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Journal of Molecular Structure 561 (2001) 175–183

Journal of
MOLECULAR
STRUCTURE

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Crystal structures of two substituted 2,5-diaryl-1,3,4-oxadiazoles

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Received 1 September 2000; revised 10 November 2000; accepted 10 November 2000

Abstract

The crystal structures of 2,5-di(4-pyridyl)-1,3,4-oxadiazole, **I**, and 2-(4-cyanophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole, **II**, were determined from single crystal data (**I**: monoclinic, *C*2/*c* (no. 15), $a = 5.3129(9)$ Å, $b = 12.142(3)$ Å, $c = 16.771(3)$ Å, $\beta = 93.41(2)°$, $R_{all} = 0.0774$; **II**: triclinic, $P\bar{1}$ (no. 2), $a = 7.3908(12)$ Å, $b = 8.7992(15)$ Å, $c = 12.036(2)$ Å, $\alpha = 77.04(2)°$, $\beta = 89.29(2)°$, $\gamma = 87.58(2)°$, $R_{all} = 0.0552$). In both structures the formation of stacks of the almost planar molecules is observed as known for other oxadiazoles. These compounds exhibit differences to other substituted 2,5-diaryl-1,3,4-oxadiazoles in the crystalline structure.

Keywords: 1,3,4-oxadiazoles; Crystal structure; X-ray diffraction

1. Introduction

Aromatic 1,3,4-oxadiazoles have attracted much interest during the past 30 years because of their use as laser dyes, photographic materials or scintillators [1]. Besides, they show a combination of interesting properties, which makes them suitable for the development of new electrical and electro-optical devices: The electronic spectrum of the 1,3,4-oxadiazole system is equivalent to that of benzene and the maxima are only slightly hypsochromically shifted. Substituted 2,5-diaryl-1,3,4-oxadiazoles show strong fluorescence in solution on stimulation by UV or β-irradiation, and some of them are electroluminescent with radiation of blue light [2]. Additionally, they have extremely high thermal and oxidative stability.

These physical and physicochemical properties can be tailored by the electronic and three-dimensional structure of the molecules as well as, in the solid state, by the crystalline structure. Systematic study of the crystal structures of differently substituted 2,5-diaryl-1,3,4-oxadiazoles should make it possible to understand the formation of certain structure elements desired for specific applications. For example, the design of oxadiazoles with a non-centrosymmetric structure is of great interest for optical applications. Besides, the knowledge of the bulk structure will be helpful to understand the formation of highly ordered thin layers, which are needed for microelectronic and micro-optoelectronic devices.

Nevertheless, little is known about the crystalline structures of aromatic 1,3,4-oxadiazoles. The few known structures [3–7] show mainly monoclinic or orthorhombic symmetry and consist of stacks of molecules with one or two orientations of these molecules within the stacks, but with a different arrangement of the stacks relative to each other.

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0022-2860/01/$ - see front matter
PII: S0022-2860(00)00921-2

Table 1
Data collection parameters and crystal data for 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**I**) and 2-(4-cyano-phenyl)-5(4-dimethylamino-phenyl)-1,3,4-oxadiazole (**II**)

Compound	**I**	**II**
Lattice parameters (Å, °)	$a = 5.3129(9)$ $b = 12.142(3)$ $c = 16.771(3)$ $\beta = 93.41(2)$	$a = 7.3908(12)$ $b = 8.7992(15)$ $c = 12.036(2)$ $\alpha = 77.04(2)$ $\beta = 89.29(2)$ $\gamma = 87.58(2)$
Molar volume (cm^3/mol)	1080.0(4)	762.1(2)
Number of formula units, Z	4	4
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
Diffractometer	Stoe IPDS	Stoe IPDS
Radiation	Mo–Kα (graphite monochrom., $\lambda =$ 71.07 pm)	Mo–Kα (graphite monochrom., $\lambda =$ 71.07 pm)
Temperature (K)	293	293
Data range (°)	$3.8 < 2\theta < 56.3$	$3.8 < 2\theta < 56.3$
Index range	$-6 \le h \le 6$ $-16 \le k \le 16$ $-22 \le l \le 22$	$-9 \le h \le 9$ $-10 \le k \le 10$ $-15 \le l \le 15$
Rotation angle (°); φ-increment	$0 < \varphi < 250$; $\Delta\varphi = 2°$	$0 < \varphi < 250$; $\Delta\varphi = 2°$
Number of images	125	125
Exposure time (min)	6	4
Detector distance (mm)	60	60
Data corrections	Polarization/Lorentz	Polarization/Lorentz
Absorption corrections	None	None
μ (cm^{-1})	69.0	126.5
Number of collected reflections	4761	6121
Number of unique reflections	899	2251
Number of reflections with $I_0 > 2\sigma(I)$	545	1565
R_{int}	0.1346	0.0908
Structure determination	SHELXS86 and SHELXS93 [9]	SHELXS86 and SHELXS93 [9]
Scattering factors	Intern. tables, vol. C	Intern. tables, vol. C
Goodness of fit	1.062	1.068
$R1$; $wR2$ ($I_0 > 2\sigma(I)$)	0.0431; 0.0912	0.0375; 0.0939
$R1$; $wR2$ (all data)	0.0774; 0.1039	0.0552; 0.1015

In this paper, we present the structures of two substituted 2,5-diaryl-1,3,4-oxadiazoles, compare their structural features to those of similarly substituted oxadiazoles, and discuss the existing similarities and differences.

2. Experimental

2.1. Preparation

2,5-di(4-pyridyl)-1,3,4-oxadiazole (**I**) was prepared by one-step condensation reaction of 4-pyridinecarboxylic acid and hydrazine hydrate in polyphosphoric acid. After precipitation in water the product was recrystallized from water (melting point: 118°C).

2-(4-cyanophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole (**II**) was synthesized via precursor route as described in [8]. The product was recrystallized from toluene (melting point: 238°C).

2.2. Structure analysis

From both compounds single crystals were transferred into glass capillaries ($d = 0.2$–0.3 mm). The scattering intensities of a suitable crystal were collected with an imaging plate diffractometer. Structure solution and refinement were carried out using the

Table 2
Positional parameters and equivalent isotropic displacement parameters for 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**I**) ($U_{eq} = 1/3[U_{22} + 1/\sin^2 \beta(U_{11} + U_{33} + 2U_{13} \cos \beta)]$ [10].)

Atom	Site	*x/a*	*y/b*	*z/c*	$U_{eq} \times 10^{-1}/pm^2$
O1	4e	0.0000	0.55218(14)	0.2500	45.3(6)
N1	8f	−0.1068(4)	0.37965(15)	0.22300(10)	54.2(6)
N2	8f	−0.7615(4)	0.6019(2)	0.05390(11)	63.7(6)
C1	8f	−0.1610(4)	0.4818(2)	0.20903(12)	43.7(6)
C2	8f	−0.3664(4)	0.5255(2)	0.15617(11)	44.2(6)
C3	8f	−0.5365(4)	0.4524(2)	0.11845(13)	50.9(6)
H3	8f	−0.5147(39)	0.3729(15)	0.1275(12)	44(5)[a]
C4	8f	−0.7287(5)	0.4947(2)	0.06821(14)	57.9(7)
H4	8f	−0.8481(53)	0.4444(20)	0.0430(15)	72(8)[a]
C5	8f	−0.5974(6)	0.6704(2)	0.0903(2)	65.0(8)
H5	8f	−0.6187(43)	0.7533(21)	0.0786(14)	68(7)[a]
C6	8f	−0.3991(5)	0.6362(2)	0.14236(14)	57.0(7)
H6	8f	−0.2772(47)	0.6912(18)	0.1664(15)	64(7)[a]

[a] Isotropic displacement parameters.

programs SHELXS86 and SHELXL93 [9]. The data collection parameters and determined crystallographic data are summarized in Tables 1–5. The H-atoms were located in successive difference Fourier syntheses.

Table 3
Selected distances (Å) and angles (°) for 2,5-di(4-pyridyl)-1,3,4-oxadiazole (I)

Bond	Distance	Bond	Angles
O1–C1	1.365(2)	C1–O1–C1	102.5(2)
N1–N1	1.409(3)	C1–N1–N1	106.2(1)
N1–C1	1.292(3)	N1–C1–O1	112.5(2)
C1–C2	1.464(3)	N1–C1–C2	127.5(2)
C2–C3	1.391(3)	O1–C1–C2	120.0(2)
C3–C4	1.383(3)	C6–C2–C3	118.4(2)
C4–N2	1.334(3)	C6–C2–C1	122.6(2)
N2–C5	1.327(3)	C1–C2–C3	119.0(2)
C5–C6	1.391(3)	C2–C3–C4	118.5(2)
C6–C2	1.373(3)	C4–C3–H3	122.3(2)
C3–H3	0.98(2)	C2–C3–H3	119.2(2)
C4–H4	0.96(3)	C3–C4–N2	123.7(2)
C5–H5	1.03(2)	N2–C4–H4	117.7(2)
C6–H6	1.00(2)	C3–C4–H4	118.6(2)
		C4–N2–C5	117.0(2)
		N2–C5–C6	123.7(2)
		N2–C5–H5	117.6(1)
		C6–C5–H5	118.8(1)
		C5–C6–C2	118.8(2)
		C2–C6–H6	121.0(1)
		C5–C6–H6	120.2(1)

3. Results and discussion

3.1. 2,5-Di(4-pyridyl)-1,3,4-oxadiazole

In the crystal, the molecules of the 2,5-di(4-pyridyl)-1,3,4-oxadiazole, **I**, Fig. 1, have an almost planar structure. All three rings of the molecule are planar but they show a slight torsion relative to each other. The deviation of the planes of the two pyridyl rings relative to the plane of the oxadiazole ring is +3.3° for one ring and −3.3° for the other. Due to the absence of significant steric hindrance the torsion angle between two neighboring rings is small, hence partial conjugation is present.

In the three-dimensional structure the molecules of **I** form stacks, Fig. 3(a). The shortest contact between the stacks in *c*-direction is 3.75 Å so that no intermolecular interactions such as hydrogen bridges/bonds can exist, even though they could be expected for this compound. The axis of the stacks is parallel to the *a*-axis of the unit cell and the molecules are inclined to this axis by 50°. The planes of the molecules are all parallel as illustrated in Fig. 2(a), and the molecules are all oriented in the same direction within one stack regarding the oxygen atom of the oxadiazole ring. The shortest interplanar distance within the stacks is 3.80 Å, and the oxadiazole ring of each molecule is situated between two pyridyl rings of neighboring molecules so that π–π interactions exist which

Table 4
Positional parameters and equivalent isotropic displacement parameters for 2-(4-cyano-phenyl)-5(4-dimethylamino-phenyl)-1,3,4-oxadiazole (**II**) ($U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha]$ [10].)

Atom	Site	*x/a*	*y/b*	*z/c*	$U_{eq} \times 10^{-1}/pm^2$
O1	2i	−0.05248(15)	0.32412(13)	0.45194(8)	70.5(3)
N1	2i	0.1358(2)	0.4318(2)	0.31602(12)	88.4(5)
N2	2i	0.2310(2)	0.3116(2)	0.39257(12)	88.5(5)
N3	2i	−0.7083(3)	0.9386(3)	0.1024(2)	119.1(7)
N4	2i	0.2572(3)	−0.2527(2)	0.84454(14)	103.0(6)
C1	2i	0.1155(2)	0.2519(2)	0.47015(13)	69.7(5)
C2	2i	−0.0285(2)	0.4358(2)	0.35348(13)	69.8(5)
C3	2i	−0.1774(2)	0.5408(2)	0.30378(13)	67.9(4)
C4	2i	−0.1409(2)	0.6627(2)	0.21019(14)	75.3(5)
H4	2i	−0.0110(25)	0.6746(21)	0.1814(15)	95(5)[a]
C5	2i	−0.2764(3)	0.7637(2)	0.15873(15)	78.8(5)
H5	2i	−0.2522(23)	0.8517(22)	0.0942(15)	94(6)[a]
C6	2i	−0.4529(2)	0.7467(2)	0.20060(14)	75.3(5)
C7	2i	−0.4902(3)	0.6271(2)	0.2947(2)	84.4(5)
H7	2i	−0.6144(27)	0.6161(23)	0.3217(16)	109(6)[a]
C8	2i	−0.3536(2)	0.5250(2)	0.3453(2)	79.2(5)
H8	2i	−0.3821(25)	0.4358(25)	0.4094(16)	103(6)[a]
C9	2i	0.1471(2)	0.1223(2)	0.56758(13)	68.4(4)
C10	2i	0.3202(3)	0.0562(2)	0.58742(14)	75.7(5)
H10	2i	0.4203(25)	0.0996(22)	0.5394(15)	95(5)[a]
C11	2i	0.3581(3)	−0.0679(2)	0.67738(15)	81.0(5)
H11	2i	0.4770(24)	−0.1076(21)	0.6853(14)	85(6)[a]
C12	2i	0.2208(3)	−0.1304(2)	0.75359(14)	80.3(5)
C13	2i	0.0459(3)	−0.0639(2)	0.7331(2)	82.4(5)
H13	2i	−0.0533(27)	−0.1016(23)	0.7847(16)	101(6)[a]
C14	2i	0.0081(3)	0.0599(2)	0.64169(15)	77.1(5)
H14	2i	−0.1194(25)	0.1083(21)	0.6264(14)	86(5)[a]
C15	2i	−0.5950(3)	0.8524(3)	0.1473(2)	91.8(6)
C16	2i	0.4409(5)	−0.3098(4)	0.8718(3)	121.8(9)
H161	2i	0.5179(39)	−0.2354(38)	0.8967(23)	164(12)[a]
H162	2i	0.4356(37)	−0.3985(37)	0.9328(25)	164(11)[a]
H163	2i	0.5062(46)	−0.3514(42)	0.8141(30)	197(16)[a]
C17	2i	0.0993(9)	−0.3069(9)	0.9255(5)	158(2)
H171	2i	0.1995(38)	−0.3967(36)	0.9828(24)	158(10)[a]
H172	2i	0.0582(45)	−0.2222(38)	0.9709(26)	180(13)[a]
H173	2i	0.1530(25)	−0.3162(33)	0.9237(22)	19(4)[a]

[a] Isotropic displacement parameters.

are perpendicular to the planes of the molecules. In this view every second molecule belongs to the same stack, the molecules seen directly next to each other are situated at a different height regarding the *b*-axis and therefore they belong to different stacks.

The structure of a closely related oxadiazole is already known: In the 2,5-diphenyl-1,3,4-oxadiazole, *DPO*, the terminal nitrogen atoms of the pyridyl substituents are replaced by CH-groups. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 5.203(2)\,\AA$, $b = 18.143(6)\,\AA$, $c = 12.184(4)\,\AA$. The two structures are compared in Figs. 2 and 3.

The view along the *a*-axis (Fig. 3) shows the arrangement of the stacks in the bc-plane. Within the stacks the molecules are oriented in the same direction for both structures. But for compound **I** the stacks are related by translation along the *b*-axis. In contrast to this highly periodic arrangement in the DPO the stacks are shifted relative to each other so

Table 5
Selected distances (Å) and angles (°) for 2-(4-cyanophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole (**II**)

Bond distance	Angles	Bond distance	Angles
O1–C1	1.368(2)	C1–O1–C2	102.82(12)
O1–C2	1.374(2)	C2–N1–N2	106.97(13)
N1–C2	1.292(2)	C1–N2–N1	106.13(14)
N1–N2	1.407(2)	N2–C1–O1	112.36(14)
N2–C1	1.294(2)	N2–C1–C9	127.4(2)
C2–C3	1.451(2)	O1–C1–C9	120.20(13)
C3–C4	1.403(2)	N1–C2–O1	111.7(2)
C4–C5	1.367(3)	N1–C2–C3	127.35(15)
C5–C6	1.395(2)	O1–C2–C3	120.75(13)
C6–C7	1.396(3)	C8–C3–C4	119.1(2)
C7–C8	1.375(3)	C8–C3–C2	122.6(2)
C8–C3	1.390(2)	C4–C3–C2	118.28(14)
C4–H4	1.02(2)	C5–C4–C3	120.9(2)
C5–H5	0.99(2)	C5–C4–H4	120.6(1)
C7–H7	0.97(2)	C3–C4–H4	118.5(1)
C8–H8	1.00(2)	C4–C5–C6	119.7(2)
C6–C15	1.431(3)	C4–C5–H5	121.8(1)
C15–N3	1.158(3)	C6–C5–H5	118.5(1)
C1–C9	1.454(2)	C5–C6–C7	119.9(2)
C9–C10	1.384(3)	C5–C6–C15	119.8(2)
C10–C11	1.376(3)	C7–C6–C15	120.2(2)
C11–C12	1.404(3)	N3–C15–C6	178.8(2)
C12–C13	1.397(3)	C8–C7–C6	120.1(2)
C13–C14	1.386(3)	C8–C7–H7	121.3(2)
C14–C9	1.399(2)	C6–C7–H7	118.6(1)
C10–H10	0.97(2)	C7–C8–C3	120.4(1)
C11–H11	0.93(2)	C7–C8–H8	119.9(2)
C13–H13	0.98(2)	C3–C8–H8	119.7(2)
C14–H14	1.02(2)	C10–C9–C14	118.4(2)
C12–N4	1.373(3)	C10–C9–C1	119.13(14)
N4–C16	1.443(4)	C14–C9–C1	122.4(2)
N4–C17	1.532(6)	C11–C10–C9	121.8(2)
C16–H161	0.98(3)	C11–C10–H10	117.8(2)
C16–H162	0.95(3)	C9–C10–H10	120.3(2)
C16–H163	0.97(4)	C10–C11–C12	120.5(2)
C17–H171	1.17(3)	C10–C11–H11	117.4(2)
C17–H172	1.05(3)	C12–C11–H11	122.1(2)
C17–H173	0.40(2)	N4–C12–C13	121.3(2)
		N4–C12–C11	121.1(2)
		C13–C12–C11	117.6(2)
		C14–C13–C12	121.7(2)
		C14–C13–H13	117.7(2)
		C12–C13–H13	120.6(2)
		C13–C14–C9	120.0(2)
		C13–C14–H14	121.8(2)
		C9–C14–H14	118.2(2)
		C12–N4–C16	120.8(2)
		C12–N4–C17	116.8(3)
		C16–N4–C17	121.7(3)

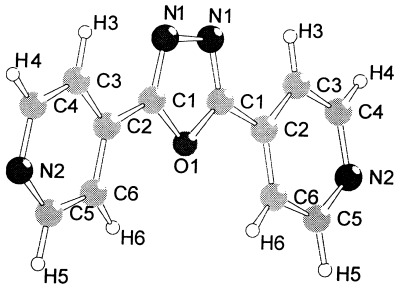

Fig. 1. Molecular structure of 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**I**).

that the oxadiazole rings are not aligned along the vertical axis. Along the horizontal axis pairs of molecules related by a center of inversion are formed in both structures.

This slight shift of the stacks can also be seen in Fig. 2 where for the DPO the layers of stacks overlap slightly which is not the case for **I**. The most obvious difference between these two structures is the orientation of neighboring stacks relative to each other: For compound **I** neighboring stacks are oriented in the same direction whereas in the DPO neighboring stacks show two different orientations ($\pm 50°$ relative to the axis of the stacks). However, the single orientation of the molecules is preferable for optical applications as it might lead to polarized emission.

In both structures common motifs of packing are found such as the parallel arrangement of the molecules in the stacks, which allows $\pi-\pi$ interactions between the oxadiazole ring of one molecule and the phenyl groups of the neighboring molecules. Despite the small molecular differences the two compounds show significant differences in their three-dimensional structure and in the orientation of their molecules in the unit cell.

One possible explanation for this difference could involve the formation of hydrogen bonds/bridges in the pyridyl structure with the terminal nitrogen but this is not observed in this structure even though there should not be any steric hindrance. Consequently, the only molecular interaction in these solid state structures is the $\pi-\pi$ interaction for which the same motif is observed so that this is not explaining the differences between the two crystal structures.

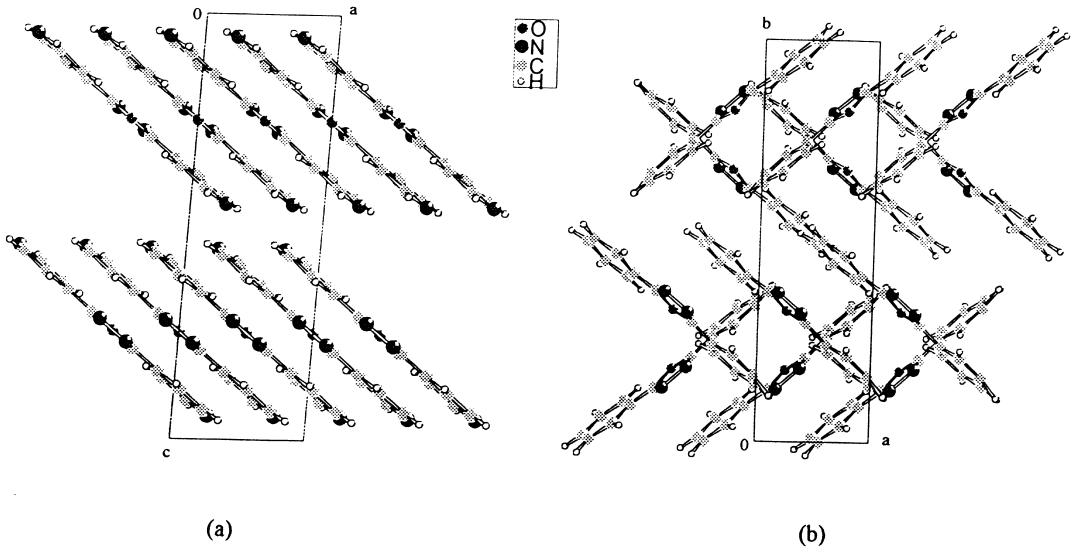

Fig. 2. Perspective view of the crystal structures along the axis of the stacks of: (a) 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**I**); (b) 2,5-diphenyl-1,3,4-oxadiazole (DPO)

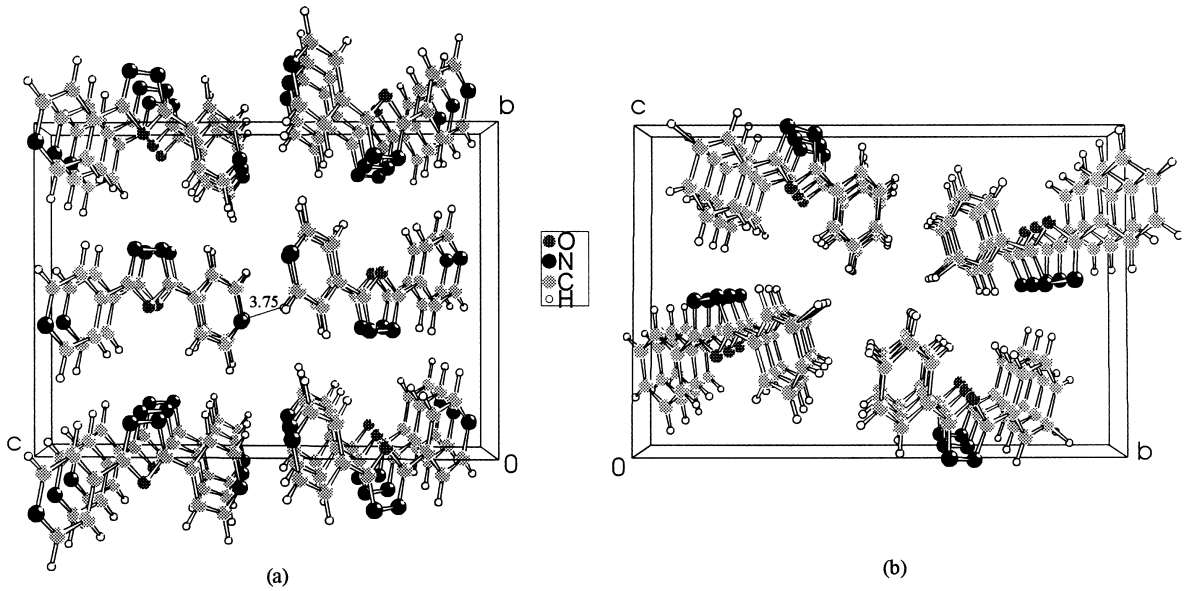

Fig. 3. Crystal structures of: (a) 2,5-di(4-pyridyl)-1,3,4-oxadiazole (**I**); (b) 2,5-diphenyl-1,3,4-oxadiazole (DPO) illustrating the arrangement of the stacks relative to each other.

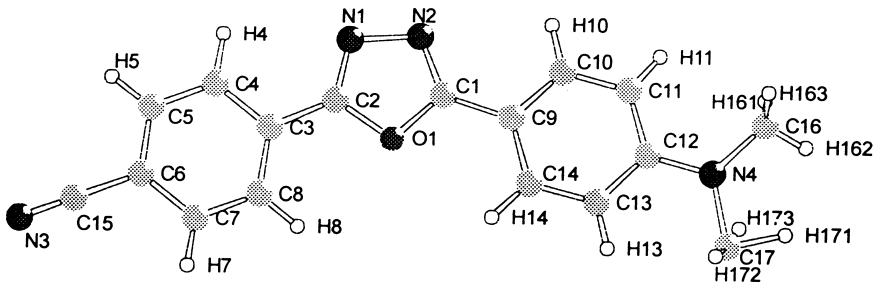

Fig. 4. Molecular structure of 2-(4-cyano-phenyl)-5(4-dimethylamino-phenyl)-1,3,4-oxadiazole (**II**).

3.2. 2-(4-Cyanophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole

This compound is the first 2,5-diphenyl-1,3,4-oxadiazole that crystallizes in the triclinic crystal system. The only other triclinic oxadiazole known so far is the 2-(4-methoxybenzyl)-5-phenyl-1,3,4-oxadiazole [11] where the conjugation is interrupted by a benzyl group so that the molecules have an angle of 117°.

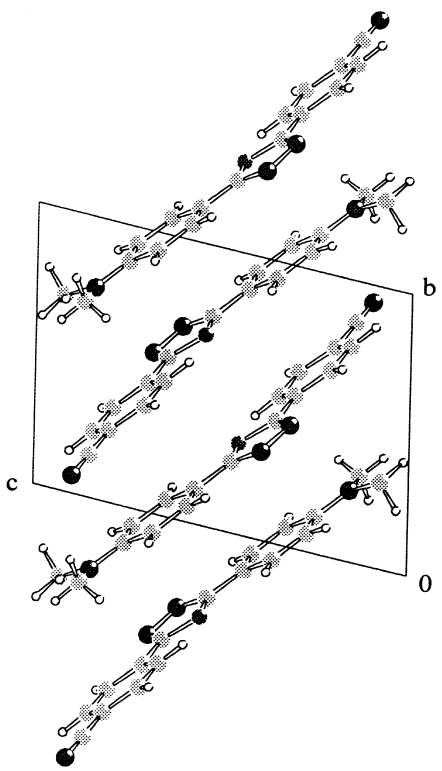

Fig. 5. Unit cell of 2-(4-cyanophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole (**II**).

In the crystal, the molecules of 2-(4-cyanophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole, **II**, Fig. 4, have an almost planar structure. The planarity of the three single rings is nearly perfect but again the rings show a slight torsion relative to each other. The rotation of the inter-ring bond between the oxadiazole ring and the benzonitrile is +6.5° and between the oxadiazole ring and the dimethylaniline is +4.2°. In this molecule the two substituents are tilted in the same direction relative to the oxadiazole ring whereas in **I** the rings are tilted in opposite directions.

In the three-dimensional structure, Fig. 5, the molecules of **II** form stacks, too. The axis of these stacks is the *b*-axis and the molecules in the stacks are inclined by 50° to this axis. Neighboring stacks are oriented in the same direction like already observed for compound **I**. The shortest distance between the stacks is around 3.5 Å which is too long for any hydrogen bonds/bridges between these layers. Within the stacks pairs of molecules are formed in which the two molecules are related by a center of inversion so that the molecules show alternately opposite orientations regarding the oxygen atoms of their oxadiazole rings. The planes of the oxadiazole rings of the molecules are separated by 3.60 Å. These pairs of molecules also show a distance of 3.54 Å to the next oxadiazole molecule so that within the stacks the molecules are almost equidistant. Between the pairs the shortest contact exists between the oxadiazole ring of one molecule and the dimethylaniline ring of the other so that the $\pi-\pi$ interaction here is not exactly perpendicular to the planes of the rings. The slight torsion of the rings allows a better $\pi-\pi$ interaction. Accordingly, the interaction of the molecules in the

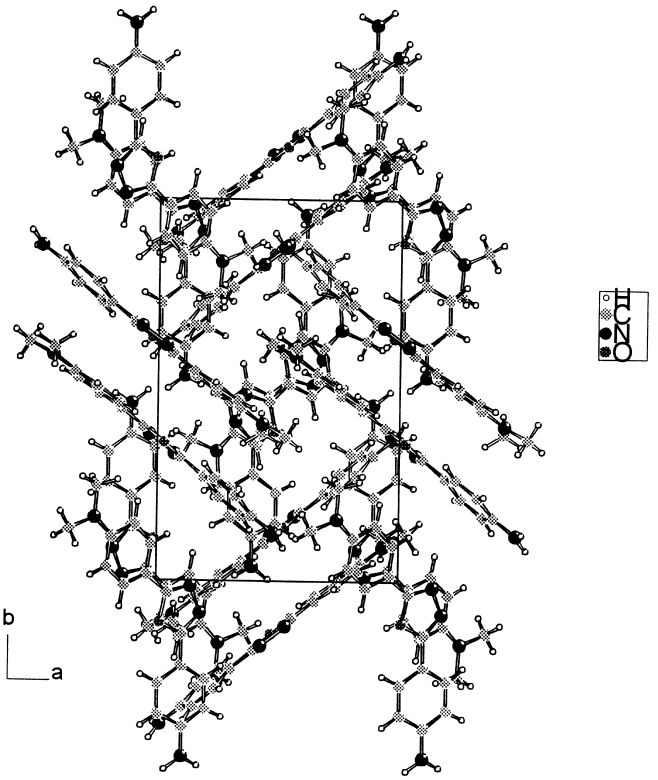

Fig. 6. Unit cell of 2-(4-amino-phenyl)-5(4-dimethylamino-phenyl)-1,3,4-oxadiazole (**III**).

stacks is different for **II** compared to that observed in **I** or DPO.

If the CN-moiety of **II** is replaced by a NH_2-group we get to the 2-(4-amino-phenyl)-5(4-dimethylamino-phenyl)-1,3,4-oxadiazole, **III**, for which the structure is also known. We observe that just a very small change in the molecular substitution leads to a completely different structure with other motifs of packing. Compound **III** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.4585\,\mathring{A}$, $b = 16.9604\,\mathring{A}$, $c = 16.0758\,\mathring{A}$ and $\beta = 109.49°$ [12]. The structure is much more complex, Fig. 6 consists of oxadiazole molecules with four different orientations. The formation of stacks of molecules like seen in the other structures is not observed. The complex packing of the molecules in this structure increases the distance between the aromatic rings to about 4 Å so that the π–π interactions are rather weak. The shortest distance between molecules in this structure is 2.5 Å between the amino groups.

This complex structure does not show the motifs of packing (like the formation of stacks) that are observed for the solid state structures of oxadiazoles so far. The small change in the molecular structure did not introduce any additional interactions between the molecules but, nevertheless, leads to a complete change in the crystalline structure.

4. Conclusions

The 2,5-diaryl-1,3,4-oxadiazole structures determined so far consist all of almost planar molecules in which the planar rings show only slight torsion relative to each other. In nearly all structures these molecules form stacks. Within these stacks the planes of the molecules are parallel to each other and separated by approximately 3.5 Å, and two possible arrangements occur: Regarding the oxygen atom of the oxadiazole ring the molecules can be oriented all

in the same direction (**I**) or alternating in opposite directions (**II**). An arrangement observed for different oxadiazoles is the shift of the molecules relative to each other in the way that the oxadiazole ring of one molecule is sandwiched between two phenyl rings of neighboring molecules to allow good $\pi-\pi$ interaction perpendicular to the planes of the molecules. However, in **II** a different arrangement of the molecules within the stacks is found where two oxadiazole rings are situated next to each other.

Generally, the planes of the molecules are inclined to the axis of the stacks by around 50°. Between neighboring stacks two different relations are observed: Neighboring stacks are oriented in the same direction (**I**, **II**) or in opposite directions (DPO) so that the neighboring stack is inclined to the axis of the stacks by $-50°$.

Small changes in the molecular structure of the oxadiazole do not have any influence on the planarity of the molecules and the existence of intermolecular $\pi-\pi$ interactions but might lead to a completely different packing of these molecules in the crystalline structure as seen for the pair **II/III**. Compound **III** crystallizes in a monoclinic space group like most of the oxadiazoles crystallize in the monoclinic or orthorhombic system but the widely observed formation of stacks is not found in this structure. The exchange of one endgroup leads again to the formation of stacks for compound **II** but this compound is exceptional in that it crystallizes in the triclinic crystal system. Surprisingly, no hydrogen bonding interactions are observed in any of these systems, which could have explained these drastic changes in the crystalline structure. Therefore, various very complex influences must be responsible for the formation of a certain structure and a definite type of packing.

Acknowledgements

We thank the European Commission under contract number FMRX-CT97-0106 (TMR-EUROLED) for financial support and for introducing the collaboration.

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