C(31A)	0.6267 (3)	0.6144 (2)	0.2100 (2)	0.044 (1)
O(30A)	0.6866 (2)	0.7353 (2)	0.2522 (2)	0.062 (1)
O(31A)	0.4650 (2)	0.5708 (2)	0.1955 (2)	0.068 (1)
C(1B)	0.1412 (2)	0.2520 (2)	0.4240 (2)	0.035 (1)
C(2B)	0.1530 (3)	0.1295 (2)	0.3481 (2)	0.036 (1)
C(3B)	0.0036 (2)	0.0338 (2)	0.3145 (2)	0.035 (1)
N(3B)	0.0135 (3)	−0.0907 (2)	0.2275 (2)	0.042 (1)
C(4B)	−0.1549 (3)	0.0553 (2)	0.3562 (2)	0.041 (1)
C(5B)	−0.1649 (3)	0.1765 (2)	0.4338 (2)	0.045 (1)
C(6B)	−0.0171 (3)	0.2753 (2)	0.4669 (2)	0.041 (1)
O(10B)	0.2840 (2)	0.4812 (1)	0.5022 (2)	0.050 (1)
O(11B)	0.4443 (2)	0.3223 (2)	0.4372 (2)	0.054 (1)
C(11B)	0.2992 (3)	0.3597 (2)	0.4575 (2)	0.038 (1)
OW(1)	0.1904 (2)	0.0097 (2)	0.9851 (2)	0.050 (1)
OW(2)	0.3627 (3)	0.8709 (3)	0.2380 (3)	0.082 (1)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

N(1A)—C(6A)	1.323 (3)	C(31A)—O(31A)	1.272 (3)
N(1A)—C(2A)	1.342 (2)	C(1B)—C(6B)	1.385 (3)
C(2A)—C(3A)	1.403 (3)	C(1B)—C(2B)	1.392 (3)
C(2A)—C(21A)	1.533 (3)	C(1B)—C(11B)	1.487 (3)
C(3A)—N(4A)	1.347 (2)	C(2B)—C(3B)	1.380 (3)
C(3A)—C(31A)	1.529 (3)	C(3B)—C(4B)	1.377 (3)
N(4A)—C(5A)	1.323 (3)	C(3B)—N(3B)	1.466 (2)
C(5A)—C(6A)	1.381 (3)	C(4B)—C(5B)	1.387 (3)
C(21A)—O(21A)	1.204 (3)	C(5B)—C(6B)	1.385 (3)
C(21A)—O(20A)	1.267 (3)	O(10B)—C(11B)	1.252 (2)
C(31A)—O(30A)	1.219 (3)	O(11B)—C(11B)	1.277 (2)

C(6A)—N(1A)—C(2A)	118.8 (2)	O(31A)—C(31A)—C(3A)	119.4 (2)
N(1A)—C(2A)—C(3A)	120.1 (2)	C(6B)—C(1B)—C(2B)	120.4 (2)
N(1A)—C(2A)—C(21A)	111.4 (2)	C(6B)—C(1B)—C(11B)	119.9 (2)
C(3A)—C(2A)—C(21A)	128.5 (2)	C(2B)—C(1B)—C(11B)	119.7 (2)
N(4A)—C(3A)—C(2A)	120.2 (2)	C(3B)—C(2B)—C(1B)	118.5 (2)
N(4A)—C(3A)—C(31A)	111.1 (2)	C(4B)—C(3B)—C(2B)	121.9 (2)
C(2A)—C(3A)—C(31A)	128.7 (2)	C(4B)—C(3B)—N(3B)	119.2 (2)
C(5A)—N(4A)—C(3A)	118.2 (2)	C(2B)—C(3B)—N(3B)	118.9 (2)
N(4A)—C(5A)—C(6A)	121.6 (2)	C(3B)—C(4B)—C(5B)	119.2 (2)
N(1A)—C(6A)—C(5A)	120.9 (2)	C(6B)—C(5B)—C(4B)	120.1 (2)
O(21A)—C(21A)—O(20A)	122.2 (2)	C(1B)—C(6B)—C(5B)	120.0 (2)
O(21A)—C(21A)—C(2A)	117.9 (2)	O(10B)—C(11B)—O(11B)	123.6 (2)
O(20A)—C(21A)—C(2A)	119.9 (2)	O(10B)—C(11B)—C(1B)	119.1 (2)
O(30A)—C(31A)—O(31A)	121.7 (2)	O(11B)—C(11B)—C(1B)	117.3 (2)
O(30A)—C(31A)—C(3A)	118.9 (2)		

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least squares with anisotropic displacement parameters for all non-H atoms. H-atom positions were located by difference methods and included in the respective refinements with both positional and isotropic displacement parameters refined.

For both compounds, data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON*92 (Spek, 1990).

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Novel Six- and Eight-Membered Heterocycles. A Trithiadiazaphosphorinane and a Pentathiadiazaphosphocine

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Abstract

We report the single-crystal X-ray structure determinations of two novel phosphorus-, nitrogen- and sulfur-containing heterocycles, namely, 4,6-bis[2-(2-methyl)-propyl]-5-oxo-5-phenyl-1,2,3,4,6,5-trithiadiazaphosphorinane, $C_{14}H_{23}N_2OPS_3$, and 6,8-bis[2-(2-methyl)propyl]-7-oxo-7-phenyl-1,2,3,4,5,6,8,7-pentathiadiazaphosphocine, $C_{14}H_{23}N_2OPS_5$. The phosphorinane compound is

unusual in that it displays a high degree of steric compression in the S—S—S bond angle, which has a value of only 96.3°. The phosphocine compound has bond angles similar to those found in S_8 rings. One S—S—S—S torsion angle, however, is compressed to 30°. The phosphocine has two conformationally identical molecules in the asymmetric unit.

Comment

There has recently been some interest in sulfur-containing cyclic systems, both for their biological activity (Behar & Danishefsky, 1993) and as precursors for diatomic sulfur (Salama, Steliou & Yu, 1992). We have been involved in attempts at generating new forms of sulfurated heterocycles of interest in these and other areas (Bottle et al., 1993). We now report the single-crystal X-ray structure determinations of two unusual phosphorus-, nitrogen- and sulfur-containing heterocycles, one six-membered, 4,6-bis[2-(2-methyl)propyl]-5-oxo-5-phenyl-1,2,3,4,6,5-trithiadiazaphosphorinane, (1), the other eight-membered, 6,8-bis[2-(2-methyl)propyl]-7-oxo-7-phenyl-1,2,3,4,5,6,8,7-pentathiadiazaphospho-cine, (2). These unusual compounds were isolated as minor by-products of the reaction of sulfur monochloride with di-tert-butylphenylphosphonic diamide. Both compounds (1) and (2) were present as equilibrium components of a complex mixture of other phosphorus-, nitrogen- and sulfur-containing heterocycles, as well as elemental sulfur. The major component of the mixture was a seven-membered tetrathia heterocycle, (3), the structure of which has been published recently (Bottle et al., 1993).

(1)   (2)   (3)
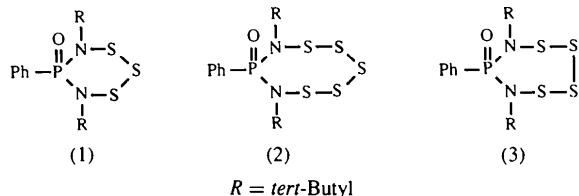
$R = tert$-Butyl

The molecular of (1) (Fig. 1) displays a remarkably symmetrical chair arrangement with the bulky tert-butyl groups and phosphonic O atom occupying pseudo-equatorial positions. This conformation allows the best extension of π bonding through the O—P—N—S system, which is supported by the torsion angles between these atoms [175.1 (1) and −175.1 (1)°]. In this regard, compound (1) differs from the seven-membered-ring analogue (3) (Bottle et al., 1993) which has angles of −107.5 (2) and 159.3 (1)°. With respect to the bond lengths and the planarity around the N atom, however, the six-membered ring of compound (1) displays similar structural characteristics to the seven-membered analogue of (3). The geometry about each N atom is quite planar, indicating much sp^2 character arising from significant $d\pi$–$p\pi$ overlap with the P atom. The S—

N and P—N bond lengths in (1) are all within 1% of those in the analogous seven-membered system. There is minor variation of the S—S bond lengths, which, at 2.058 (1) and 2.065 (1) Å in (1), are intermediate between the values of 2.043 (1) and 2.071 (1) Å found for compound (3). The most significant difference relates to the S—S—S bond angle, which has been compressed substantially to 96.3 (4)° from the usual value of 108° in S_8 (Abrahams, 1961) and of over 100° in the seven-membered-ring tetrasulfide (Bottle et al., 1993). In addition, the S—S—S—N torsion angles [66.3 (1) and −66.4 (1)°] are small for such sulfur rings, e.g. in S_8 they are close to 100° (Abrahams, 1961) and in S_6 74.5° (Caron, Donohue & Goldfish, 1961). This compression would give rise to an increase of the overall strain in the molecule, resulting in compound (1) being less favoured thermodynamically.
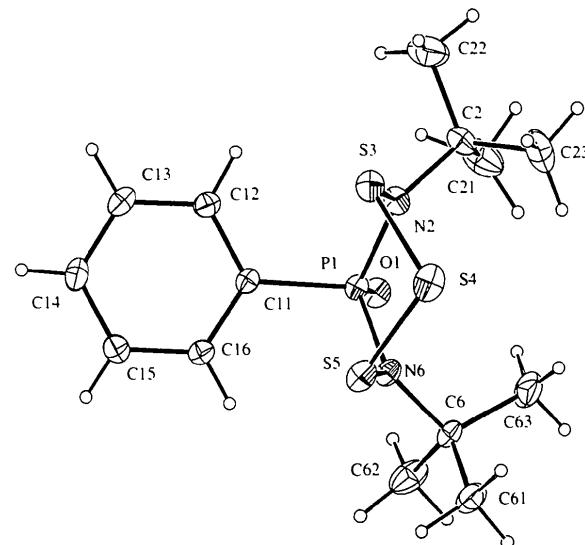
Fig. 1. Molecular configuration and atom-numbering scheme for compound (1) shown with 20% probability displacement ellipsoids.

For the eight-membered heterocyclic compound (2) (Fig. 2), there are two independent but conformationally identical molecules in the asymmetric unit. These two molecules are not related by any crystallographic symmetry. The geometries about the N atoms in these molecules are again quite planar, indicating similar $d\pi$–$p\pi$ overlap with the P atom. As expected, the N—S bond lengths (average 1.695 Å) are similar to those of related systems in which the N atom is sp^2 hybridized (Engelsein, Kalker, Lex & Linke, 1974). The S—S—S bond angles have an average value of 105.4° and are quite normal for S_8 rings (Abrahams, 1961). One of the S—S—S—S torsion angles [96.3 (2) (molecule 1) and −96.1 (2)° (molecule 2)] is also as expected for eight-membered sulfur rings. The second S—S—S—S torsion angle, however, is unusually small [−32.9 (2) (molecule 1) and −30.9 (2)° (molecule 2)].

This compression increases the overall strain in the molecule and explains why compound (2) is a minor component in the reaction mixture.
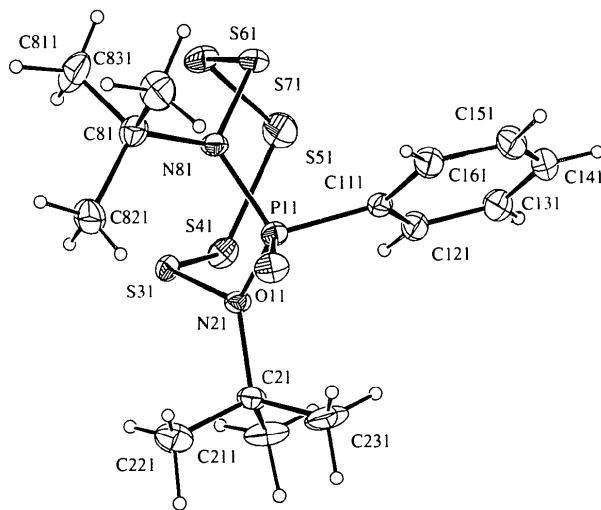
Fig. 2. Molecular configuration and atom-numbering scheme for compound (2) shown with 20% probability displacement ellipsoids.

Experimental

The phosphorinane (1) and the phosphocine (2) were prepared by the action of sulfur monochloride (S_2Cl_2, 220 mg, 1.6 mmol) on di-*tert*-butylphenylphosphonic diamide (200 mg, 0.75 mmol), with pyridine (5 ml) being used as both solvent and base. Upon addition of the S_2Cl_2, a creamy precipitate of pyridinium hydrochloride formed (confirmed by NMR). The solvent was removed under high vacuum and worked up *via* standard extraction procedures. Flash chromatography (EtOAc, $CHCl_3$ and 60–80 hexanes, 1:1:2) was used to separate the products from elemental sulfur and other by-products. The compounds were further purified by reversed-phase MPLC (medium pressure liquid chromatography) using a Büchi system. This gave phosphorinane (1) (17 mg; 6.3% yield) as a white powder, which was recrystallized from MeOH to give needles (m.p. 435–436 K), and phosphocine (2) (26 mg; 8.2% yield) as a yellow/white powder, which on recrystallization from acetonitrile gave prisms (m.p. 400–402 K). Both original specimens used for X-ray analysis were cleaved from larger crystals.

Compound (1)

Crystal data
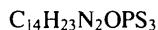
$C_{14}H_{23}N_2OPS_3$
$M_r = 362.5$
Monoclinic
$P2_1/a$
$a = 14.002\,(3)$ Å
$b = 9.0989\,(6)$ Å
$c = 15.413\,(4)$ Å
$\beta = 114.24\,(1)°$
$V = 1790.6\,(6)$ Å^3
$Z = 4$
$D_x = 1.345$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–14°$
$\mu = 0.503$ mm^{-1}
$T = 298\,(2)$ K
Prismatic
$0.35 \times 0.25 \times 0.12$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3290 measured reflections
3146 independent reflections
2557 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.049$
$\theta_{max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 10$
$l = -18 \rightarrow 16$
3 standard reflections monitored every 250 reflections
intensity decay: 0.5%

Refinement

Refinement on F^2
$R(F) = 0.0367$
$wR(F^2) = 0.1133$
$S = 0.959$
3146 reflections
282 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 0.99P]$
where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P(1)	0.7165 (1)	0.0632 (1)	0.2044 (1)	0.035 (1)
O(1)	0.6275 (1)	0.1626 (2)	0.1612 (1)	0.048 (1)
N(2)	0.8042 (2)	0.1261 (2)	0.3106 (1)	0.043 (1)
C(2)	0.7918 (2)	0.2477 (3)	0.3739 (2)	0.056 (1)
C(21)	0.6919 (4)	0.3360 (5)	0.3241 (4)	0.096 (2)
C(22)	0.8870 (4)	0.3476 (6)	0.4000 (4)	0.097 (1)
C(23)	0.7926 (5)	0.1777 (6)	0.4644 (3)	0.094 (1)
S(3)	0.9144 (1)	0.0244 (1)	0.3608 (1)	0.052 (1)
S(4)	0.8605 (1)	-0.1700 (1)	0.3949 (1)	0.065 (1)
S(5)	0.7717 (1)	-0.2353 (1)	0.2566 (1)	0.054 (1)
N(6)	0.6755 (1)	-0.1082 (2)	0.2159 (1)	0.041 (1)
C(6)	0.5663 (2)	-0.1431 (3)	0.2101 (2)	0.045 (1)
C(61)	0.5594 (3)	-0.3035 (4)	0.2342 (3)	0.065 (1)
C(62)	0.4885 (3)	-0.1162 (6)	0.1077 (3)	0.081 (1)
C(63)	0.5443 (4)	-0.0490 (5)	0.2813 (4)	0.084 (1)
C(11)	0.7895 (2)	0.0403 (3)	0.1324 (2)	0.036 (1)
C(12)	0.8712 (2)	0.1338 (3)	0.1413 (2)	0.043 (1)
C(13)	0.9140 (2)	0.1312 (3)	0.0746 (2)	0.051 (1)
C(14)	0.8756 (2)	0.0356 (4)	-0.0008 (2)	0.055 (1)
C(15)	0.7950 (2)	-0.0579 (4)	-0.0101 (2)	0.058 (1)
C(16)	0.7521 (2)	-0.0561 (3)	0.0560 (2)	0.049 (1)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

P(1)—O(1)	1.461 (2)	S(5)—N(6)	1.689 (2)
P(1)—N(2)	1.693 (2)	N(6)—C(6)	1.529 (3)
P(1)—N(6)	1.696 (2)	C(6)—C(61)	1.519 (4)
P(1)—C(11)	1.803 (2)	C(6)—C(63)	1.520 (4)
N(2)—C(2)	1.530 (3)	C(6)—C(62)	1.524 (4)
N(2)—S(3)	1.700 (2)	C(11)—C(16)	1.387 (4)
C(2)—C(21)	1.520 (5)	C(11)—C(12)	1.387 (3)
C(2)—C(22)	1.524 (5)	C(12)—C(13)	1.386 (4)
C(2)—C(23)	1.530 (5)	C(13)—C(14)	1.373 (4)
S(3)—S(4)	2.0584 (11)	C(14)—C(15)	1.373 (4)
S(4)—S(5)	2.0651 (13)	C(15)—C(16)	1.380 (4)
O(1)—P(1)—N(2)	112.07 (10)	C(6)—N(6)—S(5)	120.4 (2)
O(1)—P(1)—N(6)	110.76 (10)	C(6)—N(6)—P(1)	123.9 (2)
N(2)—P(1)—N(6)	110.61 (10)	S(5)—N(6)—P(1)	114.56 (11)
O(1)—P(1)—C(11)	112.60 (10)	C(61)—C(6)—C(63)	108.2 (3)
N(2)—P(1)—C(11)	105.42 (10)	C(61)—C(6)—C(62)	108.5 (3)
N(6)—P(1)—C(11)	105.05 (10)	C(63)—C(6)—C(62)	112.8 (3)

C(2)—N(2)—P(1)	129.4 (2)	C(61)—C(6)—N(6)	110.3 (2)		
C(2)—N(2)—S(3)	115.5 (2)	C(63)—C(6)—N(6)	109.6 (2)		
P(1)—N(2)—S(3)	114.49 (12)	C(62)—C(6)—N(6)	107.4 (2)		
C(21)—C(2)—C(22)	110.0 (4)	C(16)—C(11)—C(12)	118.8 (2)		
C(21)—C(2)—C(23)	110.0 (4)	C(16)—C(11)—P(1)	118.9 (2)		
C(22)—C(2)—C(23)	109.2 (4)	C(12)—C(11)—P(1)	121.4 (2)		
C(21)—C(2)—N(2)	112.4 (3)	C(13)—C(12)—C(11)	120.4 (2)		
C(22)—C(2)—N(2)	106.5 (3)	C(14)—C(13)—C(12)	120.1 (3)		
C(23)—C(2)—N(2)	108.6 (3)	C(13)—C(14)—C(15)	120.0 (3)		
N(2)—S(3)—S(4)	103.20 (8)	C(14)—C(15)—C(16)	120.3 (3)		
S(3)—S(4)—S(5)	96.31 (4)	C(15)—C(16)—C(11)	120.5 (3)		
N(6)—S(5)—S(4)	103.71 (8)				

Compound (2)

Crystal data

$C_{14}H_{23}N_2OPS_5$
$M_r = 426.6$
Triclinic
$P\bar{1}$
$a = 9.836\ (9)$ Å
$b = 14.01\ (1)$ Å
$c = 15.733\ (8)$ Å
$\alpha = 96.89\ (5)°$
$\beta = 91.95\ (5)°$
$\gamma = 107.70\ (4)°$
$V = 2045\ (3)$ Å³
$Z = 4$
$D_x = 1.386$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6\text{–}14°$
$\mu = 0.649$ mm⁻¹
$T = 298\ (2)$ K
Prismatic
$0.30 \times 0.25 \times 0.12$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7659 measured reflections
7200 independent reflections
4847 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.020$
$\theta_{max} = 25°$
$h = 0 \rightarrow 11$
$k = -16 \rightarrow 15$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 250 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0475$
$wR(F^2) = 0.1306$
$S = 1.045$
7200 reflections
582 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 3.24P]$
where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.83$ e Å⁻³
$\Delta\rho_{min} = -0.72$ e Å⁻³
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for* (2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P(11)	0.4787 (1)	0.3204 (1)	0.1349 (1)	0.039 (1)
O(11)	0.4384 (3)	0.4091 (2)	0.1175 (2)	0.056 (1)
S(31)	0.4174 (1)	0.1222 (1)	0.0345 (1)	0.042 (1)
S(41)	0.4103 (1)	0.0080 (1)	0.1027 (1)	0.054 (1)
S(51)	0.5999 (1)	0.0544 (1)	0.1848 (1)	0.068 (1)
S(61)	0.7460 (1)	0.1412 (1)	0.1158 (1)	0.063 (1)
S(71)	0.7540 (1)	0.2887 (1)	0.1571 (1)	0.052 (1)
N(21)	0.3575 (3)	0.2100 (2)	0.0905 (2)	0.038 (1)
N(81)	0.6360 (3)	0.3204 (2)	0.0957 (2)	0.043 (1)
C(111)	0.4981 (4)	0.3156 (3)	0.2481 (2)	0.040 (1)
C(121)	0.4417 (5)	0.2292 (3)	0.2850 (3)	0.049 (1)
C(131)	0.4545 (5)	0.2315 (4)	0.3732 (3)	0.064 (1)
C(141)	0.5223 (6)	0.3216 (5)	0.4239 (3)	0.075 (2)
C(151)	0.5789 (6)	0.4075 (4)	0.3887 (3)	0.074 (2)
C(161)	0.5680 (5)	0.4059 (4)	0.3008 (3)	0.057 (1)
C(21)	0.1965 (4)	0.1930 (3)	0.0836 (3)	0.046 (1)
C(211)	0.1171 (6)	0.0865 (5)	0.0980 (5)	0.079 (2)
C(221)	0.1531 (7)	0.2081 (7)	-0.0053 (4)	0.088 (2)
C(231)	0.1576 (6)	0.2669 (6)	0.1481 (6)	0.099 (3)
C(81)	0.6857 (5)	0.3663 (3)	0.0135 (3)	0.054 (1)
C(811)	0.7857 (8)	0.3143 (6)	-0.0286 (5)	0.087 (2)
C(821)	0.5577 (7)	0.3503 (6)	-0.0496 (4)	0.076 (2)
C(831)	0.7607 (8)	0.4774 (5)	0.0389 (5)	0.081 (2)
P(12)	0.9558 (1)	0.6981 (1)	0.3848 (1)	0.039 (1)
O(12)	0.8170 (3)	0.6266 (2)	0.3960 (2)	0.064 (1)
S(32)	1.1056 (1)	0.8947 (1)	0.4792 (1)	0.065 (1)
S(42)	1.3206 (2)	0.9358 (1)	0.4820 (2)	0.125 (1)
S(52)	1.3707 (2)	0.9188 (2)	0.3525 (2)	0.149 (1)
S(62)	1.2109 (3)	0.9471 (2)	0.2874 (2)	0.147 (1)
S(72)	1.0623 (2)	0.8081 (1)	0.2444 (1)	0.101 (1)
N(22)	1.0382 (3)	0.7698 (2)	0.4771 (2)	0.043 (1)
N(82)	0.9405 (4)	0.7791 (3)	0.3172 (2)	0.055 (1)
C(112)	1.0762 (4)	0.6359 (3)	0.3390 (2)	0.042 (1)
C(122)	1.0214 (5)	0.5596 (3)	0.2704 (3)	0.056 (1)
C(132)	1.1085 (6)	0.5088 (4)	0.2324 (3)	0.066 (1)
C(142)	1.2483 (6)	0.5319 (4)	0.2615 (3)	0.068 (1)
C(152)	1.3018 (6)	0.6054 (4)	0.3306 (4)	0.072 (2)
C(162)	1.2168 (5)	0.6576 (4)	0.3697 (3)	0.056 (1)
C(22)	1.0185 (6)	0.7272 (5)	0.5635 (3)	0.074 (2)
C(212)	1.0140 (10)	0.6197 (6)	0.5519 (5)	0.107 (3)
C(222)	0.9208 (19)	0.7701 (15)	0.6097 (10)	0.098 (5)
C(222')	0.8642 (14)	0.7254 (10)	0.5904 (7)	0.056 (2)
C(232)	1.1389 (11)	0.7826 (8)	0.6278 (5)	0.125 (3)
C(82)	0.8063 (6)	0.8121 (4)	0.3091 (3)	0.076 (2)
C(812)	0.7421 (8)	0.8186 (6)	0.3957 (5)	0.089 (2)
C(822)	0.8450 (12)	0.9149 (7)	0.2797 (7)	0.128 (3)
C(832)	0.7006 (9)	0.7352 (7)	0.2434 (5)	0.110 (3)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

P(11)—O(11)	1.466 (3)	P(12)—N(82)	1.681 (4)
P(11)—N(81)	1.685 (3)	P(12)—N(22)	1.688 (3)
P(11)—N(21)	1.693 (3)	P(12)—C(112)	1.794 (4)
P(11)—C(111)	1.796 (4)	S(32)—N(22)	1.668 (4)
S(31)—N(21)	1.688 (3)	S(32)—S(42)	2.013 (3)
S(31)—S(41)	2.016 (2)	S(42)—S(52)	2.115 (4)
S(41)—S(51)	2.114 (3)	S(52)—S(62)	2.011 (4)
S(51)—S(61)	2.021 (2)	S(62)—S(72)	2.067 (4)
S(61)—S(71)	2.067 (2)	S(72)—N(82)	1.680 (4)
S(71)—N(81)	1.678 (3)	N(22)—C(22)	1.543 (5)
N(21)—C(21)	1.527 (5)	N(82)—C(82)	1.531 (6)
N(81)—C(81)	1.542 (5)	C(112)—C(162)	1.379 (6)
C(111)—C(121)	1.375 (6)	C(112)—C(122)	1.389 (6)
C(111)—C(161)	1.393 (6)	C(122)—C(132)	1.379 (6)
C(121)—C(131)	1.385 (6)	C(132)—C(142)	1.362 (7)
C(131)—C(141)	1.372 (7)	C(142)—C(152)	1.371 (7)
C(141)—C(151)	1.355 (8)	C(152)—C(162)	1.383 (6)
C(151)—C(161)	1.380 (7)	C(22)—C(222)	1.45 (2)
C(21)—C(211)	1.506 (7)	C(22)—C(212)	1.483 (9)
C(21)—C(231)	1.504 (7)	C(22)—C(232)	1.482 (10)
C(21)—C(221)	1.506 (7)	C(22)—C(222')	1.583 (12)
C(81)—C(831)	1.503 (7)	C(222)—C(222')	0.72 (2)
C(81)—C(811)	1.517 (7)	C(82)—C(822)	1.508 (10)
C(81)—C(821)	1.520 (7)	C(82)—C(832)	1.513 (9)
P(12)—O(12)	1.458 (3)	C(82)—C(812)	1.525 (9)
O(11)—P(11)—N(81)	112.2 (2)	O(12)—P(12)—C(112)	112.1 (2)
O(11)—P(11)—N(21)	112.9 (2)	N(82)—P(12)—C(112)	105.8 (2)
N(81)—P(11)—N(21)	106.0 (2)	N(22)—P(12)—C(112)	107.5 (2)
O(11)—P(11)—C(111)	111.6 (2)	N(22)—S(32)—S(42)	110.12 (14)
N(81)—P(11)—C(111)	106.6 (2)	S(32)—S(42)—S(52)	105.95 (13)
N(21)—P(11)—C(111)	107.2 (2)	S(62)—S(52)—S(42)	103.86 (14)
N(21)—S(31)—S(41)	110.79 (13)	S(52)—S(62)—S(72)	106.31 (13)
S(31)—S(41)—S(51)	106.87 (8)	N(82)—S(72)—S(62)	109.2 (2)
S(61)—S(51)—S(41)	103.49 (9)	C(22)—N(22)—S(32)	118.2 (3)
S(51)—S(61)—S(71)	105.80 (9)	C(22)—N(22)—P(12)	120.9 (3)
N(81)—S(71)—S(61)	109.36 (14)	S(32)—N(22)—P(12)	119.0 (2)

C(21)—N(21)—S(31)	117.3 (2)		C(82)—N(82)—S(72)	118.6 (3)
C(21)—N(21)—P(11)	123.3 (2)		C(82)—N(82)—P(12)	122.0 (3)
S(31)—N(21)—P(11)	118.4 (2)		S(72)—N(82)—P(12)	118.6 (2)
C(81)—N(81)—S(71)	118.5 (3)		C(162)—C(112)—C(122)	119.1 (4)
C(81)—N(81)—P(11)	122.0 (3)		C(162)—C(112)—P(12)	123.7 (3)
S(71)—N(81)—P(11)	118.6 (2)		C(122)—C(112)—P(12)	117.2 (3)
C(121)—C(111)—C(161)	119.0 (4)		C(132)—C(122)—C(112)	120.0 (5)
C(121)—C(111)—P(11)	123.5 (3)		C(142)—C(132)—C(122)	120.9 (5)
C(161)—C(111)—P(11)	117.4 (3)		C(132)—C(142)—C(152)	119.4 (5)
C(111)—C(121)—C(131)	120.7 (4)		C(142)—C(152)—C(162)	120.9 (5)
C(141)—C(131)—C(121)	119.2 (5)		C(112)—C(162)—C(152)	119.7 (4)
C(151)—C(141)—C(131)	121.0 (5)		C(222)—C(22)—C(212)	126.8 (9)
C(141)—C(151)—C(161)	120.3 (5)		C(222)—C(22)—C(232)	91.7 (9)
C(151)—C(161)—C(111)	119.8 (5)		C(212)—C(22)—C(232)	107.0 (6)
C(211)—C(21)—C(231)	109.6 (5)		C(222)—C(22)—N(22)	107.6 (8)
C(211)—C(21)—C(221)	108.8 (5)		C(212)—C(22)—N(22)	110.3 (4)
C(231)—C(21)—C(221)	108.9 (6)		C(232)—C(22)—N(22)	111.5 (5)
C(211)—C(21)—N(21)	110.0 (3)		C(222)—C(22)—C(222')	27.2 (7)
C(231)—C(21)—N(21)	110.8 (3)		C(212)—C(22)—C(222')	104.8 (7)
C(221)—C(21)—N(21)	108.6 (4)		C(232)—C(22)—C(222')	115.9 (7)
C(831)—C(81)—C(811)	110.9 (5)		N(22)—C(22)—C(222')	107.0 (5)
C(831)—C(81)—C(821)	110.2 (5)		C(822)—C(82)—C(832)	109.8 (6)
C(811)—C(81)—C(821)	108.4 (5)		C(822)—C(82)—C(812)	108.6 (6)
C(831)—C(81)—N(81)	107.7 (4)		C(832)—C(82)—C(812)	110.7 (6)
C(811)—C(81)—N(81)	109.5 (4)		C(822)—C(82)—N(82)	109.6 (6)
C(821)—C(81)—N(81)	110.1 (4)		C(832)—C(82)—N(82)	107.8 (5)
O(12)—P(12)—N(82)	111.4 (2)		C(812)—C(82)—N(82)	110.4 (4)
O(12)—P(12)—N(22)	113.4 (2)			

For both compounds, data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON*92 (Spek, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Acetoxy-6-(1,1-dimethyl-2-propenyl)-2H-furo[2,3-h][1]benzopyran-2-one

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Abstract

The title ester {6-(1,1-dimethyl-2-propenyl)-2-oxo-2H-furo[2,3-h][1]benzopyran-5-yl acetate, $C_{18}H_{16}O_5$}, is a furanocoumarin. The pyrone, phenyl and furan rings are planar. Molecules are held together by C—H···O hydrogen bonds.

Comment

Many coumarin derivatives are of biological importance (Michel & Durant, 1976; Schmalle, Jarchow, Hausen & Schulz, 1982). The crystal structure of the title compound has been determined as part of our programme on the crystal structure analysis of these derivatives. The title compound, (I), was prepared by the acetylation of 5-hydroxy-6-(1,1-dimethyl-2-propenyl)-2H-furo[2,3-h][1]-benzopyran-2-one, a furanocoumarin isolated from the roots of *Heracleum thomsoni*, a herb growing wild in the Ladakh region of Jammu and Kashmir State, India (Banerjee, Gupta & Atal, 1980).

(I)
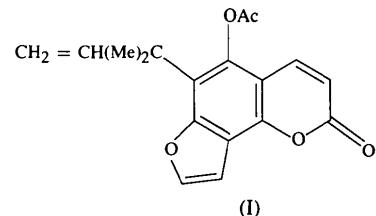
An *ORTEP*II (Johnson, 1976) drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. The furocoumarin atoms are almost coplanar as in other furocoumarin derivatives (Bideau, Bravic & Desvergne, 1979; Bravic & Bideau, 1978; Dall'Acqua, Benetollo & Bombieri, 1981). The deviations from the mean plane of the three rings range from −0.058 (3) to 0.040 (2) Å, indicating a reasonably planar system. Variations in the bond lengths and angles in the phenyl ring, which are due to the fusion of the pyrone and