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Eu(DPM)$_3$ TRANSANNULARLY INDUCED PARAMAGNETIC CHEMICAL SHIFTS IN THE PMR SPECTRA OF ENDRIN, DIELDRIN, AND PHOTODIELDRIN

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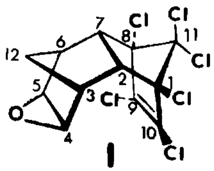
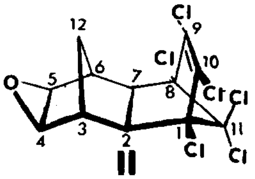
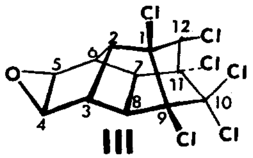
The new PMR shift reagent tris(dipivalomathanato)europium [Eu(DPM)$_3$; 1-3] was found useful for the chemical shift and structural assignments of the epoxy derivatives of the chlorinated polycyclodiene pesticides and their degradation products. Eu(DPM)$_3$ associates with epoxide oxygens and induces large paramagnetic shifts in the signals of protons in adjacent and distant rings. Studies of the effects of varied concentrations of Eu(DPM)$_3$ on the PMR spectra of the insecticides endrin (I), dieldrin (II), and the important photolysis product of II, photodieldrin (III, 4,5) showed the relationship between the distance of the protons from the europium and the magnitude of the chemical shift.



I



II



III

The PMR spectra of endrin and dieldrin are similar in most respects but one definitive feature of the endrin spectrum (6) is the splitting of the $H_{2,7}$ signal into a pair of doublets due to the coupling of H_2 with H_3 and H_6 and the coupling of H_7 with H_6 and H_3. This characteristic of the endo-endo ring fusion is obscured by the overlap of the $H_{2,7}$ and the $H_{4,5}$ signals of endrin in CCl_4

(Figure 1A). Addition of Eu(DPM)$_3$ to the endrin solution shifts both the $H_{2,7}$ and the $H_{4,5}$ signals downfield (Figure 1B) but the latter shift is approximately four times greater in magnitude so these two signals become well separated and the splitting of the $H_{2,7}$ signal can be clearly observed at a 250 Hz sweep width. Dieldrin, which possesses an endo-exo ring fusion, does not contain dihedral angles conducive to the above couplings and its $H_{2,7}$ protons resonate as a sharp singlet (6).

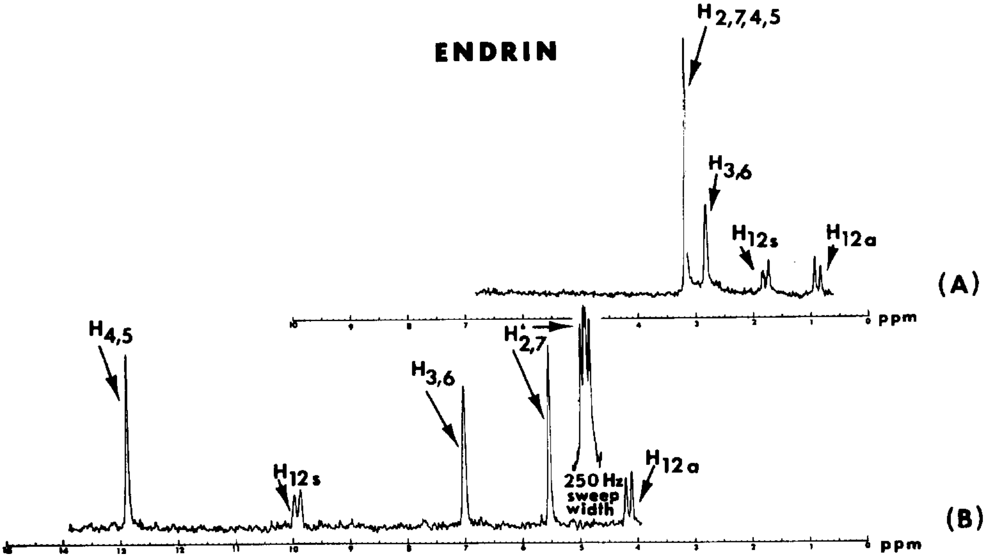


Figure 1 (A) Endrin (0.14 M) without Eu(DPM)$_3$ and (B) with 0.07 M Eu(DPM)$_3$ in CCl_4 at 100 MHz.

Graphs of $\Delta\delta$ versus R^{-3} (where R is the distance of each proton from the center of the europium atom (3) as measured from molecular models) give straight lines for all three epoxides. Figure 2 shows the plot obtained for photodieldrin using this method. All except the two protons closest to the europium (H_4 and H_5) fit the curve as might be expected (1).

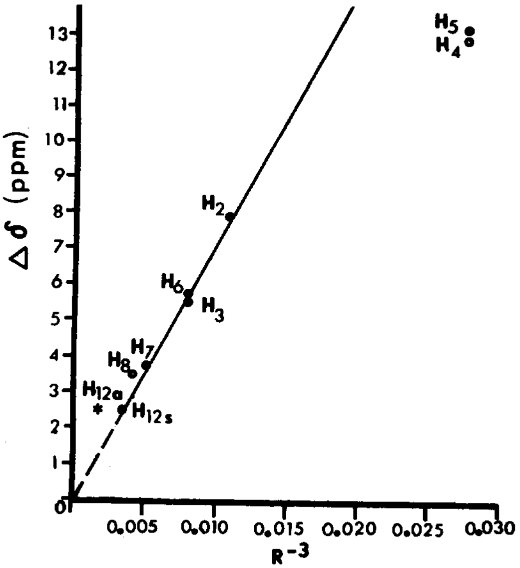


Figure 2 Change in chemical shift versus the reciprocal of the distance cubed of each proton of a 0.20 M solution of photodieldrin and 0.18 M solution of Eu(DPM)$_3$ in carbon tetrachloride.

The stereochemistry of H_{12}, which migrates during the photorearrangement reaction, has never been determined to our knowledge. It is seen from Figure 2 that Δδ of this proton plotted for the configuration syn to the epoxide (H_{12s}) conforms well with the curve whereas the anti configuration (H_{12a}; designated by the asterisk) does not. This indicates that the H_{12} is syn to the epoxide.

Close examination of the H_{12} signal revealed that it is a poorly resolved doublet with a small coupling constant ($J = 0.7$ Hz). Irradiation of either H_2 or H_7 sharpens the doublet perceptibly and triple resonance at these frequencies doubles this effect. Thus, both H_2 and H_7 have a small long-range coupling (<0.5 Hz) with H_{12}. Normally, such coupling is confined to protons separated by four bonds and in a "W" conformation with respect to one another, which would indicate that H_{12} is anti to the epoxide. However, a recent investigation by Marchand et al. (7) noted a small, but finite, non-"W" long-range coupling with the proton geminal to the position where this coupling usually occurs. Similarly, we noted this anomaly in the syn-methylene proton signal of those pesticides containing the epoxide or double bond linkage at C_4-C_5 (6). Irradiation of H_6 collapses H_{12} to a singlet making it evident that these two protons must be spatially close to one another. Examination of the model of photodieldrin reveals that H_6 and H_{12} are the "bowsprit" and "flagpole" hydrogens on a six-membered ring rigidly held in a skew-boat conformation (Figure 3). The distance between these two protons is only about 1.6 Å whereas the sum of the van der Waals radii of two hydrogens is 2.4 Å (8) so that a transannular through-space coupling of these protons is the most likely cause of the H_{12} doublet, confirming the H_{12s} assignment made on the basis of the $\Delta\delta$ produced by $Eu(DPM)_3$.

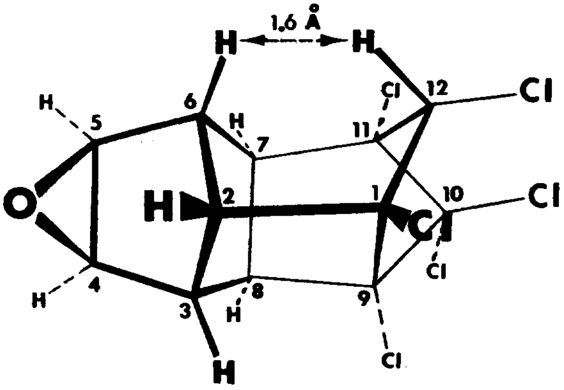


Figure 3 Stereochemical relationship between H_6 and H_{12} of photodieldrin

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