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Crystal Structures of Two Biphenyl Compounds

Abstract The crystal structures of two biphenyl compounds 3-amino -2,4 dicyano - 3',4',5' trimethoxy - 1,3 terphenyl (I) and 3-amino -2,4,dicyano -5- methyl - 4'-N,N diethyl amino biphenyl (II) are described here (CCDC NO. : 134369 & 134370). The title compounds $C_{23}H_{15}N_3O_3$ (I) and $C_{19}H_{19}N_4$ (II) crystallized in the centrosymmetric triclinic space group P 1 and non-centrosymmetric orthorhombic space group Fdd2 respectively. The unit cell parameters are : (I) $a = 10.3555(2)$, $b = 10.7103(2)$, $c = 11.0096(0)\text{\AA}$, $\alpha = 64.1(0)$, $\beta = 65.9(0)$, $\gamma = 89.6(0)^\circ$; $Z=2$ and (II) $a = 23.0364(1)$, $b = 37.2165(1)$, $c = 7.7491(0)\text{\AA}$, $\alpha = \beta = \gamma = 90.0(0)^\circ$; $Z=16$. The R factors for compound (I) and (II) are 0.053 and 0.064 respectively.

Keywords: Biphenyl, terphenyl, photophysical, laser activity, biological activity

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1. Introduction

Literature is flooded with the crystal structure determination of biphenyl derivatives and the torsion angle between these phenyl rings determines the photophysical and biological activity of a biphenyl derivative (SHUKLA, et al., 1985, NIEGER et al., 1998). The laser activity of biphenyl compound can be enhanced by bulkier substitutions on the phenyl rings. The π - electron delocalization along the biphenyl unit will be the maximum in the coplanar arrangement of the biphenyls (NIEGER et al., 1998). Biphenyl derivatives are of considerable interest because of the deviation of inter- ring torsion angle between the solid state and gaseous state (RAJNİKANT et al ., 1995, BAUODOUR, 1991). Apart from the photophysical properties, biphenyl compounds are of great importance due to the activity of these molecules on the central nervous system (REBOUL et al., 1993). Certain fluoro substituted biphenyl derivatives have greater affinities to certain receptor proteins (MCKINNEY, J.D and SINGER, 1998). In order to study the changes in the conformational aspects of biphenyls due to the various substituents on the phenyls, we have undertaken the x-ray diffraction studies on two biphenyl compounds.

2. Synthesis

The title compounds were synthesized as follows: A mixture of 3,4,5 trimethoxy benzalacetophenone (2.4 mmol) [for compound I], 4-diethylamino benzalacetone (1.0g 4.6mmol) (for compound II), malononitrile (0.6g 9.2mmol) and few drops of pyrrolidine in ethanol (20 ml) was heated under reflux for 7 hours. The reaction mixture was concentrated

under reduced pressure and purified by column chromatography over silica gel. Elution with a mixture of petroleum ether-benzene (1:5) gave the product as a yellow solid.

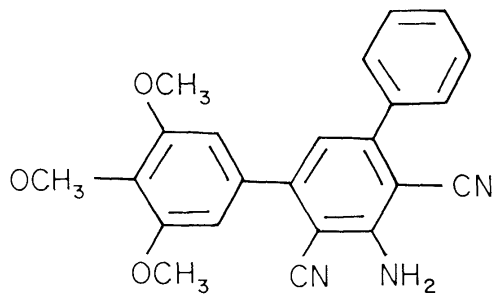


Fig. 1: Chemical diagram of the title compound (I).

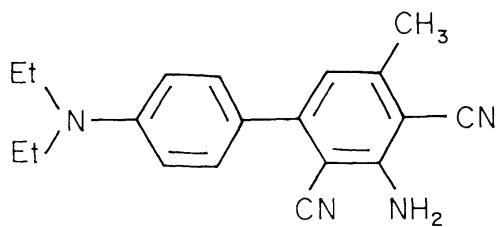


Fig. 2: Chemical diagram of the title compound (II).

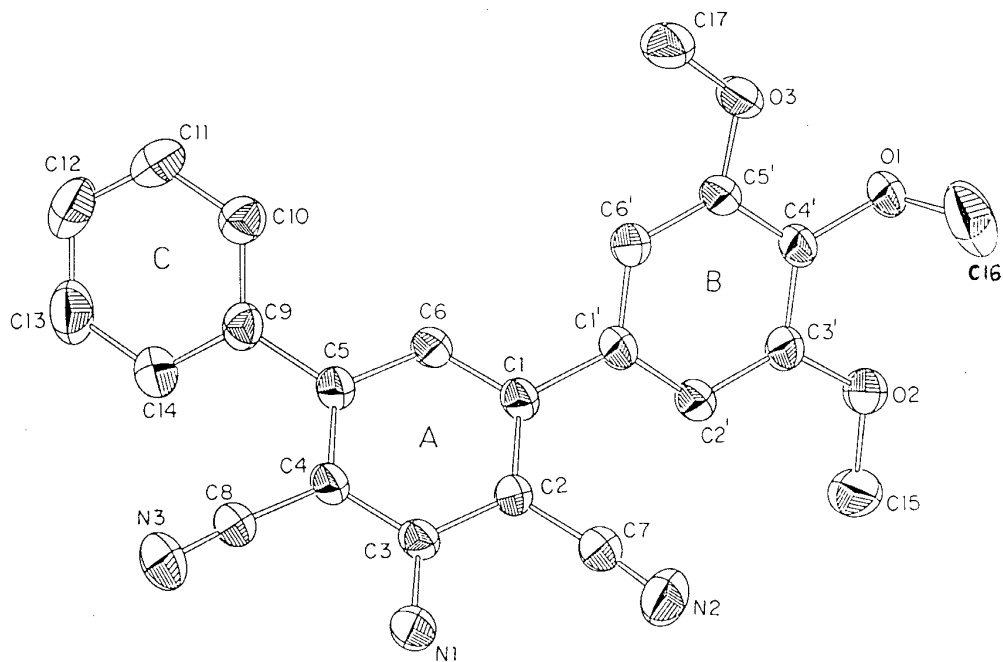


Fig. 3: Molecular structure of compound (I) showing 50% probability displacement ellipsoids with atomic numbering scheme.

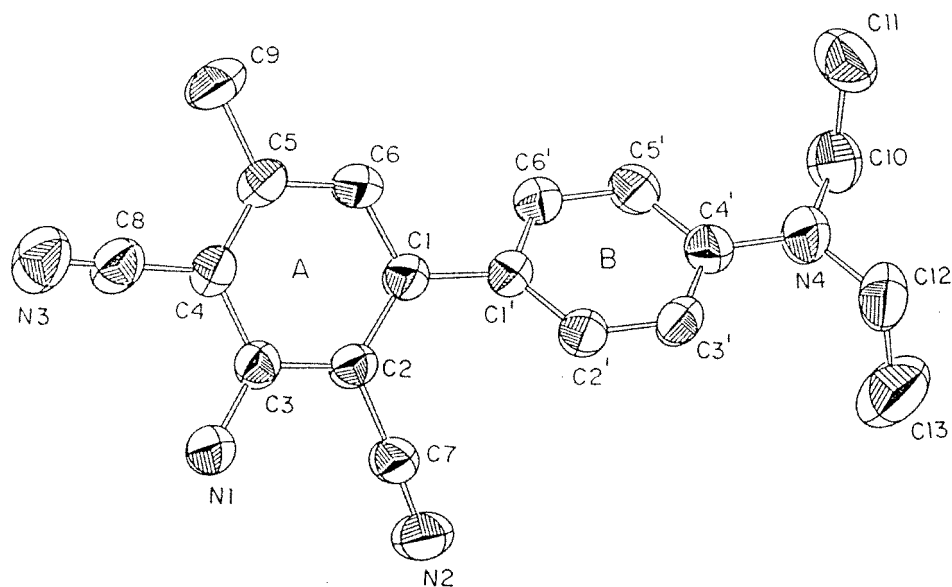


Fig. 4: Molecular structure of compound (II) showing 50% probability displacement ellipsoids with atomic numbering scheme.

	Compound (I)	Compound (II)
Empirical formula	$C_{23}H_{19}N_3O_3$	$C_{19}H_{20}N_4$
Formula weight	385.41	304.39
Temperature	293(2) K	293(2) K
Wavelength	0.71073Å	0.71073Å
Crystal system	Triclinic	Orthorhombic
space group	$P \bar{1}$	Fdd2
Unit cell dimensions	a=10.3555(2)Å b=10.7103(2)Å c=11.0096(2)Å $\alpha = 64.1(0)^\circ$ $\beta = 65.9(0)^\circ$ $\gamma = 89.6(0)^\circ$	a = 23.0364(1)Å b = 37.2165(1)Å c = 7.7491(0) Å $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume(Å ³)	980.40(3)	6643.57(3)
Z	2	16
D_x Mgm ⁻³	1.306	1.217
Absorption Coefficient (mm ⁻¹)	0.088	0.075
F(000)	404	2592
Crystal size (mm)	.38 x .22 x .20	.34 x .16 x .14
θ range for data collection	2.16° to 28.32°	2.08° to 28.30°
Index ranges	-13 ≤ h ≤ 8 -14 ≤ k ≤ 11 -14 ≤ l ≤ 13	-30 ≤ h ≤ 20- -45 ≤ k ≤ 49 -10 ≤ l ≤ 10

Reflections Collected	8012	12994
Independent reflections	4665	4072
R(int) =	0.0939	0.1171
Data / restraints / parameters	4665/0/266	4072 / 1 / 212
Goodness-of-fit on F ²	0.563	0.800
Final R indices	R1=0.0526	R1=0.0640
[I>2sigma(I)]	WR2=0.0825	WR2 = 0.1336
Extinction coefficient	0.030(6)	0.00054(14)
Largest diff. Peak and hole (e Å ⁻³)	0.250 , -0.272	0.238 , -0.259

Table 1: Crystal data and details of structure determination

Atom	x	Y	Z	U _{eq}
O(1)	1863(1)	8802(1)	8765(1)	42(1)
O(2)	2348(1)	6979(1)	7638(1)	46(1)
O(3)	2337(2)	11569(1)	7002(1)	49(1)
C(1)	3946(2)	10964(2)	2471(2)	33(1)
C(2)	3312(2)	10448(2)	1827(2)	33(1)
C(3)	3817(2)	11094(2)	241(2)	33(1)
C(2')	3129(2)	8897(2)	5069(2)	36(1)
C(1')	3381(2)	10350(2)	4139(2)	34(1)
C(5)	5642(2)	12790(2)	-37(2)	33(1)
C(6)	5105(2)	12116(2)	1526(2)	34(1)
C(6')	3130(2)	11276(2)	4745(2)	37(1)
C(4)	4984(2)	12287(2)	-672(2)	34(1)
C(3')	2615(2)	8378(2)	6619(2)	35(1)
C(5')	2607(2)	10749(2)	6295(2)	36(1)
C(9)	6858(2)	14046(2)	-979(2)	35(1)
C(4')	2333(2)	9301(2)	7239(2)	34(1)
N(1)	3165(2)	10633(2)	-374(2)	47(1)
C(7)	2055(2)	9328(2)	2725(2)	42(1)
C(10)	6871(2)	15049(2)	-504(2)	41(1)
C(8)	5378(2)	13000(2)	-2256(2)	42(1)
C(11)	7975(2)	16238(2)	-1365(2)	51(1)
C(15)	2682(2)	5990(2)	7079(2)	57(1)
C(17)	2439(3)	13039(2)	6116(2)	57(1)
N(3)	5617(2)	13521(2)	-3498(2)	66(1)
N(2)	1059(2)	8448(2)	3339(2)	66(1)
C(14)	8001(2)	14256(2)	-2335(2)	47(1)
C(13)	9098(2)	15450(2)	-3181(2)	58(1)
C(12)	9087(2)	16443(2)	-2710(2)	58(1)
C(16)	393(2)	8138(3)	9684(2)	85(1)

Table 2: Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for Compound (I). Where U_{eq} = (1/3)Σ_{i,j}a_i*a_j*a_i

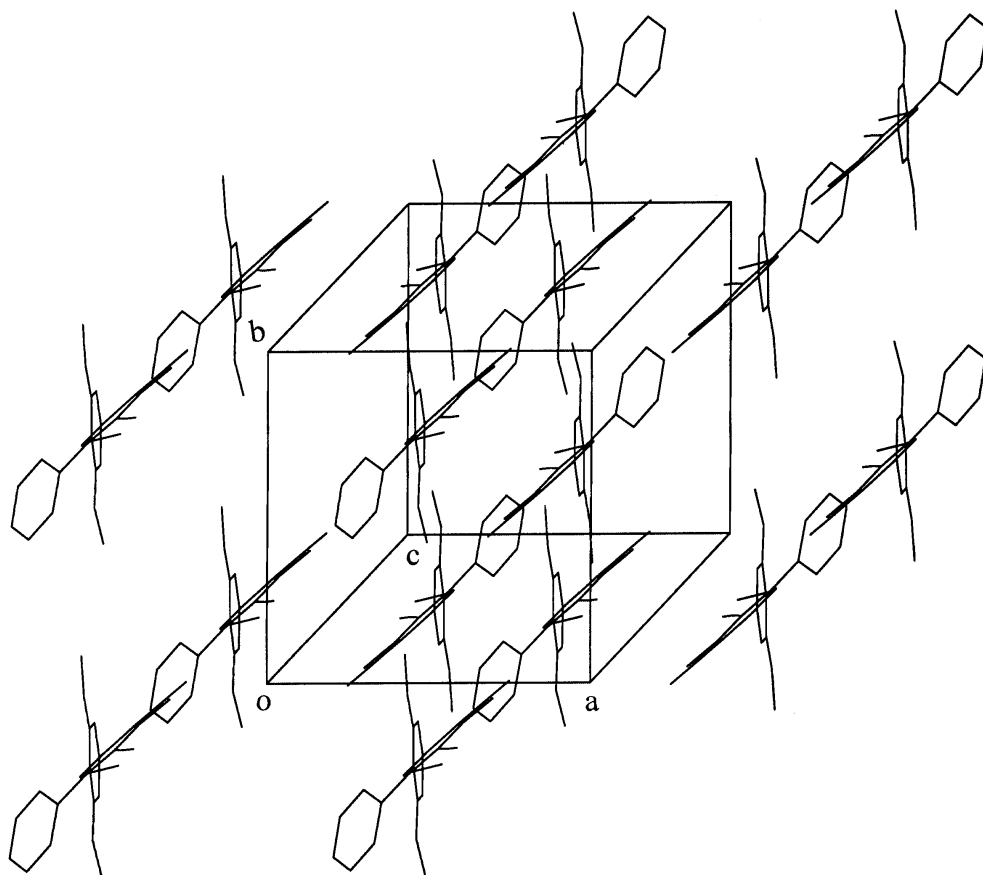


Fig. 5: Packing of the molecules (compound I) down c-axis.

ATOM	x	y	z	Ueq
C(3)	1913(1)	699(1)	9455(3)	35(1)
C(1')	2894(1)	-134(1)	9225(3)	35(1)
C(2)	2406(1)	475(1)	9612(3)	35(1)
C(1)	2381(1)	107(1)	9235(3)	34(1)
N(4)	4270(1)	-874(1)	8683(4)	57(1)
C(4)	1385(1)	536(1)	8962(4)	38(1)
C(5)	1348(1)	168(1)	8652(4)	39(1)
C(6')	2847(1)	-487(1)	9801(4)	41(1)
C(3')	3873(1)	-272(1)	8345(4)	44(1)
C(5')	3295(1)	-729(1)	9657(4)	44(1)
C(4')	3824(1)	-630(1)	8901(4)	43(1)
C(8)	876(1)	754(1)	8750(4)	48(1)
N(2)	3338(1)	771(1)	10801(4)	54(1)
C(2')	3417(1)	-33(1)	8516(4)	40(1)

C(7)	2934(1)	635(1)	10258(4)	38(1)
N(1)	1947(1)	1059(1)	9736(4)	51(1)
C(6)	1841(1)	-41(1)	8801(4)	40(1)
C(10)	4218(2)	-1241(1)	9314(5)	57(1)
N(3)	463(1)	919(1)	8572(4)	67(1)
C(9)	784(1)	-5(1)	8135(5)	62(1)
C(11)	3909(2)	-1487(1)	8069(6)	67(1)
C(12)	4820(2)	-771(1)	7920(6)	67(1)
C(13)	5222(2)	-606(1)	9256(7)	90(1)

Table 3: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound (II). Where $U_{eq} = (1/3)\sum_i \sum_j a_i^* a_j^* a_{ij}$

Compound I		Compound II	
O(1)-C(4')	1.377(2)	C(3)-N(1)	1.357(3)
O(1)-C(16)	1.405(2)	C(1')-C(1)	1.483(4)
O(2)-C(3')	1.366(2)	C(2)-C(7)	1.444(4)
O(2)-C(15)	1.417(2)	N(4)-C(4')	1.381(4)
O(3)-C(5')	1.368(2)	N(4)-C(12)	1.448(5)
O(3)-C(17)	1.420(2)	N(4)-C(10)	1.457(4)
N(2)-C(7)	1.140(2)	C(4)-C(8)	1.435(4)
C(2)-C(7)	1.492(2)	C(5)-C(9)	1.505(4)
N(1)-C(3)	1.354(2)	C(8)-N(3)	1.140(4)
C(4)-C(8)	1.433(2)	N(2)-C(7)	1.139(3)
C(8)-N(3)	1.140(2)	C(10)-C(11)	1.510(5)
C(5)-C(9)	1.485(2)	C(12)-C(13)	1.518(6)
C(2)-C(7)	1.492(2)		

Table 4: Selected bond lengths(\AA)

Compound I		Compound II	
C(4')-O(1)-C(16)	115.2(1)	N(1)-C(3)-C(4)	121.2(2)
C(3')-O(2)-C(15)	118.1(1)	N(1)-C(3)-C(2)	121.3(2)
C(5')-O(3)-C(17)	117.5(1)	C(4')-N(4)-C(12)	121.9(3)
N(1)-C(3)-C(2)	121.2(1)	C(4')-N(4)-C(10)	120.9(3)
N(1)-C(3)-C(4)	121.2(1)	N(4)-C(4')-C(5')	121.7(3)
O(2)-C(3')-C(2')	124.5(1)	N(4)-C(4')-C(3')	121.7(3)
O(2)-C(3')-C(4')	115.0(1)	N(3)-C(8)-C(4)	178.3(3)
O(3)-C(5')-C(4')	115.3(1)	N(2)-C(7)-C(2)	177.3(3)
O(3)-C(5')-C(6')	124.5(1)	N(4)-C(10)-C(11)	113.2(2)
O(1)-C(4')-C(5')	119.4(1)	N(4)-C(12)-C(13)	110.8(3)
O(1)-C(4')-C(3')	120.9(1)	C(1)-C(1')-C(2')	120.4(2)
N(2)-C(7)-C(2)	174.8(2)	C(6)-C(5)-C(9)	119.6(2)
N(3)-C(8)-C(4)	175.8(2)		

Table 5: Selected bond angles ($^\circ$)

Atom	Torsion Angle(°)
C(1)-C(2)-C(3)-N(1)	-177.2(2)
C(7)-C(2)-C(3)-N(1)	-2.2(2)
N(1)-C(3)-C(4)-C(5)	178.5(2)
N(1)-C(3)-C(4)-C(8)	2.7(2)
C(15)-O(2)-C(3')-C(2')	3.3(2)
C(15)-O(2)-C(3')-C(4')	-176.7(2)
C(1')-C(2')-C(3')-O(2)	-179.0(2)
C(17)-O(3)-C(5')-C(6')	7.6(3)
C(1')-C(6')-C(5')-O(3)	179.4(2)
O(3)-C(5')-C(4')-O(1)	-1.8(2)
O(3)-C(5')-C(4')-C(3')	-178.2(1)
O(2)-C(3')-C(4')-O(1)	1.9(2)
O(2)-C(3')-C(4')-C(5')	178.2(1)

Table 6: Selected torsion angles (°) for Compound (I).

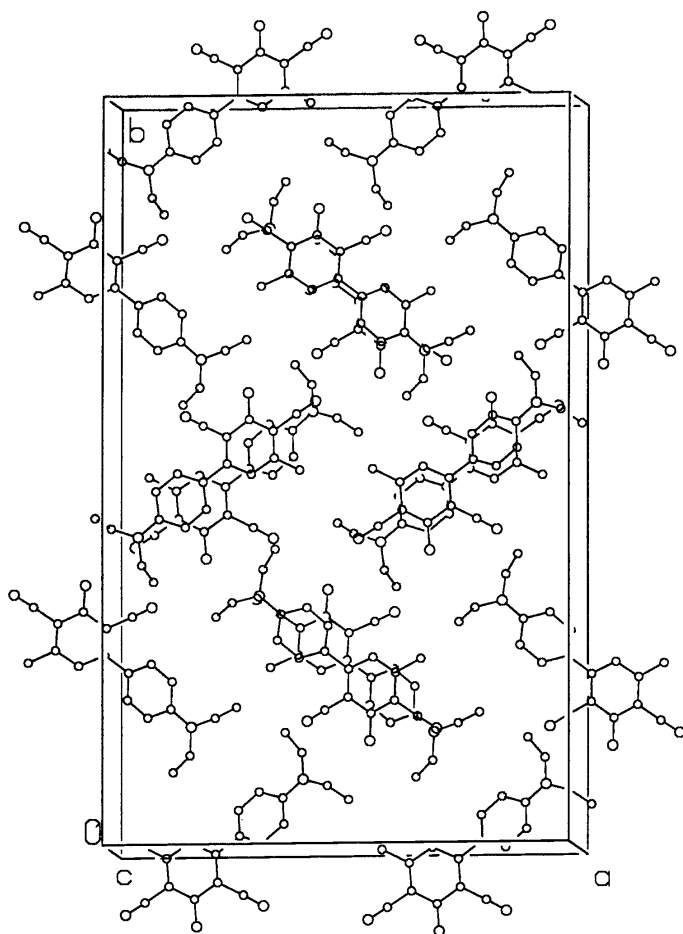


Fig. 6: Packing of the molecules (compound II) down c-axis.

3. Experimental

X-ray data for the title compounds were collected at room temperature on a Siemens, SMART CCD AREA DETECTOR

(SIEMENS, 1996a) diffractometer equipped with the MoK α radiation using ω scan mode. The data reduction and cell refinement were carried out with the help of SAINT (SIEMENS, 1996b) software. 2641 reflections were considered observed for compound (I) and 2270 were considered observed for compound II with $I > 2\sigma(I)$. The intensities were corrected for Lorentz and Polarization effects but not for absorption. The structure of the title compound (I) was solved by Direct Methods procedure using SHELXS86 (SHELDRICK, 1990) and refinement was performed by full-matrix least-squares technique on F^2 using SHELXL93 (SHELDRICK, 1993). The structure of the title compound (II) was solved by Direct Methods procedure using SHELXS97

(SHELDRICK, 1997) and refinement was performed by full-matrix least-squares technique on F^2 using SHELXL97 (SHELDRICK, 1997). All hydrogen atoms were geometrically fixed and were allowed to ride on the corresponding non-hydrogen atoms. The final R- factors for compounds (I) and (II) are 5.3% and 6.4% respectively. The crystal data are summarized in Table 1. The atomic coordinates of (I) together with the equivalent isotropic thermal parameters are listed in Table 2 and the same is listed in Table 3 for (II). The selected bond distances and selected bond angles are listed in Table 4 & 5. The selected torsion angles which describe the conformational aspects of biphenyl moiety are given in Table 6 & 7. The conformational features were analyzed by PARST97 (NARDELLI, 1995). The thermal ellipsoid diagrams were plotted using ZORTEP (ZSOLNAI, 1997).

5. Results and Discussion

Structure (I) consists of three phenyl rings A, B and C connected through (C9-C5) for rings C and A and (C1-C1') for rings A and B. All phenyl rings in both structures are in planar conformation. The dihedral angles between rings A and C, A and B for compound (I) and A and B, for compound (II) are $41.7(1)^\circ$, $49.2(1)^\circ$ and $41.4(1)^\circ$ respectively. The twisting of these rings can also be described using the following torsion angles: C6-C1-C1'-C6' = $47.6(2)^\circ$ and $37.9(2)^\circ$ [A and B for compound (I) and (II)] and C10-C9-C5-C6 = $40.7(2)^\circ$ [C and A for compound (I)]. As can be seen from the torsion angles C6'-C5'-O3-C17 [$7.6(3)^\circ$], C5'-C4'-O1-C16 [$105.9(2)^\circ$] and C4'-C3'-O2-C15 [$-176.6(2)^\circ$], the methoxy substituents show +syn periplanar, anticlinal and -anti periplanar conformations respectively. The angles at O1, O2 and O3 [C4'-O1-C16 = $115.2(1)^\circ$; C3'-O2-C15 = $118.1(1)^\circ$; C5'-O3-C17 = $117.6(1)^\circ$] are larger than 109° because of steric hindrances. All O-C distances prove a sp^3 state. The triple bond distances N3 \equiv C8 and C7 \equiv N2 : $1.140(2)\text{\AA}$ and $1.140(2)\text{\AA}$ [compound (I)] $1.143(3)\text{\AA}$ and $1.140(3)\text{\AA}$ [compound (II)] agree with the literature values (ALLEN et al., 1986). The bond angles at C8 and C7 [C4-C8-N3 = $175.8(2)^\circ$; C2-C7-N2 = $178.3(3)^\circ$] satisfy the triple bond character of C8 \equiv N3 and C7 \equiv N2 (sp hybridisation). The C1-C1' bond distances [$1.492(2)\text{\AA}$ (I) and $1.481(3)\text{\AA}$ (II)] which connect two phenyl rings A and B are comparable with the reported values (ALLEN et al., 1986). The unit cell packing is shown in fig 4 & 5. The packing of the molecules in the unit cell is stabilized by van der Waals contact.

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