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NMR and X-ray Studies Concerning Structure of 6,6'-(Oxybis(4,1-phenylene))*bis*-(2-allylpyridazin-3(2H)-one)

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Abstract: The structural NMR and X-ray studies of 6,6'-(Oxybis(4,1-phenylene))*bis*-(2-allylpyridazin-3(2H)-one), a *bis*-pyridazine derivative heterocycle, are reported in this study. Both ^{1}H- and ^{13}C- NMR confirm the proposed structure of compound. In order to establish unequivocally the structure of compound, the X-ray data analysis was performed. The compound crystallizes in the triclinic P-1(2) space group with a = 10.3699(7) Å, b = 10.6972(6) Å, c = 11.0449(4) Å, α = 87.941(5)°, β = 75.564(5)°, γ = 72.055(5)°, V= 1127.68 (12) Å^3 and Z = 2. Molecular and crystal packing parameters for the novel heterocyclic system were obtained from intensity data collected at room temperature. The two phenyl rings (from the diphenyl ether moiety) are perpendicular one to each other and, on its turn, each phenyl ring is almost coplanar with the pyridazine ring.

Keywords: ^{1}H- and ^{13}C- NMR, X-ray, crystal structure, *bis*-pyridazine.

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Introduction

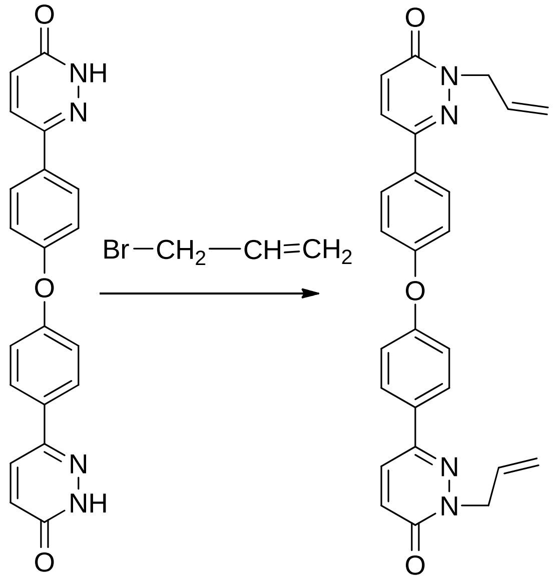
During the last decades synthesis of new 6-membered ring nitrogen heterocycles became a permanent interest of chemists, not only because of their applications but also because of the beauty of synthesis itself.[1-10]

It was previous described in the literature that 6-membered ring nitrogen heterocycles possess a large variety of applications in very different fields, such us medicinal chemistry (antibacterial and antifungal, antituberculosis, anticancer, etc.),[11-20] opto-electronics (highly fluorescent derivatives, compounds with liquid crystal and ionic liquids properties and semiconductors)[21-27] and agriculture (herbicidal activity and grow up factor for plants).[28]

To continue our research in the field of 1,2 diazines, the structure of 6,6'-(Oxybis(4,1-phenylene))*bis*-(2-allylpyridazin-3(2H)-one) was investigated by NMR and X-ray studies.

Results and discussions

In order to obtain the *N*-allyl- *bis*-pyridazinone **2**, a straightforward and efficient setup procedure was used: the direct *N*-alkylation reaction of *bis*-pyridazinone **1** with allyl bromide, Scheme 1.



Scheme 1. Reaction pathway to obtain 6,6'-(Oxybis(4,1-phenylene)) *bis*-(2-allylpyridazin-3(2H)-one).

Full details concerning the synthesis of the *bis*-pyridazine derivative heterocycle, **2**, could be found elsewhere.[16]

The NMR spectra of **2** confirm the proposed structure. In the ^{1}H-NMR, the methylene protons ($H_{1'}$) from allyl group appear at 4.84 ppm (d, $J_{1',2'}$ = 6.0 Hz, 4H (2xCH_2): $H_{1'}$), due to the powerful deshielding effect induced by the N_2-nitrogen from pyridazine moiety. The $H_{3'}$ ($H_{3'a}$, $H_{3'b}$) protons from allyl group appears at 5.28 ppm as a triplet of doublets. Having in view the values of the coupling constants ($J_{3'b,2'}$ = 10.0 Hz, $J_{3'a,2'}$ = 1.2 Hz), we are able to say that $H_{3'a}$ with $H_{2'}$ are in *cis* related to each other while $H_{3'b}$ with $H_{2'}$ are in *trans*. The $H_{2'}$ proton from allyl group appear between 6.11-6.01 ppm (2H : $H_{2'}$), being coupled with the two $H_{3'}$ protons. The two protons from pyridazine ring (H_4 and H_5) appear as doublets ($J_{4,5}$ = $J_{5,4}$ = 10.0 Hz), at 7.65 ppm, respectively 7.03 ppm, in accordance with their surroundings. The ^{13}C-NMR spectrum also confirmed the proposed structures. The most deshielded carbon is those one of the carbonyl lactame carbon (C_3) that appears at 159.42 ppm. The allyl carbons appear according with their environment: 54.51 ($C_{1'}$), 118.58 ($C_{3'}$), 131.81 ($C_{2'}$). All the remaining signals from NMR spectra are in accordance with the proposed structure.

In order to establish unequivocally the structure of the *bis*-pyridazine derivative heterocycle **2**, the X-ray data analysis was performed. Yellow needles crystals of compound **2** were obtained by crystallization from methanol. The X-ray structure of the title compound with the atom numbering scheme is shown in Figure 1.

The crystal structure and refinement data are summarized in Table 1. The H atoms were positioned geometrically and refined using a riding model with C—H distances of 0.95 – 0.99 Å, and with Uiso(H) = 1.2 Ueq(C).

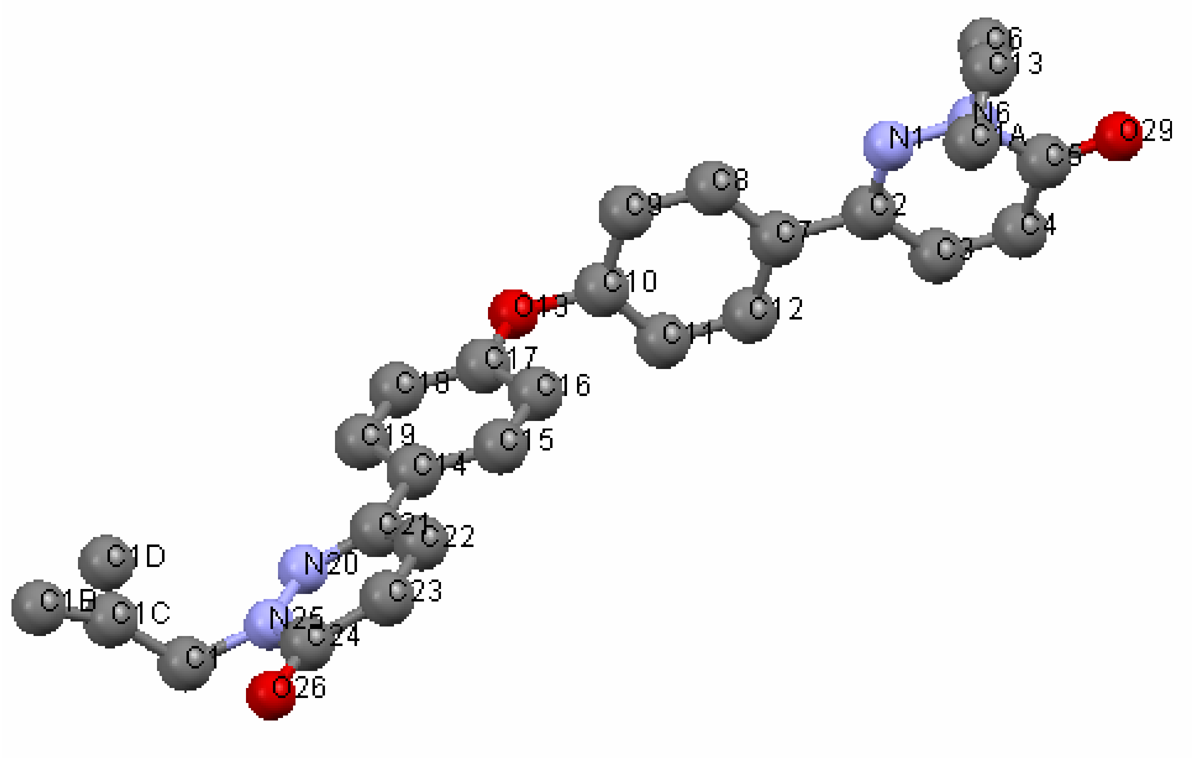


Figure 1. The molecular structure of $C_{26}H_{22}N_4O_3$ drawn at 50% probability level. H atoms are omitted for clarity.

Table 1. Crystal structure and diffraction data.

Chemical formula	$C_{26}H_{22}N_4O_3$
Formula weight	438.48
Crystal Color	Yellow
Crystal System	triclinic
Space Group	P-1
Cell parameters (Å):	
a	10.3699 (7)
b	10.6972 (6)
c	11.0449 (6)
Cell angles (^{o}):	
α	87.941 (5)
β	75.564 (5)
γ	72.055 (5)
Volume ($Å^3$)	1127.68
Z	2
ρ_{calc} (mg/mm^3)	1.221
F(000)	434.0
μ/mm^{-1}	0.684
Reflections collected	12975
Data/restraints/parameters	4242/0/282
Final R indexes [$I > 2\sigma(I)$]	R1 = 0.1319, wR2 = 0.4183
Goodness of Fit on F^2	1.896

Fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

Table 2. Fractional atomic coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times 10^3$). Ueq is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O13	4517.6(13)	7364.8(16)	5132.8(14)	81.8(4)
O26	14531.8(13)	5302.1(15)	2011.0(14)	79.8(4)
C14	8855.4(17)	6423.5(16)	3933.5(16)	54.6(4)
N25	12350.9(15)	5455.4(17)	1843.3(15)	67.8(4)
N20	10942.6(14)	5726.1(16)	2294.1(14)	64.0(4)
N1	1586.6(16)	9781.2(16)	10632.7(15)	66.7(4)
C7	2330.9(16)	9635.5(17)	8423.8(17)	56.3(4)
C21	10396.7(17)	6108.7(16)	3468.2(16)	54.2(4)
C2	1596.6(17)	10423.6(18)	9603.5(17)	58.4(4)
C15	8150.8(18)	7159.2(18)	5032.5(18)	61.9(5)
C18	6634.7(18)	6333.2(19)	3679.1(18)	64.8(5)
C10	3797.4(18)	8128(2)	6235.3(19)	65.7(5)
C17	5959.1(17)	7072.3(19)	4777.3(18)	62.8(5)
N6	970.0(18)	10461(2)	11741.7(16)	76.0(5)
C24	13269.6(18)	5559.2(18)	2521.3(19)	63.3(5)
C19	8066.4(18)	6010.7(18)	3264.2(17)	60.7(4)
C23	12628.3(19)	5970.6(19)	3800.6(19)	66.3(5)
C16	6708.0(19)	7486(2)	5465.2(19)	67.0(5)
C22	11245.5(18)	6228.6(18)	4268.9(18)	62.0(4)
O29	-73.3(19)	12335(2)	12959.1(17)	115.0(7)
C12	2598(2)	10210(2)	7283.6(19)	72.0(5)
C5	375(2)	11809(3)	11902(2)	83.0(6)
C11	3326(2)	9461(2)	6196(2)	77.0(6)
C8	2820(2)	8277(2)	8427(2)	73.2(5)
C3	924(2)	11807(2)	9651(2)	74.2(5)
C9	3543(2)	7525(2)	7342(2)	78.2(6)
C4	337(2)	12457(2)	10755(2)	89.3(7)
C1	12904(3)	4982(4)	543(2)	101.4(10)
C6	1035(3)	9639(3)	12824(2)	103.7(8)

C13	2359(4)	9329(3)	13178(3)	114.3(10)
C1A	3467(4)	9545(4)	12594(4)	123.7(11)
C1B	14352(11)	2437(9)	-25(9)	134(4)
C1C	13478(5)	3574(6)	354(6)	158.1(18)
C1D	13516(7)	2842(6)	992(6)	102(2)

Table 3 and Table 4 list the bond lengths, bond angles and torsion angles for compound **2**.

Table 3. Bond Lengths (Å) for compound **2**.

O13-C10	1.396(2)	C7-C12	1.384(3)	C23-C22	1.340(2)
O13-C17	1.384(2)	C7-C8	1.384(3)	O29-C5	1.229(3)
O26-C24	1.236(2)	C21-C22	1.428(2)	C12-C11	1.379(3)
C14-C21	1.484(2)	C2-C3	1.425(3)	C5-C4	1.425(3)
C14-C15	1.378(2)	C15-C16	1.386(2)	C8-C9	1.376(3)
C14-C19	1.399(2)	C18-C17	1.375(3)	C3-C4	1.331(3)
N25-N20	1.361(2)	C18-C19	1.375(2)	C1-C1C	1.440(6)
N25-C24	1.381(2)	C10-C11	1.360(3)	C6C13	1.459(4)
N25-C1	1.453(3)	C10-C9	1.366(3)	C13-C1A	1.254(5)
N20-C21	1.303(2)	C17-C16	1.381(2)	C1B-C1C	1.282(10
N1-C2	1.307(2)	N6-C5	1.381(3)	C1C-C1D	1.033(6)
N1- N6	1.351(2)	N6-C6	1.461(3)		
C7-C2	1.475(3)	C24C23	1.424(3)		

The data from Table 3 and 4 (especially the torsion angles) and the Figure 1, reveal interesting data concerning spatial orientations of the four rings in compound **2**. Thus, the two phenyl rings (from the diphenyl ether moiety) are perpendicular one to each other (C17O13C10C11 = 90.3^{o}; C17O13C10C9 = -91.3^{o}). On its turn, each phenyl ring is almost coplanar (slightly out of plane with about 15^{o}) with the pyridazine ring (C19C14C21N20 = 16.4^{o}; C15C14C21C22 = 17.3^{o}). It is not out of interest to mention that the vinyl group (from allyl) is almost perpendicular to the pyridazine moiety (N6C6C13C1A = -9.1^{o}), because this may be interesting from the medicinally chemistry point of view (interaction with the active sites).

Table 4. Bond angles (^{o}) and torsion angles (^{o}) for compound **2**.

Bond angles				**Torsion angles**
C17	O13	C10	117.78(13)	C8 C7 C12 C11 -0.2(3)
C16	C17	O13	123.17(17)	C2 C7 C8 H8 1.9(3)
C15	C14	C21	120.73(15)	C2 C7 C8 C9 -178.1(2)
N1	N6	C5	125.73(19)	C12 C7 C8 H8 -180.0(2)
C15	C14	C19	117.79(16)	C12 C7 C8 C9 -0.0(3)
N1	N6	C6	113.7(2)	C14 C21 C22 C23 -178.1(2)
C19	C14	C21	121.46(16)	C14 C21 C22 H22 1.9(3)
C5	N6	C6	120.5(2)	N20 C21 C22 C23 1.5(3)
N20	N25	C24	125.67(16)	N20 C21 C22 H22 -178.6(2)
O26	C24	N25	120.22(19)	N1 C2 C3 H3 -176.9(2)
N20	N25	C1	115.48(17)	N1 C2 C3 C4 3.1(3)
O26	C24	C23	125.51(18)	C7 C2 C3 H3 3.0(3)
C24	N25	C1	118.83(17)	C7 C2 C3 C4 -177.0(2)
N25	C24	C23	114.27(16)	C14 C15 C16 C17 -0.4(3)
C21	N20	N25	118.07(15)	C14 C15 C16 H16 179.6(2)
C18	C19	C14	121.40(17)	H15 C15 C16 C17 179.6(2)
C2	N1	N6	118.70(17)	H15 C15 C16 H16 -0.4(3)
C22	C23	C24	121.11(17)	H18 C18 C17 O13 -0.3(3)
C12	C7	C2	122.12(17)	H18 C18 C17 C16 179.8(2)
C17	C16	C15	119.35(18)	C19 C18 C17 O13 179.7(2)
C8	C7	C2	120.56(17)	C19 C18 C17 C16 -0.3(3)
C23	C22	C21	119.50(18)	H18 C18 C19 C14 179.7(2)
C8	C7	C12	117.30(18)	H18 C18 C19 H19 -0.3(3)
C11	C12	C7	121.4(2)	C17 C18 C19 C14 -0.3(3)
N20	C21	C14	117.15(15)	C17 C18 C19 H19 179.8(2)

N6	C5	C4	113.37(19)	O13 C10 C11 C12 179.1(2)
N20	C21	C22	121.35(16)	O13 C10 C11 H11 -0.9(3)
O29	C5	N6	120.3(2)	C9 C10 C11 C12 0.7(3)
C22	C21	C14	121.50(16)	C9 C10 C11 H11 -179.4(2)
O29	C5	C4	126.3(3)	O13 C10 C9 C8 -179.3(2)
N1	C2	C7	116.21(17)	O13 C10 C9 H9 0.7(3)
C10	C11	C12	119.7(2)	C11 C10 C9 C8 -0.9(3)
N1	C2	C3	120.53(18)	C11 C10 C9 H9 179.1(2)
C9	C8	C7	121.49(19)	O13 C17 C16 C15 -179.3(2)
C3	C2	C7	123.26(17)	O13 C17 C16 H16 0.6(3)
C4	C3	C2	119.6(2)	C18 C17 C16 C15 0.6(3)
C14	C15	C16	121.42(16)	C18 C17 C16 H16 -179.4(2)
C10	C9	C8	119.57(19)	N1 N6 C5 O29 -175.0(2)
C19	C18	C17	119.53(16)	N1 N6 C5 C4 5.8(3)
C3	C4	C5	121.8(2)	C6 N6 C5 O29 1.9(4)
C11	C10	O13	119.9(2)	C6 N6 C5 C4 -177.2(2)
C1C	C1	N25	115.0(3)	N1 N6 C6 H6A -156.6(2)
C11	C10	C9	120.55(19)	N1 N6 C6 H6B -39.7(3)
C13	C6	N6	113.8(2)	N1 N6 C6 C13 81.8(3)
C9	C10	O13	119.57(19)	C5 N6 C6 H6A 26.1(3)
C1A	C13	C6	128.2(3)	C5 N6 C6 H6B 143.1(2)
C18	C17	O13	116.31(15)	C5 N6 C6 C13 -95.4(3)
C1B	C1C	C1	160.2(7)	O26 C24 C23 H23 -0.1(3)
C18	C17	C16	120.51(17)	O26 C24 C23 C22 179.9(2)
C1D	C1C	C1	130.4(7)	N25 C24 C23 H23 179.8(2)
Torsion angles				N25 C24 C23 C22 -0.2(3)
C17 O13 C10 C11 90.3(2)				C24 C23 C22 C21 -1.0(3)
C17 O13 C10 C9 -91.3(2)				C24 C23 C22 H22 179.1(2)
C19 C14 C21 N20 16.4(3)				H23 C23 C22 C21 179.0(2)

C15 C14 C21 C22 17.3(3)	H23 C23 C22 H22 -1.0(3)
C15 C14 C21 N20 -162.3(2)	C7 C12 C11 C10 -0.1(3)
C19 C14 C21 C22 -164.1(2)	C7 C12 C11 H11 179.9(2)
C21 C14 C15 H15 -1.4(3)	H12 C12 C11 C10 179.9(2)
C21 C14 C15 C16 178.6(2)	H12 C12 C11 H11 -0.0(4)
C19 C14 C15 H15 179.9(2)	N6 C5 C4 C3 -4.8(3)
C19 C14 C15 C16 -0.1(3)	N6 C5 C4 H4 175.2(2)
C21 C14 C19 C18 -178.2(2)	O29 C5 C4 C3 176.1(2)
C21 C14 C19 H19 1.8(3)	O29 C5 C4 H4 -3.9(4)
C15 C14 C19 C18 0.5(3)	C7 C8 C9 C10 0.6(3)
C15 C14 C19 H19 -179.6(2)	C7 C8 C9 H9 -179.4(2)
C24 N25 N20 C21 -0.5(3)	H8 C8 C9 C10 -179.5(2)
C1 N25 N20 C21 177.6(2)	H8 C8 C9 H9 0.5(4)
N20 N25 C24 O26 -179.1(2)	C2 C3 C4 C5 0.8(3)
N20 N25 C24 C23 1.0(3)	C2 C3 C4 H4 -179.2(2)
C1 N25 C24 O26 2.8(3)	H3 C3 C4 C5 -179.3(2)
C1 N25 C24 C23 -177.1(2)	H3 C3 C4 H4 0.7(4)
N20 N25 C1 C1C -97.2(4)	N25 C1 C1C C1B -125(2)
N20 N25 C1 H1A 20(2)	N25 C1 C1C H1C 55.2(5)
N20 N25 C1 H1B 145(2)	H1A C1 C1C C1B 118(3)
C24 N25 C1 C1C 81.0(4)	H1A C1 C1C H1C -62(2)
C24 N25 C1 H1A -162(2)	H1B C1 C1C C1B -7(3)
C24 N25 C1 H1B -37(2)	H1B C1 C1C H1C 173(2)
N25 N20 C21 C14 178.8(2)	N6 C6 C13 H13 170.8(3)
N25 N20 C21 C22 -0.7(3)	***N6 C6 C13 C1A -9.1(5)***
N6 N1 C2 C7 177.8(2)	H6A C6 C13 H13 49.3(4)
N6 N1 C2 C3 -2.3(3)	H6A C6 C13 C1A -130.6(4)
C2 N1 N6 C5 -2.4(3)	H6B C6 C13 H13 -67.7(4)
C2 N1 N6 C6 -179.5(2)	H6B C6 C13 C1A 112.4(4)

C12 C7 C2 N1 -170.4(2)	C6 C13 C1A H1AA -168(2)
C12 C7 C2 C3 9.7(3)	C6 C13 C1A H1AB 8(3)
C8 C7 C2 N1 7.6(3)	H13 C13 C1A H1AA 12(2)
C8 C7 C2 C3 -172.3(2)	H13 C13 C1A H1AB -172(3)
C2 C7 C12 H12 -2.2(3)	H1BA C1B C1C C1 169(10)
C2 C7 C12 C11 177.8(2)	H1BA C1B C1C H1C -11(10)
C8 C7 C12 H12 179.7(2)	H1BB C1B C1C C1 -13(9)
C10 O13 C17 C18 -179.2(2)	H1BB C1B C1C H1C 167(9)
C10 O13 C17 C16 0.7(3)	

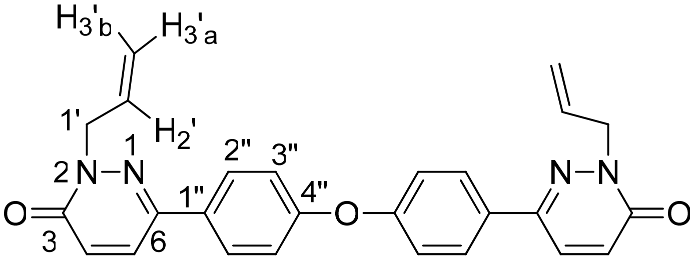
Experimental

All the reagents and solvents employed were of the best grade available and were used without further purification. Melting points were determined using an electrothermal apparatus (MELTEMP II) and are uncorrected. The NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The X-Ray diffraction experiment was performed using a SuperNova Dual diffractometer equipped with a Cu ($K\alpha$ radiation, $\lambda = 0.684$ Å) fine-focus sealed X-ray tube and a graphite monochromator. Detector resolution: 16.1593 pixels mm-1, ω scans. Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011), Tmin = 0.914, Tmax = 1.000. A total number of 12975 reflections (4242 independent) were recorded at room temperature on a small single crystal. All H atoms were located in difference electron density maps and were included in idealized positions in a riding model with isotropic thermal parameters equal to 1.2 times those of their parent atoms. In the final cycles of refinement, least-squares weights of the form were: wR_2 = 0.4532 and R_1 = 0.1319 (l>2/s(1)). Crystallographic data for 6,6’-(Oxybis(4,1-phenylene))*bis*-(2-allylpyridazin-3(2H)-one) are listed in Table 1. CCDC contains the supplementary crystallographic data for this paper.

Data processing and refinement

Using Olex2 [1], the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

Data collection: CrysAlisPro, Agilent Technologies, Version 1.171.36.28.



6,6’-(Oxybis(4,1-phenylene))bis-(2-allylpyridazin-3(2H)-one) ***(2)****:* ^{1}H-NMR (500 MHz, $CDCl_3$): δ_{ppm}: 4.84 (d, $J_{1',2'}$ = 6.0 Hz, 4H, $H_{1'}$), 5.28 (td, $J_{3',2'}$ = 10.0 Hz, 4H, $H_{3'}$), 6.01-6.11 (m, 2H, $H_{2'}$), 7.03 (d, $J_{5,4}$ = 10.0 Hz, 2H, H_5), 7.10 (d, $J_{2'',3''}$ = 8.8 Hz, 4H, $H_{2''}$), 7.65 (d, $J_{4,5}$ = 10.0 Hz, 2H, H_4), 7.77 (d, $J_{3'',2''}$ = 8.8 Hz, 4H, $H_{3''}$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ_{ppm}: 54.51 ($C_{1'}$), 118.58 ($C_{3'}$), 119.27 ($C_{2''}$), 127.60 ($C_{3''}$), 129.92 (C_4), 130.21 (C_5), 131.81 ($C_{2'}$), 143.89 ($C_{1''}$+ C_6), 157.85 ($C_{4''}$), 159.42 (C_3).

Conclusions

Herein we report a feasible study concerning the structure of 6,6’-(oxybis(4,1-phenylene))*bis*-(2-allylpyridazin-3(2H)-one). The NMR (both

H- and C-) as well as the X-ray study confirm unambiguously the structure of compound. The compound crystallizes in the triclinic P-1(2) space group with a = 10.3699(7) Å, b = 10.6972(6) Å, c = 11.0449(4) Å, α = 87.941(5)°, β = 75.564(5)°, γ = 72.055(5)°, V= 1127.68 (12) Å3 and Z = 2. The two phenyl rings (from the diphenyl ether moiety) are perpendicular one to each other and, on its turn, each phenyl ring is almost coplanar with the pyridazine ring.

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