Discussion. Fractional coordinates and B_{eq} values are given in Table 1,* the intramolecular distances in Table 2. Those of the carborane cage are in very good agreement with previously determined structures (Císařová, 1985). It is worth emphasizing the regularity of the carborane cage (see also Table 3). The motif as well as packing of molecules in the unit cell are depicted in Figs. 1 and 2, respectively. van der Waals radii for relevant atoms or the methyl group are: H = 1·2, methyl = 2·0, Cl = 1·8 Å (*Handbook of Chemistry and Physics*, 1979). In Table 4 the shortest intermolecular distances between carborane ligands and methyl groups are listed. Although these distances where H atoms are involved are the least reliable, this overview illustrates that distances for all these pairs except Cl···methyl are somewhat longer than the sum of van der Waals radii. This may be qualitatively explained by the attraction of negative Cl atoms to the positive tetramethylammonium group.

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* Lists of structure factors, anisotropic thermal parameters, bond angles, H-atom coordinates and bond lengths involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53482 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Ethyl 5-Chloro-1-cyanomethyl-3-phenylindole-2-carboxylate

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Abstract. $C_{19}H_{15}ClN_2O_2$, M_r = 338·80, triclinic, $P\bar{1}$, a = 13·984 (2), b = 10·069 (2), c = 13·248 (1) Å, α = 72·61 (1), β = 82·60 (1), γ = 69·27 (2)°, V = 1668·9 (2) Å^3, Z = 4, D_m = 1·34 (5), D_x = 1·36 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 2·03 mm^{-1}, F(000) = 704, T = 300 K, final R = 0·066 for 3915 observed reflections [$I \geq 3\sigma(I)$]. There are two independent molecules per asymmetric unit. The indole nucleus is slightly bent along the C(8)—C(9) bond. The phenyl ring connected to the indole rings is rotated about the C(3)—C(10) bond by 52·6 (5)° in molecule A and 49·9 (5)° in molecule B. The carboxyl group makes a dihedral angle of 25·3 (5)° with the mean plane of the indole rings in A and 14·7 (3)° in B. The C—C≡N chain is linear and is inclined at an angle of 86·1 (4)° to the mean plane of the indole rings in A and 83·3 (4)° in B.

Introduction. Indole and its derivatives possess various important pharmacological properties like central nervous system depressant, muscle relaxant and anti-allergic properties (Harris & Uhle, 1960; Wei & Stanley, 1970; Houlihah, 1973; White & Black, 1976; Ho, Haegman & Perisco, 1986). The title compound is an important precursor to a physiologically active tetrahydropyrazinoindole (Reynolds & Carson, 1970). It can be readily converted to 8-chloro-10-phenyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole in a single step by reductive cyclization using lithium aluminium hydride.

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Table 1. *Fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* ($Å^2 \times 10^4$) *for non-*H *atoms; e.s.d.'s are in parentheses*

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

	x	*y*	*z*	U_{eq}
N(1)	7923 (2)	2197 (3)	5837 (2)	481 (10)
C(2)	8087 (2)	2345 (4)	6803 (2)	478 (12)
C(3)	7354 (2)	1989 (3)	7536 (2)	451 (11)
C(4)	5818 (2)	1236 (3)	7286 (2)	472 (12)
C(5)	5387 (2)	939 (4)	6548 (2)	497 (12)
C(6)	5799 (3)	999 (4)	5517 (2)	561 (14)
C(7)	6648 (2)	1406 (4)	5210 (2)	522 (13)
C(8)	7091 (2)	1733 (3)	5938 (2)	450 (11)
C(9)	6706 (2)	1620 (3)	6991 (2)	429 (11)
C(10)	7215 (2)	1961 (3)	8678 (2)	452 (12)
C(11)	7156 (3)	3147 (4)	9028 (3)	575 (14)
C(12)	6984 (3)	3106 (4)	10085 (3)	667 (17)
C(13)	6887 (3)	1852 (5)	10820 (3)	709 (18)
C(14)	6959 (3)	654 (4)	10483 (3)	699 (18)
C(15)	7125 (3)	696 (4)	9418 (2)	549 (14)
Cl(16)	4267 (1)	500 (1)	6870 (1)	683 (4)
C(17)	8646 (2)	2110 (4)	4947 (2)	529 (13)
C(18)	8507 (3)	3537 (4)	4163 (3)	607 (16)
N(19)	8412 (3)	4630 (4)	3526 (3)	881 (18)
C(20)	8908 (2)	2891 (4)	6890 (2)	513 (13)
O(21)	9273 (2)	3606 (3)	6145 (2)	657 (11)
O(22)	9202 (2)	2482 (3)	7870 (2)	786 (14)
C(23)	9971 (4)	3029 (6)	8089 (4)	990 (28)
C(24)	10589 (0)	1883 (0)	8835 (0)	2227 (72)
N(1′)	2096 (2)	2833 (3)	4055 (2)	475 (10)
C(2′)	1975 (2)	2586 (3)	3108 (2)	471 (12)
C(3′)	2747 (2)	2860 (3)	2391 (2)	462 (12)
C(4′)	4246 (2)	3701 (4)	2639 (2)	505 (13)
C(5′)	4618 (3)	4129 (4)	3346 (3)	577 (14)
C(6′)	4151 (3)	4159 (4)	4352 (3)	606 (15)
C(7′)	3315 (3)	3718 (4)	4662 (2)	557 (14)
C(8′)	2934 (2)	3280 (3)	3955 (2)	460 (12)
C(9′)	3370 (2)	3264 (3)	2939 (2)	463 (12)
C(10′)	2929 (2)	2852 (4)	1264 (2)	504 (13)
C(11′)	2156 (3)	3584 (4)	533 (3)	592 (14)
C(12′)	2370 (4)	3641 (5)	−524 (3)	759 (20)
C(13′)	3349 (4)	2974 (5)	−872 (3)	770 (21)
C(14′)	4115 (3)	2258 (5)	−155 (3)	716 (18)
C(15′)	3916 (3)	2194 (4)	912 (3)	603 (15)
Cl(16′)	5690 (1)	4677 (1)	3007 (1)	845 (5)
C(17′)	1358 (2)	2756 (4)	4933 (2)	526 (13)
C(18′)	1492 (3)	1537 (4)	5745 (3)	611 (15)
N(19′)	1578 (3)	457 (4)	6373 (3)	881 (18)
C(20′)	1203 (2)	1912 (4)	3065 (2)	501 (13)
O(21′)	748 (2)	1421 (3)	3838 (2)	653 (11)
O(22′)	1073 (2)	1901 (3)	2106 (2)	782 (14).
C(23′)	319 (4)	1277 (5)	1957 (3)	838 (22)
C(24′)	−546 (0)	2436 (0)	1507 (0)	1571 (41)

Table 2. *Bond lengths* (Å) *and angles* (°) *for molecules A and B; e.s.d.'s are in parentheses*

N(1)—C(2)	1·390 (5) 1·394 (5)	C(8)—C(9)	1·419 (4) 1·410 (4)
N(1)—C(8)	1·377 (5) 1·375 (5)	C(10)—C(11)	1·379 (6) 1·391 (5)
N(1)—C(17)	1·456 (4) 1·459 (4)	C(10)—C(15)	1·392 (4) 1·391 (5)
C(2)—C(3)	1·386 (4) 1·392 (4)	C(11)—C(12)	1·385 (5) 1·386 (5)
C(2)—C(20)	1·467 (6) 1·479 (6)	C(12)—C(13)	1·384 (6) 1·383 (6)
C(3)—C(10)	1·497 (4) 1·488 (4)	C(13)—C(14)	1·375 (7) 1·370 (6)
C(3)—C(9)	1·432 (5) 1·430 (5)	C(14)—C(15)	1·394 (5) 1·396 (5)
C(4)—C(5)	1·366 (5) 1·365 (6)	C(17)—C(18)	1·465 (5) 1·477 (5)
C(4)—C(9)	1·404 (5) 1·416 (5)	C(18)—N(19)	1·146 (5) 1·133 (5)
C(5)—C(6)	1·408 (4) 1·414 (5)	C(20)—O(21)	1·209 (4) 1·207 (4)
C(5)—Cl(16)	1·743 (4) 1·737 (4)	C(20)—O(22)	1·316 (4) 1·314 (5)
C(6)—C(7)	1·366 (6) 1·367 (6)	O(22)—C(23)	1·463 (8) 1·462 (7)
C(7)—C(8)	1·384 (5) 1·379 (6)	C(23)—C(24)	1·375 (4) 1·397 (4)
C(2)—N(1)—C(8)	109·1 (2) 108·9 (2)	C(8)—C(9)—C(4)	118·7 (3) 118·3 (3)
C(2)—N(1)—C(17)	126·5 (3) 127·2 (3)	C(8)—C(9)—C(3)	107·8 (3) 108·4 (3)
C(8)—N(1)—C(17)	122·2 (3) 122·4 (3)	C(4)—C(9)—C(3)	133·5 (3) 133·1 (3)
N(1)—C(2)—C(3)	109·5 (3) 109·5 (3)	C(3)—C(10)—C(11)	122·8 (3) 121·9 (3)
N(1)—C(2)—C(20)	119·6 (3) 118·9 (3)	C(3)—C(10)—C(15)	118·9 (3) 119·1 (3)
C(3)—C(2)—C(20)	130·8 (3) 130·9 (3)	C(11)—C(10)—C(15)	118·4 (3) 118·8 (3)
C(2)—C(3)—C(9)	106·3 (3) 105·7 (3)	C(10)—C(11)—C(12)	121·2 (3) 120·2 (3)
C(2)—C(3)—C(10)	129·7 (3) 131·0 (4)	C(11)—C(12)—C(13)	120·3 (4) 121·0 (4)
C(9)—C(3)—C(10)	124·0 (3) 123·2 (3)	C(12)—C(13)—C(14)	119·0 (3) 119·1 (4)
C(9)—C(4)—C(5)	117·9 (3) 118·2 (3)	C(13)—C(14)—C(15)	120·8 (4) 120·9 (4)
C(4)—C(5)—C(6)	122·8 (3) 122·1 (4)	C(14)—C(15)—C(10)	120·3 (4) 120·1 (3)
C(4)—C(5)—Cl(16)	119·5 (2) 119·6 (3)	N(1)—C(17)—C(18)	113·2 (3) 113·1 (3)
C(6)—C(5)—Cl(16)	117·7 (3) 118·2 (3)	C(17)—C(18)—N(19)	177·8 (4) 178·9 (4)
C(5)—C(6)—C(7)	119·9 (4) 120·5 (4)	C(2)—C(20)—O(21)	123·7 (3) 122·8 (3)
C(6)—C(7)—C(8)	118·4 (3) 117·9 (3)	C(2)—C(20)—O(22)	111·5 (3) 113·2 (3)
N(1)—C(8)—C(7)	130·6 (3) 129·6 (3)	O(21)—C(20)—O(22)	124·8 (4) 124·0 (4)
N(1)—C(8)—C(9)	107·4 (3) 107·4 (3)	C(20)—O(22)—C(23)	117·6 (3) 118·4 (3)
C(7)—C(8)—C(9)	122·1 (3) 123·0 (3)	O(22)—C(23)—C(24)	105·7 (4) 108·5 (4)

The title compound was synthesized by treating ethyl 5-chloro-3-phenylindole-2-carboxylate with chloroacetonitrile in the presence of sodium hydride. The present work was undertaken since very little crystallographic information is available on non-steroidal indole derivatives (Chakraborthy & Talapatra, 1986). This work is a continuation of our investigations on some pharmacologically important indoles and their precursors.

Experimental. Colorless transparent needle-shaped crystals grown by diffusion of hexane into benzene solution; crystal of size 0·2 × 0·13 × 0·28 mm mounted on Enraf–Nonius CAD-4 diffractometer; $\omega/2\theta$ scan, maximum time spent on any reflection was 30 s, scan width $2\theta = (1 + 0{\cdot}14\tan\theta)°$, aperture width = $(3 + 0{\cdot}42\tan\theta)$ mm; cell dimensions from least-squares refinement of 18 centered reflections in the θ range 13 to 35°; density by flotation technique; intensity data collected to a maximum $2\theta = 140°$; three standard reflections monitored every 2 h, no variation; 6294 reflections measured; h 0 to 17, k −11 to 12, l −15 to 16; 3915 reflections with $I \geq 3\sigma(I)$ considered observed; data corrected for Lorentz–polarization effects; empirical absorption correction based on a series of ψ scans applied, minimum, maximum and average correction factors 0·950, 0·999 and 0·986. The structure was solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); all H atoms (except methyl H atoms) located from successive difference Fourier maps; full-matrix least-squares refinement on F with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms using *SHELX76* (Sheldrick, 1976). The temperature factor and the shift/e.s.d. in the positional parameters of C(24) were high in both molecules. In the final refinement cycle, the positional parameters of C(24) in both molecules were fixed and the H atoms attached to these atoms were not included in refinement and structure-factor calculations. The final $R = 0{\cdot}066$ and $wR = 0{\cdot}078$, $w = 1/[\sigma^2(F) + 0{\cdot}00694F^2]$, σ's based on counting statistics, the refinement terminated when the shift/e.s.d. in the positional parameters of non-H atoms was less than 0·16, the minimum and maximum residual electron densities in the final difference Fourier map were $-0{\cdot}31$ and $0{\cdot}56$ e Å^{-3}. Atomic scattering factors taken from *SHELX76*.

Discussion. The final positional parameters of non-H atoms and U_{eq} values are given in Table 1, and the bond lengths and angles are given in Table 2.* An *ORTEP* plot (Johnson, 1965) of one of the molecules with 50% probability thermal ellipsoids and atomic numbering is shown in Fig. 1.

The two rings in the indole ring system are planar and the normals to these planes are inclined at angles 2·1 (3)° in molecule *A* and 3·0 (4)° in molecule *B*. Thus the indole nucleus is slightly bent along the C(8)—C(9) bond which appears to be statistically highly significant (Falkenberg & Carlstrom, 1971). The C(3)—C(9) bond is longer than the standard aromatic C—C bond and is in agreement with the values observed in various other indole derivatives (Falkenberg & Carlstrom, 1971; Roychowdhury & Basak, 1975; Vijayalakshmi & Srinivasan, 1975; Chandrashekar & Pattabhi, 1980; Chakraborthy & Talapatra, 1986; Shoja, 1988). The bond lengths C(6)—C(7) and C(4)—C(5) = 1·366 (6) Å are considerably shorter (5σ) than the standard aromatic C—C bond. The phenyl ring connected to the indole ring system is rotated about the C(3)—C(10) bond by 52·6 (5)° in molecule *A* and 49·9 (5)° in molecule *B*. The ethyl carboxylate group, except for atom C(24), is planar and the two C—O bond lengths of this group are in agreement with the values observed in esters (Vijayalakshmi & Srinivasan, 1975). The mean plane of the ethyl carboxylate group makes a dihedral angle of 25·3 (5)° with the mean plane of the indole rings in molecule *A* and 14·7 (3)° in molecule *B*. The C=O bond is *syn* to the ester moiety about the C—O bond; the torsion angle O(21)—C(20)—O(22)—C(23) is 5·0 (5)° in *A* and 1·0 (5)° in *B*. The C—C≡N chain is linear and is inclined at an angle of 86·1 (4)° in *A* and 83·3 (4) ° in *B* to the mean planes of the indole rings. The Cl atom has a deviation of 0·076 (1) Å in *A* and 0·013 (1) Å in *B* from the mean planes of the indole rings. The average C(5)—Cl distance of 1·740 (4) Å is larger than the previously reported values (Ikemoto, Yakushi, Naito, Kurudo & Sano, 1977; Sindt & MacKay, 1979). There are no intra- or intermolecular hydrogen bonds. There are a few short contacts less than 3·4 Å. The crystal structure is stabilized mainly by van der Waals forces.

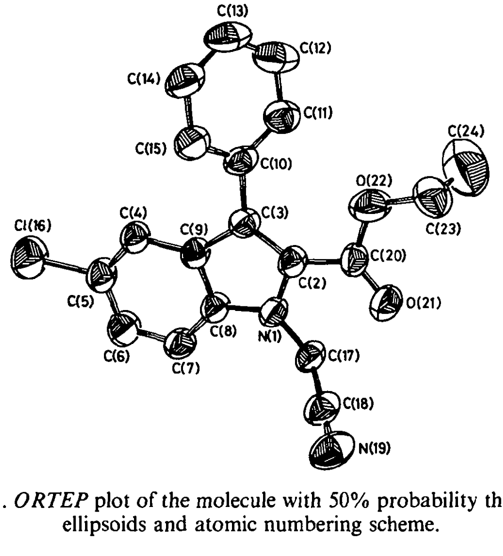

Fig. 1. *ORTEP* plot of the molecule with 50% probability thermal ellipsoids and atomic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a diagram of the molecular packing viewed down **b** have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53503 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of 6a-Thia/Selena-1,3,4,6-tetraazapentalene Derivatives: Hypervalent S/Se—N Bonds

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Abstract. 2,3,4,5-Tetrahydro-1,6-diphenyl-3,4-propano-6a-thia-1,3,4,6-tetraazapentalene-2,5-dione, (I), $C_{18}H_{16}N_4O_2S$, $M_r = 352{\cdot}42$, orthorhombic, $Iba2$, $a = 20{\cdot}490\,(10)$, $b = 21{\cdot}420\,(5)$, $c = 7{\cdot}575\,(2)$ Å, $V = 3324\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}408$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}204$ mm^{-1}, $F(000) = 1472$, $T = 293$ K, $R = 0{\cdot}051$ for 1014 observed reflections. 1,6-Diethyl-2,3,4,5-tetrahydro-3,4-propano-6a-thia-1,3,4,6-tetraazapentalene-2,5-dione, (II), $C_{10}H_{16}N_4O_2S$, $M_r = 256{\cdot}33$, monoclinic, $P2_1/n$, $a = 23{\cdot}888\,(3)$, $b = 4{\cdot}8422\,(6)$, $c = 22{\cdot}518\,(4)$ Å, $\beta = 102{\cdot}62\,(1)°$, $V = 2541{\cdot}8\,(6)$ Å^3, $Z = 8$, $D_x = 1{\cdot}340$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}5418$ Å, $\mu = 2{\cdot}214$ mm^{-1}, $F(000) = 1088$, $T = 293$ K, $R = 0{\cdot}073$ for 2615 observed reflections. 1,6-Diethyl-2,3,4,5-tetrahydro-3,4-propano-6a-selena-1,3,4,6-tetraazapentalene-2,5-dithione, (III), $C_{10}H_{16}N_4S_2Se$, $M_r = 335{\cdot}36$, monoclinic, $P2_1$, $a = 13{\cdot}025\,(4)$, $b = 10{\cdot}233\,(1)$, $c = 5{\cdot}2535\,(7)$ Å, $\beta = 98{\cdot}36\,(2)°$, $V = 692{\cdot}7\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}611$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 2{\cdot}956$ mm^{-1}, $F(000) = 340$, $T = 293$ K, $R = 0{\cdot}043$ for 1382 observed reflections. Each molecule has approximate mirror symmetry except phenyl or ethyl groups with equidistant S—N/Se—N bonds. The mean distances of S—N bonds are 1·959 (6) and 1·927 (6) Å in (I) and (II), respectively, and that of the Se—N bonds in (III) is 2·034 (6) Å. These values are longer than those of the normal S/Se—N single bonds by 9–12%. The S—C distances, 1·717 (7) for (I), 1·717 (6) Å (mean value) for (II), and the Se—C distance, 1·852 Å for (III), are intermediate between those for single and double bonds. The pentalene framework and O or S atoms of carbonyl or thiocarbonyl groups are almost coplanar. The structural features show the π-hypervalency of the 12π-system.

Introduction. It is well known that the S atom shows hypervalency (Musher, 1969). In typical hypervalent compounds, such as σ-sulfuranes (Paul, Martin & Perozzi, 1972; Kálmán, Sásvári & Kapovits, 1973) and thiathiophthenes (Hansen & Hordvik, 1973), a tetravalent or divalent S atom contacts with electronegative groups, X and Y forming linear $X\cdots S\cdots Y$ bonds. The lengths of the $S\cdots X$ and $S\cdots Y$ bonds are longer than those of S—X and S—Y single bonds and shorter than the sum of the van der Waals radii, and correspond to 0·5 of Pauling's bond order (Pauling, 1960).

Compounds (I), (II) and (III), which have tetraazathia- or tetraazaselenapentalene frames with carbonyl or thiocarbonyl groups, are expected to show hypervalency like that in 6a-thiathiophthenes.

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