

Crystal and Molecular Structure of 4-Benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carbonitrile

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ABSTRACT

The crystal structure of potential active 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carbonitrile (C₂₃H₁₅N₃O) (I) has been determined from single crystal X-ray diffraction data. Also IR, Uv-vis and NMR spectral data were determined. The title compound crystallizes in the monoclinic space group *P* 21/*c*, with *a* = 9.3167(2), *b* = 20.6677(3), *c* = 10.6143(3) Å, β = 112.665(3)°, *V* = 1886.00(8) Å³, *D*_{calc} = 1.23 g cm⁻³, *Z* = 4. In the structure, intermolecular *H*-bonds lead to the formation of a centrosymmetric dimer of the molecule. Furthermore, the compound has a wide transmission window (300 to 1100 nm) with a transparency of nearly 100% and the UV cut-off wavelength occurs at 242 nm.

Keywords: Pyrazole-3-Carbonitrile; 2,3-Furandione; Single Crystal Structure; X-Ray Diffraction; IR; NMR Spectra

1. Introduction

Pyrazole nucleus and its derivatives such as nitriles, amides or esters possess numerous chemical, biological, medicinal, and agricultural applications due to their versatile biological activities appearing as antimicrobial [1,2], antiviral [3,4], antibacterial [5], antitumor [6-8], anti-inflammatory [9,10], antihistaminic [11], pesticidal [12,13], antifungal [14], against rheumatoid arthritis [15], anticonvulsant [16], antidepressant [17], antipyretic [18], and commercially important dyestuffs [19] agents. Their excellent control activities on various plant diseases are studied, too [20,21]. Recently, reactions of cyclic oxalyl compounds have been reported to give substituted heterocyclic compounds [22-26]. The reaction of 4-benzoyl-5-phenylfuran-2,3-dione, obtained easily from dibenzoylmethane and oxalyl dichloride [22], with various phenyl hydrazones and phenylhydrazine leads to pyrazole carboxylic acids and pyridazinones [27-29]. Nitriles are widely used for transformation into amides, amines, esters, carboxylic acids etc. [30]. Hence they have been used as intermediates for the synthesis of fine chemicals such as agricultural chemicals, dyes and medicines [31]. Title compound was mainly synthesized from 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic acid together with acid chloride and its amide derivatives (Scheme 1). Furthermore, a cold solution of the acid amide in a mixture of Dimethyl formamide (DMF) and Thionylchloride (SOCl₂) was stirred at 0°C - 5°C for 2 hours to give the

nitrile product. In view of these wide ranges of biological and pharmaceutical importance [32], in the present study, we report the synthesis, spectroscopic and structural characterization and the X-ray diffraction (XRD) study of the title compound, too, as well as for the comparisons of the geometrical features with related compounds in the literature. The structure of the title compound confirms the molecular formula based on microanalysis, IR, Uv-vis and NMR spectra beside X-ray diffraction data.

2. Experimental

2.1. Synthesis of the Title Compound

The title compound was prepared by the reaction of 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic acid amide with DMF and SOCl₂ (Figure 1). A cold solution of the acid amide (0.37 g, 1.0 mmol) in a mixture of DMF (0.7 mL) and SOCl₂ (0.15 mL) was stirred at 0°C - 5°C for 2 h similarly given in [5], and the solution was left stirring overnight. Then the mixture was poured over crushed ice and the precipitate formed was filtered off, washed with water and recrystallized from methanol and dried on P₂O₅ M.p. 167°C, yield 70% (0.245 g). The authenticity of the compound has been established by microanalyses, UV, IR, ¹H and ¹³C NMR spectra.

2.2. Materials and Physical Measurements

The melting point was determined on an ElectrothermalModel 9200 apparatus and is uncorrected. The IR ab

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Table 1. Crystallographic data and structure refinement parameters.

Empirical formula	C ₂₃ H ₁₅ N ₃ O
Formula weight	349.4 g/mol
Crystal colour	colourless
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 9.3167(2)$ Å, $b = 20.6677(3)$ Å, $c = 10.6143(3)$ Å $\beta = 112.665(3)^\circ$
Volume	1886.00(8) Å ³
Z, Calculated density	4, 1.23 Mg m ⁻³
Absorption coefficient	0.077 mm ⁻¹
$F(000)$	728
Crystal size	0.25 × 0.19 × 0.15 mm
Theta range for data collection	2.3 to 26.5 deg.
Limiting indices	$-11 \leq h \leq 11$, $-25 \leq k \leq 25$, $-13 \leq l \leq 12$
Reflections collected/unique	39067/ 3862 [$R(\text{int}) = 0.065$]
Completeness to theta = 26.5	98.9 %
Max. and min. transmission	0.992 and 0.982
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2819/0/244
Goodness-of-fit on F^2	1.066
Final R indices [$I > 2$ sigma (I)]	$R1 = 0.052$, $wR2 = 0.119$
R indices (all data)	$R1 = 0.075$, $wR2 = 0.132$
Largest diff. peak and hole	0.142 e Å ⁻³ and -0.200 e Å ⁻³

Table 2. Selected bond lengths (Å) and angles (°).

N(2)-N(3)	1.358(2)	N(3)-N(2)-C(15)	103.6(2)
O(1)-C(13)	1.219(3)	N(2)-N(3)-C(18)	118.3(2)
N(3)-C(18)	1.440(3)	N(3)-C(17)-C(1)	123.2(2)
C(17)-C(14)	1.388(3)	C(1)-C(17)-C(14)	130.4(2)
C(15)-C(14)	1.410(3)	N(2)-C(15)-C(14)	113.0(2)
C(16)-N(1)	1.141(3)	C(14)-C(15)-C(16)	128.0(2)
N(2)-C(15)	1.330(3)	O(1)-C(13)-C(7)	120.4(2)
N(3)-C(17)	1.362(3)	C(7)-C(13)-C(14)	121.1(2)
C(17)-C(1)	1.473(3)	N(3)-C(18)-C(23)	119.5(2)
C(7)-C(13)	1.489(3)		
C(15)-C(16)	1.438(3)		
C(13)-C(14)	1.478(3)		

Elemental analysis of compound for carbon, hydrogen, and nitrogen are in good agreement with theoretical values. The theoretical and observed element percentages respectively are: %C: 79.07 and 78.94, %H: 4.33 and 4.45, %N: 12.03 and 12.18.

Optical transmission spectrum of the compound is shown in **Figure 5**. The range of optical transmittance

and the transparency cut-off are important parameters for a single crystal used in optical applications. It has a wide transmission window (300 to 1100 nm) with a transparency of nearly 100% and the UV cut-off wavelength occurs at 242 nm. The wide transmission range in the entire visible region is a useful property for opto-electronic applications. Hence, the title compound has become a

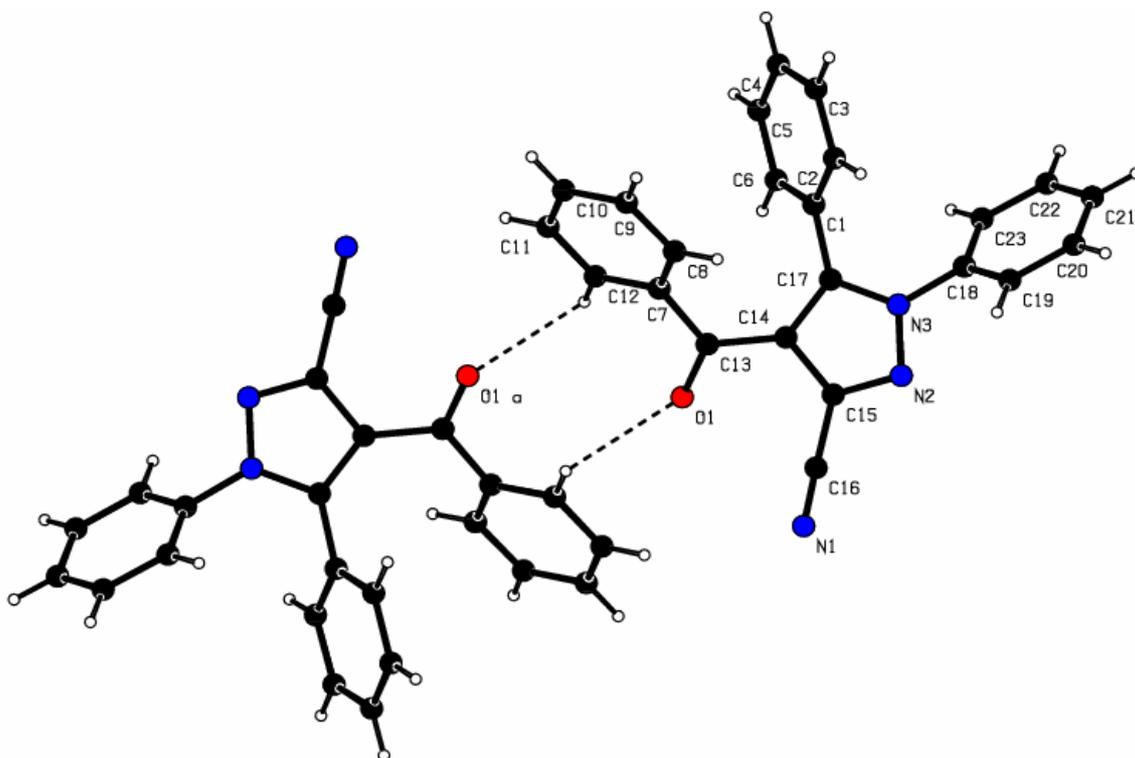


Figure 3. Part of the crystal structure of the molecule, showing the formation of a centrosymmetric dimer. Atoms marked with an (a) are at the symmetry position $(2 - x, -y, 1 - z)$.

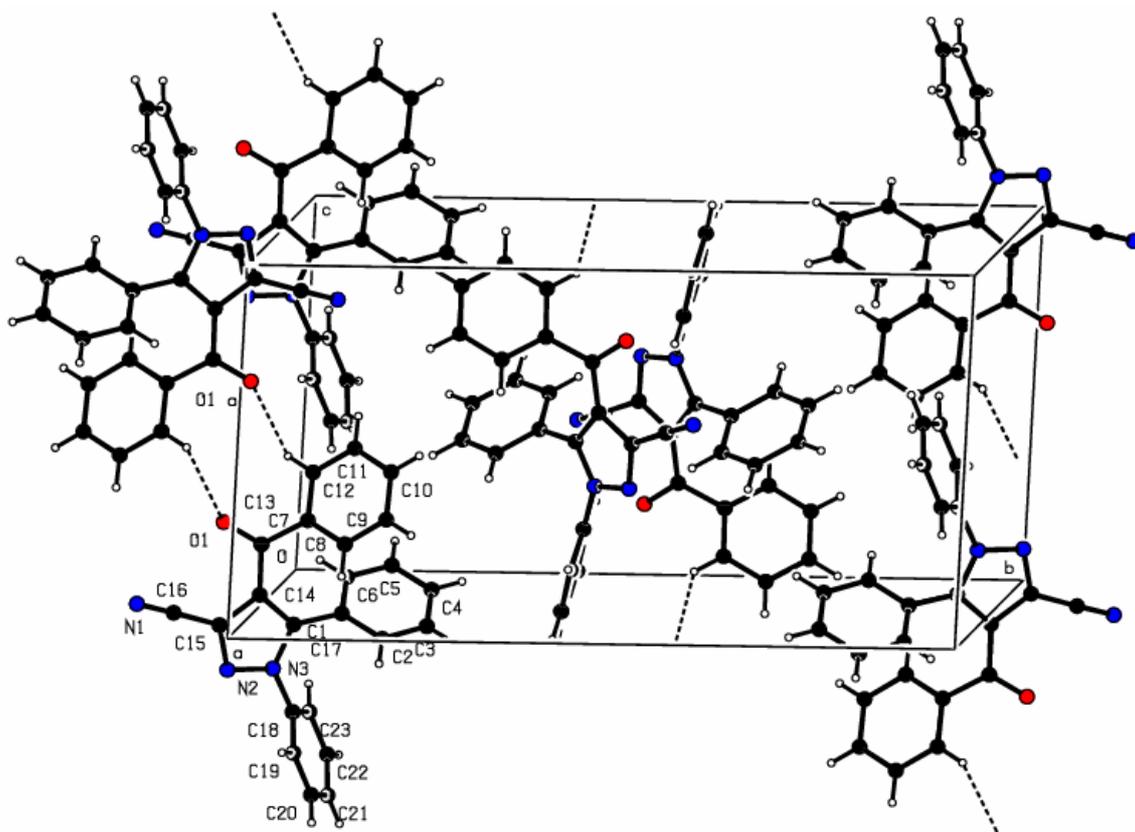


Figure 4. Packing diagram and H bonding geometry along the *a*-axis [symmetry code (a): $2 - x, -y, 1 - z$].

good candidate for optoelectronic applications.

The FT IR spectrum (**Figure 6**) of the title compound show sharp absorption bands occurred in the range $3095\text{--}3000\text{ cm}^{-1}$ due to the aromatic (C-H) stretching vibrations. The sharp and middle-intensity IR absorption band of the nitrile ($\text{C}=\text{N}$) group founds at 2246 cm^{-1} . Weak combination or overtone bands appear in the $2000\text{--}1670\text{ cm}^{-1}$ region. The strong characteristic absorption band at 1652 cm^{-1} indicate the $\text{C}=\text{O}$ (benzoyl) group of the compound [40].

The sharp skeleton bands observed at 1614 (w) , 1597 (m) , 1578 (w) , 1536 (w) , 1498 (m) , 1482 (s) , 1461 (s) cm^{-1} characterize the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ vibrations of phenyl and pyrazole rings. The additional absorption bands at

980 (m) , 937 (m) , 913 (s) , 850 (w) cm^{-1} are due to the aromatic (C-H) in-plane bending vibrations. Moreover, the strong absorption bands occurred at 765 (m) , 742 (s) , 696 (s) , 665 (m) cm^{-1} belong to the $\text{C}-\text{H}$ bond out of plane bending and $\text{C}=\text{C}$ bond bending vibrations of the substituted pyrazole and phenyl rings, respectively.

The structure of the title compound was further characterized by NMR absorption. Important structural information about can be obtained from its NMR spectra. In the ^{13}C -NMR spectrum (**Figure 7**) of the CDCl_3 solution of the compound was observed = $188.24\text{ (t, } J = 4.5\text{ Hz, Ph-C = O)}$, 145.21 (s, C-3) , and $138.26\text{ ppm (t, } J = 4.6\text{ Hz, C-5)}$. The peaks at 136.75 , 133.48 , 130.23 , 129.78 , 129.64 , 129.23 , 129.16 , 128.92 , 128.54 , 128.32 ,

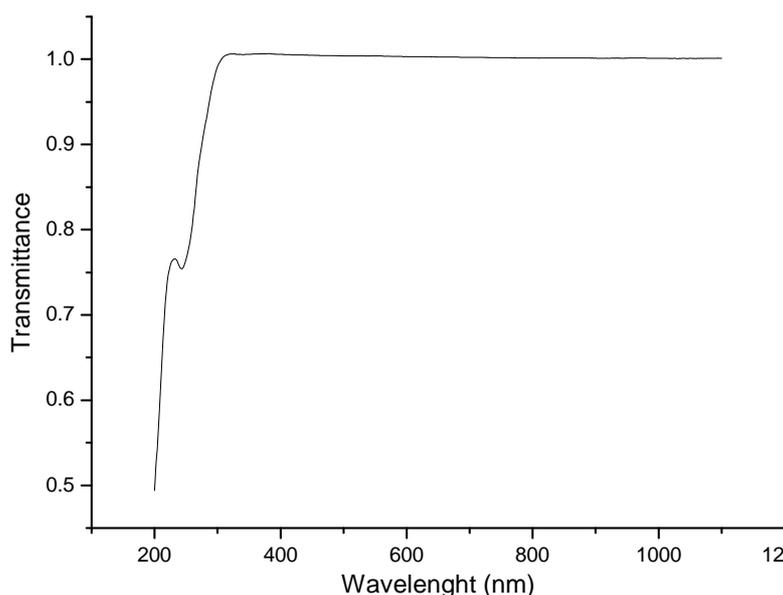


Figure 5. Optical transmission spectrum of the title compound.

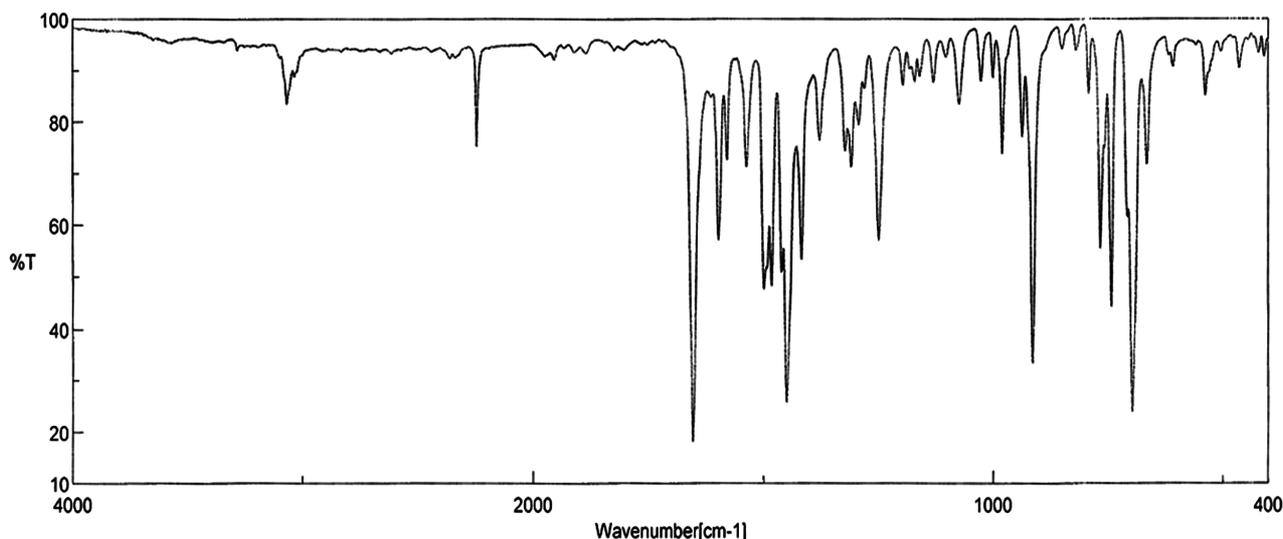


Figure 6. FT-IR spectrum for the title compound in KBr pellet.

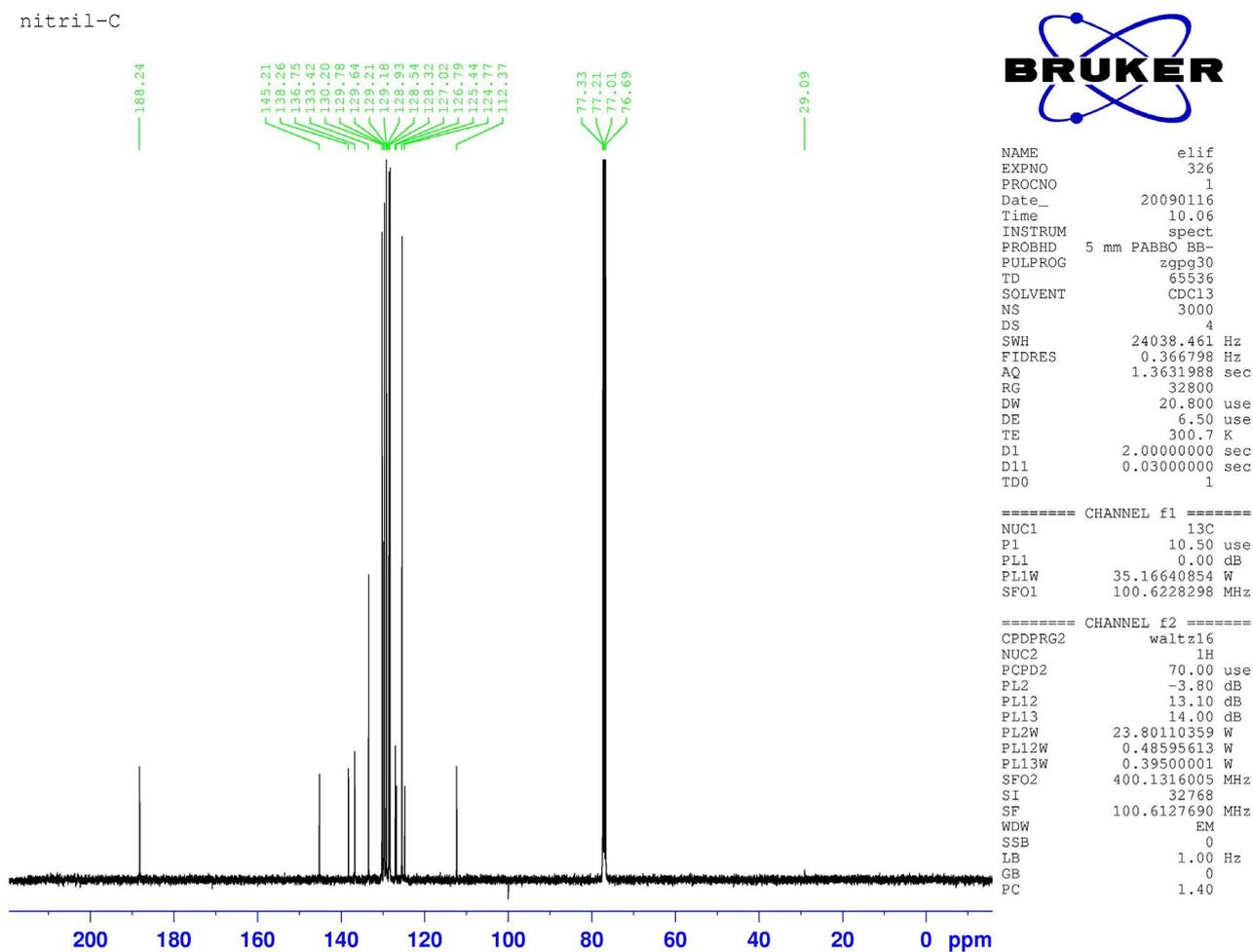


Figure 7. A part of ^{13}C -NMR spectrum of the title compound.

127.02, 126.79, 125.46, 124.77 ppm (s, C-4) are thought to represent the aromatic carbons and a singlet peak at 112.37 ppm represent the nitrile group [40].

Therefore, final confirmation of the structure of the compound was derived from its ^1H -NMR spectrum: =7.72 - 7.09 ppm a set of signals for aromatic protons.

4. Conclusion

Consequently, the novel compound is a significant preliminary compound due to the fact that original pyrazole-3-carboxylic acid derivative includes nitrile group in its structure. It is air-stable in the solid state, crystallized from methyl alcohol and insoluble in water. Additionally, it has good solubility in common organic solvents, such as CH_2Cl_2 , THF, DMF, DMSO, CHCl_3 , acetone and toluene. The authenticity of the compound has been established by UV, IR, NMR, XRD and elemental analysis techniques. The title compound characterized can be essential in medicinal and biological applications. Some pyrazole derivatives, as known, have been used to treat some diseases [1-21,30-32]. The title structure may be

important from a medicinal point of view as well as their widespread biological significance. Further investigation on the mechanism, potential activity and the optimal reaction condition is currently in progress.

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