
The second group of protons are d, e, and f, which form an almost first order AMX system: τ 5.93 (2 protons, d), τ 7.6 (2 protons, e), τ 8.0 (2 protons, f). $J_{de} = J_{df} = 1.5$ c./sec., $J_{ef} = 7$ c./sec. Since $J_{de} = J_{df}$, the signal at τ 5.93 appears as a triplet.

The 24 protons of the methyl ester groups appear as four distinct singlets of equal intensity at τ 6.05, 6.25, 6.61, and 6.97.

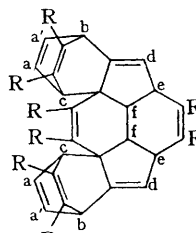
While 3,3'-bi-indenyl forms a tetra-adduct in this reaction, its tetramethyl derivative (I) forms only a di-adduct: this must be entirely due to the steric interference of the methyl groups.



(I)



(II) R=CO₂Me



(III) R=CO₂Me

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¹ Y. Altman and D. Ginsburg, *J. Chem. Soc.*, 1961, 1498.

² W. Kemp and J. Spanswick, *J. Chem. Soc. (C)*, in the press.