$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.270P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.01$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Intramolecular C—H···O—X contacts (C—H···O hydrogen bonds) in CHO—C—C—XO fragments (Å, °)*

X—O	C—H···O	H···O	H···O—X	C···O	Reference
–CHO	116	2.30	100	2.884 (2)	this work
–C=O(–C)	124	2.06	109	2.767	(*a*)
–C=O(–C)	109	2.27	103	2.769	(*a*)
$-NO_2$	106	2.27	111	2.725	(*b*)
$-NO_2$	78	2.71	88	2.701	(*c*)
–CHO	122	2.43	101	3.045	(*d*)
–CHO	92	2.48	87	2.686	(*e*)
–CHO	86	2.55	87	2.692	(*f*)
–CHO	85	2.62	88	2.735	(*g*)
–CHO	84	2.63	85	2.715	(*g*)

References: (*a*) Talipov *et al.* (1995); (*b*) Byrn *et al.* (1993); (*c*) Coppens & Schmidt (1964); (*d*) McCague *et al.* (1984); (*e*) Sterner *et al.* (1990); (*f*) De Rosa *et al.* (1994); (*g*) Puliti *et al.* (1995).

Table 2. *Intermolecular C—H···O—C′ contacts for (I) (Å, °)*

C—H···O—C′	C—H···O	H···O	H···O—C′	C···O
C5—H5···O2—C12^{i}	152	2.51	156	3.417 (2)
C7—H7···O1—C11^{ii}	140	2.58	140	3.361 (2)
C11—H11···O1—C11^{iii}	129	2.64	107	3.367 (2)
C3—H3···O2—C12^{iv}	147	2.65	147	3.486 (2)
C12—H12···O2—C12^{v}	116	2.73	103	3.302 (2)
C8—H8···O2—C12^{vi}	129	2.74	98	3.459 (2)

Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $2-x, 1-y, 1-z$; (iv) $-x, 2-y, 1-z$; (v) $1+x, y, z$; (vi) $x, \frac{3}{2}-y, -\frac{1}{2}+z$.

The first 209 reflections were remeasured 12 h later at the end of the data collection to monitor crystal decay. H atoms were refined with isotropic displacement parameters.

Data collection: *ASTRO* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Two new 2,3-substituted 5-norbornenes

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Abstract

In the bicyclo[2.2.1]heptene (norbornene) moieties of *S*-methyl 3-(4-methylphenyl)bicyclo[2.2.1]hept-5-ene-2-carbothioate, $C_{16}H_{18}OS$, (2*a*), and *S*-methyl 3-(4-nitrophenyl)bicyclo[2.2.1]hept-5-ene-2-carbothioate, $C_{15}H_{15}NO_3S$, (2*b*), the five-membered rings are in envelope conformations, while the six-membered rings adopt boat conformations. The dihedral angles between the norbornene six-membered ring moiety and the phenyl substituent are 67.22 (9) and 31.8 (2)°, for (2*a*) and (2*b*), respectively. In both compounds, molecules are joined through C—H···O interactions.

Comment

The Diels–Alder reaction of α,β-unsaturated carbonyl and carboxylic compounds with cyclopentadiene has been extensively investigated (Sauer & Sustmann, 1980; Camilo & Gruber, 1999). When no Lewis acid catalysts

are employed, mixtures of both the *endo* and *exo* adducts are obtained, usually with a predominance of the former isomer. Our interests in the stereoselectivity of catalysed reactions between α,β-unsaturated thioesters and cyclopentadiene led us to extend our studies (Wladislaw *et al.*, 1991) to the reaction between cyclopentadiene and some methyl thiocinnamates, (1*a*)–(1*c*) (Camilo *et al.*, 1998). With substitution at the *para* position by electron-withdrawing and electron-donating groups, in the presence of boroncatechol bromide, the reaction led exclusively to one of two possible adducts, (2*a*)–(2*c*) (*endo*) or (3*a*)–(3*c*) (*exo*) in good yields (Camilo, 1998). In order to determine unambiguously which of the adducts was obtained, a crystal structure determination of compounds (2/3*a*) and (2/3*b*) was undertaken.

(1) (2) (3)

(*a*) R = Me
(*b*) R = NO_2
(*c*) R = Cl

The main result of this work is the determination that, as can be seen in Figs. 1 and 2, only the *endo* adducts [(2*a*) and (2*b*)] were produced. In both compounds, the norbornene moieties are essentially identical: in fact, a least-squares fit (Kabsch, 1976) gives an r.m.s. deviation between equivalent atoms of 0.019 Å. Therefore, the following comments and data refer to compound (2*a*). The boat conformation of the norbornene six-membered ring (C1–C6) is evidenced by the Cremer & Pople (1975) puckering parameters: q_2 = 0.953 (6), q_3 = 0.011 (2) and Q_T = 0.953 (6) Å, and θ = 89.3 (1) and φ_2 = 178.6 (2)°. Similarly, the two five-membered rings are in envelope conformations, as shown by their puckering parameters: q_2 = 0.622 (3) and 0.553 (3) Å, and φ_2 = −34.0 (2) and −35.5 (3)°, for rings (C1–C4, C7) and (C4–C6, C1, C7), respectively, these two rings being at 80.5 (1)° to each other. The bond lengths and angles are, within experimental errors, in good agreement with the reported values (Mackay *et al.*, 1994; Puviarasan *et al.*, 1998). Also, the torsion angle about C8—S is almost equal in both compounds, being 0.9 (3) and 1.1 (4)° in (2*a*) and (2*b*), respectively. The dihedral angle between the phenyl and the nitro group in (2*b*) is 10.8 (3)°.

The main differences between the two molecules are the relative orientations of the phenyl and the carbothioate groups with respect to the norbornene moiety, as can be seen from the torsion angles: C2—C3—C10—C11 = 74.3 (3) and −13.8 (3)° for (2*a*) and (2*b*), respectively, and O—C8—C2—C3 = 13.6 (3) and −84.7 (5)° for (2*a*) and (2*b*), respectively. This, in turn, gives rise to an intramolecular short contact in (2*a*) [C3···O 2.910 (3), H3···O 2.50 Å]. Moreover, as can be seen in Table 2, the molecules of (2*a*) are linked through C—H···O interactions, forming an infinite chain parallel to the *a* direction, while in (2*b*) (Table 4) the molecules form centrosymmetric dimers, which in turn are linked through another C—H···O interaction involving the O atom of the nitro group.

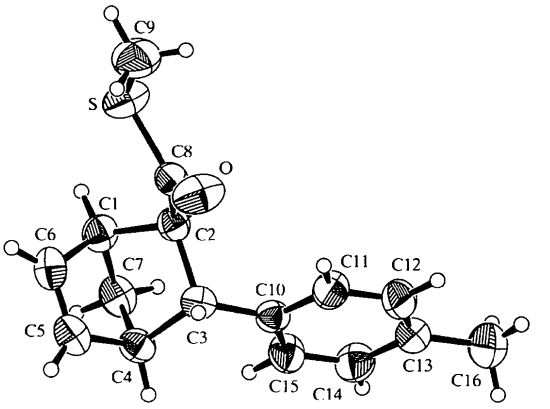

Fig. 1. The molecular structure of compound (2*a*) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

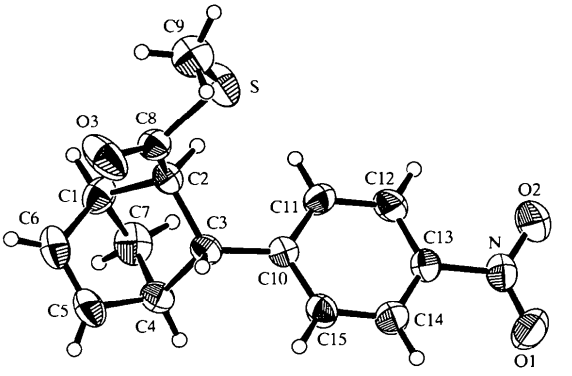

Fig. 2. The molecular structure of compound (2*b*) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

Experimental

The title compounds were synthesised as described by Camilo (1998). Colourless crystals of the two compounds were obtained from solutions in ethanol.

Compound (2*a*)

Crystal data

$C_{16}H_{18}OS$
M_r = 258.36

Mo $K\alpha$ radiation
λ = 0.71073 Å

Triclinic
$P\bar{1}$
a = 5.763 (1) Å
b = 10.153 (2) Å
c = 12.022 (2) Å
α = 83.37 (1)°
β = 86.46 (1)°
γ = 78.83 (1)°
V = 684.9 (2) Å^3
Z = 2
D_x = 1.253 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 9.08–13.67°
μ = 0.222 mm^{-1}
T = 293 K
Irregular
0.30 × 0.20 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2800 measured reflections
2531 independent reflections
1570 reflections with $F^2 > 2\sigma F^2$

R_{int} = 0.021
θ_{max} = 25.47°
$h = -6 \rightarrow 0$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 30 min
intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.115
S = 1.019
2531 reflections
165 parameters
H-atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.2415P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.198 e Å^{-3}
$\Delta\rho_{min}$ = −0.238 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S—C8	1.766 (2)	O—C8	1.203 (3)
S—C9	1.785 (3)	C5—C6	1.314 (3)
C8—S—C9	101.3 (1)	O—C8—S	122.1 (2)
C1—C7—C4	93.4 (2)	C2—C8—S	112.8 (2)
O—C8—C2	125.1 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7A···O^i	0.97	2.75	3.571 (3)	143

Symmetry code: (i) $1 + x, y, z$.

Compound (2*b*)

Crystal data

$C_{15}H_{15}NO_3S$
M_r = 289.34
Monoclinic
$P2_1/c$
a = 9.763 (1) Å
b = 12.097 (2) Å
c = 12.164 (1) Å
β = 107.292 (8)°
V = 1371.7 (3) Å^3
Z = 4
D_x = 1.401 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 8.12–13.53°
μ = 0.242 mm^{-1}
T = 293 K
Irregular
0.25 × 0.20 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2698 measured reflections
2541 independent reflections
1369 reflections with $F^2 > 2\sigma F^2$

R_{int} = 0.039
θ_{max} = 25.46°
$h = -11 \rightarrow 0$
$k = -14 \rightarrow 0$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 30 min
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.165
S = 1.039
2541 reflections
182 parameters
H-atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0834P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.225 e Å^{-3}
$\Delta\rho_{min}$ = −0.276 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2b)*

S—C8	1.747 (4)	N—C13	1.470 (4)
S—C9	1.794 (4)	O3—C8	1.194 (4)
N—O1	1.218 (4)	C5—C6	1.323 (5)
N—O2	1.221 (4)		
C8—S—C9	101.8 (2)	C4—C7—C1	94.3 (3)
O1—N—O2	123.3 (3)	O3—C8—C2	125.6 (3)
O1—N—C13	118.4 (3)	O3—C8—S	122.2 (3)
O2—N—C13	118.4 (3)	C2—C8—S	112.3 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2b)*

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15···O3^i	0.93	2.43	3.345 (5)	170
C9—H9C···O1^{ii}	0.96	2.57	3.498 (5)	162

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$.

H atoms were located on stereochemical grounds and refined with fixed geometry (riding model), with an isotropic displacement parameter amounting to 1.5 (for methyl-H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the carrier atom.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

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trans-2,6-Bis(ethylamino)-2,4,4,6,8,8-hexapiperidinocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazatetraene

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Abstract

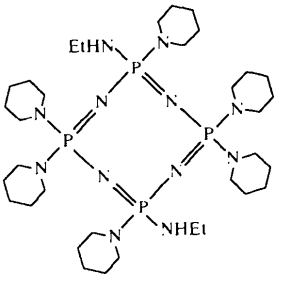
The title compound, $C_{34}H_{72}N_{12}P_4$, consists of a chair-shaped cyclic tetrameric phosphazene ring with six bulky piperidino and two ethylamino side groups. The two ethylamino side groups are in *trans* positions. The bulky substituents are instrumental in determining the eight-membered-ring conformation. The endocyclic N—P—N angles, which have different substituents, are not the same as the P—N—P angles of the macrocyclic ring.

Comment

During the last two decades, the structures and properties of the bulky phenoxy derivatives of hexachlorocyclo-2λ^5,4λ^5,6λ^5-triphosphazene, $N_3P_3Cl_6$, and octachlorocyclo-2λ^5,4λ^5,6λ^5,8λ^5-tetraphosphazene, $N_4P_4Cl_8$, have attracted great interest in the synthesis of new, small-molecule organocyclophosphazenes (Allcock, Dembek *et al.*, 1992) and high polymeric phosphazenes with inorganic backbones (Allcock, 1985; Allcock *et al.*, 1987) and aryloxy side groups which may be useful as high refractive index glasses (Olshavsky & Allcock, 1995), ferroelectric and non-linear optical polymers (Allcock *et al.*, 1991), liquid crystalline materials (Allcock & Kim, 1991) and biomedical materials (Cohen *et al.*, 1990). Some of the phosphazene polymers are thought to be useful as cancer chemotherapeutic agents (Chernov *et al.*, 1959; van der Huizen, 1984). A relationship has been determined between the structures of the cyclophosphazenes and cytostatic activity (van der Huizen, 1984) and for effective tumour growth inhibition, electron-donating groups (*e.g.* aziridine, pyrrolidine, and primary and secondary amines) in the P—N ring skeletons seem to be essential. The important physical or chemical properties of phosphazene polymers are imposed by the structure of the organic, inorganic or metal–organic side groups (Allcock, 1985). The organophosphazene derivatives are used in polymer synthesis and the resulting polymers are expected to have unique physical properties (Allcock, 1972; Allcock *et al.*, 1987). Polyphosphazenes with aryloxy, alkoxy and metallocenyl side groups are of special interest (Allcock *et al.*, 1984).

There are two crystal modifications, generally called the *K* and *T* forms, of $N_4P_4Cl_8$, which is a standard compound for tetrameric phosphazenes (Hazekamp *et al.*, 1962; Wagner & Vos, 1968). The crystal structures of some $N_4P_4Cl_8$ derivatives such as $[N_4P_4(NMe_2)_8]$, (1), (Bullen, 1962), $[N_4P_4Cl_4(NEt_2)_4]$, (2), (Hökelek & Kılıç, 1990), $[N_4P_4Cl_7(OC_6H_2$-2,6-$^tBu_2$-4-Me)], (3), (Hökelek *et al.*, 1996) and $[N_4P_4(NC_4H_8O)_6(NHCH_2CH_3)]$, (4), (Hökelek *et al.*, 1998) have been determined.

The main objective of this study was to determine the influences of the relatively hindered side groups, and also of steric and electronic factors, on the macrocyclic tetraphosphazene ring. The title molecule, (I), is shown



(I)

in Fig. 1. Its structure consists of a non-planar cyclic tetrameric phosphazene ring in a chair conformation with two ethylamino (in 2,6-*trans* positions) and six bulky piperidino side groups. The N atoms are displaced