

Fig. 1. Molecular drawing (ORTEP: Johnson, 1976) of the aromatic cation  $C_{15}H_{10}N^+$  with the atomic numbering scheme.

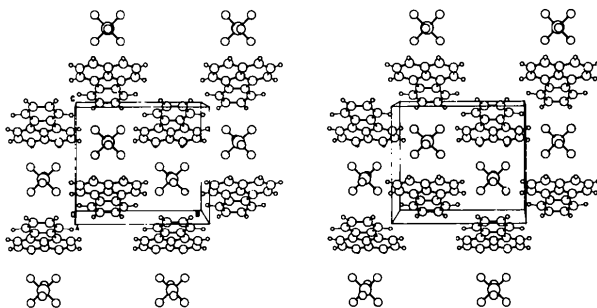


Fig. 2. Stereodrawing (PLUTO: Motherwell & Clegg, 1978) of the crystal structure viewed down *a*.

**Related literature.** A short and efficient synthesis of the title compound is reported separately (Fourmigué, Bechgaard, Auban, Jérôme, Boubekeur &

Batail, 1989; Fourmigué, Boubekeur, Batail & Bechgaard, 1989). The salient structural difference between this aromatic cation and its neutral analog, the fluoranthene (Hazell, Jones & Sowden, 1977) is a significant contraction [ $-0.025(5) \text{ \AA}$ ] of the N—C bond lengths and a similar shortening [ $-0.024(5) \text{ \AA}$ ] of the C(5)—C(6) bonds.

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## Structure of 7,16-Dimethyl-7H<sup>+</sup>,16H<sup>+</sup>-1,4,10,13-tetrathia-7,16-diazoniacyclooctadecane Dipicrate

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**Abstract.**  $C_{14}H_{32}N_2S_4^{2+} \cdot 2C_6H_2N_3O_7^-$ ,  $M_r = 812.79$ , monoclinic,  $P2_1/a$ ,  $a = 16.542(5)$ ,  $b = 23.750(9)$ ,  $c = 9.402(3) \text{ \AA}$ ,  $\beta = 105.067(14)^\circ$ ,  $V = 3567 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.513 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 0.328 \text{ mm}^{-1}$ ,  $F(000) = 1696$ ,  $T = 293 \text{ K}$ ,  $R = 0.0703$  for 1998 unique observed reflections. The asymmetric unit comprises two independent half-macrocycles and two independent picrates. The ring conformation is such that all six heteroatoms are exo-dentate. Each N-bound hydrogen of the macrocyclic

dication is linked by a strong hydrogen bond to the phenolic oxygen of one picrate anion, yielding a neutral, centrosymmetric species.

**Experimental.** Compound prepared by reaction of 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane and picric acid (1:2 molar ratio) in nitromethane. Lath-shaped yellow crystal,  $0.132 \times 0.304 \times 0.832 \text{ mm}$ , mounted about *b* on a Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo *K* $\alpha$  X-radiation, cell parameters from three  $0k0$  and 15  $h0l$  reflections. For data collection,  $\omega$  scans

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
S(1)	0.29391 (21)	0.65020 (14)	-0.0927 (4)	0.0490 (23)
C(2)	0.3160 (8)	0.5898 (5)	-0.0277 (12)	0.048 (9)
C(3)	0.3919 (8)	0.5969 (5)	-0.1569 (12)	0.052 (9)
S(4)	0.40158 (23)	0.53806 (14)	0.2828 (3)	0.0563 (25)
C(5)	0.4495 (7)	0.4835 (4)	0.1963 (11)	0.038 (8)
C(6)	0.4809 (7)	0.4410 (5)	0.3178 (11)	0.041 (8)
N(7)	0.5086 (6)	0.3863 (4)	0.2657 (9)	0.037 (7)
C(7N)	0.5126 (8)	0.3437 (5)	0.3824 (12)	0.051 (9)
C(8)	0.5910 (7)	0.3928 (5)	0.2311 (12)	0.043 (9)
C(9)	0.6108 (7)	0.3413 (4)	0.1505 (12)	0.041 (8)
S(10)	0.23086 (23)	0.59004 (15)	0.3798 (4)	0.060 (3)
C(11)	0.1817 (7)	0.5215 (5)	0.3397 (14)	0.049 (9)
C(12)	0.1022 (8)	0.5229 (5)	0.2203 (12)	0.052 (9)
S(13)	0.06281 (24)	0.45157 (15)	0.1694 (4)	0.066 (3)
C(14)	0.0238 (7)	0.4325 (5)	0.3269 (11)	0.039 (8)
C(15)	-0.0296 (7)	0.3809 (5)	0.2793 (11)	0.041 (8)
N(16)	-0.0586 (5)	0.3559 (3)	0.4049 (9)	0.033 (6)
C(16N)	-0.0898 (8)	0.2979 (5)	0.3616 (13)	0.050 (9)
C(17)	-0.1250 (7)	0.3921 (4)	0.4420 (11)	0.038 (8)
C(18)	-0.1508 (7)	0.3680 (5)	0.5775 (13)	0.054 (9)
O(1')	0.5787 (5)	0.6216 (3)	0.0363 (8)	0.049 (6)
C(1')	0.6287 (7)	0.6457 (5)	0.1379 (12)	0.033 (8)
C(2')	0.6731 (7)	0.6165 (5)	0.2700 (12)	0.036 (8)
N(2')	0.6554 (6)	0.5568 (4)	0.2850 (13)	0.051 (9)
O(21')	0.6539 (6)	0.5275 (4)	0.1798 (10)	0.063 (7)
O(22')	0.6457 (7)	0.5401 (4)	0.3986 (11)	0.083 (8)
C(3')	0.7287 (8)	0.6400 (5)	0.3905 (13)	0.048 (9)
C(4')	0.7496 (8)	0.6962 (5)	0.3832 (14)	0.046 (10)
N(4')	0.8112 (8)	0.7227 (6)	0.5032 (13)	0.062 (10)
O(41')	0.8564 (6)	0.6913 (4)	0.5946 (10)	0.068 (7)
O(42')	0.8136 (6)	0.7735 (5)	0.5074 (10)	0.080 (8)
C(5')	0.7080 (7)	0.7304 (5)	0.2637 (13)	0.039 (8)
C(6')	0.6521 (8)	0.7042 (5)	0.1478 (13)	0.043 (9)
N(6')	0.6131 (7)	0.7417 (5)	0.0235 (13)	0.061 (9)
O(61')	0.6142 (8)	0.7918 (4)	0.0480 (10)	0.107 (10)
O(62')	0.5792 (7)	0.7200 (4)	-0.0934 (10)	0.081 (8)
O(1'')	0.9471 (5)	0.6186 (4)	0.3400 (9)	0.054 (6)
C(1'')	0.8969 (8)	0.6298 (5)	0.2211 (12)	0.037 (8)
C(2'')	0.8894 (7)	0.6826 (5)	0.1466 (11)	0.036 (8)
N(2'')	0.9382 (7)	0.7295 (5)	0.2211 (12)	0.055 (9)
O(21'')	0.9610 (8)	0.7317 (4)	0.3513 (14)	0.122 (1)
O(22'')	0.9579 (7)	0.7663 (4)	0.1471 (12)	0.098 (9)
C(3'')	0.8391 (7)	0.6938 (5)	0.0120 (12)	0.038 (8)
C(4'')	0.7876 (8)	0.6523 (5)	-0.0615 (12)	0.047 (10)
N(4'')	0.7322 (7)	0.6616 (5)	-0.2033 (11)	0.056 (9)
O(41'')	0.7277 (6)	0.7099 (4)	-0.2547 (9)	0.081 (8)
O(42'')	0.6929 (6)	0.6218 (5)	-0.2748 (10)	0.080 (8)
C(5'')	0.7925 (7)	0.5980 (5)	-0.0018 (11)	0.037 (8)
C(6'')	0.8420 (7)	0.5883 (5)	0.1313 (12)	0.034 (8)
N(6'')	0.8427 (6)	0.5318 (4)	0.1964 (11)	0.045 (8)
O(61'')	0.8381 (6)	0.4922 (4)	0.1080 (9)	0.063 (7)
O(62'')	0.8486 (6)	0.5276 (3)	0.3255 (9)	0.068 (7)

Table 2. Bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.'s

S(1)—C(2)	1.805 (12)	S(10)—C(11)	1.816 (13)
S(1)—C(9)	1.808 (12)	S(10)—C(18)	1.784 (12)
C(2)—C(3)	1.512 (17)	C(11)—C(12)	1.491 (17)
C(3)—S(4)	1.812 (12)	C(12)—S(13)	1.833 (13)
S(4)—C(5)	1.818 (11)	S(13)—C(14)	1.820 (12)
C(5)—C(6)	1.512 (15)	C(14)—C(15)	1.508 (16)
C(6)—N(7)	1.500 (14)	C(15)—N(16)	1.508 (14)
N(7)—C(7N)	1.483 (15)	N(16)—C(16N)	1.491 (15)
N(7)—C(8)	1.489 (15)	N(16)—C(17)	1.505 (14)
C(8)—C(9)	1.519 (16)	C(17)—C(18)	1.555 (16)
C(9)—S(1)—C(2)	103.1 (5)	C(18)—S(10)—C(11')	103.3 (6)
S(1)—C(2)—C(3)	113.9 (8)	S(10)—C(11)—C(12)	113.3 (9)
C(2)—C(3)—S(4)	110.7 (8)	C(11)—C(12)—S(13)	111.1 (9)
C(3)—S(4)—C(5)	103.5 (5)	C(12)—S(13)—C(14)	101.2 (5)
S(4)—C(5)—C(6)	104.0 (7)	S(13)—C(14)—C(15)	105.3 (8)
C(5)—C(6)—N(7)	113.9 (9)	C(14)—C(15)—N(16)	111.6 (9)
C(6)—N(7)—C(7N)	107.9 (8)	C(15)—N(16)—C(16N)	108.0 (8)
C(6)—N(7)—C(8)	110.9 (8)	C(15)—N(16)—C(17)	110.9 (8)
C(7N)—N(7)—C(8)	111.5 (9)	C(16N)—N(16)—C(17)	111.6 (8)
N(7)—C(8)—C(9)	110.7 (9)	N(16)—C(17)—C(18)	110.7 (9)
S(1)—C(9)—C(8)	112.2 (8)	S(10)—C(18)—C(17)	110.9 (8)
C(2)—S(1)—C(9)—C(8)	-60.2 (9)	C(11)—S(10)—C(18)—C(17)	-60.7 (9)
C(9)—S(1)—C(2)—C(3)	-58.2 (9)	C(18)—S(10)—C(11)—C(12)	-56.4 (10)
S(1)—C(2)—C(3)—S(4)	173.0 (6)	S(10)—C(11)—C(12)—S(13)	172.9 (6)
C(2)—C(3)—S(4)—C(5)	80.2 (9)	C(11)—C(12)—S(13)—C(14)	73.6 (9)
C(3)—S(4)—C(5)—C(6)	164.0 (7)	C(12)—S(13)—C(14)—C(15)	165.8 (8)
S(4)—C(5)—C(6)—N(7)	168.9 (7)	S(13)—C(14)—C(15)—N(16)	173.4 (7)
C(5)—C(6)—N(7)—C(7N)	-162.8 (9)	C(14)—C(15)—N(16)—C(16N)	-164.6 (9)
C(5)—C(6)—N(7)—C(8)	74.8 (11)	C(14)—C(15)—N(16)—C(17)	72.8 (11)
C(6)—N(7)—C(8)—C(9)	-168.8 (9)	C(15)—N(16)—C(17)—C(18)	-176.6 (9)
C(7N)—N(7)—C(8)—C(9)	71.0 (11)	C(16N)—N(16)—C(17)—C(18)	62.9 (11)
N(7)—C(8)—C(9)—S(1)	175.2 (7)	N(16)—C(17)—C(18)—S(10)	-179.0 (7)

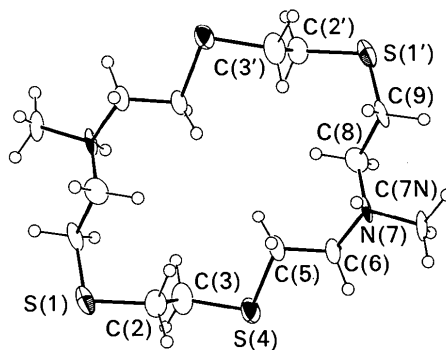


Fig. 1. View with atom-numbering scheme for one macrocyclic dication lying across a crystallographic inversion centre. Thermal ellipsoids are drawn at the 30% probability level, excepting those of H which have artificial radii of 0.10 Å for clarity.

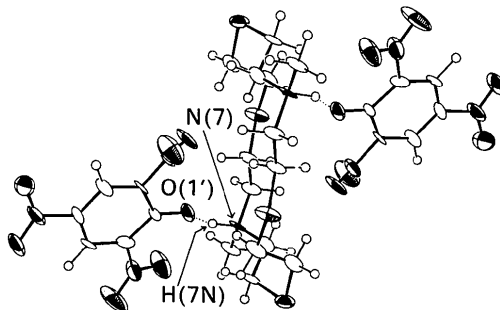


Fig. 2. Each N-bound hydrogen participates in strong hydrogen bonding to the phenolic oxygen of a picrate ion, giving the neutral species shown.

with scan width  $[1.0 + 0.5(\sin \mu / \tan \theta)]^\circ$ ,  $2\theta_{\max} = 45^\circ$ ,  $h \ 0 \rightarrow 17$ ,  $k \ 0 \rightarrow 25$ ,  $l \ -10 \rightarrow 9$ , no significant crystal movement or decay, semi-empirical absorption correction applied (using  $\varphi$  scan on 0.12.0, max. and min. corrections 1.60, 0.80 respectively), 4848 reflections measured, 4562 unique ( $R_{\text{int}} = 0.086$ ), giving 1998 with  $F \geq 6\sigma(F)$  for structure solution [by means of automatic direct methods (Sheldrick, 1986)] and refinement [using full-matrix least squares on  $F$  (Sheldrick, 1976)]. Anisotropic thermal parameters for all non-H atoms, H atoms refined in fixed, calculated positions. At convergence,  $R$ ,  $wR = 0.0703$ ,  $0.0788$ ,  $S = 1.174$  for 468 parameters,  $(\Delta/\sigma)_{\max}$  in final cycle 0.032, max. and min. residues in final difference Fourier synthesis 0.39,  $-0.64 \text{ e \AA}^{-3}$  respectively. The weighting scheme  $w^{-1} = \sigma^2(F) + 0.001028F^2$  gave satisfactory agreement

analyses. Scattering factors were inlaid (Sheldrick, 1976). Atom coordinates and equivalent isotropic thermal parameters are given in Table 1 while selected molecular-geometry parameters appear in Table 2.\* The atom-numbering scheme for the cation is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985). The centrosymmetric, hydrogen-bonded species comprising one macrocyclic dication and two picrate monoanions is shown in Fig. 2; selected hydrogen-bonding parameters are listed in Table 3. Molecular-geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

**Related literature.** The unmethylated, neutral molecule 1,4,10,13-tetrathia-7,16-diazacyclooctadecane (Ammon, Chandrasekhar, Bhattacharjee, Shinkai & Honda, 1984) likewise lies across an inversion centre. However, it does not participate in significant hydrogen bonding, and has a different ring conformation

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51900 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected hydrogen-bonding parameters for N—H $\cdots$ O—C

Distances (Å)			
H(7N) $\cdots$ O(1')	1.848 (12)	H(16N) $\cdots$ O(1'')	1.684 (12)
Angles (°)			
N(7)—H(7N) $\cdots$ O(1')	150.5 (9)	N(16)—H(16N) $\cdots$ O(1'')	152.2 (9)
H(7N) $\cdots$ O(1')—C(1')	140.1 (8)	H(16N) $\cdots$ O(1'')—C(1'')	144.5 (9)

with no exdentate S atoms. Four *anti* C—N and eight *gauche* C—S bond conformations are observed for this species. In contrast, the title compound shows two C—N bonds *anti* and two *gauche*, with six *gauche* and two *anti* C—S bond conformations.

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## Structure of *S*-Phenyl *O*-3'-Thymidinyl Methylphosphonothioate\*

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**Abstract.** *S*-Phenyl *O*-3'-thymidinyl methylphosphonothioate-tetrahydrofuran (1/1), C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>6</sub>PS.C<sub>4</sub>H<sub>8</sub>O, *M<sub>r</sub>* = 484.51, monoclinic, *P*2<sub>1</sub>, *a* = 10.7577 (17), *b* = 9.0981 (16), *c* = 12.4311 (28) Å, β = 100.425 (16)°, *V* = 1196.5 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.34 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 1.99 cm<sup>-1</sup>, *F*(000) = 512, *T* = 296 K, *R* = 0.039, *wR* = 0.048 for 3156 unique observed reflections. *S*-Phenyl *O*-3'-thymidinyl methylphosphonothioate has been obtained in crystalline form as its monotetrahydrofuranate. In the crystal, each molecule is linked by two intermolecular hydrogen bonds to two different adjacent molecules. Acceptor for both types of hydrogen bonds is the phosphoryl group of the

phosphonothioate moiety. The 5'-hydroxyl H atom (O $\cdots$ H 2.01; O $\cdots$ O 2.839 Å) and the N<sup>3</sup> hydrogen of the thymidine residue (O $\cdots$ N 2.952 Å) function as donors. The title compound is one of a series of nucleotide synthons directed towards introducing chiral internucleotidic linkages into DNA. DNA modified in this manner may have several applications in biology and medicine. Phosphonothioate-containing mononucleotides can easily be *P*-diastereomerically resolved which is a significant improvement over previous synthons of this type.

**Experimental.** The title compound was obtained as its tetrahydrofuran (THF) adduct from the high *R<sub>f</sub>* *P*-diastereomer of *S*-phenyl *O*-(5'-*O*-tritylthymidine-3'-yl) methylphosphonothioate (0.5 mmol) (Brill & Caruthers, 1988) by treatment with 20% TFA in

\* Nucleotide Chemistry. Part XXVII. Part XXVI: Grandas, Marshall, Nielsen & Caruthers (1989).