of 103·9 (4)° inside the five-membered ring and 114·4 (4)° outside. A second sp^3 atom having an angle of 114·4 (4)° is C(3) which indicates a moderate strain due, apparently, to steric reasons. The major angular deviations in the sp^2 atoms are observed at C(1) [110·6 (5)°] and C(8b) [109·8 (5)°] which are also due to their involvement in the five-membered ring. The α,β-unsaturated keto system in the molecules assumes a near-ideal coplanar arrangement as evidenced by the least-squares plane of O(6), C(6), C(7), C(5a), C(8b), C(7), C(5), and C(2a) [maximum deviation 0·090 (6) Å for C(2a)]. Both unsaturated six-membered rings have near-ideal sofa conformations (Duax, Weeks & Rohrer, 1976) with C(8) 0·63 Å from one five-atom plane and C(3) 0·71 Å from the other. The five-membered C ring has the envelope conformation with C(8b) 0·39 Å from the four-atom plane while the other five-membered ring has the half-chair conformation with O(*K*2) 0·19 Å above the three-atom plane and C(*K*2) 0·17 Å below. The closest contact between two molecules is through the hydrogen bond at H(O3): the O(3)···O(6) distance is 2·909 (5) Å and the angle at H(O3) is 158·1 (5)°. The hydrogen bonding results in a polymeric chain around the twofold screw axis.

We thank NSF (CHE 78-20347) for the partial funding of the Enraf–Nonius CAD-4 instrument used for this study.

References

Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Top. Stereochem.* **9**, 271–383.

Enraf–Nonius (1983). *Structure Determination Package.* Enraf–Nonius, Delft.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Nassim, B., Schlemper, E. O. & Crabbé, P. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 2337–2347.

Acta Cryst. (1985). C**41**, 1667–1669

Structure of (*S*)-*N*-[Methyl(phenyl)phosphinothioyl]camphorimide

By Clair J. Cheer* and Edward F. Martz

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, *USA*

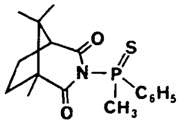
and David N. Harpp* and B. F. Friedlander

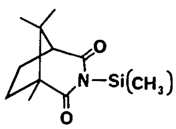
Department of Chemistry, McGill University, Montreal, PQ, Canada H3A 2K6

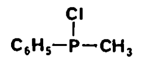
(*Received* 23 *July* 1984; *accepted* 16 *July* 1985)

Abstract. $C_{17}H_{22}NO_2PS$, $M_r = 335{\cdot}40$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}5279\,(34)$, $b = 20{\cdot}4614\,(38)$, $c = 6{\cdot}9103\,(11)$ Å, $V = 1771{\cdot}4$ Å^3, $Z = 4$, $D_m = 1{\cdot}31\,(1)$, $D_x = 1{\cdot}26$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}69$ cm^{-1}, $F(000) = 712$, $T = 295\,(2)$ K, $R(wR) = 0{\cdot}0410\,(0{\cdot}0437)$ for 1627 observed independent reflections [$F > 2{\cdot}5\sigma(F)$], goodness-of-fit = 1·039. The material was obtained as a mixture of diastereoisomers by condensing (+)-*N*-(trimethylsilyl)camphorimide (2) with chloro(methyl)phenylphosphine (3), followed by sulfuration with elemental sulfur. The higher-melting less-soluble (−) diastereoisomer produced crystals suitable for X-ray studies. The absolute configuration at phosphorus was inferred to be *S* from the known absolute configuration of (+)-camphor [Oonk (1965). PhD thesis, Univ. of Utrecht]. The imide group is not planar; the N atom lies out of the plane of the C=O groups. It is also out of the plane of the P and imide C atoms.

Introduction. As part of a program designed to prepare chiral sulfur and phosphorus compounds (Harpp, Vines, Montillier & Chan, 1976), we synthesized *N*-[methyl(phenyl)phosphinothioyl]camphorimide (1). We felt that it might serve as a general reagent from which to construct a variety of chiral P^{IV} derivatives by displacement with various nucleophiles. A number of these synthetic transformations have been successful and will be reported elsewhere.


(1)


(2)


$C_6H_5-\overset{Cl}{P}-CH_3$
(3)

---

* To whom all correspondence should be addressed.

Experimental. A mixture of diastereoisomers of (1) was prepared (Friedlander, 1980) by first condensing (+)-*N*-(trimethylsilyl)camphorimide (2) with chloro(methyl)phenylphosphine (3). This was followed by sulfuration with elemental sulfur in benzene. The benzene-insoluble material was repeatedly recrystallized from CH_2Cl_2/hexane to give a diastereoisomer having $[\alpha]_D^{25\,^{\circ}\mathrm{C}}$ $-139°$, m.p. 486–488 K. The mass spectra, proton magnetic resonance spectra and combustion analyses were consistent with the structure of (1). [The other diastereoisomer ($[\alpha]_D^{25\,^{\circ}\mathrm{C}}$ $-164°$, m.p. 472–474 K) was isolated from the benzene-soluble fraction above.] Air-stable crystals of (1) resulted from slow evaporation of a hexane/ethyl acetate solution.

Crystal, approximately 0·15 × 0·15 × 0·3 mm, used for initial data collection. Density determined by flotation in carbon tetrachloride/hexane. Nicolet R3M/E auto-diffractometer. Lattice parameters determined by least-squares fit of 25 automatically centered reflections in range $28·0 < 2\theta < 30·0°$. 1859 reflections (of which 120 check reflections and 11 systematically absent) collected in range $3·5 < 2\theta < 50°$, index range *h* 0–9, *k* 0–15, *l* 1–25, variable-speed (1·00–29·30° min^{-1}) θ–2θ scans, 3 check reflections (0,0,12, 407, 1,1,13) measured every 45 reflections. Omission of *hk*0 data inadvertent. Second crystal, approximately 0·10 × 0·10 × 0·20 mm, used to collect additional data in index range *h* 0–9, *k* 0–15, *l* 0, using same parameters as above. 102 additional reflections collected [of which 10 systematically absent and 12 check reflections (0,0,12, 407, 1,1,13)]. Two data sets scaled (scale factors 1·2303 and 0·8130 for the two data sets, respectively) and merged to give final data set of 1808 unique reflections, one of which, 020, partly obscured by beam stop and omitted. Of remaining 1807, 1627 had intensities greater than $2·5\sigma(F)$, were considered observed

Table 2. *Bond lengths* (Å) *and bond angles* (°)

S–P	1·933 (6)	P–N	1·750 (6)
P–C(1)	1·810 (6)	P–C(7)	1·790 (7)
N–C(8)	1·403 (6)	N–C(13)	1·431 (6)
O(1)–C(8)	1·210 (5)	O(2)–C(13)	1·195 (6)
C(1)–C(2)	1·375 (7)	C(1)–C(6)	1·382 (7)
C(2)–C(3)	1·392 (7)	C(3)–C(4)	1·365 (8)
C(4)–C(5)	1·371 (8)	C(5)–C(6)	1·379 (7)
C(8)–C(9)	1·505 (7)	C(9)–C(10)	1·531 (7)
C(9)–C(14)	1·532 (7)	C(10)–C(11)	1·520 (8)
C(11)–C(12)	1·558 (7)	C(12)–C(13)	1·519 (7)
C(12)–C(14)	1·546 (6)	C(12)–C(17)	1·523 (7)
C(14)–C(15)	1·530 (7)	C(14)–C(16)	1·508 (7)
S–P–N	114·8 (2)	S–P–C(1)	115·5 (2)
N–P–C(1)	102·4 (2)	S–P–C(7)	114·2 (2)
N–P–C(7)	105·2 (3)	C(1)–P–C(7)	103·2 (3)
P–N–C(8)	120·9 (3)	P–N–C(13)	117·3 (3)
C(8)–N–C(13)	119·9 (3)	P–C(1)–C(2)	120·6 (3)
P–C(1)–C(6)	119·3 (3)	C(2)–C(1)–C(6)	120·1 (4)
C(1)–C(2)–C(3)	119·0 (4)	C(2)–C(3)–C(4)	121·2 (5)
C(3)–C(4)–C(5)	119·3 (5)	C(4)–C(5)–C(6)	120·7 (5)
C(1)–C(6)–C(5)	119·8 (4)	N–C(8)–O(1)	120·9 (3)
N–C(8)–C(9)	115·4 (3)	O(1)–C(8)–C(9)	123·7 (4)
C(8)–C(9)–C(10)	107·6 (3)	C(8)–C(9)–C(14)	111·7 (3)
C(10)–C(9)–C(14)	103·9 (3)	C(9)–C(10)–C(11)	105·0 (4)
C(10)–C(11)–C(12)	105·7 (4)	C(11)–C(12)–C(13)	106·6 (3)
C(11)–C(12)–C(14)	103·3 (3)	C(13)–C(12)–C(14)	107·6 (3)
C(11)–C(12)–C(17)	113·2 (4)	C(13)–C(12)–C(17)	109·6 (4)
C(14)–C(12)–C(17)	115·7 (3)	N–C(13)–O(2)	119·4 (3)
N–C(13)–C(12)	116·2 (3)	O(2)–C(13)–C(12)	124·4 (4)
C(9)–C(14)–C(12)	98·9 (3)	C(9)–C(14)–C(15)	110·3 (3)
C(12)–C(14)–C(15)	111·2 (3)	C(9)–C(14)–C(16)	113·4 (4)
C(12)–C(14)–C(16)	114·0 (3)	C(15)–C(14)–C(16)	108·7 (3)

Table 1. *Atom coordinates* (×10^4) *and temperature factors* (Å^2 ×10^3)

	x	*y*	*z*	*U**
S	8900 (1)	4163 (1)	6740 (2)	63 (1)
P	9280 (1)	4220 (1)	4034 (1)	41 (1)
N	9815 (2)	3503 (1)	3050 (4)	37 (1)
O(1)	8187 (2)	3047 (1)	2488 (5)	62 (1)
O(2)	11391 (2)	3700 (1)	4566 (5)	71 (1)
C(1)	10288 (3)	4821 (2)	3444 (6)	44 (1)
C(2)	10572 (3)	4934 (2)	1553 (6)	57 (1)
C(3)	11355 (4)	5398 (2)	1156 (8)	70 (2)
C(4)	11826 (4)	5748 (2)	2605 (8)	70 (2)
C(5)	11523 (4)	5638 (2)	4483 (7)	65 (2)
C(6)	10760 (3)	5175 (2)	4916 (6)	53 (1)
C(7)	8195 (3)	4434 (2)	2474 (8)	66 (2)
C(8)	9148 (3)	3006 (2)	2344 (5)	42 (1)
C(9)	9710 (3)	2446 (2)	1366 (5)	43 (1)
C(10)	10214 (4)	2709 (2)	−495 (6)	65 (2)
C(11)	11294 (3)	2976 (2)	122 (6)	63 (1)
C(12)	11405 (3)	2804 (2)	2309 (6)	42 (1)
C(13)	10916 (3)	3367 (2)	3435 (5)	43 (1)
C(14)	10664 (3)	2205 (1)	2553 (5)	40 (1)
C(15)	11149 (4)	1595 (2)	1623 (7)	63 (1)
C(16)	10388 (4)	2052 (2)	4628 (6)	63 (1)
C(17)	12558 (3)	2706 (2)	2946 (8)	68 (2)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

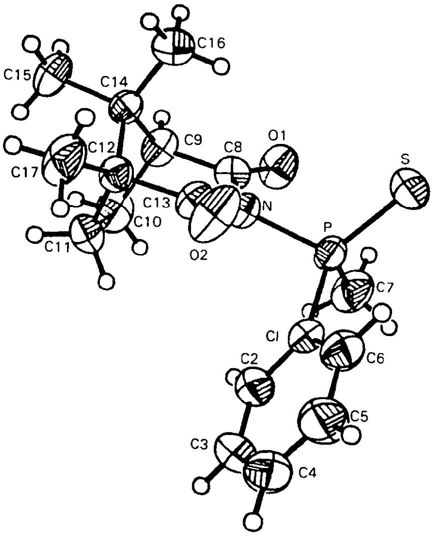


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (*S*)-*N*-[methyl(phenyl)phosphinothioyl]camphorimide, (1). Thermal ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

and used in refinement. Structure solved using program package *SHELXTL* (Nicolet XRD Corp., Freemont, CA) version of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); positional and anisotropic thermal parameters for non-hydrogen atoms refined, based on F, by blocked-cascade least squares, all hydrogen atoms located from difference Fourier map. Hydrogen atoms fixed at idealized (C—H = 0·96 Å) positions, thermal parameters set at 1·2 times equivalent isotropic thermal parameter of bonded atoms, not refined. Final discrepancy indices, $R = 0{\cdot}0410$, $wR = 0{\cdot}0437$, $R_G = 0{\cdot}0515$ and GOF = 1·039 for 1627 reflections with $F > 2{\cdot}5\sigma(F)$. Weighting scheme: $w = 1/[\sigma^2(F_o) + 0{\cdot}00142(F_o)^2]$, $\sigma(F_o)$ determined from counting statistics, $wR = \sum(||F_o| - |F_c||w^{1/2})/\sum(|F_o|w^{1/2})$, $R_G = \{\sum[w(||F_o| - |F_c||)^2]/\sum[w(|F_o|)^2]\}^{1/2}$, 211 parameters refined. Max. $\Delta/\sigma = 0{\cdot}029$ in final least-squares cycle. Final difference Fourier map showed max. and min. peaks of 0·159 and −0·201 e Å^{-3}. All calculations performed using Data General Eclipse computer with *SHELXTL* programs, which use complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. Final atomic parameters are listed in Table 1 and bond lengths and angles in Table 2. The structure is shown in Fig. 1. The absolute configuration at phosphorus is *S*, inferred by reference to the known stereochemistry of (+)-camphor (Oonk, 1965; see also Allen & Rogers, 1971) [and hence (+)-*N*-(trimethylsilyl)camphorimide (2) (Oonk, 1965)]. The correct enantiomorph was fortuitously chosen by the *SHELXTL* program. The imide function deviates significantly from planarity, the N atom lies 0·4163 Å below* the least-squares plane composed of O(1), C(8), C(13) and O(2). The nitrogen itself lies 0·1202 Å below* the C(8), C(13), P plane.

---

* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates, torsion angles and details of least-squares molecular planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42382 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Defined using the perspective shown in Fig. 1.

References

Allen, F. H. & Rogers, D. (1971). *J. Chem. Soc. B*, pp. 632–636.

Friedlander, B. F. (1980). PhD thesis, McGill Univ., Montreal, Canada.

Harpp, D. N., Vines, S. M., Montillier, J.-P. & Chan, T. H. (1976). *J. Org. Chem.* **41**, 3987–3991.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 55, 99 and 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain-la-Neuve, Belgium.

Oonk, H. A. J. (1965). PhD thesis, Univ. of Utrecht, The Netherlands.

Acta Cryst. (1985). C**41**, 1669–1672

4-Dimethylamino-1-phenyl-1,2,3,5-tetrazin-6-one (I), 5-Dimethylamino-2,3-dihydro-3-oxo-2-*p*-tolylimino-1*H*-1,2,4-triazol-2-ium-1-ide Monohydrate (II) and 1-*o*-Chlorophenylimino-3,5-bis(dimethylamino)-1,2,4-triazolium Tetrafluoroborate (III)

By Peter F. Lindley and Adrial R. Walton

Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, England

and Ahmet E. Baydar and Gerhard V. Boyd*

Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX, England

(*Received* 25 *March* 1985; *accepted* 2 *July* 1985)

Abstract. (I): $C_{10}H_{11}N_5O$, $M_r = 217{\cdot}2$, orthorhombic, *Pbca*, $a = 23{\cdot}510$ (1), $b = 11{\cdot}169$ (1), $c = 7{\cdot}777$ (1) Å, $U = 2042$ (1) Å^3, $Z = 8$, $D_x = 1{\cdot}413$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}828$ mm^{-1}, $F(000) = 912$, $T = 278$ (1) K, $R = 0{\cdot}050$ for 645 significant reflections. (II): $C_{11}H_{13}N_5O.H_2O$, $M_r = 249{\cdot}3$, triclinic, $P\bar{1}$, $a = 7{\cdot}930$ (1), $b = 12{\cdot}186$ (1), $c = 6{\cdot}919$ (1) Å, $\alpha =$

---

* Current address: Department of Chemistry, Queen Elizabeth College, Campden Hill, London W8 7AH, England.