THE X-RAY MOLECULAR STRUCTURE OF (*Z*)-1-(4,5-DIPHENYL-1,2,3-TRIAZOL-2-YL)-1,2-DIPHENYLETHYLENE AT 200 K

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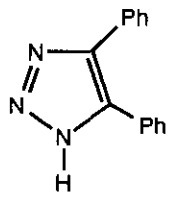
Abstract- The molecular and crystal structure of (*Z*)-1-(4,5-diphenyl-1,2,3-triazol-2-yl)-1,2-diphenylethylene has been determined by X-Ray analysis at 200K. The above (*Z*)-isomer was crystallized from the mixture of two 2*H*-triazole stereoisomers.

4,5-Diphenyl-1*H*-1,2,3-triazole (**1**) is a compound with interesting chemical properties. By pyrolysis it gives either 2,3,5,6-tetraphenylpyrazine or 2-phenylindole, depending on the temperature.[1,2] The corresponding 1-amino derivative (**2**) affords upon treatment with lead tetraacetate diphenylacetylene.[3] It yields a 2-trialkylstannyl derivative when reacted with bis(tributyltin) oxide.[4] Finally, the 1,3-chlorotropy of the 1-chloro derivative (**3**) was reported[5] but it was proved later that the compound was the 2-chloro derivative (**4**).[6]



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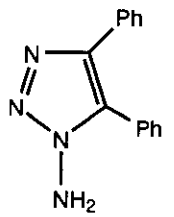

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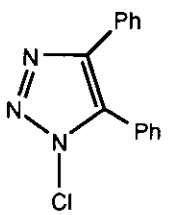

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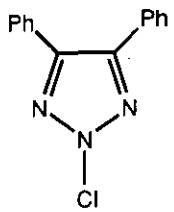

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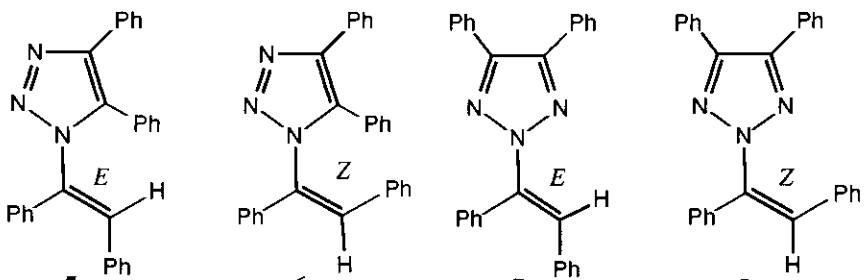
There are several synthetic procedures to prepare 4,5-diphenyl-1,2,3-triazole(**1**). The oldest one[7] involves deamination of the 1-amino derivative (**2**) with sodium nitrite or amyl nitrite [this procedure was also used in ref. 2]. Starting from 5,6-diphenyltriazinone, a [6→5] ring contraction affords **1** upon treatment with chloramine in 94% yield.[8,9] Photolysis of phenyldiazo-1,2,3-triazole in benzene affords **1** in 13% yield.[10] Manganese dioxide oxidation of 4-phenyl-1,2-diaminoimidazole also leads to **1** but in a low yield (10%).[11]

The compound also results from the reaction of 2,3-diphenylthiirene 1,1-dioxide with lithium azide (7.7% yield).[12] Katritzky has proposed the use of 2-(4-pyridyl)ethyl azide as a versatile alternative to HN_3 for 1,3-dipolar cycloadditions;[13] using this reagent he reported the preparation of **1** in three steps. Huisgen synthesized **1** by debenzylation of 1-benzyl-4,5-diphenyl-1,2,3-triazole.[14]

Nevertheless, the more straightforward procedure is that of Woerner and Reimlinger which consists in the reaction of sodium azide with tolan (diphenylacetylene).[15,16] A related procedure uses trimethylsilyl azide followed by hydrolysis with water or ethanol.[17] 4,5-Diphenyl-1*H*-1,2,3-triazole (**1**) melts at ~140 °C[1-17] and its UV,[9] ^{13}C NMR,[6] and MS[4,18] properties have been reported.

RESULTS AND DISCUSSION

In order to prepare appreciable amounts of compound (**1**) necessary for structural studies we decided to follow the Woerner and Reimlinger approach.[15] Its main inconvenient was the low yield (16%). Instead of using their experimental procedure (sodium azide, 20 h at 140 °C in DMSO) we used ammonium azide, 25 h at 120 °C in DMF (see Experimental) and we did not obtain the desired compound (**1**), but two isomeric compounds which were isolated in 14% yield (11% and 3% respectively). The mixture of these isomers presents a ^1H NMR spectrum quite similar to that of **1** having only signals about 7 ppm but its MS spectrum and analysis show that the molecular formula of both is $C_{28}H_{21}N_3$. This points out to a product of addition of **1** on the triple bond of tolan. Addition of NH-1,2,3-triazoles to triple bonds are known but they generally involve activated triple bonds (*e.g.* propiolate, acetylenedicarboxylate).[15,16,19] To establish the structure of the major isomer (that formed in 11% yield) we decided to use X-Ray crystallography.



Crystal and molecular structure of (*Z*)-1-(4,5-diphenyl-1,2,3-triazol-2-yl)-1,2-diphenylethylene (8).

Compound (**8**) is a 2*H*-triazole isomer which exhibits a disordered structure (Figure 1), the >C=CH- group attached to N2 is present in two orientations with respect to the triazole ring (see experimental). A comparison of the geometry of eleven 2*H*-1,2,3-triazole derivatives (Cambridge Structural Database)[20] showed that all bond distances and angles in the triazole ring of **8** are consistent with the corresponding average values from the CSD. The molecule possesses an almost two-fold axis passing through the N2 atom and the midpoint of the C4-C5 bond. The exocyclic angles at N2, C20 and C26 (Figure 1 and Table 1) are asymmetric (*i.e.* N3-N2-C181 > N1-N2-C181), one is wider while the other is narrower and the differences are highly significant when compared between them and with the 2*H*-triazole derivatives reported above [122(2)°, the standard deviation of the sample being in parenthesis]. This angular distortion

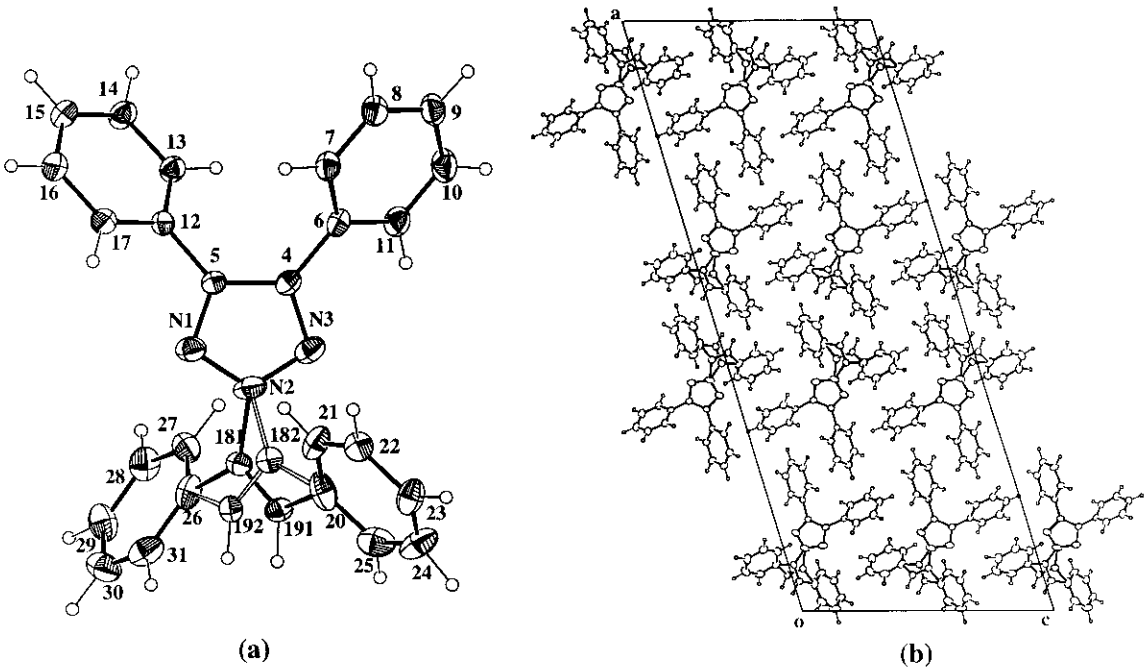


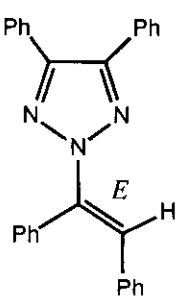
Figure 1. (a) A view of the molecular structure along with the numbering scheme and showing the disorder model. (b) Packing diagram down the **b** axis. Ellipsoids are drawn at 30% probability level.

Table 1. Selected geometrical parameters (Å, °). C(6-11) and C(12-17) stand for the centroid of the C6...,C11 and C12,..., C17 phenyl rings respectively.

N1-N2	1.340(4)	N1-C5	1.325(3)	N2-N3	1.334(4)
N3-C4	1.332(3)	C4-C5	1.412(4)	N2-C181	1.486(6)
N2-C182	1.492(9)	C4-C6	1.475(3)	C5-C12	1.474(3)
C181-C191	1.331(9)	C182-C192	1.340(13)		
C5-N1-N2	103.8(2)	N1-N2-N3	114.9(2)	N2-N3-C4	104.4(2)
N3-C4-C5	107.8(2)	C4-C5-N1	109.1(2)	C181-N2-C182	38.5(4)
N1-N2-C181	114.7(3)	N3-N2-C181	128.6(3)	N3-C4-C6	122.0(2)
N1-N2-C182	133.7(4)	N3-N2-C182	106.9(4)	C5-C4-C6	130.1(2)
C4-C6-C7	119.7(2)	N1-C5-C12	120.2(2)	C5-C12-C13	119.5(2)
C4-C6-C11	121.6(2)	C4-C5-C12	130.5(2)	C5-C12-C17	121.3(2)
C191-C20-C21	133.9(3)	C182-C20-C21	101.4(4)	C192-C26-C27	97.9(4)
C191-C20-C25	107.6(4)	C182-C20-C25	140.1(5)	C192-C26-C31	143.0(4)
C181-C26-C27	111.3(3)	C181-C26-C31	130.4(4)		
N3-C4-C6-C7	-135.1(3)	N1-C5-C12-C13	-130.6(3)	N1-N2-C181-C26	43.2(6)
N2-C181-C26-C27	35.3(6)	N1-N2-C181-C191	-139.5(4)	N3-N2-C182-C192	-142.4(6)
N2-C182-C20-C21	40.2(9)	N1-N2-C182-C192	63.5(9)	N3-N2-C182-C20	38.6(9)
N2-C181-C191-C20	10.5(8)	N2-C182-C192-C26	13.9(11)	C181-C191-C20-C21	34.1(8)
C182-C192-C26-C27	28.3(13)	C26-C181-C191-C20	-172.0(4)	C26-C192-C182-C20	-166.8(6)

Hydrogen interaction	X-H	H...Y	X...Y	X-H...Y
C27-H27...N1	1.01(4)	2.77(3)	3.147(4)	102(2)
C17-H17...N1	1.01(3)	2.85(4)	3.011(4)	89(2)
C29-H29...N1(x,-1+y,z)	0.96(5)	2.77(5)	4.581(4)	146(3)
C10-H10...N1(x,-y, 1/2+z)	1.00(5)	2.99(5)	3.693(4)	127(3)
C11-H11...N3	1.01(4)	2.82(4)	3.034(4)	92(3)
C21-H21...N3	0.90(4)	2.89(4)	3.167(4)	100(3)
C11-H11...N3(x,1+y,z)	1.01(4)	2.64(4)	3.440(4)	135(4)
C15-H15...C(6-11)(1/2-x,1/2+y,3/2-z)	1.00(4)	2.93(4)	3.783(9)	148(3)
C14-H14...C(12-17)(1/2-x,-1/2+y,3/2-z)	1.02(3)	2.90(3)	3.748(3)	141(3)

is likely an artefact arising from the large thermal displacement parameters of the mentioned atoms. The thermal values are probably an indication of the coexistence of two triazole rings slightly rotated one with respect to the other [1/2(C181-N2-C182)°, Table 1]; the deformation is too small to observe a splitting of the triazole atoms into two sites. The phenyl rings at C4 and at C5 are almost related by a binary axis and those in the >C=CH- group are *trans* oriented with respect to the double bond. Two independent C-H···phenyl interactions hold the molecules, related by two-fold axis, along the **b** axis to form columns that are then connected by C-H···N interactions (Table 1 and Figure 1b).



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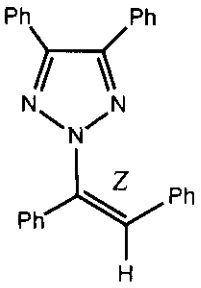

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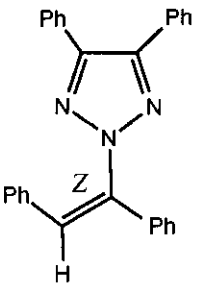
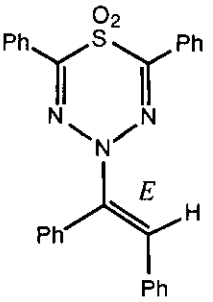


8b



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Note that the disorder does not imply the other configuration [*E*(**7**)] but a rotation about the N2-C18 single bond (**8a** ⇌ **8b**). Jarvis and Stahly[12a] have reported the X-Ray structure of a related compound (**9**) with (*E*) stereochemistry, the product does not result from the addition of the 1,3,4,5-thiatriazine-1,1-dioxide to tolan but from SO_2 extrusion in the stilbene moiety.

Concerning the regioselectivity (formation of a 2-substituted 1,2,3-triazole), it is worth reporting that amination of **1** yields a mixture of 1- and 2-amino-1,2,3-triazoles in approximately equal amounts.[21] On the other hand, 4(5)-phenyl-1,2,3-triazole reacts with ethyl propiolate and sodium methoxide to gave the adduct with the olefin at position 2.[19]

NMR studies

1-(4,5-Diphenyl-1,2,3-triazol-2-yl)-1,2-diphenylethylene was obtained as a mixture of (*E*)/(*Z*) isomers (mp 122-123 °C) which was separated by column chromatography on silica gel (eluent chloroform/ethanol 9/1). The major isomer (80%), R_f = 0.75, melts at 155-156 °C and the minor one (20%), R_f = 0.44, melts at 138-139 °C. Crystals for X-Ray structure determination were obtained directly from the mixture of isomers by slow evaporation of an ethanol solution. The monocrystal, which was collected before the evaporation was complete, contains only the major isomer (*Z*)(**8**). It remains to establish the structure of the minor isomer, most probably either (*Z*)(**6**) or (*E*)(**7**). For a 1*H*-4,5-diphenyltetrazole, like **6**, two signals are expected for the heterocyclic carbons in ^{13}C NMR spectroscopy.[13] The ^{13}C NMR spectra of each isolated isomer, recorded at 75 MHz in DMSO-d_6, are rather complicated since twenty-six out of the twenty-eight carbons appear between 125 and 137 ppm. On the other hand, both heterocyclic carbons appear at 145.4 (major) and 144.1 ppm (minor) thus establishing that both isomers are 2-substituted 1,2,3-triazoles, (*Z*)(**8**) (major) and (*E*)(**7**) (minor), differing only in the configuration of the CC double bond.

The ^{1}H NMR spectra were recorded at 300 MHz in the same solvent. The spectra are quite complicated having twenty-one protons (twenty aromatic and one olefinic) between 6.75 and 7.65 ppm. The olefinic proton (which should be a singlet) is in the 7.2-7.5 ppm zone mixed with the majority of the aromatic protons. The most interesting signals are those appearing between 6.75 and 6.95 ppm. The major isomer shows a broad doublet at 6.85 ppm ($J \sim 6.5$ Hz) which corresponds to two aromatic protons while the minor isomer shows two well resolved doublets, one at 6.80 ppm ($J = 7.9$ Hz) and another at 6.77 ppm ($J = 7.2$ Hz) corresponding to four aromatic protons. The phenyl groups at positions 4 and 5 should be magnetically equivalent, as a result of an almost free rotation about the N2-C18 bond (see crystal structure), *therefore, these signals must correspond to protons of the stilbene moiety and since they show only one ortho* coupling constant they must be *ortho* protons. To determine if they belong to the 1- or to the 2-phenyl group in the major isomer is more difficult. Comparison with the reported ^{1}H NMR data for *cis*- and *trans*-stilbene[22] allows to propose tentaively that in the case of the (*Z*)(**8**) isomer, the broad doublet belongs to the *ortho* protons of the 1-phenyl ring while in the case of the (*E*)(**7**) isomers the two very closed signals near 6.8 ppm are the four ortho protons of 1- and 2-phenyl rings. The broadening of the spectrum in the case of the major isomer (all signals, not only that at 6.85 ppm) indicates the presence of a dynamic phenomena probably related to the rotation about the N2-C18 bond. An integration of these *ortho* signals in the ^{1}H NMR of the crude mixture, taking into account that there is a 4/2 ratio between **8** and **7**, allows an independent estimation of the 80/20 relative amounts of both isomers.

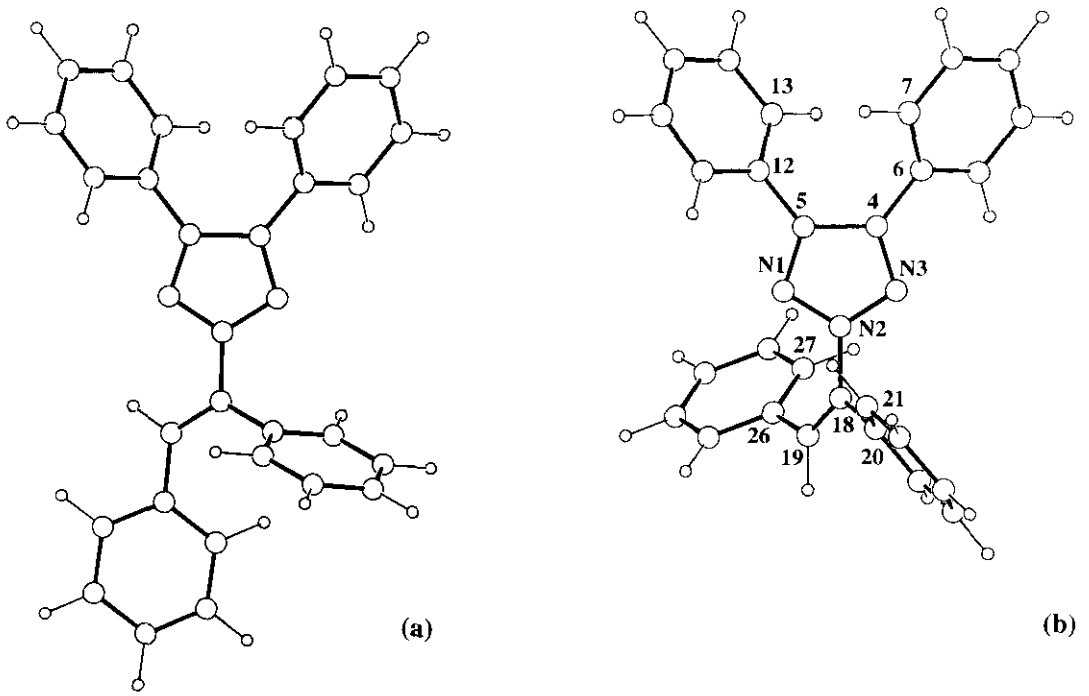

Figure 2. Views of the (*E*)(**7**) (**a**) and (*Z*)(**8**) isomers (**b**) after the geometrical optimization using the AM1 Hamiltonian. In (**b**): C26-C19-C18-C20 = - 177.5, N3-C4-C6-C7 = - 139.9, N1-C5-C12-C13 = - 138.2, N2-C18-C19-C26 = 2.9, N1-N2-C18-C19 = 58.1, N3-N2-C18-C20 = 56.1, N2-C18-C20-C21 = 47.7, C18-C19-C26-C27 = 51.2, N1-N2-C18 = 125.5 and N3-N2-C18 = 122.4°.

AM1 Calculations. We have calculated both the (*E*)(**7**) and (*Z*) (**8**) isomers of the compound using the semi-empirical AM1 Hamiltonian.[23] The optimized geometry of (*Z*)-isomer agrees with that obtained from X-Ray crystallography, in particular the torsion of the phenyl rings at positions 4 and 5: N3-C4-C6-C7 (-135.1° X-Ray; -139.9° AM1) and N1-C5-C12-C13 (-130.6° X-Ray; -138.2° AM1). A picture of both configurations is represented in Figure 2. The (*Z*) isomer (228.9 kcal mol^{-1}) is more stable than the (*E*) one (229.3 kcal mol^{-1}) by 0.4 kcal mol^{-1}, value in reasonable agreement with the experimental results [80% (*Z*)-20% (*E*)] which corresponds to 0.8 kcal mol^{-1} at 298 K.

EXPERIMENTAL

The melting point was determined with a hot-stage microscope and is uncorrected. NMR spectra were recorded on a Bruker DPX 300 spectrometer (^1H at 300 MHz and ^{13}C at 75 MHz) in DMSO-d_6 (chemical shifts in ppm from TMS).

1-(4,5-Diphenyl-1,2,3-triazol-2-yl)-1,2-diphenylethylene. A mixture of diphenylacetylene (35.4 g, 199 mmol), sodium azide (14.4 g, 218 mmol), and ammonium chloride (12 g) in 100 mL of DMF was stirred at 120 °C for 25 h. The precipitate (NaCl) was filtered off and washed with 50 mL of DMF. The filtrate was evaporated under the vacuum and the residue was treated by 5 x 50 mL of ethyl acetate. After drying over sodium sulfate and evaporation of ethyl acetate, 11.9 g (yield 14%) of the mixture of the isomers (*E,Z*)-1-(4,5-diphenyl-1,2,3-triazol-2-yl)-1,2-diphenylethylene was obtained. Molecular formula $C_{28}H_{21}N_3$. M^+(%) = 399 (100). Anal. Calcd for $C_{28}H_{21}N_3$: C, 84.18; H, 5.30; N, 10.52. Isomer (*Z*): Found: C, 84.07; H, 6.10; N, 9.83. Isomer (*E*): Found: C, 84.06; H, 5.37; N, 10.02.

X-Ray Analysis. Two data sets of the title compound were collected. The first one was recorded at rt and the structure was solved by direct methods, SIR92.[24] Refinements on *Fo* in the *Cc* and the *C2/c* space groups, compatible with the systematic absences, were carried out. In the *C2/c* space group, disorder of the >C=CH- group attached to N2 and high thermal displacement parameters, mainly those of N1, N2, N3, C20 and C26 atoms (Figure 1) were observed. This means superposition of two molecules related by a two-fold axis passing through N2 and the midpoint of the C4-C5 bond. Therefore, refinements in the *Cc* group were performed with two independent molecules related by this axis but the refinement gave the same nonsensical molecular geometry as in the *C2/c* group (see discussion and Table 1) besides high correlations factors. In order to get a better understanding of the coexistence of the two molecules, with almost coincident triazole rings (not split in two sites at room temperature) a new data set was collected at 200 K. However, similar features, as previously described, were observed and the *C2/c* space group was chosen to describe the structure. Table 2 summarizes just the experimental details and the most relevant parameters of the refinement corresponding to this data set. Like in the room temperature data set, the C18 and C19 atoms appear to be split over two positions (occupancy factors at 200 K: 0.62(1) for C181, C191 and 0.38(2) for C182 and C192) but neither disorder model for the triazole ring not for the stilbene phenyl rings (C20 to C25 and C26 to C31) could be obtained. The hydrogen atoms, located in a difference Fourier map, were included as isotropic in the last cycles of refinement. Scattering factors were taken from the *International Tables for X-Ray Crystallography*,[25] while the calculations were carried out with the XTAL,[26] PESOS,[27] and PARST[28] set of programs running on a DEC3000-300X workstation.

Table 2. Crystal analysis parameters.

Crystal data			
Chemical formula	$C_{28}H_{21}N_3$	Crystal system	Monoclinic
Mr	399.49	Space group	*C2/c*
a (Å)	43.9196(41)	α (°)	90
b (Å)	5.6291(2)	β (°)	106.836(5)
c (Å)	17.9197(8)	γ (°)	90
Z	8	*Dx* (gr/cm^3)	1.25
V (Å^3)	4240.4(5)	Radiation	CuKα
Wavelength (Å)	1.5418	Crystal colour	Colourless
No. of reflections for lattice parameters	63	Crystal description	Prism
θ range for lattice parameters (°)	2-45	Crystal size (mm)	0.50x0.27x 0.10
Absorption coefficient (cm^{-1})	5.75	Temperature (K)	200
Data collection			
Diffractometer type	Philips PW1100, four circle. Graphite oriented monochromator		
Measurement time	1 min./reflection	Detector apertures (°)	1 x 1
Collection method	ω/2θ scans	θ_{max} (°)	65
No. of standard reflections (interval)	2 (90 min.)	Scan width (°)	1.6
No. of independent reflections	3608		
No. of observed reflections, I > 3σ(I)	3337		
Refinement			
Treatment of hydrogen atoms	See experimental part		
Refinement	Least-squares on *Fo*, Full matrix		
Secondary extinction correction (10^4)	0.200(9)		
No. of parameters refined	386	Degrees of freedom	2951
Ratio of freedom	8.6	<Shift/error>	0.04
Weighting scheme: Empirical as to give no trends in $<\omega\Delta^2F>$ vs. <|Fobs|> and $<\sin\theta/\lambda>$			
$(\Delta\rho)_{max}$ (e/Å^3)	0.22	Max. thermal value (Å^2): U33[C24]=0.119(3)	
R, R*w*	0.069, 0.071		

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