Polarisation and Polarisability Study of Some Chlorinated Cyclodiene Insecticides

By **Kingsley E. Calderbank** * and **Raymond K. Pierens**, School of Chemistry, University of Sydney, N.S.W. 2006, Australia

The dipole moments and molar Kerr constants are reported for Aldrin, Dieldrin, Isodrin, Endrin, the keto-isomer of Endrin, Heptachlor, and Heptachlor *cis*-oxide as solutes in carbon tetrachloride. These data are used to obtain polarity and polarisability parameters for the structurally significant groups present.

MANY addition compounds prepared from hexachlorocyclopentadiene by Diels–Alder reaction display considerable insecticidal activity. Soloway [1] has indicated a number of structural conditions involving the type, number, and disposition of electronegative centres necessary for insecticidal properties. The polarity and polarisability of a molecule is also dependent on the above factors and hence reliable structural parameters for these properties should prove useful.

Despite a previous experimental dipole study by Arbuzov *et al.*[2] and a series of calculations of theoretical dipole moments by Riemschneider [3] there appears to be no generally applicable values available. In this paper we report the dipole moments and molar Kerr constants for a number of chlorinated cyclodiene compounds, and use these data to deduce parameters for the structurally significant groups present in the insecticides examined.

TABLE 1

Polarisations, refractions, dipole moments, and molar Kerr constants from observations on carbon tetrachloride solutions at 25°

Solute	Concentration range $10^5 w_2$	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2/$ cm^3	$R_D/$ cm^3	μ/D †	$10^{12}{}_\infty({}_mK_2)$ ‡
Aldrin	1 072—3 100	4.62	0.024	0.09	−43.9	244	76.7	2.83	−148
Dieldrin	927—3 097	1.28	0.063	0.10	−5.26	117	78.6	1.30	−17.1
Isodrin	842—3 823	5.33	0.029	0.09	−71.4	271	76.7	3.05	−238
Endrin	1 023—4 931	1.84	0.081	0.09	−11.5	138	76.8	1.68	−39.3
Keto-isomer of Endrin	123—263	10.3	0.106	0.12	62.1	477	81.0	4.38	197
Heptachlor	1 050—2 772	2.15	0.057	0.13	−18.8	149	76.1	1.84	−63.3
Heptachlor *cis*-epoxide	541—980	2.02	0.057	0.07	6.57	151	76.2	1.86	22.6

† Assumes that $_DP = 1.05R_D$. ‡ The molar Kerr constant of the solute at infinite dilution. 1 e.s.u. mol^{-1} = 1.113×10^{-18} C^2 m^5 J^{-2}.

EXPERIMENTAL

Materials, Apparatus, etc.—Commercial samples of Aldrin, Dieldrin, Isodrin, and Heptachlor were recrystallized to give melting points in good agreement with those listed in ref. 4. A sample of commercial Endrin was repeatedly recrystallized from ethanol and from carbon tetrachloride until the i.r. band at 5.7 μm[5] indicated that <0.2% of the keto-isomer was present. Also the ^{1}H n.m.r. shifts (δ 9.07 and 8.22)[6] of the 12,12a-methylene protons confirmed the identity of our sample.

The keto-isomer of Endrin (1,8,*exo*-9,10,11,11-hexachloropentacyclo[6.2.1.1.^{3,6}0.^{2,7}.0^{4,10}]dodecan-5-one) was prepared according to the method of Soloway *et al.*[7] Direct oxidation[8] of Heptachlor gave the *cis*-epoxide [*endo*-1,4,5,6,7,8,8-heptachloro-2,3-epoxy(*cis*-O,1-Cl)-2,3,3a,4,7,7a-hexahydro-(*trans*-1H,7aH)-4,7-methanoindene].

The apparatus, techniques, the solvent purification and its physical constants, and the symbols used have been described before.[9] The results have been summarised in Table 1.

Previous Measurements.—The molar Kerr constants for these solutes have not been recorded previously. Dipole moments † in benzene at 25 °C for the following have been reported:[2] Aldrin, 2.06; Dieldrin, 1.50; Endrin 4.22; ‡ Isodrin, 3.07; and Heptachlor, 1.83 D.

---

† The dipole moments are quoted throughout in Debye units = 10^{-18} e.s.u., 1 D = 3.336×10^{-30}C m.

‡ It would appear from our dipole moment results in Table 1 that this value refers not to Endrin but to the isomeric ketone.

[1] S. B. Soloway, *Adv. Pest Control Research*, 1965, **6**, 85.

[2] B. A. Arbuzov, A. N. Vereshchagin, and B. S. Batyeva, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, (*a*) 1966, 2080; (*b*) 1967, 10.

[3] R. Riemschneider and B. B. Graviz, *Botyu-Kagaku*, 1960, **25**, 123; R. Riemschneider and F. D. Grabitz, *ibid.*, 1961, **26**, 99; R. Riemschneider and V. Wuscherpfennig, *Z. Naturforsch*, 1962, **17b**, 725.

[4] 'The Merck Index of Chemicals and Drugs,' Merck, New Jersey, 7th edn., 1960.

[5] Infra Red Spectral Data, Serial No. 1689, American Petroleum Institute Research Project 44.

[6] L. H. Keith and A. L. Alford, *Tetrahedron Letters*, 1970, **28**, 2489.

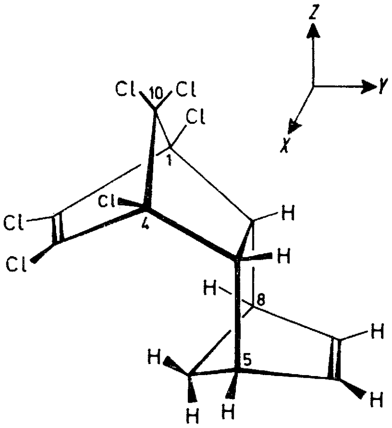
[7] S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377.

[8] W. B. Burton, Belg. P.609,983, (*Chem. Abs.*, 1963, **58**, 1434a).

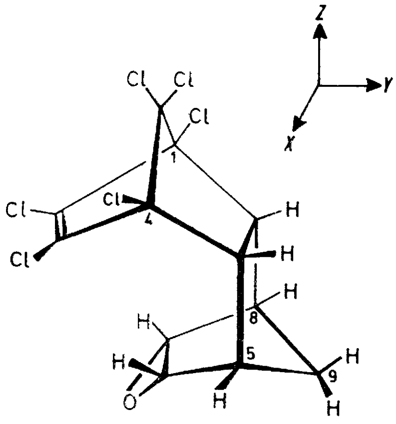
[9] R. J. W. Le Fèvre, 'Dipole Moments,' Methuen, London, 3rd edn., 1953; C. G. Le Fèvre and R. J. W. Le Fèvre in 'Physical Methods of Chemistry,' ed. A. Weissberger and B. Rossiter, Wiley, New York, 1972; R. J. W. Le Fèvre and S. C. Solomons, *Austral. J. Chem.*, 1968, **21**, 1703.

RESULTS AND DISCUSSION

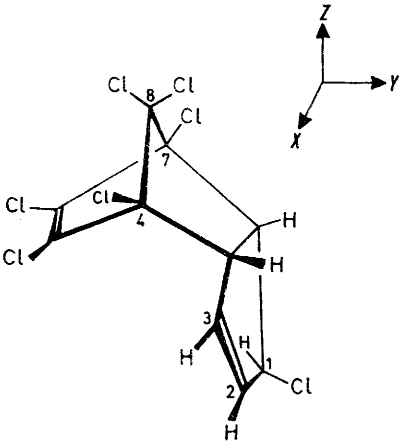
Dipole Moments.—Determination of suitable polarity parameters. Arbuzov *et al.*[2b] calculated dipole moments for the various forms of the possible structural isomers of Aldrin, Isodrin, Dieldrin, and Endrin. Within these molecules there exist certain common structural units: *viz.* the hexachloronorbornene grouping $C_7H_2Cl_6$ (' the chlorinated moiety '), the methano-bridgehead structure, and the four carbon bonds which join this bridgehead to the ' chlorinated moiety ' and to the ethylenic bond (for Aldrin and Isodrin) or to the epoxide ring (for Dieldrin and Endrin).



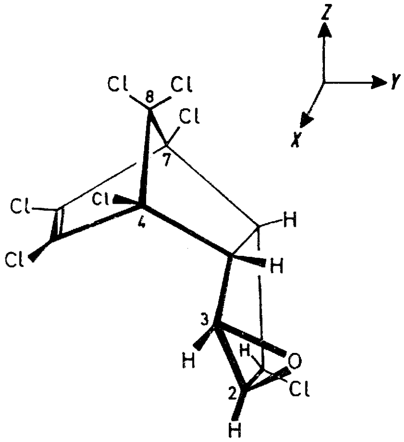
(I)



(II)



(III)



(IV)

It should be noted that recently published *X*-ray structures[10] for Aldrin (I) and Endrin (II) indicate that the methano-bridgehead structure is not completely physically equivalent in these compounds; however the minor deviations have negligible effect on polarity calculations. For each of these molecules we have chosen a Cartesian axis system as indicated in (I) and (II). The *Z* axis lies in the plane of symmetry of the hexachloronorbornene grouping and is the bisector of the C(1)C(10)C(4) angle. The *Y* axis also lies in this symmetry plane and is directed to that side of *Z* remote from the chlorinated double bond.

From the experimental dipole moments of Aldrin, Isodrin, Dieldrin, and Endrin, and the *X*-ray structural parameters of Aldrin and Endrin (and consequently the assumed structural parameters of Isodrin and Dieldrin) together with the value for the moment of the epoxide grouping in Dieldrin and Endrin it is possible to calculate the group moments for the ' chlorinated moiety ', the methano-bridgehead, and the non-chlorinated double bond. We have taken the moment of the epoxide ring to be 1.90 D.[11,12] Hence four simultaneous equations in terms of the group moments of the methano-bridgehead and of the non-chlorinated double bond, and the *Y* and *Z* component moments of the ' chlorinated moiety ' can be constructed. The line of action of the methano-grouping moment and that of the double bond have been assumed to be along the bisector of the C(5)C(9)C(8) angle and along the line joining the mid-points of the ethylenic bond and the C(5)C(8) line respectively. Using an iter-

---

[10] T. P. De Lacey and C. H. L. Kennard, *J.C.S. Perkin II*, 1972, 2153.

[11] B. A. Arbuzov, L. A. Grozina, and A. N. Vereshchagin, *Theoreticheskaya Eksp. Khimiya*, 1968, **4**, 367.

[12] R. J. W. Le Fèvre, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc.* (*B*), 1968, 148.

ative Newton–Raphson computational procedure the following dipole moment components were found to best represent the experimental data; -0.43_8, -0.13_6, -1.81_7, and 1.95_8 D for the methano-bridgehead, the double bond, and the moment components of the ' chlorinated moiety ' along the Y and Z axes, respectively.

The components (μ_X, μ_Y, μ_Z) of the resultant moments for Aldrin, Dieldrin, Isodrin, and Endrin are listed in Table 2.

TABLE 2

Calculated component moments

	μ_X	μ_Y	μ_Z
Aldrin	0	−1.65	2.30
Dieldrin	0	−1.25	0.35
Isodrin	0	−2.07	2.24
Endrin	0	−1.66	0.26

Application of polarity parameters. These parameters are now tested by their use in the calculation of dipole moments for Heptachlor (III) and Heptachlor *cis*-oxide (IV). For these molecules the reference set of orthogonal axes are defined in an analogous manner to those used previously. For Heptachlor, using a C–Cl bond moment of 1.84 D,[13] the relevant component moments deduced previously together with the X-ray structural data,[14] a calculated moment of 1.95 D is obtained. This is in good agreement with the experimental value (1.84 D, Table 1). The epoxide grouping of Heptachlor oxide can assume a *cis*- or a *trans*-disposition with respect to the chlorine on C(1). Using an approach similar to that for Heptachlor and a value of 110.5 (obtained from the structural data for Endrin [10]) for the angle between the bisector of the epoxide group and the line joining the midpoints of C(1)C(3a) and C(2)C(3), we calculate the expected moments for the *cis*- and the *trans*-forms to be 1.85 and 2.38 D respectively. Comparison of these values with the experimental (1.86 D, Table 1) confirms the *cis*-structure.

Electric Birefringence.—Bond polarisability anisotropies have been used to predict the conformations of solutes in solution (see for example ref. 15). In this technique, bond or group polarisability anisotropies * extracted from structurally suitable molecules, together with polarity data, are used in a tensorial and vectorial analysis [16] to yield molar Kerr constants ($_{\mathrm{m}}K$) expected for the particular conformation being considered. Comparison between calculated and observed $_{\mathrm{m}}K$ values allows choice to be made between candidate structures. In the present situation it was our hope to obtain polarisability parameters for the various structural units that occur regularly in the molecules of these insecticides.

If we assume that all the bonds in the molecules are such that we can use previously determined C–Cl polarisability anisotropies *i.e.* from *cis*-1,2-dichloroethylene $b_1 = 7.79_5$, $b_2 = 9.46$, $b_3 = 6.08$ [17] and from methyl chloride $b_L(\text{C–Cl}) = 3.18$, $b_T(\text{C–Cl}) = 2.20$ [18] or from cyclohexyl chloride $b_L(\text{C–Cl}) = 3.82$, $b_T(\text{C–Cl}) = 1.85$ [18] and together with the bond parameters previously listed, we can calculate molar Kerr constants. In Table 3 are the calculated values together with those measured.

TABLE 3

Calculated molar Kerr constants

	Using C–Cl bond polarisability values from		
	Methyl chloride	Cyclohexyl chloride	Observed
Aldrin	−235	−265	−148
Dieldrin	−11	−10	−17
Isodrin	−265	−295	−238
Endrin	−34	−41	−39
Heptachlor	−40	−73	−63
Heptachlor *cis*-oxide	−57	−71	+23
Heptachlor *trans*-oxide	−64	−64	

It can be seen that this approach does not yield a satisfactory set of polarisability parameters.

An alternative procedure would be to adopt the approach we used successfully to obtain polarity parameters. In order to simplify the situation we have made the assumption that apart from those in the ' chlorinated moiety ' the bonds within the molecules may be described by polarisability parameters [17,19,20] applicable in less strained environments. Using the observed $_{\mathrm{m}}K$ values of Aldrin, Dieldrin, and Endrin and the total molar refraction ($R_D = 1.05\,{}_{\mathrm{E}}P$,† ${}_{\mathrm{E}}P = 4\pi N\Sigma b_1/9$) for Aldrin (Table 1) four simultaneous equations can be set up with unknowns b_L, b_T, and b_V for the ' chlorinated moiety ' and ϕ, the angle between b_L of the chlorinated grouping (which lies in the YZ plane) and Z of the axes system defined previously; b_V lies along the X axis. In these calculations the parameters for the epoxide ring were obtained from those of ethylene oxide.[21] The solution for these equations gave for the ' chlorinated moiety ' in Aldrin, Dieldrin, and Endrin, $b_L = 20.81$, $b_T = 18.26$, $b_V = 18.36$, and $\phi = 158°$. These values, when used to calculate an $_{\mathrm{m}}K$ for Isodrin give a value (-118×10^{-12}) less negative than that observed (-238×10^{-12}).

We acknowledge with gratitude the help of Dr. R. G. Gilbert in the interpretation and manipulation of computer programs and the gifts of chemicals from Shell Development Co., Modesto, California and Drug Houses of Australia Ltd.

[5/1992 *Received, 13th October, 1975*]

---

* The polarisability semi-axis of bonds and groups b_L, b_T, or b_V or molecules b_1, b_2, b_3, are quoted throughout in Å^3 units.

† ${}_{\mathrm{E}}P$ Has been evaluated by including bond data from R. J. W. Le Fèvre and K. D. Steel, *Chem. and Ind.*, 1961, 670.

[13] C. Y. Chen and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1965, 558.

[14] K. G. Shields and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 1375.

[15] M. L. Kemp and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1965, 7094; K. E. Calderbank, R. J. W. Le Fèvre, and R. K. Pierens, *J. Chem. Soc.* (*B*), 1970, 1115, 1608.

[16] R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

[17] R. Bramley, C. G. Le Fèvre, R. J. W. Le Fèvre, and B. P. Rao, *J. Chem. Soc.*, 1959, 1183.

[18] R. J. W. Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; R. J. W. Le Fèvre and B. J. Orr, *J. Chem. Soc.* (*B*), 1966, 37.

[19] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 273.

[20] R. K. Pierens, *Austral. J. Chem.*, 1974, **27**, 399.

[21] M. J. Aroney, K. E. Calderbank, and H. J. Stootman, *Austral. J. Chem.*, 1974, **27**, 1563.