

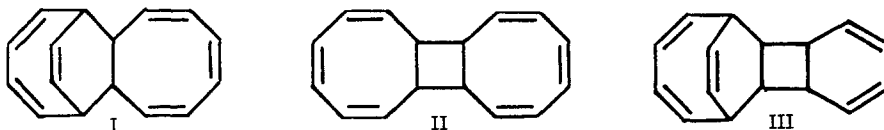
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
¹³C SPECTRUM OF A DIMER OF CYCLOOCTATETRAENE(1)

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The structure of the cyclooctatetraene dimer of m. p. 53° has been a matter of controversy. Structure I was proposed by Jones(3) and could be reconciled with a proposed mechanism of conversion of the dimer to bullvalene(4). Schröder(5) has proposed structure II because the material afforded the all *cis*-cyclobutanetetracarboxylic acid on ozonolysis and peracid oxidation. However, there is still a possibility that I could yield cyclobutanetetracarboxylic acid on oxidation by way of its valence tautomer III.



To try to settle the structural problem we have investigated the natural-abundance ¹³C spectrum of the dimer which was obtained from old samples of cyclooctatetraene by repeated chromatography on silica gel and alumina. Crystallization from ethanol under nitrogen gave pale yellow crystals of m. p. 51-2°. The 15.08 MHz ¹³C nmr spectrum was determined at 40° with the Varian DFS-60 spectrometer(6) and noise-decoupling technique(7, 8) described earlier. The time-averaged spectrum obtained from a 1 g sample of the dimer dissolved in 20% dioxan, which also serves as an internal standard, after five 25-sec scans is shown in Fig. 1. The observation of only four equally intense peaks in addition to the dioxan reference confirms that the dimer has Structure II and definitely eliminates Structure I (or III).

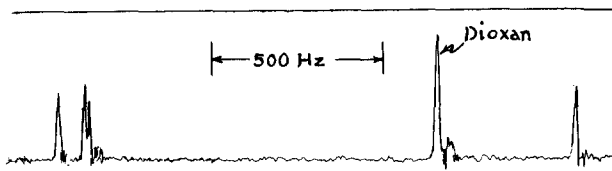


Fig. 1. Magnetic resonance spectrum of ¹³C in natural abundance of the cyclooctatetraene dimer of m. p. 53° at 15.08 MHz. With narrower sweeps, the second resonances from the left show up as two equally intense peaks split to the baseline.

The chemical shifts and one-bond coupling constants shown in Table I are in accord with II as the structure of the dimer(9). The chemical shifts were obtained from single-frequency proton-decoupled spectra taken with a 50-Hz sweep range. Under these conditions, each of the peaks had a linewidth of less than 1 Hz. The C-2 assignment is based on the finding that this

carbon is directly bound to the most shielded alkenic proton which was assumed to be H-2. The ^{13}C -H coupling constants were derived from uncoupled spectra.

Table I^a
Chemical Shifts^a and C-H Coupling Constants for
Cyclooctatetraene Dimer of m. p. 53°

Carbon	δ_{CS_2} , ppm ^a	$J_{^{13}\text{C}-\text{H}}$, Hz
1	149.6	138.5 ± 3
2	64.7	158.5 ± 5
3	59.4	156.5 ± 3
4	64.0	158.5 ± 5

^aChemical shifts relative to CS_2 were calculated on the basis that $\delta_{\text{CS}_2} - \delta_{\text{dioxan}} = 125.5$.

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