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# On the 2,5-Diazolic Heterocyclic System. I. Crystal and Molecular Structure of 3,4-Diphenyl-1,2,5-selenadiazole and 3,4-Diphenyl-1,2,5-thiadiazole

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The crystal structures of 3,4-diphenyl-1,2,5-selenadiazole (space group $P2_1/c$, cell parameters $a=6{\cdot}55$, $b=24{\cdot}55$, $c=7{\cdot}57$ Å, $\beta=101{\cdot}4°$) and 3,4-diphenyl-1,2,5-thiadiazole (space group $P2_1/c$, cell parameters $a=11{\cdot}05$, $b=7{\cdot}13$, $c=18{\cdot}71$ Å, $\beta=125{\cdot}8°$) were determined by Patterson and Fourier methods and refined by least-squares methods to the final $R$ values of 0·052 and 0·061 respectively. The relevant bond lengths inside the thiadiazolic nucleus (S–N 1·632 and C–N 1·333 Å as average values) agree very well with the values obtained by microwave spectroscopy and electron diffraction studies on 1,2,5-thiadiazole and indicate some electron delocalization inside the thiadiazolic nucleus, greater than in the selenadiazolic nucleus (Se–N 1·811 and C–N 1·300 Å as average values). In both compounds only very weak, if any, conjugation exists between the heteroaromatic nucleus and the phenyl groups. A very short intermolecular Se···N distance (2·95 Å) is noted and discussed.

## Introduction

This paper reports part of a study undertaken on the structures of molecules containing the 2,5-diazolic nucleus, with Se, S or O as the other heteroatom present in the cycle.

While the molecular structures of 1,2,5-thiadiazole (Momany & Bonham, 1961; Dobyns & Pierce, 1963) and of 1,2,5-oxadiazole (Saegebarth & Cox, 1965) have been already determined, no precise information is available about the structure of the 1,2,5-selenadiazolic nucleus. The aim of this work is to determine the molecular geometry of the 1,2,5-selenadiazolic nucleus and to study the interactions between heterocyclic nuclei and phenylic substituents. Obviously, the geometrical parameters determined can be correlated with the molecular electronic structure and can supply useful information, chiefly about the electron delocalization inside the heterocyclic nucleus and about the conjugation between the heterocyclic nucleus and the phenylic substituents.

## Experimental

Crystals suitable for an X-ray investigation were obtained by Professor V. Bertini, Institute of Organic Chemistry, Pisa University, who also gave us much useful information about these compounds. Unit-cell dimensions and space group were obtained from precession and rotation photographs, with Cu $K\alpha$ radiation; the crystal data are listed in Table 1. Three-dimensional intensity data were recorded photographically, by the equi-inclination Weissenberg technique, with the same radiation and the multiple film technique; seven layers with $a$ as rotation axis ($h=0$ to 6) were recorded and 1774 observed reflexions were obtained for the Se compound, whereas seven layers with $b$ as rotation axis ($k=0$ to 6) were recorded and 1873 independent reflexions were observed for the S compound. Integrated intensities were measured on a Nonius microdensitometer. Lorentz and polarization corrections were made in the usual way; correction was also made for $\alpha_1$–$\alpha_2$ spot doubling. No correction was made for absorption effects, owing to the very small dimensions of the crystals. Interlayer scaling factors were determined during the refinement.

Table 1. *Crystal data, with standard deviations*

| | 3,4-Diphenyl-1,2,5-selenadiazole $C_{14}H_{10}N_2Se$ | 3,4-Diphenyl-1,2,5-thiadiazole $C_{14}H_{10}N_2S$ |
|---|---|---|
| M.W. | 285·2 | 238·3 |
| $a$(Å) | 6·55 (1) | 11·05 (2) |
| $b$ | 24·55 (2) | 7·13 (1) |
| $c$ | 7·57 (1) | 18·71 (3) |
| $\beta$ (°) | 101·4 (2) | 125·8 (2) |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $Z$ | 4 | 4 |
| $D_x$ (g cm$^{-3}$) | 1·586 | 1·322 |

## Structure determination and refinement

### 3,4-*Diphenyl*-1,2,5-*selenadiazole*

The coordinates of the Se atom were determined from a three-dimensional Patterson synthesis. A Fourier synthesis, phased on the heavy atom, showed the positions of the C and N atoms. The parameters were refined by block-diagonal and full-matrix least-squares methods, with individual isotropic thermal parameters, by the least-squares programs incorporated in the X-RAY 70 System (Stewart, 1970). At this stage the reliability index $R=\sum||F_o|-|F_c||/\sum|F_o|$ was 0·094.

Subsequently, we introduced anisotropic temperature factors and the weighting scheme:

$$\sqrt{w}=1/(a+|F_o|+b|F_o|^2)$$

proposed by Cruickshank (1965) with $a=15$ and $b=0{\cdot}03$, reducing $R$ to 0·059. A three-dimensional dif-

Table 2. 3,4-*Diphenyl*-1,2,5-*selenadiazole*: *positional and anisotropic thermal parameters* (× $10^4$) *of 'heavy' atoms, with estimated standard deviations*

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Se | 2470 (1) | 10292 (1) | 8521 (1) | 164 (2) | 9 (1) | 138 (1) | −2 (1) | 29 (1) | −1 (1) |
| N(1) | 53 (8) | 10042 (2) | 7196 (6) | 174 (15) | 7 (1) | 112 (9) | 4 (2) | 31 (9) | 3 (2) |
| N(2) | 3252 (8) | 9615 (2) | 9346 (6) | 129 (14) | 9 (1) | 117 (8) | −2 (2) | 28 (8) | 1 (2) |
| C(1) | 12 (9) | 9517 (2) | 7404 (7) | 100 (14) | 11 (1) | 94 (9) | 6 (3) | 35 (9) | −1 (2) |
| C(2) | 1764 (9) | 9284 (2) | 8623 (7) | 99 (15) | 10 (1) | 100 (9) | 7 (3) | 28 (9) | −2 (2) |
| C(3) | −1747 (9) | 9208 (2) | 6303 (7) | 134 (15) | 9 (1) | 96 (9) | −4 (3) | 17 (9) | 6 (2) |
| C(4) | −3772 (9) | 9417 (2) | 6074 (8) | 162 (17) | 12 (1) | 136 (11) | 6 (3) | 9 (10) | −2 (3) |
| C(5) | −5405 (10) | 9143 (3) | 4957 (9) | 298 (25) | 12 (1) | 164 (13) | −15 (4) | −28 (10) | −5 (3) |
| C(6) | −5064 (11) | 8686 (3) | 4051 (9) | 186 (21) | 17 (1) | 149 (12) | −23 (4) | −18 (10) | 12 (3) |
| C(7) | −3072 (13) | 8480 (3) | 4236 (10) | 119 (19) | 22 (1) | 157 (12) | −13 (4) | 10 (11) | 16 (3) |
| C(8) | −1397 (10) | 8737 (3) | 5388 (8) | 112 (16) | 14 (1) | 128 (10) | −2 (3) | 5 (10) | 8 (3) |
| C(9) | 2031 (9) | 8702 (2) | 9145 (7) | 131 (16) | 10 (1) | 95 (5) | 2 (3) | 3 (9) | −2 (2) |
| C(10) | 449 (11) | 8417 (3) | 9719 (10) | 224 (21) | 11 (1) | 143 (12) | 10 (3) | 21 (12) | 1 (3) |
| C(11) | 715 (13) | 7883 (3) | 10280 (11) | 288 (22) | 13 (1) | 179 (14) | 25 (4) | −5 (14) | −5 (3) |
| C(12) | 2577 (13) | 7621 (3) | 10272 (10) | 402 (28) | 10 (1) | 156 (13) | 2 (4) | −9 (14) | 5 (3) |
| C(13) | 4188 (12) | 7900 (3) | 9718 (10) | 291 (25) | 13 (1) | 207 (16) | −14 (4) | 11 (5) | 13 (3) |
| C(14) | 3903 (11) | 8439 (2) | 9156 (8) | 156 (19) | 14 (1) | 173 (13) | −2 (3) | 13 (12) | 9 (3) |

ference synthesis calculated at this stage showed well-defined peaks in positions where H atoms were expected. Further refinement, based on anisotropic temperature factors for Se, C, N atoms and isotropic temperature factors for H atoms reduced $R$ to 0·052.

The scattering factors used in the structure factor calculations were taken from *International Tables for X-ray Crystallography* (1962). The final parameters are listed in Tables 2 and 3 along with their estimated standard deviations.*

Table 3. 3,4-*Diphenyl*-1,2,5-*selenadiazole*: *positional parameters of hydrogen atoms* (× $10^3$); *the e.s.d.'s for* $x$, $y$ *and* $z$ *parameters are* ~0·018, 0·005, 0·016 *respectively, and the thermal parameters were fixed at the value* $B = 5·0$ Å$^2$

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(4) | −339 | 968 | 670 |
| H(5) | −335 | 941 | 501 |
| H(6) | 359 | 848 | 322 |
| H(7) | 317 | 818 | 345 |
| H(8) | −22 | 857 | 526 |
| H(10) | −91 | 862 | 990 |
| H(11) | −43 | 768 | 1060 |
| H(12) | 319 | 731 | 1107 |
| H(13) | 533 | 770 | 958 |
| H(14) | 486 | 859 | 874 |

### 3,4-*Diphenyl*-1,2,5-*thiadiazole*

The phase problem was solved by a three-dimensional Patterson synthesis, by which the S atom position was determined; C and N atoms were located by means of a Fourier synthesis; the refinement by a least-squares method reduced $R$ to the value 0·12. Introduction of the weighting scheme of Cruickshank, with $a = 6·0$ and $b = 0·06$, and allowance for individual anisotropic motion, then reduced $R$ to the value 0·073. A $\Delta F$ synthesis now showed the H atom positions. Further refinement reduced $R$ to the value 0·061. The final parameters are listed in Tables 4 and 5.

Table 4. 3,4-*Diphenyl*-1,2,5-*thiadiazole*: *positional and anisotropic thermal parameters* (× $10^4$) *of 'heavy' atoms, with estimated standard deviations*

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S | 10 (1) | 1892 (1) | 830 (1) | 109 (1) | 163 (2) | 40 (1) | 1 (1) | 46 (1) | 4 (1) |
| N(1) | −32 (3) | 2775 (4) | 90 (2) | 91 (3) | 141 (7) | 34 (1) | 9 (3) | 32 (2) | 5 (2) |
| N(2) | 1747 (3) | 1221 (4) | 1454 (2) | 116 (4) | 154 (7) | 31 (1) | 3 (4) | 38 (2) | 8 (2) |
| C(1) | 1330 (3) | 2603 (4) | 209 (2) | 88 (4) | 90 (7) | 27 (1) | −3 (3) | 27 (2) | 4 (2) |
| C(2) | 2363 (3) | 1691 (4) | 1037 (2) | 95 (4) | 106 (7) | 24 (1) | 0 (3) | 25 (2) | −2 (2) |
| C(3) | 1667 (3) | 3416 (4) | −396 (2) | 85 (4) | 116 (7) | 29 (1) | 19 (4) | 27 (2) | 9 (2) |
| C(4) | 720 (4) | 3029 (5) | −1287 (2) | 107 (4) | 169 (9) | 29 (1) | 14 (4) | 28 (2) | 10 (2) |
| C(5) | 980 (4) | 3823 (6) | −1868 (2) | 146 (6) | 232 (10) | 33 (2) | 28 (5) | 42 (2) | 16 (3) |
| C(6) | 2185 (5) | 5032 (6) | −1558 (3) | 144 (6) | 250 (11) | 51 (2) | 59 (6) | 63 (3) | 44 (3) |
| C(7) | 3115 (4) | 5456 (6) | −671 (3) | 104 (5) | 218 (11) | 52 (2) | 11 (5) | 45 (3) | 33 (3) |
| C(8) | 2881 (4) | 4636 (5) | −79 (2) | 91 (4) | 169 (9) | 38 (2) | −2 (4) | 30 (2) | 8 (3) |
| C(9) | 3936 (3) | 1178 (4) | 1423 (2) | 95 (4) | 107 (7) | 26 (1) | 10 (4) | 23 (2) | 8 (2) |
| C(10) | 4296 (4) | 264 (5) | 907 (2) | 113 (4) | 169 (9) | 32 (1) | 24 (4) | 34 (2) | 9 (2) |
| C(11) | 5767 (4) | −256 (6) | 1266 (3) | 127 (5) | 208 (10) | 50 (2) | 32 (5) | 53 (3) | 18 (3) |
| C(12) | 6879 (4) | 169 (6) | 2140 (3) | 95 (5) | 188 (10) | 55 (2) | 13 (5) | 37 (3) | 27 (3) |
| C(13) | 6526 (4) | 1087 (6) | 2647 (2) | 104 (5) | 169 (9) | 38 (2) | −13 (5) | 18 (2) | 8 (3) |
| C(14) | 5071 (4) | 1585 (5) | 2301 (2) | 111 (4) | 135 (9) | 30 (1) | −1 (4) | 21 (2) | −4 (2) |

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31440 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. 3,4-*Diphenyl*-1,2,5-*thiadiazole*: *positional* ($\times 10^3$) *and thermal parameters of hydrogen atoms*; *the e.s.d.'s for x,y,z parameters are* 0·004, 0·006, 0·002 *respectively*, *and the e.s.d. for the isotropic thermal parameter is* 0·7 Å$^2$

| | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| H(4) | −25 | 216 | 849 | 1·0 |
| H(5) | 23 | 351 | 748 | 2·2 |
| H(6) | 251 | 571 | 808 | 2·7 |
| H(7) | 394 | 637 | 953 | 3·2 |
| H(8) | 357 | 512 | 56 | 1·6 |
| H(10) | 346 | 2 | 25 | 2·0 |
| H(11) | 592 | −113 | 86 | 2·7 |
| H(12) | 790 | 20 | 237 | 3·2 |
| H(13) | 748 | 135 | 337 | 2·8 |
| H(14) | 475 | 222 | 262 | 2·8 |

## Description and discussion of the structure

### *Molecular structures*

Figs. 1 and 2 show the molecular structures of 3,4-diphenyl-1,2,5-selenadiazole and 3,4-diphenyl-1,2,5-thiadiazole as seen along the normals to the diazolic nuclei. Bond lengths and angles for the two compounds are given in Tables 6 and 7. The diazolic nucleus in each compound shows well defined planarity; the defining atoms deviate from the least-squares planes by <0·01 Å. The angles between the phenyl groups and the diazolic nucleus are very similar in both compounds, namely 44·6 and 48·1° in the Se compound, 50·5 and 49·8° in the S compound. Steric interactions between substituents tilt the phenyl groups toward opposite points of the plane of the heterocyclic nucleus: the angles of this plane with the lines C(3)–C(6) and C(9)–C(12) have the values 3°20′ and −2°30′ respectively in the Se compound, 4°10′ and −3°20′ respectively in the S compound. Moreover, the bond angles C(1)–C(2)–C(9) and C(2)–C(1)–C(3) are bent from the theoretical value of 120°, corresponding to $sp^2$ hybridization, to greater values.

Table 6. *Bond lengths for the two compounds, with estimated standard deviations*

| | X=Se | X=S |
|---|---|---|
| X——N(1) | 1·807 (5) Å | 1·635 (4) Å |
| X——N(2) | 1·814 (4) | 1·630 (3) |
| N(1) –C(1) | 1·298 (7) | 1·327 (5) |
| N(2) –C(2) | 1·303 (7) | 1·342 (6) |
| C(1)—C(2) | 1·442 (7) | 1·435 (4) |
| C(1)—C(3) | 1·490 (7) | 1·500 (6) |
| C(3)—C(4) | 1·402 (8) | 1·382 (4) |
| C(4)—C(5) | 1·393 (9) | 1·396 (7) |
| C(5)—C(6) | 1·357 (11) | 1·395 (6) |
| C(6)—C(7) | 1·381 (11) | 1·380 (6) |
| C(7)—C(8) | 1·409 (9) | 1·404 (7) |
| C(8)—C(3) | 1·389 (9) | 1·406 (5) |
| C(2)—C(9) | 1·484 (7) | 1·486 (5) |
| C(9)—C(10) | 1·390 (10) | 1·401 (6) |
| C(10)-C(11) | 1·379 (10) | 1·398 (6) |
| C(11)-C(12) | 1·380 (12) | 1·387 (5) |
| C(12)-C(13) | 1·391 (12) | 1·383 (8) |
| C(13)-C(14) | 1·392 (9) | 1·383 (6) |
| C(14)-C(9) | 1·385 (8) | 1·396 (4) |
| C——H (average value) | 0·96 (14) | 1·03 (12) |

Table 7. *Bond angles for the two compounds, with estimated standard deviations*

| | X=Se | X=S |
|---|---|---|
| N(1)—X——N(2) | 92·1 (2)° | 99·2 (2)° |
| X——N(1)—C(1) | 107·9 (4) | 107·2 (2) |
| X——N(2)—C(2) | 106·8 (4) | 107·2 (2) |
| N(1)—C(1)—C(2) | 116·0 (5) | 113·7 (4) |
| N(2)—C(2)—C(1) | 117·1 (5) | 112·8 (3) |
| C(1)—C(2)—C(9) | 126·2 (5) | 127·0 (4) |
| C(2)—C(1)—C(3) | 125·8 (5) | 126·8 (3) |
| C(1)—C(3)—C(4) | 119·4 (5) | 119·1 (3) |
| C(1)—C(3)—C(8) | 121·1 (5) | 121·1 (3) |
| C(4)—C(3)—C(8) | 119·3 (5) | 119·7 (4) |
| C(3)—C(4)—C(5) | 119·4 (6) | 120·2 (3) |
| C(4)—C(5)—C(6) | 121·4 (6) | 120·5 (3) |
| C(5)—C(6)—C(7) | 119·9 (6) | 119·6 (5) |
| C(6)—C(7)—C(8) | 120·2 (6) | 120·4 (4) |
| C(7)—C(8)—C(3) | 119·8 (6) | 119·7 (3) |
| C(2)—C(9)—C(10) | 120·8 (6) | 120·2 (2) |
| C(2)—C(9)—C(14) | 120·5 (5) | 120·7 (4) |
| C(10)-C(9)—C(14) | 118·6 (5) | 119·1 (3) |
| C(9)—C(10)-C(11) | 121·2 (7) | 120·8 (3) |
| C(10)-C(11)-C(12) | 120·0 (8) | 119·2 (5) |
| C(11)-C(12)-C(13) | 119·8 (6) | 120·1 (4) |
| C(12)-C(13)-C(14) | 119·7 (7) | 121·2 (3) |
| C(13)-C(14)-C(9) | 120·7 (7) | 119·7 (4) |

The heterocyclic rings have point symmetry $2mm$ ($C_{2v}$) within experimental error. The geometrical features of the thiadiazolic nucleus as obtained in the present work, averaging between equivalent bond lengths and angles, are compared in Table 8 with the corresponding values in 1,2,5-thiadiazole. Good agreement is shown for all the parameters; only for the C–C bond length is a difference possibly significant, which could be linked to very weak, if any, conjugation between the heterocyclic ring and the phenyl groups. The absence of marked conjugation between

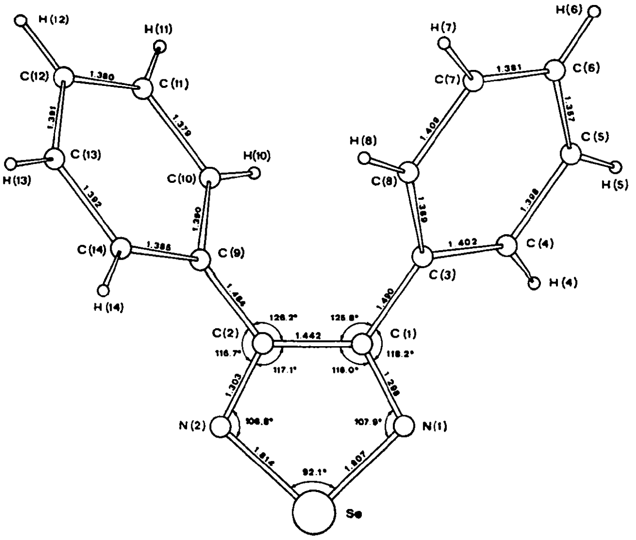

Fig. 1. Molecular structure of 3,4-diphenyl-1,2,5-selenadiazole as seen along the normal to the diazolic nucleus.

the rings, indicated by the constancy of geometrical features in the non-substituted heteroatomic nucleus and in the diphenyl derivative, is in keeping with the values of the torsional angles around C(1)–C(3) and C(2)–C(9) lines, which prevent large intramolecular electron delocalization, and with the values of C(1)–C(3) and C(2)–C(9) bond lengths (1·490 and 1·484 Å) which correspond quite well to the C($sp^2$)–C($sp^2$) single-bond distance.

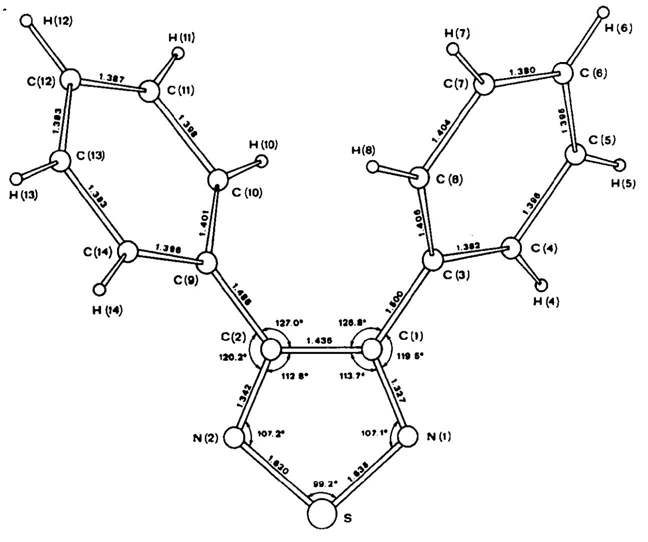

Fig. 2. Molecular structure of 3,4-diphenyl-1,2,5-thiadiazole as seen along the normal to the diazolic nucleus.

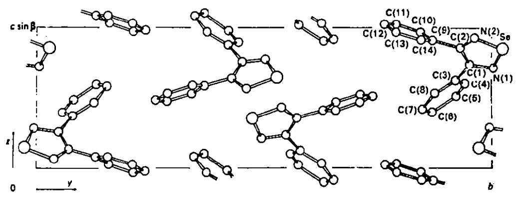

Fig. 3. Crystal packing of 3,4-diphenyl-1,2,5-selenadiazole.

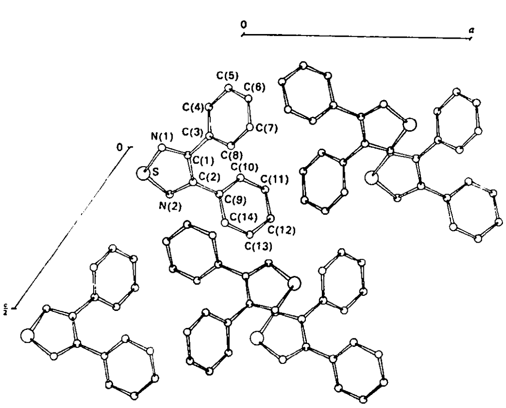

Fig. 4. Crystal packing of 3,4-diphenyl-1,2,5-thiadiazole.

Table 8. *Geometrical features of the* 1,2,5-*thiadiazolic nucleus*

| | Microwave spectroscopy[1] | Electron diffraction[2] | X-ray diffraction[3] |
|---|---|---|---|
| S–N | 1·631 (3) Å | 1·632 (5) Å | 1·635 (4) Å |
| N–C | 1·328 (3) | 1·329 (8) | 1·333 (4) |
| C–C | 1·420 (3) | 1·413 (10) | 1·435 (4) |
| C–H | 1·079 (3) | 1·080 (10) | — |
| N–S–N | 99°33′ (10′) | 99°24′ (12′) | 99°12′ (12′) |
| S–N–C | — | 106°30′ (24′) | 107° 6′ (12′) |

(1) Dobyns & Pierce (1963). (2) Momany & Bonham (1963). (3) Present work.

As regards the Se compound no comparison can be made with 1,2,5-selenadiazole because no accurate structural study of this compound has been made: the only known data are from a microwave spectroscopy study of Blackmann, Brown, Burden & Kent (1967), who pointed out the planarity of the molecule and, assuming C–C, C–N and C–H distances from 1,2,5-thiadiazole, calculated the value 1·80 Å for the N–Se distance and 94·3° for the N–Se–N bond angle. In any case, as 3,4-diphenyl-1,2,5-selenadiazole shows the same structural features pointed out for the S compound, namely torsional angles around C(1)–C(3) and C(2)–C(9) preventing significant interannular electron delocalization and C(1)–C(3) 1·500, C(2)–C(9) 1·486 Å lengths corresponding to the C($sp^2$)–C($sp^2$) single-bond distance, the same conclusions about the absence of significant conjugation between heterocyclic and phenyl rings can be drawn.

As regards the relevant question of the electron delocalization inside the heterocyclic nucleus we can remark that S–N bond (1·632 Å) has a considerable double bond character: in fact from the Pauling (1960) equation and assuming bond distances 1·74 Å for S–N single bond and 1·56 Å for S–N double bond, we calculate a double-bond order of 0·33. Correspondingly we can observe a lengthening of the C=N bond distance (mean value 1·335 Å) relative to the value of 1·300 Å found in the Se compound and in 1,2,5-oxadiazole (Saegebarth & Cox, 1965). According to Saegebarth & Cox these effects could be explained by 3*d* orbitals used for *dπ*-bonding by S. The absence of such effects in 3,4-diphenyl-1,2,5-selenadiazole is in accord with the observations by Brill (1973) who remarks that 'the second row elements P, S, Cl could use higher energy orbitals to some degree in the presence of highly electronegative substituents' such as the first row elements N, O and F which are fairly good *pπ*-donors; 'the tendency to use outer *d* orbitals appears ... to decrease going down the periodic table from the second row'.

## Crystal packing

The packing of the molecules in the crystal is described by Figs. 3 and 4. Tables 9 and 10 report the short intermolecular distances. As regards 3,4-diphenyl-1,2,5-thiadiazole, the intermolecular interactions are exclusively of the van der Waals type. The crystal packing of 3,4-diphenyl-1,2,5-selenadiazole requires some attention: in fact a very short Se···N(2) intermolecular distance occurs. Its length (2·95 Å) is definitely less than the sum of the van der Waals radii of the atoms, which is 3·5 Å (Pauling, 1960).

As a consequence, closer packing is obtained so that the unit-cell volume of 3,4-diphenyl-1,2,5-selenadiazole (1194 Å$^3$) is similar to that of 3,4-diphenyl-1,2,5-thiadiazole (1195 Å$^3$), notwithstanding the greater dimensions of the Se atom relative to the S atom.

Table 11 shows some other examples of very short contacts between Se and electron-rich atoms such as N and O. These data indicate the presence in such compounds of strong intermolecular interactions, which probably are of the 'charge transfer' type, with electrons transferred from the electron-rich N or O to the radially extended empty *d* orbitals of Se.

Table 9. 3,4-*Diphenyl*-1,2,5-*selenadiazole*: *short intermolecular distances, with symmetry operations*

| | | | |
|---|---|---|---|
| Se—Se$^{\text{iv}}$ | 3·89 Å | N(1)—C(1)$^{\text{vi}}$ | 3·64 Å |
| Se—N(2)$^{\text{iv}}$ | 2·95 | N(1)—C(3)$^{\text{vi}}$ | 3·58 |
| Se—C(1)$^{\text{v}}$ | 3·79 | N(1)—C(4)$^{\text{vi}}$ | 3·78 |
| Se—C(3)$^{\text{vi}}$ | 3·79 | N(2)—C(8)$^{\text{ii}}$ | 3·48 |
| Se—C(4)$^{\text{vi}}$ | 3·76 | C(6)—C(10)$^{\text{i}}$ | 3·68 |
| Se—C(5)$^{\text{vi}}$ | 3·73 | C(6)—C(11)$^{\text{i}}$ | 3·75 |
| Se—C(6)$^{\text{vi}}$ | 3·78 | C(7)—C(8)$^{\text{vi}}$ | 3·64 |
| N(1)–N(1)$^{\text{vi}}$ | 3·32 | C(8)—C(8)$^{\text{vii}}$ | 3·52 |
| N(2)–N(2)$^{\text{iv}}$ | 2·98 | C(6)—C(12)$^{\text{ix}}$ | 3·75 |
| | | C(11)–C(12)$^{\text{viii}}$ | 3·56 |

The atoms of the different asymmetric units are related to the atoms of the fundamental unit by the following symmetry operations:

| | | | |
|---|---|---|---|
| i | $1+x$ | $y$ | $1+z$ |
| ii | $1+x$ | $y$ | $z$ |
| iii | $-1+x$ | $y$ | $z$ |
| iv | $1-x$ | $2-y$ | $2-z$ |
| v | $-x$ | $2-y$ | $2-z$ |
| vi | $-x$ | $2-y$ | $1-z$ |
| vii | $-1-x$ | $2-y$ | $1-z$ |
| viii | $-x$ | $\frac{3}{2}-y$ | $\frac{1}{2}+z$ |
| ix | $1-x$ | $\frac{3}{2}-y$ | $-\frac{1}{2}+z$ |

Table 10. 3,4-*Diphenyl*-1,2,5-*thiadiazole*: *short intermolecular distances, with symmetry operations*

| | | | |
|---|---|---|---|
| S—N(1)$^{\text{ii}}$ | 3·68 Å | N(1)—C(8)$^{\text{i}}$ | 3·72 Å |
| S—C(1)$^{\text{ii}}$ | 3·59 | N(2)—C(5)$^{\text{iv}}$ | 3·70 |
| S—C(3)$^{\text{i}}$ | 3·68 | N(2)—C(6)$^{\text{iv}}$ | 3·57 |
| S—C(7)$^{\text{i}}$ | 3·79 | N(2)—C(12)$^{\text{iii}}$ | 3·53 |
| S—C(8)$^{\text{i}}$ | 3·61 | C(2)—C(13)$^{\text{iii}}$ | 3·72 |
| N(1)–N(1)$^{\text{i}}$ | 3·17 | C(4)—C(12)$^{\text{v}}$ | 3·70 |
| N(1)–N(2)$^{\text{ii}}$ | 3·62 | C(13)–C(14)$^{\text{iii}}$ | 3·69 |
| N(1)–C(1)$^{\text{i}}$ | 3·52 | C(14)–C(14)$^{\text{iii}}$ | 3·66 |
| N(1)–C(3)$^{\text{i}}$ | 3·56 | | |

The atoms of the different asymmetric units are related to the atoms of the fundamental unit by the following symmetry operations:

| | | | |
|---|---|---|---|
| i | $-x$ | $1-y$ | $-z$ |
| ii | $-x$ | $-y$ | $-z$ |
| iii | $1-x$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
| iv | $x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |
| v | $x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |

Table 11. *Short* Se···O *and* Se···N *intermolecular distances*

| | | |
|---|---|---|
| *trans*-Ethanediseleninic anhydride[a] | Se···O | 2·70 Å<br>3·11 |
| D-Carboxyphenylmethylselenium oxide[b] | Se···O | 2·92 |
| 1,4-Diselenocyanatobenzene[c] | Se···N | 3·32 |
| Nitrogen selenide[d] | Se···N | 3·06 |

(*a*) Gould & Post (1956). (*b*) Dahlén (1973). (*c*) McDonald & Pettit (1970). (*d*) Bärnighausen, Volkmann & Jander (1966).

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