

Predictions of the Nature and Strength of Soil Sorption of Organic Pollutants by Molecular Topology

Aleksandar Sabljic

This study was undertaken to find a simple and accurate structural parameter for the prediction of the soil sorption coefficients (K_{om} 's) of organic pollutants and to help resolve controversy about the mechanism of soil sorption. The methods used are molecular topology and quantitative structure-activity relationship analysis. We obtained extremely good linear correlation between the first-order molecular connectivity indexes ($^1\chi$) and K_{om} 's for a large group of nonionic organic compounds. In addition, the correlation equation successfully predicts soil sorption data of seven experimentally uncertain halogenated hydrocarbons. The $^1\chi$ index also correlates very well with the molecular van der Waals surface area. Our results support the postulate that soil sorption is a surface area dependent adsorption process.

The widespread use of organic pesticides led to extensive interest (Hance, 1980; Kenaga and Goring, 1980; Chiou, 1981) in the adsorption of such solutes from aqueous solution by soils because of the influence of this process on pesticide performance, mobility in the soil, and residue problems. The soil sorption coefficient (K_{om}), defined as the ratio between the concentrations of a given chemical sorbed by the soil and dissolved in the soil water normalized to the total organic carbon content of the soil, is currently used as a quantitative measure of the soil sorption (Kenaga and Goring, 1980). The experimental determination of K_{om} values is often a costly and time-consuming process. It is also very inaccurate (Chiou et al., 1979; Kenaga and Goring, 1980) for compounds of low water solubility, such as DDT, lindane, and PCB's. Water solubility (WS) and 1-octanol/water partition coefficients (K_{ow}) have been proposed (Chiou et al., 1979; Karickhoff et al., 1979; Kenaga and Goring, 1980; Chiou, 1981) as alternative, more accurate estimates of K_{om} . Unfortunately, it is impossible to determine these parameters accurately for compounds whose WS is below 1 ppm (Biggar et al., 1967; Haque and Schmedding, 1975), i.e., the same pollutants whose K_{om} 's cannot be measured accurately. In addition, several investigators have reported no or poor correlation between WS (Harris and Warren, 1964; Talbert and Fletchall, 1965; Hance, 1965; Briggs, 1969) or K_{ow} (Briggs, 1969) and soil sorption coefficients. Thus, a convenient, accurate way to predict soil sorption coefficients of a large numbers of chemical compounds is urgently needed, especially since the implication of the "Toxic Substances Control Act" is that all classes of chemicals must be assessed as to their environmental hazard.

In this investigation, molecular topology (Gutman and Trinajstić, 1973; Fox, 1983) and quantitative structure-activity relationship (QSAR) analysis have been applied to this problem, with the aim of finding the structural parameter that will most adequately describe the relationship between the molecular structure of organic compounds and their adsorption by soil and whose accuracy, unlike the experimentally determined parameters, will be independent of the magnitude of the parameter. The results of this investigation should also help resolve the current controversy concerning the process of soil sorption.

Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20205, and Theoretical Chemistry Group, Department of Physical Chemistry, Institute Rudjer Bošković, 41001 Zagreb, P.O.B. 1016, Croatia, Yugoslavia.

Table I. Observed (Chiou et al., 1979, 1983; Karickhoff et al., 1979; Kenaga and Goring, 1980; Koch, 1983) and Calculated Soil Sorption Coefficients (K_{om}) and First-Order Molecular Connectivity Indexes ($^1\chi$) of Polycyclic Aromatic Hydrocarbons and Halogenated Hydrocarbons

compound	$\log K_{om}^{obsd}$	$\log K_{om}^{calcd}$	$^1\chi$
naphthalene	3.11	3.18	4.966
anthracene	4.42	4.26	6.933
phenanthrene	4.36	4.27	6.949
tetracene	5.81	5.34	8.899
pyrene	4.92	4.81	7.933
ethylbenzene	1.98	2.61	3.931
2-methylnaphthalene	3.93	3.40	5.360
9-methylantracene	4.81	4.50	7.360
chlorobenzene	2.10	2.32	3.394
1,2-dichlorobenzene	2.26	2.54	3.805
1,3-dichlorobenzene	2.23	2.53	3.788
1,4-dichlorobenzene	2.40	2.53	3.788
1,2,4-trichlorobenzene	2.70	2.76	4.198
1,2,3,5-tetrachlorobenzene	3.20	2.98	4.609
pentachlorobenzene	3.50	3.22	5.037
2-chlorobiphenyl	3.23	3.96	6.377
2,2'-dichlorobiphenyl	3.68	4.18	6.788
2,4'-dichlorobiphenyl	3.90	4.17	6.771
2,5,2',5'-tetrachlorobiphenyl	4.67	4.62	7.575
2,3,4,2',5'-pentachlorobiphenyl	4.50	4.85	8.003
2,4,5,2',5'-pentachlorobiphenyl	4.63	4.84	7.986
2,3,4,2',3',4'-hexachlorobiphenyl	5.05	5.09	8.430
2,3,4,5,6,2',5'-heptachlorobiphenyl	5.95	5.31	8.841
DDT	5.38	5.33	8.874
DDE	4.70	5.17	8.575
dichloromethane	1.44	1.23	1.414
trichloromethane	1.65	1.40	1.732
tetrachloromethane	1.85	1.55	2.000
1,2-dichloroethane	1.28	1.50	1.914
1,2-dibromoethane	1.56	1.50	1.914
1,1,1-trichloroethane	2.02	1.55	2.000
1,1,2,2-tetrachloroethane	1.66	1.90	2.643
1,2-dichloropropane	1.43	1.70	2.270
1,2-dibromo-3-chloropropane	2.11	1.99	2.808
1,2-dibromoethene	1.65	1.50	1.914
tetrachloroethene	2.32	1.90	2.643
1,3-dichloropropene	1.42	1.78	2.414

It has long been assumed that soil sorption could be described as the adsorption of solute on the surface of the organic matter of the soil (Hance, 1967, 1980; Furrmidge and Osgerry, 1967; Bailey and White, 1970; Carringer et al., 1975). More recently, two groups (Chiou et al., 1979; Karickhoff et al., 1979) have proposed an alternate concept

of soil sorption in which solute partitioning takes place between water and the soil organic matter.

Thirty-seven compounds were initially investigated: eight PAH's and their alkyl derivatives, seven chlorobenzenes, eight PCB's plus DDT and DDE, and twelve chloro- and bromoalkanes or alkenes (Table I). This particular group of compounds was chosen because of their large production and widespread use, their resistance to chemical and biological degradation, their ability to accumulate in food chains and to affect the growth and reproduction of organisms at all levels of the food chains, and their ability to cross the blood/brain barrier. They thus constitute the major group of environmental hazards to all living species, including man. In addition, this is the largest group of structurally related compounds whose experimentally measured K_{om} 's (Chiou et al., 1979, 1983; Karickhoff et al., 1979; Kenaga and Goring, 1980; Koch, 1983) cover 5 orders of magnitude. The structural parameters used in the present investigation are the molecular connectivity indexes (χ) (Randić, 1975; Kier and Hall, 1976). These indexes have been successfully applied in quantitative structure-property and structure-activity relationship studies (Randić, 1975; Kier and Hall, 1976; Balaban et al., 1980; Sabljic and Trinajstić, 1981; Sabljic and Protić-Sabljić, 1983; Trinajstić, 1983) and, in particular, in ecotoxicological investigations (Sabljic and Protić, 1982a,b; Schultz et al., 1982; Kier and Hall, 1982; Koch, 1983; Sabljic, 1983).

METHOD OF CALCULATION

The concept of molecular connectivity was introduced by Randić (1975) and further developed and extensively used by Kier and Hall (1976). Only a brief description of the calculation of the first-order molecular connectivity index (originally designated as the branching index) used in this study is given here. Several extensive reviews have been published recently (Kier and Hall, 1976; Balaban et al., 1980; Sabljic and Trinajstić, 1981; Trinajstić, 1983) that can be consulted for a detailed description of the theory and calculation of molecular connectivity indexes.

The first-order molecular connectivity indexes ($^1\chi$) are calculated from the non-hydrogen part of the molecular skeletons. Each non-hydrogen atom is described by its δ value, which is equal to the number of adjacent non-hydrogen atoms. This index is then calculated from the atomic δ values in accordance with the expression

$$^1\chi = \sum_{s=1}^n (\delta_i \delta_j)_s^{-0.5}$$

where i and j correspond to the pairs of adjacent non-hydrogen atoms and the summation is over all bonds between non-hydrogen atoms. Molecular connectivity indexes were calculated by the GRAPH computer program (Sabljic and Trinajstić, 1981). Regression analysis was accomplished by using the modeling laboratory (MLAB) component developed by the National Institutes of Health Division of Computer Research and Technology (Knott, 1979). All calculations were carried out on a DECsystem10 computer at the National Institutes of Health, Bethesda, MD.

RESULTS AND DISCUSSION

Zero-, first-, and second-order molecular connectivity indexes were calculated for the 37 compounds. The best linear relationship was obtained between $\log K_{om}$ and the first-order molecular connectivity index ($^1\chi$). The regression equation is

$$\log K_{om} = (0.55 \pm 0.02)^1\chi + (0.45 \pm 0.12) \quad (1)$$

with the correlation coefficient equal to 0.973. The

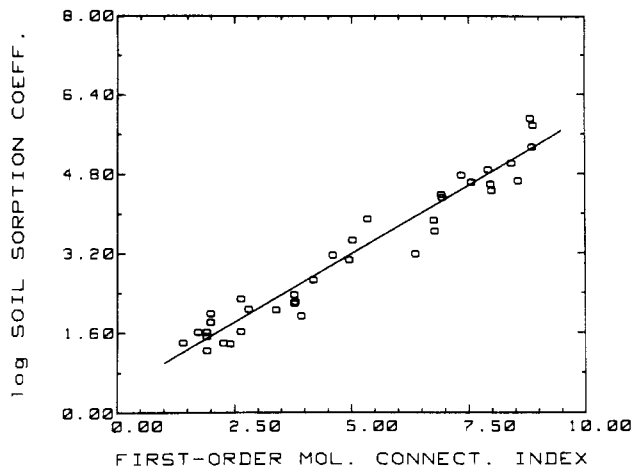


Figure 1. Observed soil sorption coefficients ($\log K_{om}^{obsd}$) plotted as a function of the first-order molecular connectivity indexes ($^1\chi$) of 37 polycyclic aromatic hydrocarbons and halogenated hydrocarbons from Table I.

graphical representation of this fit is given in Figure 1.

Statistically eq 1 accounts for 95% of the variation in the $\log K_{om}$ data. This is as good as can be expected since the accuracy of the K_{om} data is approximately 10% for compounds with high water solubility (low K_{om}) and up to 1 order of magnitude poorer for weakly soluble compounds (high K_{om}) (Kenaga and Goring, 1980). The alternative correlations $\log WS$ vs. $\log K_{om}$ and $\log K_{ow}$ vs. $\log K_{om}$ were also examined, and both were found to be inferior to eq 1. The fit for these empirical parameters was 85% and 77% of the variation in the $\log K_{om}$ data, respectively. The water solubility data used in this correlation are those reported by Chiou et al. (Chiou et al., 1979, 1983; Chiou, 1981), while the 1-octanol/water partition coefficients are primarily those collected by Kenaga and Goring (1980), as well as several by Chiou et al. (1983). The detailed analysis of the calculated and observed $\log K_{om}$ data presented in Table I shows that they are very similar (correlation coefficient is 0.973) even for compounds with the high $\log K_{om}$ values. Thus, it seems that the precision of the experimental K_{om} data is much higher than is generally accepted (Kenaga and Goring, 1980).

Since the correlation between $^1\chi$ index and $\log K_{om}$, eq 1, was found to be better than the correlations with experimental parameters, it is worth examining its predictive ability. Halogenated hydrocarbons whose K_{om} data are still uncertain (Chiou et al., 1979; Kenaga and Goring, 1980; Kenaga, 1980; Briggs, 1981; Chiou et al., 1983; Koch, 1983) were chosen for this test. The results of the test are presented in Table II. It can be seen that the $^1\chi$ index is very accurate in predicting experimental soil sorption data. For bromobenzene, lindane, and 2,4,4'-trichlorobiphenyl, the calculated K_{om} 's are within the experimental range while, for the others, the calculated values are very close.

The results presented in this study are unbiased: No hydrocarbon or halogenated hydrocarbon, whose K_{om} has been measured, was omitted. In all other studies (Chiou et al., 1979, 1983; Kenaga and Goring, 1980; Briggs, 1981) only a small subset of published experimental results on halogenated hydrocarbons are considered. We are, however, aware of a possible limitation of eq 1. Since eq 1 is based on hydrocarbon and halogenated hydrocarbon results, it may be invalid for the highly polar molecules.

In conclusion, we would like to examine our results with regard to the two contrasting models about the nature of soil sorption, viz., surface adsorption or solute partitioning.

Table II. Comparison of Observed^a and Calculated (by Equation 1) Soil Sorption Coefficients (K_{om}) for a Group of Halogenated Compounds and Benzene

compound	$^1\chi$	$\log K_{om}^{calcd}$	$\log K_{om}^{obsd}$
bromobenzene	3.394	2.32	2.18-2.80
lindane	5.464	3.44	2.96-3.46
2,4,4'-trichlorobiphenyl	7.165	4.37	3.50-4.38
hexachlorobenzene	5.464	3.46	3.59-4.25
benzene	3.000	2.09	1.26-1.92
2,4,5,2',4',5'-hexachlorobiphenyl	8.397	5.07	5.34-6.08
aldrin	8.276	4.98	2.61-4.45

^a Experimental data ($\log K_{om}^{obsd}$) are given as the range of reported values (Chiou et al., 1979; Kenaga and Goring, 1980; Kenaga, 1980; Briggs, 1981; Chiou et al., 1983; Koch, 1983) where the lowest and the highest reported values define the range.

The $^1\chi$ index can be viewed as a quantitative measure of the area occupied by the projection of the non-hydrogen skeleton of molecule. Since the large majority of the studied compounds are "quasi" two dimensional, their $^1\chi$ index should correlate very well with their surface areas. This prediction was found to be true; for all the compounds examined the correlation coefficient between the $^1\chi$ index and the calculated van der Waals surface area (Bondi, 1964) is 0.921. This result indirectly supports the proposed physical meaning of the $^1\chi$ index. In addition, it shows that this index is an excellent parameter for rapid and simple estimations of the surface areas of predominantly planar molecules from their structural formulas. Since the two-dimensional representation of the molecular structure ($^1\chi$ index) is sufficient to explain all quantitative variations in the soil sorption data, the process of soil sorption may be viewed as an attractive interaction between two planes, the magnitude of which is directly proportional to the surface area of the solute molecule. This interaction is similar to the recently measured (Israelachvili and Pashley, 1982) attractive force between two hydrophobic surfaces immersed in aqueous electrolyte solutions. In the latter case, the attractive force is proportional to the surface areas of the interacting surfaces and is attributed to hydrophobic interaction. Thus, it can be concluded that our QSAR study supports the hypothesis that soil sorption is a surface area dependent adsorption process. In addition, the correlation between the $^1\chi$ index and $\log K_{ow}$ was examined in order to test the possibility that this index also adequately describes the process of solute partitioning. The fit was only 79% for the variation of the $\log K_{ow}$ data. This is significantly lower than the correlation between the $^1\chi$ indexes and soil sorption coefficients (95%). Thus, this result also suggests that the soil sorption and partitioning process reflect different mechanisms.

In this investigation, a simple nonempirical parameter ($^1\chi$) has been found that both correlates extremely well with the soil sorption coefficients (K_{om} 's) of the two chemical groups that constitute major environmental hazards and has remarkably good predictive power. Its relative simplicity and the possibility to substantially reduce the empirical component in ecotoxicological QSAR studies make the molecular topology approach used here far more attractive than correlations between empirical parameters, which, lacking theoretical basis, are of limited usefulness. We emphasize that each theoretical prediction should be experimentally confirmed. Thus, the $^1\chi$ index should be used as a predictive tool for ranking potentially hazardous chemicals and for creating priority list for testing, so that experimental efforts can be focused on the potentially most dangerous chemicals. In addition, the

proposed method can also be used to predict the properties of chemicals that are not yet synthesized.

In the future, the molecular topology approach may also be helpful in developing new ecological models that will give more insight into the expected distribution pattern and behavior of chemicals in the environment. In these models, different distribution coefficients are combined to describe a type of ecosystem. Since the molecular connectivity indexes were found to correlate with the soil sorption coefficients (distribution between water and soil), bioconcentration factors (distribution between water and biota) (Sabljic and Protic, 1982b; Koch, 1983), 1-octanol/water partition coefficients (Kier and Hall, 1976), and acute toxicity (Schultz et al., 1982; Kier and Hall, 1982; Sabljic, 1983; Koch, 1983) of organic pollutants, it should be possible from molecular topology alone to evaluate the overall distribution pattern and possible adverse effects of chemicals in ecosystems.

Registry No. Naphthalene, 91-20-3; anthracene, 120-12-7; phenanthrene, 85-01-8; tetracene, 92-24-0; pyrene, 129-00-0; ethylbenzene, 100-41-4; 2-methylnaphthalene, 91-57-6; 9-methylanthracene, 779-02-2; chlorobenzene, 108-90-7; 1,2-dichlorobenzene, 95-50-1; 1,3-dichlorobenzene, 541-73-1; 1,4-dichlorobenzene, 106-46-7; 1,2,4-trichlorobenzene, 120-82-1; 1,2,3,5-tetrachlorobenzene, 634-90-2; pentachlorobenzene, 608-93-5; 2-chlorobiphenyl, 2051-60-7; 2,2'-dichlorobiphenyl, 13029-08-8; 2,4'-dichlorobiphenyl, 34883-43-7; 2,5,2',5'-tetrachlorobiphenyl, 35693-99-3; 2,3,4,2',5'-pentachlorobiphenyl, 38380-02-8; 2,4,5,2',5'-pentachlorobiphenyl, 37680-73-2; 2,3,4,2',3',4'-hexachlorobiphenyl, 38380-07-3; 2,3,4,5,6,2',5'-heptachlorobiphenyl, 52712-05-7; DDT, 50-29-3; DDE, 72-55-9; dichloromethane, 75-09-2; trichloromethane, 67-66-3; tetrachloromethane, 56-23-5; 1,2-dichloroethane, 107-06-2; 1,2-dibromoethane, 106-93-4; 1,1,1-trichloroethane, 71-55-6; 1,1,2,2-tetrachloroethane, 79-34-5; 1,2-dichloropropane, 78-87-5; 1,2-dibromo-3-chloropropane, 96-12-8; 1,2-dibromoethane, 540-49-8; tetrachloroethene, 127-18-4; 1,3-dichloropropene, 542-75-6; bromobenzene, 108-86-1; lindane, 58-89-9; 2,4,4'-trichlorobiphenyl, 7012-37-5; hexachlorobenzene, 118-74-1; benzene, 71-43-2; 2,4,5,2',4',5'-hexachlorobiphenyl, 35065-27-1; aldrin, 309-00-2.

LITERATURE CITED

- Bailey, G. W.; White, J. L. *Residue Rev.* **1970**, *32*, 29-92.
 Balaban, A. T.; Ciriac, A.; Motoc, I.; Simon, Z. "Steric Fit in Quantitative Structure-Activity Relationship"; Springer-Verlag: Berlin, West Germany, 1980.
 Biggar, J. W.; Dutt, G. R.; Riggs, R. L. *Bull. Environ. Contam. Toxicol.* **1967**, *2*, 90-100.
 Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441-451.
 Briggs, G. G. *Nature (London)* **1969**, *223*, 1288.
 Briggs, G. G. *J. Agric. Food Chem.* **1981**, *29*, 1050-1059.
 Carringer, R. D.; Weber, J. B.; Monaco, T. *J. Agric. Food Chem.* **1975**, *23*, 568-572.
 Chiou, C. T. In "Hazard Assessment of Chemicals. Current Developments Vol. 1"; Saxena, J.; Fisher, F., Eds.; Academic Press: New York, 1981; pp 117-153, and references cited therein.
 Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science (Washington, D.C.)* **1979**, *206*, 831-832.
 Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227-231.
 Fox, J. L. *Chem. Eng. News* **1983**, *61* (19), 45-49.
 Furmidge, C. G. L.; Osgerry, J. M. *J. Sci. Food Agric.* **1967**, *18*, 269-273.
 Gutman, I.; Trinajstić, N. *Top. Curr. Chem.* **1973**, *42*, 49-93.
 Hance, R. J. *Weed Res.* **1965**, *5*, 98-107.
 Hance, R. J. *Nature (London)* **1967**, *214*, 630-631.
 Hance, R. J. *Chem. Br.* **1980**, *16*, 128-131, and references cited therein.
 Haque, R.; Schmedding, D. *Bull. Environ. Contam. Toxicol.* **1975**, *14*, 13-18.
 Harris, C. I.; Warren, G. F. *Weeds* **1964**, *12*, 120-126.
 Israelachvili, J.; Pashley, R. *Nature (London)* **1982**, *300*, 341-342.
 Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241-248.

Kenaga, E. E. *Ecotoxicol. Environ. Saf.* 1980, 4, 26-38.
 Kenaga, E. E.; Goring, C. A. I. In "Aquatic Toxicology"; Eaton, J. C.; Parish, P. R.; Hendricks, A. C., Eds.; American Society for Testing and Materials: Philadelphia, PA, 1980; pp 78-115, and references cited therein.
 Kier, L. B.; Hall, L. H. "Molecular Connectivity in Chemistry and Drug Research"; Academic Press: New York, 1976.
 Kier, L. B.; Hall, L. H. *Bull. Environ. Contam. Toxicol.* 1982, 29, 121-126.
 Knott, G. D. *Comput. Programs Biomed.* 1979, 10, 271-280.
 Koch, R. *Toxicol. Environ. Chem.* 1983, 6, 87-96.
 Randić, M. *J. Am. Chem. Soc.* 1975, 97, 6609-6615.
 Sabljčić, A. *Bull. Environ. Contam. Toxicol.* 1983, 30, 80-83.

Sabljić, A.; Protić, M. *Bull. Environ. Contam. Toxicol.* 1982a, 28, 162-165.
 Sabljčić, A.; Protić, M. *Chem.-Biol. Interact.* 1982b, 42, 301-310.
 Sabljčić, A.; Protić-Sabljić, M. *Mol. Pharmacol.* 1983, 23, 213-218.
 Sabljčić, A.; Trinajstić, N. *Acta Pharm. Jugosl.* 1981, 31, 189-214.
 Schultz, T. W.; Kier, L. B.; Hall, L. H. *Bull. Environ. Contam. Toxicol.* 1982, 28, 373-378.
 Talbert, R. E.; Fletchall, O. H. *Weeds* 1965, 13, 46-52.
 Trinajstić, N. "Chemical Graph Theory"; CRC Press: Boca Raton, FL, 1983.

Received for review August 8, 1983. Accepted September 19, 1983.

Dinitroanilines as Photostabilizers for Pyrethroids

Prem Dureja,¹ John E. Casida, and Luis O. Ruzo*

A variety of 4-substituted 2,6-dinitroanilines stabilize pyrethroids to photodecomposition as thin films on silica gel or glass based on chemical analyses and bioassays. The 12 pyrethroids stabilized in this way include the pyrethrins, allethrin, kadethrin, resmethrin, tetramethrin, and cyphenothrin. Highly effective stabilizers of this type include trifluralin and its analogues with 1-propylamino, 1-amino, 4-methylsulfonyl, 4-sulfamoyl, and 4-dimethylsulfamoyl substituents. These dinitroanilines are more effective stabilizers than 4-nitrophenol, 8-hydroxyquinoline, phenothiazine, and 104 other compounds examined. A cyphenothrin-trifluralin (5:1) mixture is as photostable as cypermethrin on silica gel. The photostability of cyphenothrin on silica gel or in solution is enhanced by 1 part of trifluralin or its 1-amino analogue to 10 000 parts of pyrethroid. The photoquenching action of the dinitroanilines at high ratios involves competition for light, but at very low ratios they may complex with the excited state of the pyrethroid.

The photostability of the pyrethrins and the synthetic pyrethroids has been improved in two ways. Photostabilizers including antioxidants and ultraviolet (UV) screens extend the effective life of photolabile compounds such as the chrysanthemates (Abe et al., 1972; Blackith, 1952; Chen and Casida, 1969; Glynne Jones, 1960; Miskus and Andrews, 1972; Pieper and Rappaport, 1982; Tattersfield and Martin, 1934; Ueda et al., 1974; Warner, 1963). Alternatively, the photolabile sites are replaced with more stable and usually halogenated groups to obtain structurally modified and photostabilized pyrethroids (Elliott and Janes, 1978; Miyamoto et al., 1981; Ruzo, 1982, 1983). The photostabilizer approach has potential advantages in improving the cost effectiveness of established compounds, in maintaining the favorable toxicology of chrysanthemates and nonhalogenated pyrethroids, and in controlling persistence as desired for specific control situations by varying the photostabilizer or its concentration. This potential has not been realized, in part due to the lack of photostabilizers of adequate effectiveness. We have therefore continued to search for improved photostabilizers for chrysanthemates and other insecticides.

MATERIALS AND METHODS

Chemicals. The pyrethroids examined were as follows: a 40% pyrethrins I and 46% pyrethrins II mixture referred to as "pyrethrins" and *S*-bioallethrin from McLaughlin

Gormley King Co., Minneapolis, MN; (1*RS*)-*cis*-resmethrin of >98% purity from S. B. Penick & Co., Orange, NJ; (1*RS*)-*trans*-tetramethrin and (1*RS*, α *RS*)-*cis*-cyphenothrin of >95% purity from Sumitomo Chemical Co., Osaka, Japan; (i*RS*)-fenpropathrin and (i*SS*)-fenvalerate of >95% purity from Shell Development Co., Modesto, CA; kadethrin, (1*S*)-*cis*-phenothrin, (1*R*)-*cis*-permethrin, (1*R*, α *S*)-*cis*-cypermethrin, and deltamethrin of >98% purity from Roussel Uclaf, Paris, France. Structures for these pyrethroids are given by Casida et al. (1983). [¹⁴C]Cyphenothrin (2.7 mCi/mmol) was prepared by coupling (1*R*)-*cis*-[1-¹⁴C]chrysanthemoyl chloride (Ueda et al., 1974) and (i*RS*)- α -cyano-3-phenoxybenzyl alcohol (Ruzo et al., 1977) with pyridine in benzene and purification by thin-layer chromatography (TLC) (silica gel, carbon tetrachloride-ether, 3:1, *R_f* 0.56).

Pesticide chemicals were obtained from the basic manufacturers or the Health Effects Research Laboratory, U.S. Environmental Protection Agency (Research Triangle Park, NC). The procedure of Hall and Giam (1972) was used to react 4-chloro-3,5-dinitrobenzotrifluoride (Aldrich Chemical Co., Milwaukee, WI) with *n*-propylamine to obtain the monopropylamino analogue of trifluralin (mp 55-58 °C) and with ammonium hydroxide to obtain the amino analogue of trifluralin (mp 141-144 °C). The corresponding phenol was made by refluxing a mixture of chlorodinitrobenzotrifluoride and equimolar Na₂CO₃ in water for 24 h, cooling and acidification with HCl, filtration and washing the crystals with ether, and recrystallization from methanol (mp 208 °C). The methyl ether was obtained by treating the phenol in ether with diazomethane and crystallization from methanol (mp 40-41 °C). These trifluralin analogues gave appropriate mass spectra and nuclear magnetic resonance spectra. Other chemicals used were from commercial sources.

Pesticide Chemistry and Toxicology Laboratory, Department of Entomological Sciences, University of California, Berkeley, California 94720.

¹Present address: Department of Agriculture Chemicals, Indian Agricultural Research Institute, New Delhi 110012, India.