

DISCUSSION

DDT persists in soils for long periods of time, and its half-life has been estimated to be between 3 and 20 years (Kiigemagi and Terriere, 1972; Menzie, 1972). A possible way to reduce the longevity of this insecticide is to introduce or change substituents on the molecule to favor microbial utilization. Thus, Alexander and Lustigman (1966) reported that the presence of chloro, sulfonate, and nitro groups retarded the rate of biodegradation of monosubstituted benzenes, but carboxyl and hydroxyl groups favored the decomposition of the chemicals. Comparable information for DDT and related compounds might lead to the development of suitable and short-lived replacements. Although many studies have indeed been conducted of the insecticidal activity of molecules of this class with different substituents or substituents in different positions, published information on the biodegradation of many of these compounds is lacking.

In the present investigations, the para,para'-substituted dichloro, dimethoxy, dihydroxy, and dinitro compounds tested were utilized poorly if at all. Conversely, the unsubstituted chemicals or the para-substituted monohydroxy and monomethoxy chemicals were attacked readily. 1,1,1',1'-Tetraphenyldimethyl ether, a product synthesized microbiologically from diphenylmethane (Subba-Rao and Alexander, unpublished data), and its chlorinated analogue 1,1,1',1'-tetra(p-chlorophenyl)dimethyl ether were resistant to biodegradation in soil suspensions. These two molecules were included in the studies as the chlorinated ether had been suspected to be formed from chlorinated diphenylmethane in soil or water.

Biodegradability of DDT analogues has been expressed by Kapoor et al. (1973) in terms of the amount of polar metabolites generated during the metabolic transforma-

tion. However, the finding of polar products does not necessarily mean extensive metabolism or even total mineralization of the parent molecule, inasmuch as diphenylacetic acid, bis(p-chlorophenyl)acetic acid, and p-chlorophenylacetic acid, though water soluble, were not found to be decomposed appreciably in BOD bottles. Additional evidence for the resistance of these compounds can be found in the absence of microbial growth in enrichments containing such chemicals as sole sources of carbon.

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Crystal and Molecular Structure of Carbamate Insecticides. 1. Mesurol

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The crystal and molecular structure of Mesurol (4-methylthio-3,5-dimethylphenyl *N*-methylcarbamate, C₁₁H₁₅NO₂S) has been determined by three-dimensional x-ray analysis. The crystals are triclinic with space group $P\bar{1}$ and with unit cell dimensions $a = 11.786$ (2), $b = 12.149$ (5), and $c = 8.896$ (3) Å, $\alpha = 101.84$ (3), $\beta = 90.88$ (2), and $\gamma = 74.95$ (2)°, and $Z = 4$. The structure was refined to a final conventional discrepancy factor of 0.062 for 2301 observed reflections ($|F_o| > 3\sigma_{F_o}$). The molecule consists of three approximately planar sections; the methylthio and carbamate groups twist by about 80 and 60°, respectively, out of the plane of the 3,4-dimethylphenyl group. In the carbamate group, the C-O single bond distance in both molecules (average 1.370 (4) Å) indicates a possible lengthening ($\sim 3\sigma$) relative to those usually found in esters.

In recent years the production and use of both carbamate and organophosphorus insecticides have greatly increased as they replace the much less biodegradable and carcinogenic chlorinated hydrocarbon insecticides. The mode of action of the carbamate and organophosphorus insecticides is accepted to be via the inhibition of the enzyme acetylcholinesterase. The enzyme appears to be phosphorylated or carbamoylated at a serine hydroxyl with release of a leaving group. The enzyme then loses the

phosphoryl or carbamoyl group by a very slow reaction with water, and during this period the enzyme cannot react with acetylcholine (Krupka, 1964). We feel that it is important to obtain as much information as possible concerning the details of these interactions at the molecular level and, hence, have initiated a program of crystal-structure determinations of selected organophosphorus and carbamate insecticides to yield firm structural data for use by investigators in this area. We have previously reported the details of crystal structures of three organophosphorus insecticides, ronnel (Baughman and Jacobson, 1975), Coroxon (Gifkins and Jacobson, 1976), and azinphosmethyl (Rohrbaugh et al., 1976). We

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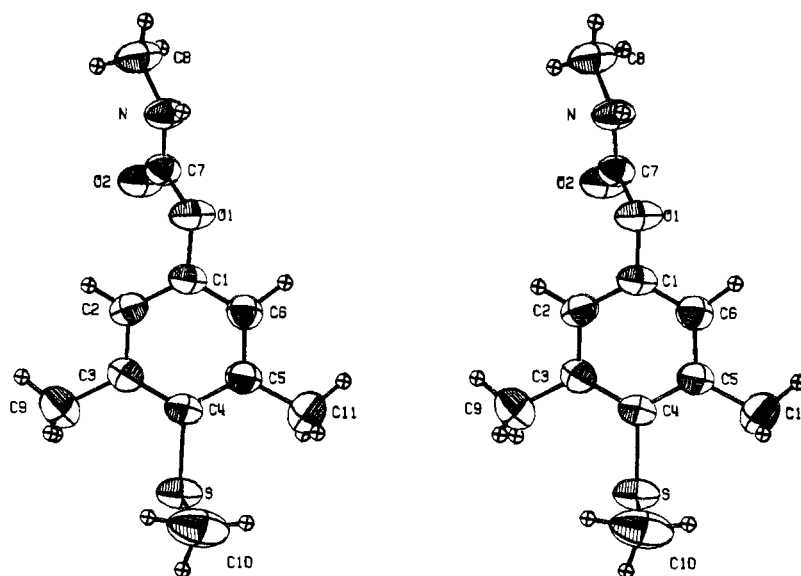


Figure 1. The two symmetry-independent Mesurol molecules.

now wish to report the structure of Mesurol (methiocarb), the first in a series of carbamate insecticides.

EXPERIMENTAL SECTION

Crystal data: $C_{11}H_{15}NO_2S$, mol wt 225.10, triclinic $P\bar{1}$, $a = 11.786$ (2), $b = 12.149$ (5), and $c = 8.896$ (3) Å, $\alpha = 101.84$ (3), $\beta = 90.88$ (2), and $\gamma = 74.95$ (2)°, $V = 1202.97$ Å³, $\rho_c = 1.243$ g/cm³, $Z = 4$, Mo $K\alpha$ ($\lambda = 0.70954$ Å), $\mu = 2.63$ cm⁻¹.

The crystals were obtained in the form of colorless plates by recrystallization from a xylene solution. Preliminary oscillation and precession photographs indicated that the crystals belonged to the triclinic crystal system. The unit cell parameters and their estimated standard deviations were obtained by a least-squares fit (Williams, 1964) to the $\pm 2\theta$ values of 18 independent high-angle reflections whose centers were determined by half-height techniques on a previously aligned four-circle diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.70954$ Å).

For data collection, a crystal of approximate dimensions $0.07 \times 0.2 \times 0.3$ mm was mounted such that the c axis was coincident with the φ axis of the diffractometer. Data were collected at room temperature using an automated four-circle diffractometer interfaced to a PDP-15 computer (Rohrbaugh and Jacobson, 1974). Graphite monochromated Mo $K\alpha$ radiation was used for data collection. Intensities were measured by the stationary-crystal, stationary-counter method and background counts were taken at the beginning and end of each measurement by offsetting in $\omega - 2\theta$. Within a 2θ sphere of 50°, all independent reflections were measured in this manner.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 50 reflections. These reflections did not vary to any significant degree during the entire period of data collection.

Intensity data were corrected for Lorentz and polarization effects but absorption and extinction corrections were not deemed necessary. The maximum and minimum transmission factors are estimated to be 0.982 and 0.924. The estimated variance in each intensity was calculated by

$$\sigma_I^2 = C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2 \quad (1)$$

where C_T and C_B are the total count and the background count, respectively, and the factor 0.03 represents an

estimate of nonstatistical errors. The estimated deviations in the structure factor were calculated by the finite difference method (Lawton and Jacobson, 1968). Of the 4238 reflections measured, 2301 were considered observed, i.e. had intensities such that $|F_o| > 3\sigma_{F_o}$.

Solution and Refinement. A Howells, Phillips, and Rogers (1950) test indicated that the space group had a center of symmetry and the space group $P\bar{1}$ was assumed with two symmetry-independent molecules in the asymmetric unit. Examination of a sharpened Patterson map yielded coordinates for the positions of the two independent sulfur atoms, but pseudosymmetry appeared in the electron-density map calculated on the basis of the structural amplitudes obtained by phasing with these positions, due to the fact that the vector between the sulfur atoms was $(1/4, 0, 1/2)$. Therefore, a superposition procedure was carried out in order to break the pseudosymmetry. The resultant map clearly showed the positions of all the nonhydrogen atoms and also gave additional verification that the space group was indeed $P\bar{1}$.

The atomic positions were refined by full-matrix least-squares procedures (Busing et al., 1962) using first isotropic and then anisotropic thermal parameters. At $R = \sum(|F_o| - |F_c|) / \sum|F_o| = 8.0\%$, a difference electron-density synthesis was computed, from which the positions of all hydrogen atoms were found. All parameters except for thermal parameters of the hydrogen atoms were further refined in a full-matrix least-squares procedure minimizing the function $\sum \omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma_{F_o}^2$. The final discrepancy factors are: $R = 0.062$ and $R_w = \{\sum \omega(|F_o| - |F_c|)^2 / \sum \omega|F_o|^2\}^{1/2} = 0.072$.

The atomic scattering factors were those of Hanson et al. (1960), except for hydrogen for which the scattering factor of Stewart et al. (1965) was used.

The final positional and thermal parameters are listed in Table I. The standard deviations were calculated from the inverse matrix of the final least-squares refinement cycle.

DISCUSSION

A computer-generated perspective drawing (Johnson, 1971) of the two symmetry independent molecules in the unit cell is shown in Figure 1. Nonhydrogen bond distances and angles along with their standard deviations are given in Table II, while bond lengths and angles associated with the hydrogen atoms are listed in Table III. The

Table I

(a) Final Atomic Positional and Thermal ^a Parameters ($\times 10^4$) for Nonhydrogen Atoms									
Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	5 750 (1) ^b	6608 (1)	2812 (2)	77 (1)	143 (2)	168 (2)	-48 (1)	-17 (1)	32 (2)
O(1)	10 357 (3)	7602 (3)	4313 (4)	84 (3)	160 (4)	161 (6)	-63 (3)	-29 (3)	74 (4)
O(2)	10 646 (3)	8113 (3)	2068 (4)	84 (3)	153 (4)	137 (6)	-51 (3)	-20 (3)	63 (4)
N	11 848 (3)	8340 (4)	4055 (4)	81 (4)	127 (5)	138 (6)	-50 (3)	-29 (4)	51 (4)
C(1)	9 278 (4)	7381 (4)	3881 (5)	64 (4)	115 (6)	137 (8)	-32 (4)	-13 (4)	47 (5)
C(2)	8 336 (4)	8259 (4)	3661 (6)	86 (5)	91 (5)	161 (9)	-37 (4)	3 (5)	20 (5)
C(3)	7 241 (4)	8040 (4)	3350 (6)	72 (5)	91 (5)	159 (8)	-16 (4)	-6 (5)	23 (5)
C(4)	7 138 (4)	6900 (4)	3261 (5)	61 (4)	102 (5)	240 (8)	-24 (4)	0 (4)	26 (5)
C(5)	8 110 (4)	6007 (4)	3482 (6)	70 (5)	96 (5)	156 (8)	-24 (4)	-5 (5)	32 (5)
C(6)	9 182 (4)	6262 (4)	3780 (5)	80 (5)	100 (5)	149 (8)	-22 (4)	-11 (5)	46 (5)
C(7)	10 938 (4)	8048 (4)	3351 (5)	69 (4)	100 (5)	135 (8)	-24 (4)	-4 (5)	45 (5)
C(8)	12 627 (5)	8813 (5)	3275 (7)	91 (5)	159 (7)	211 (11)	-69 (5)	-15 (6)	66 (7)
C(9)	6 214 (5)	9020 (5)	3079 (8)	98 (6)	123 (6)	309 (15)	-9 (5)	-30 (7)	49 (8)
C(10)	5 203 (6)	6585 (8)	4671 (8)	108 (7)	289 (11)	230 (12)	-73 (7)	7 (7)	102 (10)
C(11)	8 041 (5)	4776 (5)	3381 (7)	132 (7)	103 (6)	278 (13)	-46 (5)	24 (7)	60 (7)
S(')	8 406 (1)	6470 (1)	7822 (2)	68 (1)	134 (2)	165 (2)	-21 (1)	2 (1)	28 (2)
O(1')	3 277 (3)	7612 (3)	9328 (4)	64 (3)	150 (4)	161 (6)	-16 (3)	-7 (3)	75 (4)
O(2')	2 698 (3)	8203 (3)	7122 (4)	73 (3)	191 (5)	139 (6)	-37 (3)	-13 (3)	75 (4)
N(')	1 391 (4)	8335 (4)	9034 (4)	67 (4)	119 (4)	140 (7)	-21 (3)	2 (4)	41 (4)
C(1')	4 486 (4)	7364 (5)	8901 (5)	67 (4)	121 (6)	124 (8)	-21 (4)	-7 (4)	49 (5)
C(2')	4 981 (4)	8237 (4)	8721 (6)	77 (5)	92 (5)	186 (9)	-16 (4)	-10 (5)	41 (6)
C(3')	6 197 (4)	7954 (4)	8422 (6)	79 (5)	88 (5)	190 (10)	-33 (4)	-18 (5)	33 (6)
C(4')	6 867 (4)	6813 (4)	8284 (5)	68 (4)	86 (5)	137 (8)	-19 (4)	-11 (4)	21 (5)
C(5')	6 348 (4)	5938 (4)	8462 (5)	77 (4)	87 (5)	149 (8)	-22 (4)	-15 (5)	30 (5)
C(6')	5 128 (4)	6228 (4)	8761 (6)	78 (5)	98 (6)	16 (9)	-30 (4)	-14 (5)	35 (5)
C(7')	2 460 (4)	8073 (5)	8370 (5)	72 (4)	93 (5)	135 (8)	-20 (4)	-2 (5)	29 (5)
C(8')	341 (4)	8808 (5)	8243 (7)	75 (5)	153 (7)	199 (11)	-27 (5)	-17 (6)	49 (7)
C(9')	6 732 (5)	8929 (5)	8194 (9)	113 (6)	106 (6)	380 (16)	-39 (5)	17 (8)	63 (8)
C(10')	9 018 (5)	6503 (7)	9675 (8)	88 (6)	254 (10)	249 (13)	-39 (6)	-24 (7)	71 (10)
C(11')	7 036 (5)	4697 (5)	8337 (8)	117 (6)	103 (6)	317 (14)	-26 (5)	-13 (7)	51 (7)

(b) Final Atomic Positional ($\times 10^3$) Parameters ^c for the Hydrogen Atoms								
Atom	x	y	z	Atom	x	y	z	
H(1)	1195 (5)	828 (5)	509 (7)	H(1')	136 (5)	823 (5)	999 (7)	
H(2)	841 (5)	907 (5)	381 (6)	H(2')	449 (5)	915 (5)	901 (7)	
H(3)	998 (5)	566 (5)	381 (6)	H(3')	473 (5)	558 (5)	881 (6)	
H(4)	1301 (5)	820 (6)	215 (7)	H(4')	30 (5)	825 (5)	727 (7)	
H(5)	1322 (6)	893 (5)	382 (8)	H(5')	-28 (5)	897 (5)	884 (7)	
H(6)	1218 (6)	941 (6)	283 (8)	H(6')	45 (5)	935 (5)	787 (7)	
H(7)	642 (6)	977 (6)	303 (8)	H(7')	617 (6)	965 (6)	829 (8)	
H(8)	567 (6)	928 (6)	391 (8)	H(8')	730 (6)	897 (6)	901 (8)	
H(9)	578 (6)	884 (6)	230 (8)	H(9')	709 (6)	866 (6)	729 (8)	
H(10)	565 (6)	580 (6)	482 (8)	H(10')	892 (6)	582 (6)	999 (8)	
H(11)	438 (6)	672 (6)	465 (9)	H(11')	985 (7)	629 (6)	961 (8)	
H(12)	496 (7)	760 (6)	514 (9)	H(12')	871 (6)	726 (6)	1000 (8)	
H(13)	772 (5)	475 (5)	438 (7)	H(13')	767 (6)	456 (6)	912 (8)	
H(14)	771 (5)	456 (5)	241 (7)	H(14')	733 (6)	438 (6)	723 (8)	
H(15)	884 (5)	420 (5)	323 (7)	H(15')	667 (6)	419 (6)	826 (8)	

^a The anisotropic thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)]$. ^b In this and succeeding tables, figures in parentheses correspond to standard deviations for the least significant figures. ^c The isotropic thermal parameter of the hydrogen atom was fixed at the isotropic equivalent of the nonhydrogen atom to which it was attached.

agreement in distances and angles between the two symmetry independent molecules is quite good. There are few significant differences and none greater than 4σ . The differences in planarities are also slight as illustrated in Table IV. Such small differences might be expected due to differences in packing forces, i.e., the different environment experienced by the two molecules. Because of the very slight differences between these two symmetry independent molecules, the rest of the discussion of internal distances and angles will apply equally to both.

In general, the molecule can be considered as consisting of approximately three planar sections (cf. Table IV), namely the carbamate, C_4 -methylthio, and dimethylphenyl groups. The carbamate and methylthio groups twist by about 60 and 80° out of the plane of the dimethylphenyl group, respectively (cf. Figure 1).

One of the most interesting aspects of this structure is to be found in an examination of the dimensions of the carbamate group, particularly due to the dearth of

structural information on carbamate groups to be found in the literature. The C(7)-O(1) distance (Table II) in both molecules (average 1.370 (4) Å) indicates a possible lengthening ($\sim 3\sigma$) relative to those usually found in esters (1.358 Å) (Sutton, 1965). The C(1)-O(1) bond distance, 1.409 (5) Å, is also somewhat lengthened when compared to those found in salicylic acid (1.36 Å) (Cochran, 1953), catechol (1.373, 1.369 Å) (Wunderlich and Mootz, 1971), and pyrogallol (1.38, 1.37, 1.37 Å) (Maartmann-Moe, 1965). On the other hand, the C(7)-N and the C(7)-O(2) bond lengths are approximately the same as those found in most amides (Sutton, 1965) and urea (Caron and Donohue, 1969), and in carboxylic acids (Takusagawa et al., 1971), respectively. These variations in distances along with the observed bond angles about C(7) suggest a structure having a delocalized double bond from O(2) to C(7) to N, with O(1) having slightly reduced electron density due to electron withdrawal to the rest of the carbamate group as well as electron withdrawal to the aromatic ring system.

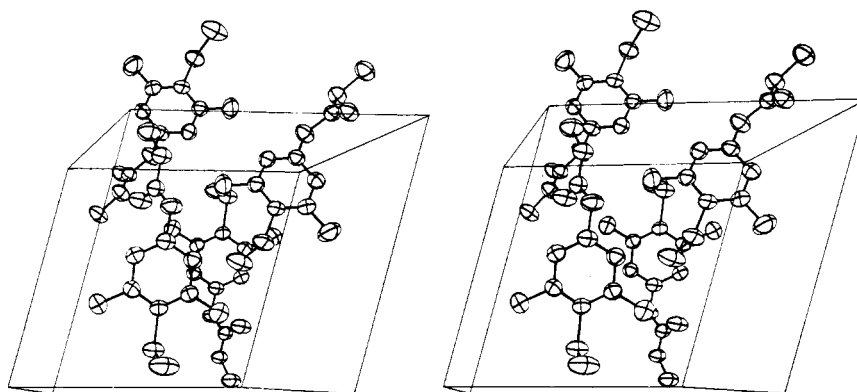


Figure 2. The crystal structure of Mesuroil as viewed down the *c* axis. The *b* axis is horizontal.

Table II. Selected Bond Lengths and Angles

	Molecule I	Molecule II
	Å	Å
C(1)-C(2)	1.369 (6)	1.373 (6)
C(1)-C(6)	1.378 (6)	1.373 (6)
C(1)-O(1)	1.399 (5)	1.418 (5)
C(2)-C(3)	1.397 (6)	1.401 (6)
C(3)-C(4)	1.407 (6)	1.386 (6)
C(3)-C(9)	1.517 (7)	1.527 (7)
C(4)-C(5)	1.402 (6)	1.392 (6)
C(4)-S	1.785 (5)	1.787 (4)
C(5)-C(6)	1.386 (6)	1.404 (6)
C(5)-C(11)	1.504 (7)	1.497 (7)
C(7)-O(1)	1.376 (5)	1.363 (5)
C(7)-O(2)	1.199 (5)	1.201 (5)
C(7)-N	1.325 (5)	1.331 (5)
C(8)-N	1.453 (6)	1.459 (6)
C(10)-S	1.793 (6)	1.786 (7)
	Deg	Deg
C(2)-C(1)-C(6)	121.4 (4)	122.7 (4)
C(2)-C(1)-O(1)	121.1 (4)	120.9 (4)
C(6)-C(1)-O(1)	117.4 (4)	116.4 (4)
C(1)-C(2)-C(3)	120.3 (4)	118.3 (5)
C(2)-C(3)-C(4)	118.4 (4)	120.1 (4)
C(2)-C(3)-C(9)	119.4 (4)	117.6 (5)
C(4)-C(3)-C(9)	122.1 (4)	122.2 (4)
C(3)-C(4)-C(5)	120.8 (4)	120.8 (4)
C(3)-C(4)-S	118.5 (3)	119.0 (4)
C(5)-C(4)-S	120.7 (4)	120.1 (4)
C(4)-C(5)-C(6)	118.8 (4)	118.8 (4)
C(4)-C(5)-C(11)	122.5 (4)	122.8 (4)
C(6)-C(5)-C(11)	118.7 (4)	118.5 (5)
C(5)-C(6)-C(1)	120.3 (4)	119.3 (4)
O(1)-C(7)-O(2)	123.0 (4)	123.7 (4)
O(1)-C(7)-N	109.4 (4)	109.5 (4)
O(2)-C(7)-N	127.7 (4)	126.8 (4)
C(1)-O(1)-C(7)	118.9 (3)	118.8 (3)
C(7)-N-C(8)	120.5 (4)	121.3 (4)
C(4)-S-C(10)	101.4 (3)	101.9 (2)

The dimensions found for this group would therefore correlate quite well with any theory that proposes ready disruption of the C(7)-O(1) bond, as is usually assumed

Table III. Hydrogen Bonds, Short Intermolecular Distance, and Angles

	(i) Hydrogen Bonds			
	H···O, Å	N···O, Å	N-H···O, deg	H···O=C, deg
N-H(1)···O(2') (1 + <i>x</i> , <i>y</i> , <i>z</i>) ^a	2.01 (6)	2.914 (5)	161 (6)	139 (2)
N'-H(1')···O(2) (-1 + <i>x</i> , <i>y</i> , 1 + <i>z</i>)	2.09 (6)	2.937 (5)	159 (6)	139 (2)
	(ii) Other Short Intermolecular Distances			
	H···O, Å	C···O, Å	C-H···O, deg	H···O-C(1), H···O-C(7), deg
C(8)-H(9)···O(1') (1 + <i>x</i> , <i>y</i> , -1 + <i>z</i>)	2.47 (6)	3.527	155 (6)	110 (2) 122 (2)
C(8')-H(9')···O(1) (1 + <i>x</i> , <i>y</i> , <i>z</i>)	2.58 (6)	3.501 (6)	154 (6)	110 (2) 123 (2)

^a Symmetry operation applied is given in parentheses.

in a discussion of the metabolic process involving carbamate insecticides and in their reaction with acetylcholinesterase (Kolbezen et al., 1954).

The maximum differences in C-C bond lengths in the aromatic ring appear to be significant judging from their estimated standard deviations (cf. Table II). However, if one considers just the 3,5-dimethyl-4-thiophenyl group itself, one would expect it would have C_{2v} symmetry, and the observed distances and angles indicate that indeed C_{2v} symmetry is closely followed, the primary deviation being between the C(2)-C(1)-O(1) and C(6)-C(1)-O(1) bond angles; such differences would be expected due to the substitution of the carbamate group which breaks the C_{2v} symmetry in the molecule as a whole and due to the O(1)-H(2) intramolecular contact. Similar effects are observed in both molecules. The dilation of the C(4)-C(5)-C(11) and C(4)-C(3)-C(9) bond angles appears to be merely due to a symmetric repulsion between the sulfur and the methyl atoms C(9) and C(11) (S-H(9), 2.85, S-H(14), 2.88 Å vs. 3.05 Å, the sum of the van der Waals radii).

A view of the unit cell is shown in Figure 2. Although one might envision N-H(1)···O(1) or N-H(1)···O(2) hydrogen bonding such as to form either chains or dimers, the only hydrogen bond type found is that involving O(2) (Table III) to link the molecules in an infinite chain.

Since neither the single bond nor the other intermolecular interactions appear short enough to indicate any appreciable interaction between molecules, it can be assumed that solid state effects do not materially influence the molecular configuration found. This is also borne out by the observation that the two symmetry independent molecules, although in a different environment, exhibit essentially the same molecular configuration.

In light of the paucity of structural information involving carbamate groups and in particular carbamate insecticides, we plan to carry out additional investigations of other carbamate insecticides of varying toxicity in order to shed more light on the structural differences, if any, that might

Table IV. Least-Squares Planes and Deviations (Å)^a

Atom	I	II	I'	II'
S	-0.044	-0.062	0.813	0.465
O(1)	0.111	0.108	0.000*	0.000*
O(2)	-1.894	-1.888	0.000*	0.000*
N	-0.492	-0.543	0.000*	0.000*
C(1)	0.006*	0.007*	0.189	0.119
C(2)	-0.002	-0.004*	1.344	1.241
C(3)	-0.001*	0.004*	1.560	1.349
C(4)	0.000*	-0.003*	0.561	0.328
C(5)	0.003*	0.003*	-0.621	-0.806
C(6)	-0.006*	-0.007*	-0.796	-0.906
C(7)	-0.866	-0.879	0.013	0.003
C(8)	-1.361	-1.440	-0.019	-0.042
C(9)	-0.036	-0.035	2.835	2.590
C(10)	1.671	1.662	1.303	1.098
C(11)	-0.010	0.008	-1.718	-1.929

^a I, $-0.195X - 0.038Y + 0.980Z = 0.790$; II, $0.191X + 0.029Y + 0.981Z = 8.873$; I', $-0.569X + 0.743Y + 0.353Z = 3.157$; II', $0.101X + 0.907Y + 0.408Z = 11.474$. The planes are defined by the atoms with an asterisk.

be found at the molecular level.

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Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes, torsional angles around the bonds, and distances and angles involving hydrogen atoms (13 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Carbamate Insecticides. 2. Aldicarb

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The crystal and molecular structure of aldicarb (2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime, C₇H₁₄N₂O₂S) has been determined by single-crystal x-ray diffraction techniques. It crystallizes in an orthorhombic unit cell, *Pcab*, with unit cell dimensions $a = 10.204$ (7), $b = 21.155$ (9), and $c = 10.003$ (7) Å and eight molecules per cell. The structure was refined to a final crystallographic discrepancy factor of 9.3% for 532 observed reflections ($|F_o| > 3\sigma_{F_o}$). Large thermal parameters resulted from the refinement due to the close proximity to a phase transition (at 13 ± 3 °C). The low-temperature phase was found to be monoclinic, *P2₁/a*, with $a = 10.25$, $b = 20.99$, and $c = 10.07$ Å and $\beta = 91.97^\circ$. The C-O single bond distance in the carbamate group was found to be significantly lengthened (1.414 Å) relative to equivalent distances found in carboxylic acid esters. Such a lengthening would correlate well with any theory involving disruption of this bond in a reaction of this molecule with acetylcholinesterase enzyme.

In recent years the chlorinated hydrocarbon insecticides have largely been replaced by the carbamate and organophosphorus insecticides. The mode of action of the carbamate and/or organophosphorus insecticides is ac-

cepted to be via the inhibition of the enzyme acetylcholinesterase. In order to better understand the stereochemical requirements necessary for efficient carbamoylation or phosphorylation of the enzyme, we have undertaken a series of structural studies of various insecticides in this laboratory (Baughman and Jacobson, 1975; Gifkins and Jacobson, 1976; Rohrbaugh et al., 1976; Takusagawa and Jacobson, 1977). It is hoped that such

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