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Organophosphorus Insecticides. 18. Famphur: *O*,*O*-Dimethyl *O*-[*p*-(*N*,*N*-Dimethylsulfamoyl)phenyl] Phosphorothioate

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Abstract

A $\delta(+)\text{P}\cdots\delta(+)\text{H}$ distance of 5.10 Å is observed in the solid state of the title compound, $C_{10}H_{16}NO_5PS_2$, and falls within the range of literature values for the separation of $\delta(-)\cdots\delta(-)$ charges in the active site of insect acetylcholinesterase (AChE). Two intramolecular C—H···O contacts reduce the rotational degrees of freedom of famphur.

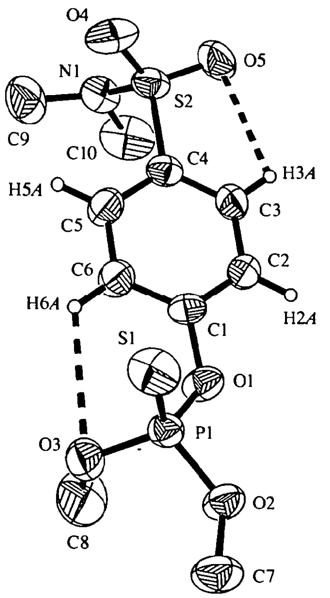
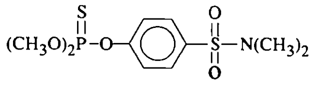


Fig. 1. View of the famphur molecule showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as small spheres of arbitrary radii and methyl H atoms have been omitted for clarity.

Comment

As part of an ongoing study of the structures of organophosphorus (OP) insecticides (Baughman & Allen, 1995, and references therein), a determination of the structure of *O*,*O*-dimethyl *O*-[*p*-(*N*,*N*-dimethylsulfamoyl)phenyl] phosphorothioate (famphur), (I), was undertaken. Accurate three-dimensional structure determinations of a series of OPs should give a better insight into any structure–activity-related interactions between the $\delta(-)\cdots\delta(-)$ centers in acetylcholinesterase (AChE) and $\delta(+)\text{P}\cdots\delta(+)$ centers in an OP insecticide.



(I)

Hollingworth, Fukuto & Metcalf (1967) give the distance range in AChE as 5.0–5.5 Å and O'Brien (1963) gives it as 4.5–5.9 Å. In famphur (Fig. 1), the $\delta(+)\text{P}\cdots\delta(+)\text{H5}A$ distance of 5.10 Å falls in the tighter range. The remaining $\text{P}\cdots\text{H}_{\text{ring}}$ distances fall outside this range: H2*A*, 3.97; H3*A*, 5.78; and H6*A*, 2.89 Å. Since all ring H atoms except for H6*A* are involved in contacts with $\delta(-)$ atoms, it would seem that the ring H atoms have sufficient $\delta(+)$ charge to partner with the $\delta(+)$P atom in enzyme inhibition.

Elongation of the P—O1 bond (*versus* P—O2 and P—O3) and shortening of the C1—O1 bond (*versus* O2—C7 and O3—C8) has been noted in all similar compounds in this series and is undoubtedly a contributing factor to the ease of hydrolysis of these compounds.

Atoms C7 and C8 point roughly in opposite directions [S1—P1—O2—C7 = 57.8 (3), S1—P1—O3—C8 = 178.4 (3) and C7—O2···O3—C8 = −96.8 (3)°]. This conclusion parallels the known preference of dipoles (*e.g.* MeO's) to point in opposite directions (Ternay, 1976). The phosphate group is tipped generally towards the H6*A* side of the molecule as the planes defined by P1, O1, C1 and the ring C atoms are at an angle of 35.4 (3)° with respect to each other and the S1 atom points back towards the H2*A* side of the molecule [S1—P1—O1—C1 = −42.4 (3)°] (see also Fig. 1). This is likely to be a result of a weak intermolecular hydrogen bond between the O3 and H6*A* atoms (Table 2). Unlike the case in leptophos oxon (Baker & Baughman, 1995), where a hydrogen bond exists between an oxygen doubly bonded to the P atom, the O3···H6*A* bond in famphur involves an sp^3-O atom. The interaction of O5 with H3*A* (see Table 2) causes the C4, S2, N1 plane to be at an angle of 65.9 (2)° with respect to the ring C atoms.

Atom N1 exhibits some pyramidalization as the sum of the three angles about it is 349.5°; all three angles are between 114.7 (4) and 118.4 (3)°, and N1 is only 0.286 (4) Å above the plane defined by atoms S2, C9 and C10. An increased interaction of the S2 atom with the π system of the phenyl ring is indicated by the S2—C4 distance of 1.772 (3) Å, which is shorter than the average C_{alkyl}—S distance (1.82 Å) observed in six compounds in this series. The shorter C_{ring}—S distance in famphur is within 3σ of the C_{ring}—S distance [1.785 (5) Å] in the carbamate insecticide mesurol (Takusagawa & Jacobson, 1977). In famphur, the two identical S=O distances [1.426 (3) Å] and the O=S=O angle [119.4 (2)°] compare quite favorably with the average of eight distances [1.432 Å] and four angles [118.3°] reported for four phenylsulfonyl-containing compounds (Zukerman-Schpector & Monteiro, 1996; Chen *et al.*, 1996; Bolte & Berger, 1996). These distances are shorter than the single-bond S—O distances [1.512 (2) and 1.511 (4) Å] for the DMSO ligands in $[Cd(NCS)_2(4\text{-dmap})_2].2DMSO$ and $[Cd(NCSe)_2(4\text{-dmap})_2].2DMSO$, respectively (Secondo *et al.*, 1997), indicating that S=O double-bond character is present in famphur.

Table 1. *Selected geometric parameters (Å, °)*

S1—P1	1.9009 (12)	P1—O1	1.591 (2)
S2—O4	1.426 (3)	O1—C1	1.396 (3)
S2—O5	1.426 (3)	O2—C7	1.443 (4)
S2—N1	1.618 (3)	O3—C8	1.450 (5)
S2—C4	1.772 (3)	N1—C10	1.455 (5)
P1—O3	1.556 (2)	N1—C9	1.461 (5)
P1—O2	1.561 (2)		
O4—S2—O5	119.4 (2)	O2—P1—O1	95.17 (12)
O4—S2—N1	106.7 (2)	O3—P1—S1	111.02 (11)
O5—S2—N1	106.9 (2)	O2—P1—S1	118.73 (10)
O4—S2—C4	107.77 (15)	O1—P1—S1	116.57 (10)
O5—S2—C4	107.23 (15)	C1—O1—P1	125.2 (2)
N1—S2—C4	108.41 (14)	C10—N1—C9	114.7 (4)
O3—P1—O2	107.21 (13)	C10—N1—S2	116.4 (3)
O3—P1—O1	106.54 (14)	C9—N1—S2	118.4 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···O5	0.96	2.48	2.885 (5)	105
C6—H6*A*···O3	0.96	2.72	3.348 (5)	124

Experimental

The title compound was obtained from the Quality Assurance Section, Pesticides and Toxic Substances Laboratory, USEPA, Research Triangle Park, NC, USA.

Crystal data

$C_{10}H_{16}NO_5PS_2$
$M_r = 325.33$
Monoclinic
$P2_1/c$
$a = 12.786\ (2)$ Å
$b = 10.290\ (2)$ Å
$c = 13.095\ (2)$ Å
$\beta = 118.70\ (1)°$
$V = 1511.2\ (4)$ Å^3
$Z = 4$
$D_x = 1.430$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 7.4$–$12.5°$
$\mu = 0.471$ mm^{-1}
$T = 293\ (2)$ K
Block cut from larger crystal
$0.44 \times 0.38 \times 0.28$ mm
Colorless

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3623 measured reflections
2669 independent reflections
1961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.009$

$\theta_{max} = 25.05°$
$h = -1 \rightarrow 15$
$k = -1 \rightarrow 12$
$l = -15 \rightarrow 14$
3 standard reflections every 50 reflections intensity decay: average of 1.2% in $\sigma(I)$'s

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.125$
$S = 1.052$
2660 reflections
173 parameters
H atoms riding (C—H 0.96 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.7937P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.262$ e Å^{-3}
$\Delta\rho_{min} = -0.246$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0055 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991*a*). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL/PC* and *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1316). Services for accessing these data are described at the back of the journal.

References

Baker, S. M. & Baughman, R. G. (1995). *J. Agric. Food Chem.* **43**, 503–506.
Baughman, R. G. & Allen, J. L. (1995). *Acta Cryst.* **C51**, 521–523.
Bolte, M. & Berger, B. (1996). *Acta Cryst.* **C52**, 1987–1989.
Chen, Y.-S., Khan, M., Rao, S. N., Krishnaiah, M. & Narayana Raju, K. V. (1996). *Acta Cryst.* **C52**, 1847–1849.
Hollingworth, R. M., Fukuto, T. R. & Metcalf, R. L. (1967). *J. Agric. Food Chem.* **15**, 235–241.
O'Brien, R. D. (1963). *J. Agric. Food Chem.* **11**, 163–166.
Secondo, P. M., Land, J. M., Collier, H. L. & Baughman, R. G. (1997). *Inorg. Chem.* Submitted.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1991*a*). *P3/P4-PC Diffractometer Program.* Version 4.23. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1991*b*). *XDISK. Data Reduction Program.* Version 4.20.2PC. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Takusagawa, F. & Jacobson, R. A. (1977). *J. Agric. Food Chem.* **25**, 329–333.
Ternay, A. L. Jr (1976). *Contemporary Organic Chemistry*, p. 822. Philadelphia: W. B. Saunders.
Zukerman-Schpector, J. & Monteiro, H. J. (1996). *Acta Cryst.* **C52**, 1767–1770.