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On the 2,5-Diazolic Heterocyclic System. II. Crystal and Molecular Structure of 3,4-Diphenyl-1,2,5-oxadiazole

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The crystal structure of 3,4-diphenyl-1,2,5-oxadiazole (space group $P2_1/c$, cell parameters $a=15{\cdot}26$, $b=6{\cdot}07$, $c=12{\cdot}61$ Å, $\beta=94{\cdot}2°$) was determined by direct methods and refined by a least-squares method to the final R value of 0·089. The molecular parameters were compared with those of the corresponding S and Se compounds and with those of 1,2,5-oxadiazole. Bond lengths in the diazolic nucleus appeared longer than the corresponding values in 1,2,5-oxadiazole. This feature together with conformational details of the whole molecule (torsional angle of 19° between the heterocyclic nucleus and one phenyl group) indicated good interannular conjugation.

Introduction

In the previous paper (Mellini & Merlino, 1976) we described the crystal and molecular structures of 3,4-diphenyl-1,2,5-selenadiazole and 3,4-diphenyl-1,2,5-thiadiazole, pointing out that these compounds differ substantially in π-electron delocalization inside the heterocyclic nucleus, but are alike as regards the very weak interactions between the heterocyclic nucleus and the phenyl substituents. Now we describe and discuss the crystal and molecular structure of 3,4-diphenyl-1,2,5-oxadiazole, whose different behaviour prompted us to write a separate paper.

Experimental

Crystals suitable for X-ray structural investigation were supplied by Professor V. Bertini. As for the related compounds described in the preceding paper, unit-cell dimensions and space group were obtained from precession and rotation photographs, using Cu $K\alpha$ radiation; the crystal data are listed in Table 1. The intensity data were recorded with Ni-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) by means of Weissenberg photographs, with the multiple-film technique and integrating process. Six layers with b as rotation axis ($k=0$ through 5) were recorded and 1079 independent reflexions were observed. The intensities, measured with a Nonius microdensitometer were corrected for Lorentz and polarization factors, as well as for α_1–α_2 spot doubling. No correction was made for absorption owing to the small dimensions of the crystal and the low value of the absorption coefficient.

Structure determination

By means of the program *DATFIX*, incorporated in the X-RAY 70 System (Stewart, 1970), the overall isotropic temperature factor, the scale factors and the normalized structure factor magnitudes E were calculated. The structure was solved by direct methods, using the symbolic addition procedure. The origin of the unit cell was fixed by assigning phases to three reflexions of permitted parities. Symbols a,b,c were assigned to three additional reflexions, introduced as necessary during the development of the phase determination. Sign and symbol assignments are shown in Table 2. The application of the method was simplified by the preparation of lists of reflexion combinations in the $\sum_2$ formula, by means of the program *SIGMA*2 (Stewart, 1970). Signs and symbols were derived by hand application of the $\sum_2$ formula for 98 reflexions with $E\geq 1{\cdot}91$. Several relations among the symbols were obtained, from which the following solution for symbols was found: $a=b=-$, $c=+$. The sign determination was then extended to all the reflexions with $E\geq 1{\cdot}5$ by automatic application of the $\sum_2$ formula by means of the program *PHASE* (Stewart, 1970).

A three-dimensional E map, calculated with the contribution of the 234 E values, whose signs were deter-

Table 1. *Crystal data, with standard deviations*

M. W.	222·2
a	15·26 (2) Å
b	6·07 (1)
c	12·61 (2)
β	94·2 (1)°
Space group	$P2_1/c$
Z	4
D_x (g cm^{-3})	1·264

Table 2. *Signs and symbols used in the application of the* $\sum_2$ *relations*

h	k	l	E	Sign or symbol
13	2	−1	2·77	+
11	3	−2	2·52	+
2	1	2	2·61	+
6	2	2	3·20	a
13	5	−5	2·52	b
18	0	0	4·23	c

mined by the above described procedure, clearly showed the positions of all the 'heavy' atoms in the structure. Block-diagonal least-squares refinement reduced $R=\sum||F_o|-|F_c||/\sum|F_o|$ to 0·019: individual isotropic temperature factors and scale factors were among the refined parameters. Two refinement cycles with anisotropic temperature factors reduced R to 0·13. A three-dimensional Fourier synthesis calculated at this stage revealed the positions of the H atoms. More full-matrix least-squares refinement cycles were made. The weighting scheme $\sqrt{w}=1/(a+|F_o|+b|F_o|^2)$ was introduced, with $a=5{\cdot}0$ and $b=0{\cdot}09$. Refinement was concluded at $R=0{\cdot}089$.

The scattering factors used in the structure factor calculations were taken from *International Tables for X-ray Crystallography* (1962). Tables 3 and 4 give the final positional and thermal parameters, with their e.s.d.'s.*

Description and discussion of the structure

The molecular features of 3,4-diphenyl-1,2,5-oxadiazole are illustrated in Fig. 1; some bond lengths and angles are given in the figure but are fully reported in Tables 5 and 6, together with their e.s.d.'s. We must remark on the well-defined planarity of the three nuclei, with deviations of the atoms locating the planes from the least-squares planes less than 0·1 Å.

Table 3. *Positional and anisotropic thermal parameters* (× 10^4) *of 'heavy atoms', with estimated standard deviations*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	2539 (3)	10582 (7)	5016 (3)	111 (23)	432 (20)	109 (4)	51 (7)	0 (3)	−103 (7)
N(1)	3125 (3)	10706 (9)	4202 (3)	98 (4)	497 (25)	85 (4)	126 (7)	11 (3)	−39 (8)
N(2)	1958 (3)	8832 (9)	4883 (4)	95 (4)	443 (24)	95 (4)	61 (8)	14 (3)	−29 (8)
C(1)	2883 (3)	8940 (8)	3580 (4)	64 (3)	219 (19)	75 (4)	39 (6)	5 (3)	−15 (7)
C(2)	2158 (3)	7793 (8)	4004 (4)	65 (3)	274 (20)	73 (4)	53 (6)	15 (3)	6 (7)
C(3)	3378 (3)	8452 (8)	2658 (3)	48 (2)	155 (17)	79 (4)	6 (5)	5 (2)	−1 (6)
C(4)	3408 (3)	10005 (9)	1844 (2)	55 (3)	184 (20)	101 (5)	10 (5)	13 (3)	5 (7)
C(5)	3908 (4)	9539 (11)	991 (5)	52 (3)	253 (23)	129 (6)	9 (6)	15 (3)	−17 (9)
C(6)	4359 (3)	7590 (10)	940 (5)	57 (3)	356 (28)	108 (5)	−33 (7)	24 (3)	−37 (10)
C(7)	4327 (3)	6079 (9)	1746 (5)	78 (4)	371 (28)	107 (5)	−37 (8)	21 (4)	17 (10)
C(8)	3836 (3)	6478 (8)	2600 (4)	61 (3)	214 (19)	100 (5)	8 (6)	7 (3)	2 (7)
C(9)	1658 (3)	5870 (8)	3618 (4)	48 (2)	228 (19)	95 (4)	22 (5)	13 (2)	27 (7)
C(10)	1674 (3)	5203 (9)	2566 (5)	50 (3)	312 (23)	119 (5)	−11 (6)	24 (3)	−31 (8)
C(11)	1197 (4)	3375 (11)	2197 (6)	53 (3)	374 (28)	187 (8)	−14 (7)	−15 (4)	−58 (12)
C(12)	706 (4)	2172 (12)	2849 (7)	67 (4)	361 (30)	192 (10)	−5 (8)	11 (5)	47 (14)
C(13)	673 (5)	2817 (13)	3870 (8)	92 (5)	477 (39)	197 (11)	−43 (11)	18 (6)	174 (18)
C(14)	1155 (5)	4633 (12)	4277 (5)	91 (4)	467 (32)	110 (6)	−4 (9)	25 (4)	89 (11)

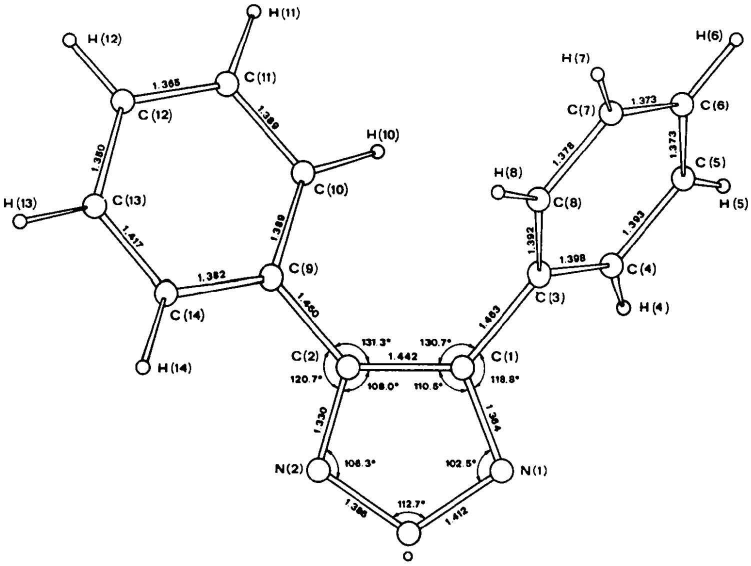

Fig. 1. Molecular structure of 3,4-diphenyl-1,2,5-oxadiazole as seen along the normal to the diazolic nucleus.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31441 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Positional* ($\times 10^3$) *and thermal* (Å^2) *parameters of* H *atoms*

The e.s.d.'s are 0·004, 0·012, 0·005, 2, for x,y,z,B parameters respectively.

	x	y	z	B
H(4)	307	1144	194	4·3
H(5)	389	1074	45	5·4
H(6)	464	720	39	4·1
H(7)	460	493	181	5·7
H(8)	388	535	325	4·8
H(10)	203	604	206	4·9
H(11)	141	310	123	12·1
H(12)	26	62	264	10·6
H(13)	31	211	434	6·8
H(14)	124	537	508	4·9

Table 5. *Bond lengths* (Å) *with estimated standard deviations*

O——N(1)	1·412 (7)
O——N(2)	1·386 (7)
N(1)—C(1)	1·364 (7)
N(2)—C(2)	1·330 (7)
C(1)—C(2)	1·442 (7)
C(1)—C(3)	1·463 (7)
C(3)—C(4)	1·398 (7)
C(4)—C(5)	1·393 (8)
C(5)—C(6)	1·373 (9)
C(6)—C(7)	1·373 (8)
C(7)—C(8)	1·378 (8)
C(8)—C(3)	1·392 (7)
C(2)—C(9)	1·460 (7)
C(9)—C(10)	1·389 (8)
C(10)-C(11)	1·389 (8)
C(11)-C(12)	1·365 (11)
C(12)-C(13)	1·350 (13)
C(13)-C(14)	1·417 (11)
C(14)-C(9)	1·382 (9)
C——H (average value)	1·02 (10)

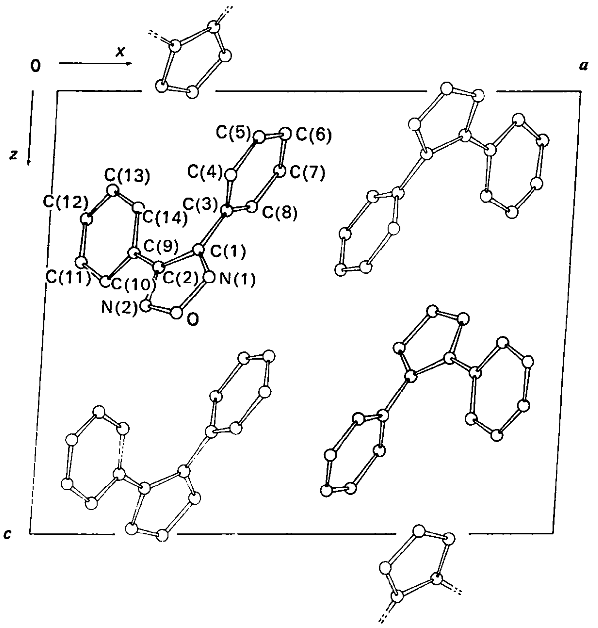

Fig. 2. Crystal packing of 3,4-diphenyl-1,2,5-oxadiazole.

Table 6. *Bond angles* (°) *with estimated standard deviations*

N(1)—O——N(2)	112·7 (4)
O——N(1)—C(1)	102·5 (4)
O——N(2)—C(2)	106·3 (4)
N(1)—C(1)—C(2)	110·5 (4)
N(2)—C(2)—C(1)	108·0 (4)
C(1)—C(2)—C(9)	131·3 (4)
C(2)—C(1)—C(3)	130·7 (4)
C(1)—C(3)—C(4)	119·6 (4)
C(1)—C(3)—C(8)	120·5 (4)
C(4)—C(3)—C(8)	119·9 (4)
C(3)—C(4)—C(5)	118·7 (5)
C(4)—C(5)—C(6)	121·0 (6)
C(5)—C(6)—C(7)	119·8 (6)
C(6)—C(7)—C(8)	120·7 (5)
C(7)—C(8)—C(3)	119·8 (5)
C(2)—C(9)—C(10)	120·4 (4)
C(2)—C(9)—C(14)	121·6 (5)
C(10)-C(9)—C(14)	118·0 (5)
C(9)—C(10)-C(11)	120·5 (5)
C(10)-C(11)-C(12)	121·6 (7)
C(11)-C(12)-C(13)	118·6 (7)
C(12)-C(13)-C(14)	121·3 (8)
C(13)-C(14)-C(9)	119·9 (7)

Saegebarth & Cox (1965) studied 1,2,5-oxadiazole by microwave spectroscopy, obtaining the following parameters: bond lengths O–N 1·380, N–C 1·300, C–C 1·421, C–H 1·076 Å, all values with a standard deviation of 0·003 Å; bond angles N–O–N 110·4, O–N–C 105·8°, both with a standard deviation of 0·3°.

If we compare the data from Saegebarth & Cox (1965) with our results we can observe that the diphenyl derivative shows a general lengthening of all bond lengths inside the heterocyclic nucleus and a reduction in symmetry from *2mm* (C_{2v}) to *m* (σ_h). The asymmetry of the heterocyclic nucleus is clearly linked to the different disposition of the two phenyl substituents relative to the nucleus. In fact, while one of the two phenyl substituents is rotated by 61·2°, the other makes an angle of only 19°, which indicates good conjugation between the nucleus and the latter phenyl group. Steric interactions prevent complete planarity and constrain the former phenyl group to high torsional angle, and explain also the values of the C(9)-C(2)-C(1) and C(2)-C(1)-C(3) bond angles, 131·3 and 130·7° respectively, well above the corresponding values in the two other compounds of the series (Mellini & Merlino, 1976). Intramolecular steric interactions are reported in Table 7. In this table the short intramolecular contacts in 3,4-diphenyl-1,2,5-oxadiazole are compared with the corresponding contacts in the S and Se compounds. It can be seen that the only relevant differences are for N(2)···H(14), C(8)···H(10) and H(8)···H(10) interactions.

A simple Hückel calculation was made to derive approximate bond orders, introducing the same parameters used by Luzkii, Scepel, Shvaika & Klimiscia (1969) in their study of some derivatives of oxadiazoles corrected taking account of the torsional angles between the heterocyclic nucleus and the phenyl

Table 7. *Short intramolecular distances* (Å)

	3,4-Diphenyl-1,2,5-selenadiazole	3,4-Diphenyl-1,2,5-thiadiazole	3,4-Diphenyl-1,2,5-oxadiazole
N(1)—C(4)	2·91	2·99	3·06
N(1)—C(8)	3·54	3·57	3·49
N(1)--H(4)	2·69	2·75	2·88
N(1)—H(8)	3·88	3·86	3·69
N(2)—C(10)	3·50	3·60	3·66
N(2)—C(14)	2·92	3·04	2·89
N(2)—H(10)	3·73	3·80	3·95
N(2)—H(14)	2·79	2·79	2·39
C(3)—C(9)	3·19	3·23	3·19
C(8)—C(10)	3·36	3·49	3·38
C(8)—H(10)	3·38	3·34	2·80
C(10)-H(8)	3·34	3·53	3·41
H(8)—H(10)	3·63	3·67	3·13

Table 8. *Short intermolecular distances* (Å)

O——C(7)^{iii}	3·51	N(1)—C(5)^{ii}	3·80
O——C(6)^{iii}	3·51	N(2)—C(5)^{iii}	3·79
O——C(5)^{ii}	3·78	N(2)—C(10)^{iii}	3·49
O——C(4)^{ii}	3·71	N(2)—C(11)^{iii}	3·64
O——C(10)^{iii}	3·60	N(2)—C(12)^{i}	3·69
O——C(11)^{iii}	3·60	N(2)—C(13)^{i}	3·31
O——C(13)^{i}	3·38	C(2)—C(5)^{iii}	3·80
O——C(14)^{i}	3·34	C(2)—C(12)^{i}	3·69
N(1)-C(7)^{iii}	3·73	C(11)-C(12)^{iv}	3·71
N(1)-C(6)^{iii}	3·42	C(12)-C(12)^{iv}	3·79

Symmetry notation

i	x	$1+y$	z
ii	x	$\frac{5}{2}-y$	$\frac{1}{2}+z$
iii	x	$\frac{3}{2}-y$	$\frac{1}{2}+z$
iv	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

groups; the results of the calculation indicated bond orders higher for O–N(1) and N(1)–C(1) bonds than for O–N(2) and N(2)–C(2), in contrast to the structural data determined in the present investigation. This point deserves further attention from both the experimental and theoretical points of view.

The general lengthening of the bond distances inside the oxadiazolic nucleus [together with the shortening of C(11)–C(12) and C(12)–C(13), 1·350 and 1·365 Å respectively] is clear evidence of electron drift from the nucleus towards the conjugated phenyl group. On the other hand, in the preceding paper on the structure of the S and Se compounds we concluded that no significant conjugation exists between heterocyclic and phenyl rings in those compounds. This is in line with the results of extended Hückel calculations by Galasso & De Alti (1971) on the preferred conformation and electronic structure of phenyl derivatives of pyrrole, furan and thiophene, and by Galasso & Trinajstic (1972) on the stereochemistry of the isomeric bipyrroles, bifurans, bithiophenes and biselenophenes. Their calculations indicate that for phenyl derivatives of furan and for bifurans the greatest conformational stability is obtained for a planar or nearly planar conformation, as opposed to the situation for the corresponding S and Se compounds, indicating that in the furan derivatives the π-conjugation energy is by far the most relevant factor.

Crystal packing

The packing of the molecules in the crystal is described by Fig. 2. Table 8 gives the short (less than 3·80 Å) intermolecular distances. The values in the table as well as Fig. 2 show that the intermolecular interactions are exclusively of the van der Waals type.

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