

Structures of 2,3-Diethyl-6,7-dihydro-5*H*-2aλ⁴-seleno-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1(2*H*),4(3*H*)-diselone and 1,4-Bis(ethylimino)-5,6-dihydro-2,2aλ⁴,3-triseleno-4a,6a-diazacyclopenta[*cd*]pentalene

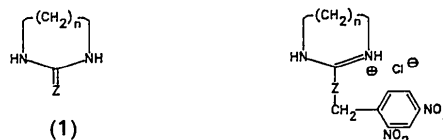
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Abstract. 2,3-Diethyl-6,7-dihydro-5*H*-2aλ⁴-seleno-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1(2*H*),4(3*H*)-diselone (7), C₁₀H₁₆N₄Se₃, *M_r* = 429.146, monoclinic, *P*2₁, *a* = 5.322 (2), *b* = 10.531 (3), *c* = 12.939 (2) Å, β = 99.20 (2)°, *V* = 715.85 Å³, *Z* = 2, *D_x* = 1.99 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 74.84 cm⁻¹, *F*(000) = 412, *T* = 295 K, *R* = 0.055 for 1568 reflections with *F* ≥ 3σ(*F*). 1,4-Bis(ethylimino)-5,6-dihydro-2,2aλ⁴,3-triseleno-4a,6a-diazacyclopenta[*cd*]pentalene (8), C₉H₁₄N₄Se₃, *M_r* = 415.199, monoclinic, *P*2₁/*a*, *a* = 8.005 (1), *b* = 13.717 (2), *c* = 11.950 (1) Å, β = 93.42 (1)°, *V* = 1309.76 Å³, *Z* = 4, *D_x* = 2.10 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 81.78 cm⁻¹, *F*(000) = 792, *T* = 295 K, *R* = 0.053 for 1793 reflections with *F* ≥ 3σ(*F*). Compound (7) was found to contain elongated Se—N bonds, while compound (8) contains elongated Se—Se bonds in its fused ring system. In both structures evidence was found for some conjugation in the fused ring systems of the molecules.

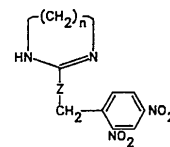
Introduction. In the course of work on the synthesis of new types of 1,6,6aλ⁴-triheterapentalene structure, we have found (Lai, 1990) that cyclic thioureas and selenoureas (1) undergo alkylation with 2,4-dinitrobenzyl chloride to give salts (2) which, when deprotonated with aqueous sodium carbonate, afford the bases (3). These bases react with heterocumulenes RNCX (*X* = O, S, Se) with elimination of 2,4-dinitrotoluene and concomitant addition of two molecules of the heterocumulene to give products which, on the basis of elemental composition, ¹H and ¹³C NMR spectra and mechanistic considerations, seemed likely to possess structure (4) or structure (5). We have recently shown that the product from the reaction of the tetrahydropyrimidine [(3): *n* = 3, *Z* = S] with cyclohexylisosenocyanate possesses the N—S—N structure (6) (Billing, Boeyens, Denner, Hellyar, Lai, Mathee & Reid, 1992). We now report, on the basis of X-ray single-crystal structure determinations, that whereas the product from the reac-

tion of the tetrahydropyrimidine [(3): *n* = 3, *Z* = Se] with ethyl isosenocyanate possesses the tetraaza-selenapentalene structure (7), the product from the reaction of the imidazoline [(3): *n* = 2, *Z* = Se] with ethyl isosenocyanate possesses the diazatriseselenapentalene structure (8).



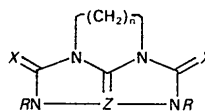
(1)

(2)

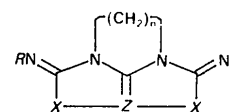


(3)

(1)–(3): *n* = 2, 3, 4
Z = S, Se

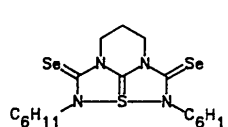


(4)

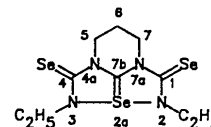


(5)

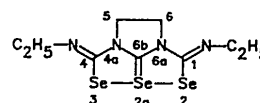
(4) and (5): *n* = 2, 3, 4
X = O, S, Se
Z = S, Se



(6)



(7)



(8)

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Experimental. Compound (7) crystallized from dichloromethane–hexane (1:3) as yellow needle-shaped crystals; m.p. 468–469 K. Analysis: calculated for C₁₀H₁₆N₄Se₃ C 27.99, H 3.76, N 13.06%; found C 27.96, H 3.70, N 13.01%. ¹H NMR (200 MHz, CDCl₃): δ 1.40 (*t*, 6H, 2 × CH₃) 2.39 (quintet, 2H, 6-CH₂), 3.95 (*q*, 4H, 2- + 3-CH₂CH₃) and 4.66 p.p.m. (*t*, 4H, 5- + 7-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 14.37 (2 × CH₃), 20.19 (6-CH₂), 45.17 and 49.29. (2-CH₂CH₃ + 3-CH₂CH₃ + 5-CH₂ + 7-CH₂), 159.41 (7b-C=Se) and 167.42 p.p.m. (1- + 4-C=Se). Compound (8) crystallized from dichloromethane–hexane (1:3) as orange crystals; m.p. 448–451 K. Analysis: calculated for C₉H₁₄N₄Se₃ C 26.04, H 3.40, N 13.50, Se 57.06%; found C 26.10, H 3.33, N 13.50, Se 56.96%. ¹H NMR (200 MHz, CDCl₃): δ 1.22 (*t*, 6H, 2 × CH₃), 3.22 (*q*, 4H, 1- + 4-CH₂CH₃) and 4.39 p.p.m. (*s*, 4H, 5- + 6-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 15.19 (2 × CH₃), 47.00 (5- + 6-CH₂), 51.07 (1- + 4-CH₂CH₃), 149.40 (1- + 4-C=N) and 171.57 p.p.m. (6b-C=Se).

For compound (7), a yellow needle of 1.72 × 0.12 × 0.12 mm mounted with the needle axis along φ was used for data collection on a CAD-4 diffractometer; ω -2 θ scans, maximum scan speed 5.49° min⁻¹. The lattice parameters were determined from a least-squares fit of 25 reflections in the range 12 < θ < 17°. Three standard reflections monitored every hour showed only random fluctuations. Data were corrected for Lorentz–polarization and absorption effects, the latter *via* ψ scans (maximum/minimum transmission 0.99/0.78). 4385 measured reflections (2 < θ < 30°; -7 < h < 7, 0 < k < 14, -18 < l < 18) were averaged to give 1568 unique reflections with $F > 3\sigma(F)$, $R_{\text{int}} = 0.051$, used for the least-squares refinement, on F , of 154 parameters. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically and allowed to refine with a common isotropic displacement factor. The refinement converged at $R = 0.055$ and $wR = 0.034$ with $w \propto 1/\sigma^2(F)$. No parameter shifts exceeded 0.001 σ for the final cycle of refinement. The maximum and minimum heights in the final $\Delta\rho$ map were 1.01 and -0.73 e Å⁻³ respectively.

For compound (8), an orange needle of 0.35 × 0.13 × 0.10 mm was used for data collection on a CAD-4 diffractometer; ω -2 θ scans, maximum scan speed 4.12° min⁻¹; graphite-monochromated Mo $K\alpha$ radiation. The lattice parameters were determined from a least-squares fit of 25 reflections in the range 12 < θ < 19°. Data were corrected for Lorentz–polarization, decay (6.8%, based on three standard reflections) and absorption effects; ψ scans were used for the absorption correction (maximum/minimum transmission 0.99/0.39). 4808 measured reflections (2 < θ < 25°; -11 < h < 11, 0 < k < 19, -16 < l < 16)

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for compound (7)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Se(1)	786 (2)	-4869	8971 (1)	58 (1)
Se(2)	6466 (2)	-1652 (2)	8435 (1)	43 (1)
Se(3)	10355 (2)	-1728 (2)	5448 (1)	65 (1)
N(1)	3927 (14)	-2690 (8)	9116 (6)	42 (2)
N(2)	4118 (13)	-3847 (8)	7657 (6)	40 (2)
N(3)	6908 (13)	-2927 (8)	6626 (6)	44 (2)
N(4)	8695 (14)	-1107 (9)	7356 (7)	48 (2)
C(1)	3080 (17)	-3706 (11)	8610 (8)	43 (3)
C(2)	5747 (16)	-2947 (10)	7456 (6)	38 (2)
C(3)	8627 (18)	-1827 (15)	6550 (8)	55 (3)
C(4)	6409 (18)	-3905 (11)	5826 (7)	56 (3)
C(5)	5698 (17)	-5140 (11)	6328 (8)	60 (3)
C(6)	3516 (16)	-4940 (11)	6919 (7)	56 (3)
C(7)	3292 (17)	-2330 (11)	10115 (7)	55 (3)
C(8)	5087 (21)	-2925 (12)	10999 (8)	72 (4)
C(9)	10111 (16)	102 (13)	7486 (8)	62 (3)
C(10)	8814 (22)	1154 (11)	6885 (9)	75 (4)

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for compound (8)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Se(1)	267 (2)	8447 (1)	2022 (1)	40 (1)
Se(2)	1851 (2)	8455 (1)	3982 (1)	32 (1)
Se(3)	3451 (2)	8046 (1)	5939 (2)	40 (1)
N(1)	-179 (16)	6492 (9)	1200 (11)	42 (3)
N(2)	1073 (16)	6644 (8)	2959 (10)	33 (3)
N(3)	2479 (16)	6481 (8)	4584 (10)	34 (3)
N(4)	3591 (17)	5969 (8)	6294 (11)	45 (4)
C(1)	323 (19)	7069 (10)	1973 (13)	35 (4)
C(2)	1794 (20)	7095 (9)	3840 (13)	34 (4)
C(3)	3191 (21)	6698 (10)	5683 (13)	40 (4)
C(4)	2229 (23)	5461 (9)	4212 (13)	52 (5)
C(5)	1258 (25)	5566 (9)	3052 (14)	60 (5)
C(6)	-952 (21)	6911 (11)	181 (13)	45 (4)
C(7)	-1726 (23)	6121 (13)	-573 (14)	59 (5)
C(8)	4258 (26)	6136 (11)	7438 (14)	69 (6)
C(9)	2838 (22)	6000 (13)	8262 (14)	56 (5)

were averaged to give 1793 unique reflections with $F > 3\sigma(F)$, $R_{\text{int}} = 0.024$, used for the least-squares refinement, on F , of 146 parameters. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically (C–H 1.08 Å) and allowed to refine with a common isotropic displacement factor. The refinement converged at $R = 0.053$ and $wR = 0.049$ with $w \propto 1/\sigma^2(F)$. No parameter shifts exceeded 0.004 σ in the final cycle of refinement. The maximum and minimum heights in the final $\Delta\rho$ map were 0.85 and -0.92 e Å⁻³, respectively.

The structures were solved by direct methods using *SHELXS86* and refined with *SHELXL76* (Sheldrick, 1976, 1990). Atomic scattering factors were used as given in *SHELXL76*. Corrections for anomalous scattering were taken from Cromer & Liberman (1970). Diagrams were produced using *SCHAKAL88* (Keller, 1988).

Discussion. Final atomic coordinates for 2,3-diethyl-6,7-dihydro-5*H*-2a λ^4 -selena-2,3,4a-tetraazacyclo-

pent[*cd*]indene-1(2*H*),4(3*H*)-diselone (7) and 1,4-bis(ethylimino)-5,6-dihydro-2,2a λ^4 ,3-triseleno-4a,6a-diazacyclopenta[*cd*]pentalene (8) are listed in Tables 1 and 2.*

Molecular structure of (7). The structure of (7) is shown in Fig. 1, which also defines the crystallographic numbering scheme. Selected bond distances and angles are listed in Table 3. Compound (7) contains elongated Se—N bonds of length 2.044 (8) and 2.053 (7) Å, which are accordingly greater by 9.3 and 9.8%, respectively, than the two-centre two-electron Se—N covalent bond of length 1.87 Å based on the sum of the covalent radii of Se and N (Pauling, 1960). These Se—N bond lengths are very similar to those recently reported for the thiocarbonyl analogue (9) [2.022 (6) and 2.045 (6) Å (Iwasaki, Murakami, Yamazaki, Yasui, Tomura & Matsumura, 1991)]. The lengths of corresponding bonds and the size of corresponding bond angles in the two halves of the triheteropentalene framework of (7) are very similar, differing from one another at most by 0.052 Å and 2.8°, respectively. The lengths of the C—C, C—N and C—Se bonds are also very similar to those of the corresponding bonds in the thiocarbonyl analogue (9) (Iwasaki, Murakami, Yamazaki, Yasui, Tomura & Matsumura, 1991). Bond angles in compound (7) also differ very little (maximum 1.0°) from the corresponding bond angles in (9).

In compound (7), the C=Se bond lengths of 1.841 (10) Å for C(1)=Se(1) and 1.819 (10) Å for C(3)=Se(3) lie midway between the length of a C—Se single bond [1.97 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987); 1.94 Å, sum of

* Lists of structure factors, anisotropic displacement parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55762 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1012]

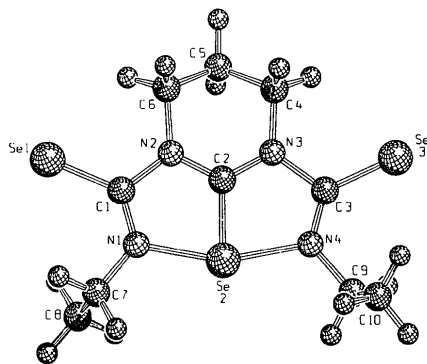


Fig. 1. Molecular structure and atomic labelling scheme for compound (7).

Table 3. Selected bond lengths (Å) and angles (°) for compound (7)

C(1)—Se(1)	1.841 (10)	N(1)—Se(2)	2.044 (8)
N(4)—Se(2)	2.053 (7)	C(2)—Se(2)	1.860 (9)
C(3)—Se(3)	1.819 (10)	C(1)—N(1)	1.297 (12)
C(7)—N(1)	1.438 (11)	C(1)—N(2)	1.437 (11)
C(2)—N(2)	1.338 (11)	C(6)—N(2)	1.497 (12)
C(2)—N(3)	1.321 (10)	C(3)—N(3)	1.489 (15)
C(4)—N(3)	1.455 (12)	C(3)—N(4)	1.285 (13)
C(9)—N(4)	1.475 (14)	C(5)—C(4)	1.528 (14)
C(6)—N(5)	1.504 (11)	C(8)—C(7)	1.505 (13)
C(10)—C(9)	1.462 (14)		
N(4)—Se(2)—N(1)	159.4 (4)	C(2)—Se(2)—N(1)	79.8 (4)
C(2)—Se(2)—N(4)	79.6 (4)	C(1)—N(1)—Se(2)	115.1 (7)
C(7)—N(1)—Se(2)	120.8 (7)	C(7)—N(1)—C(1)	124.0 (9)
C(2)—N(2)—C(1)	116.3 (8)	C(6)—N(2)—C(1)	123.7 (8)
C(6)—N(2)—C(2)	120.0 (8)	C(3)—N(3)—C(2)	116.1 (9)
C(4)—N(3)—C(2)	120.7 (8)	C(4)—N(3)—C(3)	123.2 (9)
C(3)—N(4)—Se(2)	116.2 (8)	C(9)—N(4)—Se(2)	120.2 (7)
C(9)—N(4)—C(3)	123.4 (9)	N(1)—C(1)—Se(1)	127.7 (8)
N(2)—C(1)—Se(1)	120.6 (8)	N(2)—C(1)—N(1)	111.6 (9)
N(2)—C(2)—Se(2)	117.1 (6)	N(3)—C(2)—Se(2)	118.0 (7)
N(3)—C(2)—N(2)	124.9 (9)	N(3)—C(3)—Se(3)	119.4 (10)
N(4)—C(3)—Se(3)	130.5 (10)	N(4)—C(3)—N(3)	110.1 (9)
C(5)—C(4)—N(3)	109.3 (8)	C(6)—C(5)—C(4)	111.1 (9)
C(5)—C(6)—N(2)	109.2 (8)	C(8)—C(7)—N(1)	111.2 (9)
C(10)—C(9)—N(4)	113.8 (8)		

covalent radii of Se and C] and the estimated length of a C=Se double bond [1.74 Å (Pauling, 1960)]. This indicates that the C=Se groups are conjugated with neighbouring N atoms. The N(1)—C(1) and N(4)—C(3) bonds in (7) are short [1.297 (12) and 1.285 (13) Å, respectively], being only slightly longer than an N=C double bond [1.28 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)]. In contrast, the N(2)—C(1) and N(3)—C(3) bonds [1.437 (11) and 1.489 (15) Å respectively] are much closer in length to that of an N—C single bond [1.48 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)]. The large differences in these pairs of N—C bond lengths indicate that the C(1)=Se(1) group is strongly conjugated with N(1), but only to a small extent with N(2), and that the C(3)=Se(3) group is likewise strongly conjugated with N(4) but not with N(3).

The C(2)—Se(2) bond length of 1.860 (9) Å of compound (7) is intermediate between that of a C—Se single bond (1.97 Å) and the estimated length of a C=Se double bond (1.74 Å) and is virtually the same as the C—Se bond length in tetramethylselenourea [1.863 (4) Å (Foss & Maartmann-Moe, 1987)].

The lengths of the N(2)—C(2) and the N(3)—C(2) bonds [1.338 (11) and 1.321 (10) Å, respectively] lie closer to that of an N=C double bond (1.28 Å) than to that of an N—C single bond (1.48 Å) (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). This indicates that N(2) and N(3) are conjugated with the C(2)=Se(2) group. The bonding system in compound (7) is thus segmented into three islands of conjugation, namely the N(1)—C(1)—Se(1) unit, the N(4)—C(3)—Se(3) unit and the N(2)N(3)—C(2)—Se(2) unit. Similar conclusions have been reached

concerning the structure of compound (6) (Billing, Boeyens, Denner, Hellyar, Lai, Matthee & Reid, 1992).

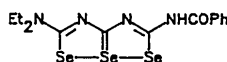
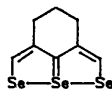
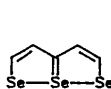
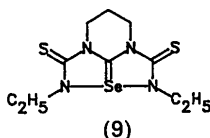


Table 4. Selected bond lengths (Å) and angles (°) for compound (8):

Se(2)—Se(1)	2.597 (2)	C(1)—Se(1)	1.892 (14)
Se(3)—Se(2)	2.658 (2)	C(2)—Se(2)	1.874 (12)
C(3)—Se(3)	1.884 (13)	C(1)—N(1)	1.263 (18)
C(6)—N(1)	1.452 (18)	C(1)—N(2)	1.416 (17)
C(2)—N(2)	1.323 (17)	C(5)—N(2)	1.490 (15)
C(2)—N(3)	1.320 (17)	C(3)—N(3)	1.431 (17)
C(4)—N(3)	1.479 (16)	C(3)—N(4)	1.269 (17)
C(8)—N(4)	1.456 (18)	C(5)—C(4)	1.555 (20)
C(7)—C(6)	1.518 (21)	C(9)—C(8)	1.559 (24)
C(1)—Se(1)—Se(2)	91.2 (4)	Se(3)—Se(2)—Se(1)	167.5 (1)
C(2)—Se(2)—Se(1)	84.6 (4)	C(2)—Se(2)—Se(3)	82.9 (5)
C(3)—Se(3)—Se(2)	91.2 (5)	C(6)—N(1)—C(1)	117.8 (13)
C(2)—N(2)—C(1)	127.9 (11)	C(5)—N(2)—C(1)	120.3 (11)
C(5)—N(2)—C(2)	111.6 (11)	C(3)—N(3)—C(2)	127.8 (12)
C(4)—N(3)—C(2)	111.0 (11)	C(4)—N(3)—C(3)	120.8 (11)
C(8)—N(4)—C(3)	118.8 (13)	N(1)—C(1)—Se(1)	129.9 (12)
N(2)—C(1)—Se(1)	113.2 (10)	N(2)—C(1)—N(1)	116.9 (13)
N(2)—C(2)—Se(2)	123.0 (10)	N(3)—C(2)—Se(2)	124.6 (11)
N(3)—C(2)—N(2)	112.5 (11)	N(3)—C(3)—Se(3)	112.8 (10)
N(4)—C(3)—Se(3)	131.2 (12)	N(4)—C(3)—N(3)	115.9 (13)
C(5)—C(4)—N(3)	103.4 (11)	C(4)—C(5)—N(2)	101.6 (11)
C(7)—C(6)—N(1)	110.7 (13)	C(9)—C(8)—N(4)	109.5 (15)

Molecular structure of (8). The structure of (8) is shown in Fig. 2, which also defines the crystallographic numbering scheme. Selected bond distances and angles are listed in Table 4. The Se—Se bond lengths of 2.597 (2) and 2.658 (2) Å are greater by 10.9 and 13.6%, respectively, than the two-centre two-electron Se—Se covalent bond length [2.34 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)]. Long Se—Se bonds have been found in three other triselenapentalenes whose structures have been determined, namely (10) [Se—Se 2.579 (3) and 2.586 (3) Å (Hordvik & Julshamm, 1971)], (11) [Se—Se 2.554 (3) and 2.568 (3) Å (Hordvik & Porten, 1973)] and (12) [two independent molecules: (A) Se—Se 2.554 (1) and 2.582 (1) Å, (B) Se—Se 2.514 (1) and 2.641 (1) Å (Richter, Sieler, Hansen, Köhler, Beyer & Hoyer, 1991)]. The average Se—Se bond lengths in compounds (8) and (10)–(12) are slightly smaller than the average Se—Se bond lengths in several inorganic salts whose anions or cations contain a sequence of three Se atoms, namely rubidium triselenocyanate hemihydrate, Rb⁺.(SeCN)₃[−].½H₂O [Se—Se 2.656 (3) Å (Hauge,

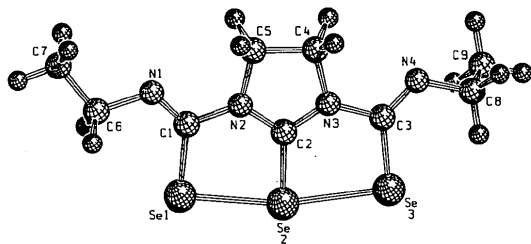


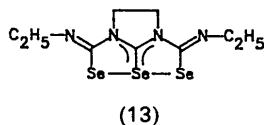
Fig. 2. Molecular structure and atomic labelling scheme for compound (8).

1971)], potassium triselenocyanate hemihydrate, K⁺.(SeCN)₃[−].½H₂O [Se—Se 2.648 (4) and 2.689 (4) Å (Hauge & Sletten, 1971)], tris(selenourea) dichloride hydrate, [(NH₂)₂CSe]₃²⁺.2Cl[−].H₂O [Se—Se 2.597 (2) and 2.717 (2) Å (Hauge, Opedal & Årskog, 1975)] and tris(selenourea) dibromide hydrate, [(NH₂)₂CSe]₃²⁺.2Br[−].H₂O [Se—Se 2.624 (2) and 2.712 (2) Å (Hauge, Opedal & Årskog, 1975)].

The C(2)—Se(2) bond length of 1.874 (12) Å in compound (8) is intermediate between that of a C—Se single bond (1.97 Å) and is slightly greater than the length of the corresponding bonds in compounds (7) [1.860 (9) Å] and (9) [1.852 (7) Å (Iwasaki, Murakami, Yamazaki, Yasui, Tomura & Matsumura, 1991)]. The lengths of the N(2)—C(2) and the N(3)—C(2) bonds in compound (8) [1.323 (17) and 1.320 (17) Å, respectively] lie between that of an N—C single bond (1.48 Å) and that of an N=C double bond (1.28 Å) and are slightly smaller than the N(2)—C(2) and the N(3)—C(2) bonds in compounds (7) [1.338 (11) and 1.321 (10) Å, respectively] and (9) [1.326 (9) and 1.331 (9) Å, respectively (Iwasaki, Murakami, Yamazaki, Yasui, Tomura & Matsumura, 1991)]. This indicates that N(2) and N(3) are conjugated with C(2)=Se(2) in compound (8), but that the conjugation is marginally less than that between N(2), N(3) and C(2)=Se(2) in compounds (7) and (9).

The N(1)—C(1) and N(4)—C(3) bonds with lengths of 1.263 (18) and 1.269 (17) Å, respectively, are essentially localized N=C double bonds [N=C double-bond length 1.28 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)]. Correspondingly, the lengths of the N(2)—C(1) and N(3)—C(3) bonds [1.416 (17) and 1.431 (17) Å, respectively] are closer to an N—C single bond length (1.48 Å), and the C(1)—Se(1) and C(3)—Se(3) bond lengths are close to that of a C—Se single bond

(1.97 Å). These data indicate that the N(1)=C(1) and N(4)=C(3) bonds are not appreciably conjugated with the attached pairs of heteroatoms N(2), Se(1) and N(3), Se(3), respectively. The molecule of (8) can therefore be represented approximately by (13).



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Structure of a Covalently Linked Cross-Section Representative of a Hydrogen-Bonded dA·dT Base Pair

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Abstract. 3-(3',5'-Di-O-acetyl-2'-deoxy-β-D-ribofuranosyl)-9-(2'-deoxy-β-D-ribofuranosyl)-11-methyl-3H-pyrimido[1'',6'':1',2']imidazo[4',5':4,5]imidazo-[2,1-]purin-8(9H)-one acetonitrile solvate monohydrate, C₂₆H₂₈N₈O₉·C₂H₃N·H₂O, *M_r* = 655.63 (596.56 + 41.05 + 18.02), monoclinic, *P*2₁, *a* = 5.659 (2), *b* = 15.097 (3), *c* = 17.138 (5) Å, β = 96.73 (3)°, *V* = 1454 (1) Å³, *Z* = 2, *D_x* = 1.497 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 1.09 cm⁻¹, *F*(000) = 688, *T* = 198 K, *R* = 0.054 and *wR* = 0.056 for 1532 observed reflections. The atoms of the central five-ring heteroaromatic array are coplanar with a root-mean-square deviation of ± 0.03 Å. The torsion angle of the glycosidic linkage, C(3a)—N(3)—C(1)—O(1'), for attachment at the purine-N, is -174.4 (7)°, and the angle C(8)—N(9)—C(1'')—O(1''), for attachment at the pyrimidine-N, is -159.3 (7)°. Both are in the *anti*

range. The N(12)···N(13) distance is 2.56 (1) Å, compared with the N—H···O distance of 2.85 Å in a dA·dT Watson–Crick base pair, and the N(6)···N(7) distance is 2.609 (10) Å, *cf.* N···H—N of 2.9 Å. Thus, compound (1) is a spatial mimic of a Watson–Crick double-helical dA·dT cross section. The sugar puckers are ²*E* (C2'-*endo*), with *P* = 169.8 and τ_{*m*} = 37.2, and ³*E* (C3'-*endo*), with *P* = 16.0 and τ_{*m*} = 38.9. Intermolecular hydrogen bonding in the crystal occurs between H(O5'') of one molecule and N(13) of an adjacent molecule, and likewise between H(O3'') and N(12) of the second.

Introduction. We have introduced the concept of covalently linked double-helical cross sections that are representative of A·U, dA·dU and dA·U duplexes (Devadas & Leonard, 1986, 1990). While comparison of the overall geometry of a Watson–Crick