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ORIGINAL PAPER

# Michael addition of phenylacetonitrile to the acrylonitrile group leading to diphenylpentanedinitrile. Structural data and theoretical calculations

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Knoevenagel condensation of phenylacetonitrile with 4-diphenylaminophenylacetonitrile in the presence of piperidine was carried out to obtain a novel conjugated compound. In addition to the expected compound 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (*I*), the 3-((4-diphenylamino)phenyl)-2,4-diphenylpentanedinitrile (*II*) was also obtained with a good yield. Compound *II* was obtained as a result of the Michael addition of phenylacetonitrile with 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (*I*). Conversely, when the same reaction was performed in the presence of KOH as catalyst, only the $\alpha,\beta$-unsaturated nitrile (*I*) was afforded with a 92 % yield. The structures were confirmed with IR, EI-MS and NMR spectroscopy. Single crystals *I* and *II* were formed and their structures were determined by X-ray single-crystal diffraction analysis. Crystal *I* belongs to the monoclinic system with space group $P2_1/n$ having unit cell parameters of $a = 16.8589(5)$ Å, $b = 6.68223(17)$ Å, $c = 19.8289(7)$ Å, $\beta = 111.133(4)^\circ$ and $Z = 4$. Crystal *II* belongs to the same monoclinic system with space group $P2_1/c$, having unit cell parameters of $a = 10.8597(4)$ Å, $b = 24.7533(10)$ Å, $c = 9.7832(4)$ Å, $\beta = 91.297(3)^\circ$ and $Z = 4$. In addition to the structural data analysis, some theoretical calculations that reveal the nature of relevant structure–property relationships are also reported.


**Keywords:** phenylacetonitrile, $\alpha,\beta$-unsaturated nitrile, *N*-diphenylaminophenyl derivative, cyano-substituted compound, Michael addition, crystal structure

## Introduction

Unsaturated nitriles play a key role in several pathways proposed for the pre-biotic synthesis of biological molecules (Guillemin et al., 1998). Arylacrylonitriles are important synthons for the synthesis of several biologically active molecules used in the preparation of perfumes (Fraysse, 1980), flavonoid pigments (Fringuelli et al., 1994), sexual pheromones and vitamin A, etc. They are directly involved as plant growth regulators in increasing the soybean crop (Mori, 1976), and as inhibitors of prostaglandin synthetase (Peat et al., 1981; Michel et al., 1984). The traditional preparation of arylacrylonitriles involves the reaction of aromatic aldehydes with arylacetonitriles (Knoevenagel reaction, as well as Meyer and Frost reaction) (Knoevenagel, 1896; Frost, 1889). The compounds can be obtained under basic conditions in a polar solvent (NaOH, KOH, NaOEt, $K_2CO_3$ in MeOH, EtOH or THF) (D'sa et al., 1998; Guil-

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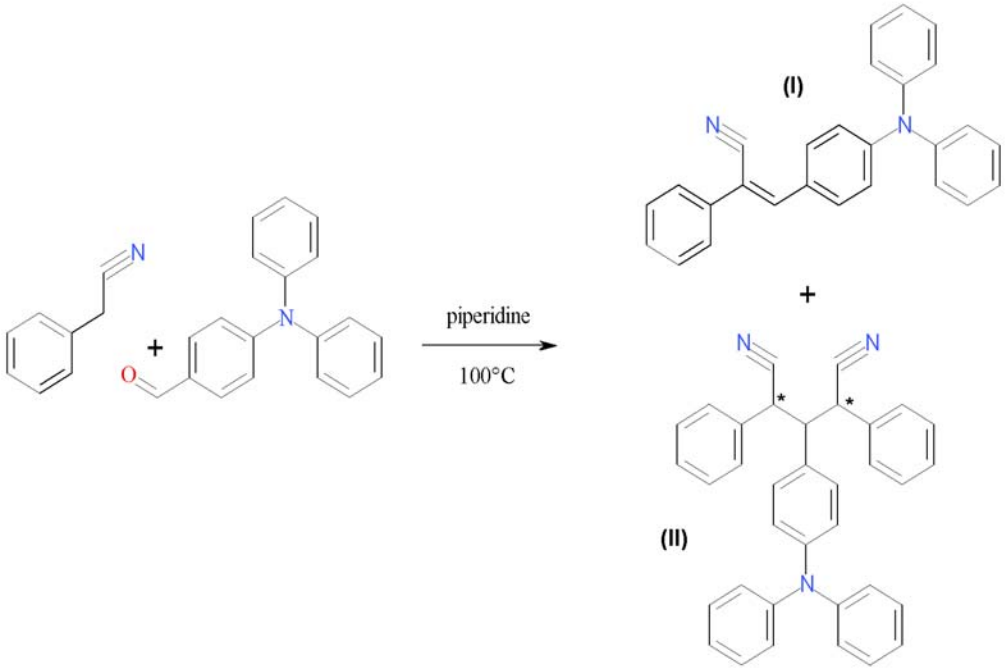


**Fig. 1.** In situ formation of 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (*I*) mixed with 3-(4-diphenylamino)phenyl-2,4-diphenylpentanedinitrile (*II*).

lot et al., 2005). Recently, Loupy et al. (2005) applied solvent-free procedures, using powdered KOH as the base at ambient temperature, in the reaction of phenylacetonitrile with 4-methoxybenzaldehyde to yield the *Z* and *E* acrylonitrile isomers, accompanied by compounds resulting from the Michael addition. Using non-catalysed solvent-free conditions for the reaction of 4-methoxybenzaldehyde with phenylacetonitrile, these investigators obtained $\alpha,\beta$-unsaturated nitrile ($Z + E$) as the main product; they also occasionally observed, by GC-MS detection, a product from the Michael addition. The reaction of phenylacetonitrile with aromatic and aliphatic aldehydes at ambient temperature in the presence of KOH using 4-trifluoromethanophenyl afforded the compound 3-(4-$F_3$C(phenyl)-2,4-diphenylpentanedinitrile) with 8–13 % yield. However, when a highly hindered aromatic aldehyde, such as mesitaldehyde, was used, the reaction afforded an almost quantitative yield (98 %) of the $\alpha,\beta$-unsaturated nitrile.

The present group has reported several studies on syntheses of $\alpha,\beta$-unsaturated nitriles by Knoevenagel condensation without catalyst and under solvent-free conditions (Percino et al., 2010, 2011, 2012; Pérez-Gutiérrez et al., 2011), as well as the preparation of conjugated pyridine-(*N*-diphenylamino) or *N*-dimethylamino carbazole)acrylonitrile derivatives. Good yields were obtained by following the Knoevenagel method in the presence of piperidine or KOH as the catalyst. The present work reports on the in situ synthesis of 2,4-diphenyldinitrile, as a side reaction of the Michael addition when the Knoevenagel condensation of phenylacetonitrile and *N*-diphenylaminophenyaldehyde was carried out using piperidine as the catalyst. The compounds 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (*I*) and 3-(4-diphenylamino) phenyl)-2,4-diphenylpentanedinitrile (*II*) were isolated even though the aldehyde is highly hindered. The compounds were characterised using IR, $^1$H-NMR, MS techniques and single crystal X-ray analysis. Theoretical calculations were also performed in order to evaluate the nature of the relevant structure-property relationships, such as $\pi$-delocalisation on the whole molecule of *I* as contrasted with molecule *II*.

## Experimental

Phenylacetonitrile and 4-diphenylaminophenylacetonitrile were obtained from Aldrich (Mexico) and purified prior to use. Melting points were measured with an SEV (Systems and Equipments of Glass, SEV Mexico) (0–300 ℃) apparatus and are reported as uncorrected values. The IR spectra of the products were recorded on a Vertex (model 70, Bruker Optics, Germany) 750 FT-IR spectrophotometer by attenuated total reflectance (ATR). The $^1$H NMR spectra were obtained using compounds dissolved in $CDCl_3$ on a Varian 400 MHz NMR spectrometer (Varian NMR, Walnut Creek, CA, USA). The electron ionisation (EI) spectra were acquired on a Jeol MStation 700-D mass spectrometer (Jeol USA, Peabody, MA, USA).

The synthesis of compounds *I* and *II* was performed by mixing 1 : 1 : 1 (molar ratios) of phenylacetonitrile, 4-diphenylaminophenylacetonitrile and piperidine, as shown in Fig. 1. Piperidine acted as

**Table 1.** Crystallography data for *I* and *II* compounds

| | *I* | *II* |
|---|---|---|
| Empirical formula | $C_{27}H_{20}N_2$ | $C_{35}H_{27}N_3$ |
| Crystal system | Monoclinic | Monoclinic |
| Colour, Habit | Yellow, rod | Pale yellow, plate |
| Formula mass | 372.45 | 489.60 |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $T$/K | 110(2) | 110(2) |
| $a$/Å | 16.8589(5) | 10.8597(4) |
| $b$/Å | 6.68223(17) | 24.7533(10) |
| $c$/Å | 19.8289(7) | 9.7832(4) |
| $\alpha$/° | 90.00 | 90.00 |
| $\beta$/° | 111.133(4) | 91.297(3) |
| $\gamma$/° | 90.00 | 90.00 |
| $V$/Å$^3$ | 2083.59(11) | 2629.18(18) |
| $Z$ | 4 | 4 |
| Dc/(g cm$^{-3}$) | 1.187 | 1.237 |
| $F$/(000) | 784 | 1032 |
| $\mu$/mm$^{-1}$ | 0.070 | 0.073 |
| $\lambda$/Å | 0.71073 | 0.71073 |
| Crystal size/(mm$^3$) | 0.62 × 0.19 × 0.15 | 0.75 × 0.32 × 0.07 |
| $2\theta_{max}$/° | 25.00 | 24.35 |
| $N$ | 15652 | 13551 |
| $N°$ ($I > 2.0\sigma(I)$) | 3074 | 3619 |
| R1 | 3.30 | 5.85 |
| wR2 | 8.24 | 14 |
| Goodness-of-fit | 1.036 | 1.150 |
| Largest diff peak and hole/(e Å$^{-3}$) | –0.17 and 0.13 | –0.31 and 0.42 |

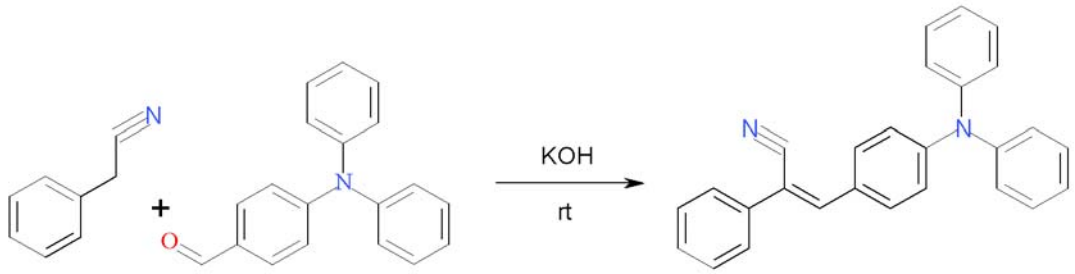


**Fig. 2.** Reaction to obtain 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (*I*).

both catalyst and solvent. The reaction mixture was refluxed at 100℃ for 36 h. During the reaction, the mixture appeared to be oily with a brownish-red colour. The mixture was neutralised with a HCl (2 M) solution to precipitate the products in powder form and which were subsequently washed with $H_2O$. The products were purified by recrystallisation with a solvent mixture of ethylacetate : hexane (4 : 1 vol.). The compound was characterised by IR, $^1$H-NMR and EI mass spectrometry. The compound (*II*) was obtained in the form of single crystals using the following procedure: the 3-(4-diphenylamino)phenyl)-2,4-diphenylpentanedinitrile (16.8 mg, 0.034 mmol) was dissolved in 6.5 mL of ethanol and set aside at 4℃ for 4 days.

The reaction conditions to obtain 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (*I*) were as shown in Fig. 2. Compound *I* was obtained with a 92 % yield, in accordance with the following procedure: phenylacetonitrile (0.15 mL, 1.28 mmol) was added to a solution of *p*-(diphenylaminophenyl) aldehyde (0.35 g, 1.28 mmol) in ethanol (10 mL) at 60℃ and at ambient temperature. The mixture was stirred and then KOH powder (0.072 g, 1.28 mmol) was added. After 30 min. a yellow precipitate was formed, which was filtered and washed with $H_2O$. The product was purified by recrystallisation with methanol. Crystals of (*I*) were obtained with 10 mg of (*I*) dissolved in 15 mL of cyclohexane and kept at ambient temperature; after 72 h the yellow crystals were formed.

All reflection intensities were measured at 110(2) K using a KM4/Xcalibur (detector: Sapphire3) with enhanced graphite-monochromated Mo $K\alpha$ radiation ($\lambda$ = 0.71073 Å) using the CrysAlisPro program (Version 1.171.35.11, Oxford Diffraction, 2011). The CrysAlisPro This program was used to refine the cell

dimensions and for data reduction. The structures were solved with the SHELXS-97 program (Sheldrick, 1998) and were refined on $F^2$ with SHELXL-97 (Sheldrick, 1998). Analytical numeric absorption corrections based on a multi-faceted crystal model were applied using CrysAlisPro. The temperature of the data collection was controlled using the Cryojet system (manufactured by Oxford Instruments). The H atoms (except for specified atoms) were located at calculated positions using the instructions AFIX 13 or AFIX 43 with isotropic displacement parameters having values 1.2 times Ueq of the attached C atoms. The crystallography data for *I* and *II* compounds are presented in Table 1.

## Results and discussion

### *Reactions with acrylonitriles*

There have been several recent approaches to the preparation of arylacrylonitriles with aromatic aldehydes. Solvent-free methods at various temperatures were used successfully to synthesise different $\alpha,\beta$-unsaturated nitriles as well as for a series of isomers of 3-(4-substituted phenyl)-2-arylacrylonitriles (aryl, phenyl or pyridyl) with chloro-, fluoro- substituents (Percino et al., 2010, 2011, 2012; Pérez-Gutiérrez et al. 2011). Procedures using piperidine and elevated temperature afforded compounds with dimethylamino-, diphenylamino- and *N*-ethyl-3-carbazole- substituents. These reports did not indicate any secondary reactions.

Lorente et al. (1995) reported the isolation of substituted 1-aminocyclohexene-2,4-dicarbonitriles obtained by the reaction of $\alpha,\beta$-unsaturated nitriles (two equivalents) with benzyl cyanide making use of a stronger base than piperidine, such as sodium methoxide or sodium 2-propoxide in methanol. The outcome of this reaction is attributed to the dependence of the reaction on the catalyst and of the molar ratios of the reactants, because when l-amino-3,4,5-triphenylcyclohexene-2,4-dicarbonitrile was used with another equivalent of cinnamonitrile in a sodium methoxide-methanol solution, the cyclohexene l-amino-3,4,5-triphenylcyclohexene-2,4-dicarbonitrile was obtained. However, Guillot et al. (2005) compared two synthetic methods: one using KOH as a catalyst at ambient temperature and another performed at a higher temperature (110 °C) under microwave (MW) irradiation. These authors reported that using KOH at ambient temperature led to the preparation of 3-phenyl-2,4-diphenylpentanedinitrile, as detected by GC-MS. The presence and the yield of this compound depended on the steric hindrance of the aldehyde reactant.

In the current work, the compound *II* is formed in situ under reaction conditions that include piperidine (Fig. 1), because *II* was not present with the KOH catalyst (Fig. 2). The use of piperidine as a catalyst made it possible to obtain both compounds: *II* with a yield of 21 % mixed with *I* with a 42 % yield. Product *II* is characterised in *anti* configuration in two enantiomeric forms, *anti* (2*R*,4*R*) and *anti* (2*S*,4*S*). Recent studies of the Michael addition of some aldehydes to malonates in the presence of organic catalysts have been reported using different solvents; here the reactions were found to be highly enantioselective (Saidalimu et al., 2013). However, in this case, in the presence of piperidine, the reaction does not proceed enantioselectively. By contrast, with the use of KOH as a catalyst at ambient temperature (Fig. 2), the primary product was the $\alpha,\beta$-unsaturated nitrile (*I*) (92 %). This outcome could be explained by the low reactivity of the —COH group through the —$N(Ph)_2$ moiety, which is a strong electron-donating group with a greater influence than the highly hindered aromatic aldehyde. It is suggested that both catalyst and solvent play a determinant role in the diastereo- and enantioselectivity of the Michael addition reaction (Saidalimu et al., 2013).

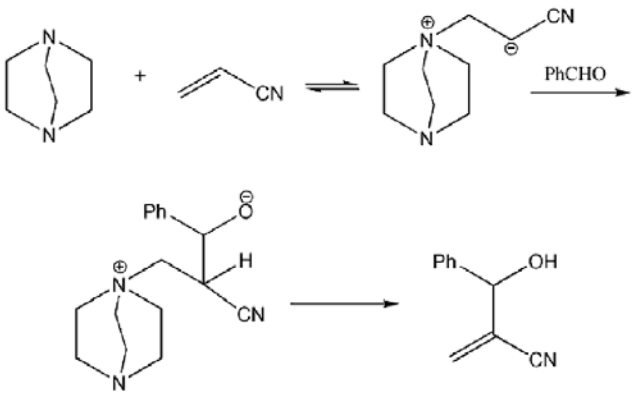


**Fig. 3.** Baylis–Hillman reaction (Lubineau & Augé, 1999; Augé et al., 1994).

According to a report by Jenner, the amines can react via Michael addition under aqueous conditions (Jenner, 1996), especially with $\alpha,\beta$-unsaturated nitriles, using a combination of pressure and catalysis by ytterbium triflate which strongly promotes the addition of amines to $\alpha,\beta$-ethylenic compounds (Lubineau & Augé, 1999). Physicochemical activation by water is highly efficient except when the substituent is —$OOCH_3$ due to the rapid retro-Michael reactions. A related reaction is the Baylis–Hilman reaction, which proceeds readily in water with a good rate enhancement (Fig. 3) (Lubineau & Augé, 1999).

Sağırli and co-workers recently reported a number of poly-substituted cyclopentenes obtained by a multicomponent catalyst-free reaction using a combination of $\beta$-nitrostyrene, benzylidenemalononitriles and 2-morpholinoethyl isocyanide (Sağırli et al., 2013). These authors proposed the mechanism shown in Fig. 4. Both of these mechanisms were helpful in explaining the formation of (*II*) as shown in Fig. 5.

**Table 2.** IR, $^1$H-NMR and EI mass spectrometry data of *I* and *II* compounds

(2-(Phenyl)-3-(4-diphenylaminophenyl)acrylonitrile) *I*:
Yellow powder solid, (yield, 42 % section 3.2.1 and 92 % section 3.2.2); M.p.: 162–164 °C
IR (KBr), $\tilde{\nu}$/cm$^{-1}$: 3033 (w), 2216 (s, C≡N), 1586 (broad, C=C$_{Ar}$ and C=C), 1492 (s, $\nu$(C—H) double bond), 829 (s, C—H, CR$_1$R$_2$=CR$_3$H)
$^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.795–7.766 (dd, 2H), 7.658–7637 (dd, 2H), 7.446–7.407 (m, 3H), 7.373–7.297 (m, 5H), 7.258 (s, 1H), 7.173–7.104 (m, 5H), 7.070–7.042 (dd, 2H) EI, $m/z$ ($I_r$/%): 372 (100) (M), 371 (10) (M$^+$)

(3-(4-Diphenylamino)phenyl)-2,4-diphenylpentanedinitrile) *II*:
Pale yellow powder (21 %) M.p.: 116–118 °C
IR (KBr), $\tilde{\nu}$/cm$^{-1}$: 3033 (w), 2209 (s, C≡N), and 2238 (w, C≡N), 1586 (broad, C=C$_{Ar}$), 1492 (s, $\nu$(C—H) aliphatic), 829 (s, C—H, CR$_1$R$_2$=CR$_3$H)
$^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.793–7.772 (dd, 2H), 7.663–7.634(dd, 2H), 7.448–6.9387 (m, 20H), 6.809–735 (q, 4H), 4.77–4.764 (dd, 1H), 4.407–4.381 (dd, 1H), 3.425–385, (dd, 1H)
EI, $m/z$ ($I_r$/%): 488 (15) (M$^+$), 372 (100) (M)

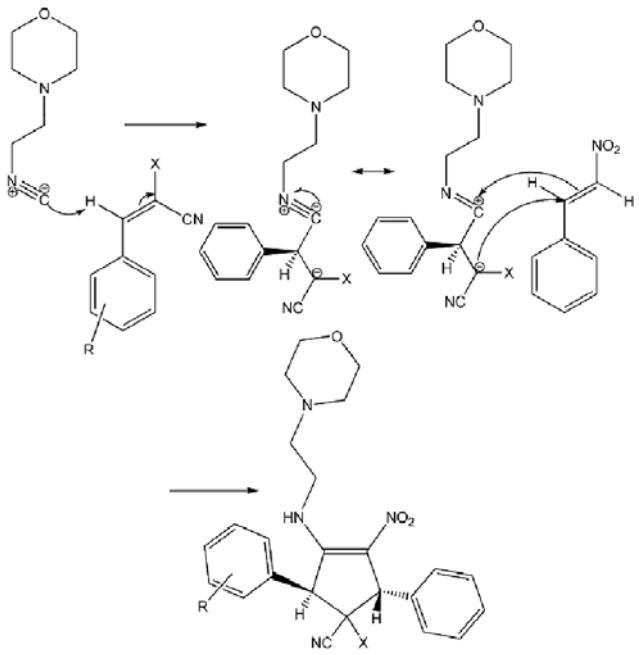

**Fig. 4.** Proposed mechanism for formation of poly-substituted cyclopentenes (Sağırli et al., 2013).

The synthesised compounds *I* and *II* were characterised by IR, $^1$H-NMR, EI MS data, X-ray crystallography and physical characterisation. These results are given in Tables 2 and 3. For $\alpha$,$\beta$-conjugated nitrile *I*, the double bond $\nu$(—C=C—) at $\approx$ 1625 cm$^{-1}$ was not observed (Bellamy, 1975; Nakanishi & Solomon, 1977) as identified in compounds containing N(CH$_3$)$_2$ at 1613–1610 cm$^{-1}$ and this behaviour could be attributed to the overlap of the signals arising from the $\nu$(—C=C—) from the aromatic and pyridine rings. This result provided evidence that the electrons in the compounds exhibited a higher extent of delocalisation (Percino et al., 2011). The electrons from the $\pi$ bonds are delocalised or distributed over the whole system (acting as a group of interacting conjugated atoms). The out-of-plane C—H deformation in *I* appeared at 829 cm$^{-1}$. This signal disappeared completely in compound *II*. The band at 2216 cm$^{-1}$ was assigned to the —C≡N group and is an indication that, even with the —C≡N attached to the alkene double bond, the presence of the —N(Ph)$_2$ in the *p*-position induced a strong conjugation. For *II,* the band at 2209 cm$^{-1}$ and one with smaller intensity at 2238 cm$^{-1}$ could be indicative of two —C≡ N groups in the 2 and 4 positions, due to the asymmetry of the molecule. The band at 2890 cm$^{-1}$ is due to the stretching $\nu$(C—H).

The $^1$H-NMR data in the CD$_3$Cl solution showed the general de-shielding effect of the protons of the $\alpha$,$\beta$-unsaturated nitrile compounds. Thus, the proton H(3) in compound *I* appeared at 7.258 ppm, (7.540 ppm corresponds to the chemical shift of a proton in a double bond) (Williams & Fleming, 1980). The same protons associated with the —N(CH$_3$)$_2$ substituent were reported at 7.41 ppm for the respective phenyl groups. Compound *II* is of an asymmetrical structure, hence the $^1$H-NMR results showed three different methine carbon atoms, which appeared at 4.77–4.764 ($J$ = 5.2 Hz, dd, 1H, H(2)), 4.407–4.381 ($J$ = 10.4 Hz, dd, 1H, H(4)), and 3.399–3.411 ($J$ = 5.6 Hz, $J$ = 10.4 Hz, dd, 1H, H(3)), clearly indicating the formation of 2,4-diphenylpentanedinitrile.

### *Crystallography studies*

The data and structure refinements obtained from single crystals of *I* and *II* are given in the Supplementary Information. For both compounds, the data were collected at 110(2) K after the crystals were flash-cooled from ambient temperature. The *I* and *II* structures derived from X-ray studies indicated that structures *I* and *II* were ordered, solved and refined in the space group monoclinic, with $P2_1/c$ and $P2_1/n$, respectively, having 4 molecules per cell for both structures. The ORTEP structures of *I* and *II* are shown in Fig. 6. The X-ray investigation showed that compound *I* had the *Z*-geometry about the ethylene bridge which links the aromatic rings. Table 3 gives the selected bond lengths with estimated standard deviations for compounds *I* and *II*, as well as the dihedral angles between the acrylonitrile linkage and the

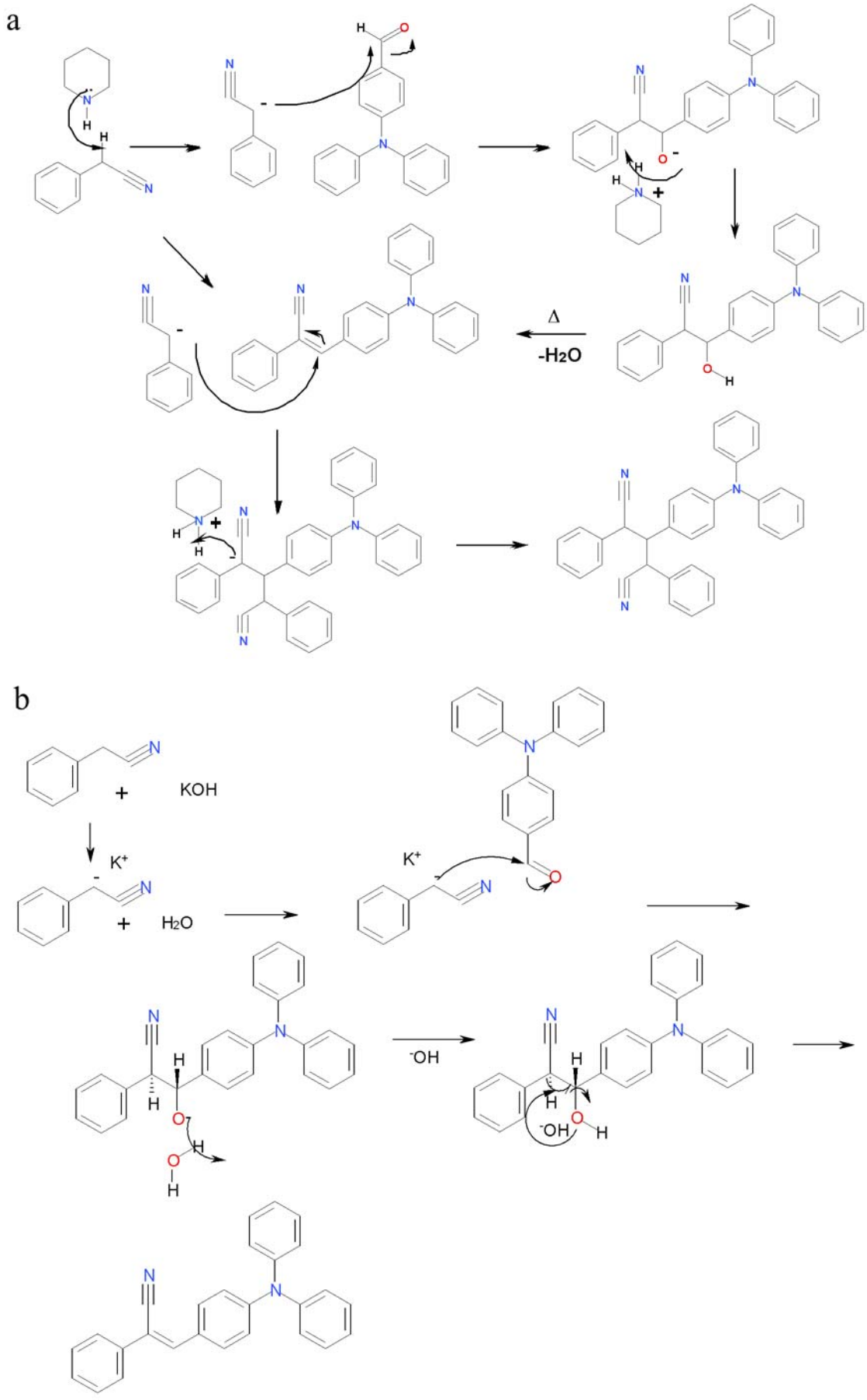


**Fig. 5.** Proposed mechanisms for formation of compounds *I* and *II* in the presence of piperidine (a) and *I* in KOH (b).

**Table 3.** Selected bond lengths, bond and torsion angles for *I* and *II*

| Bond length/Å | | | |
|---|---|---|---|
| *I* | | *II* | |
| C(13)—C(14) | 1.3973(16) | C(19)—C(20) | 1.556(4) |
| C(13)—C(18) | 1.3980(16) | C(19)—C(28) | 1.560(4) |
| C(13)—N(1) | 1.3997(15) | C(20)—C(22) | 1.517(4) |
| C(14)—C(15) | 1.3792(16) | C(21)—N(2) | 1.151(3) |
| C(15)—C(16) | 1.4010(16) | C(20)—C(21) | 1.479(4) |
| C(16)—C(17) | 1.4011(15) | C(28)—C(29) | 1.469(4) |
| C(16)—C(19) | 1.4557(15) | C(28)—C(30) | 1.518(4) |
| C(17)—C(18) | 1.3797(16) | C(29)—N(3) | 1.161(4) |
| C(19)—C(20) | 1.3495(16) | | |
| C(20)—C(22) | 1.4839(15) | | |
| **Bond angles/°** | | | |
| C(19)—C(20)—C(22) | 123.96(10) | C(7)—N(1)—C(13) | 118.25(19) |
| C(19)—C(20)—C(21) | 120.50(10) | C(1)—N(1)—C(13) | 118.2(2) |
| C(16)—C(19)—C(20) | 129.59(10) | C(15)—C(16)—C(19) | 119.0(2) |
| C(17)—C(16)—C(19) | 124.12(10) | C(17)—C(16)—C(19) | 122.6(2) |
| C(15)—C(16)—C(19) | 118.51(10) | C(20)—C(19)—C(28) | 113.7(2) |
| C(19)—C(20)—C(22) | 123.96(10) | C(12)—C(7)—N(1) | 118.8(2) |
| | | C(8)—C(7)—N(1) | 122.2(2) |
| | | C(2)—C(1)—N(1) | 120.8(2) |
| | | C(6)—C(1)—N(1) | 119.7(2) |
| **Torsion angles/°** | | | |
| C(17)—C(16)—C(19)—C(20) | 29.69(17) | C(16)—C(19)—C(20)—C(22) | 55.8(3) |
| C(16)—C(19)—C(20)—C(21) | 6.53(17) | C(6)—C(1)—N(1)—C(13) | –147.2(2) |
| C(19)—C(20)—C(22)—C(23) | –154.21(11) | C(2)—C(1)—N(1)—C(13) | 32.4(4) |
| C(19)—C(20)—C(22)—C(27) | 26.45(16) | C(12)—C(7)—N(1)—C(13) | 41.1(3) |
| C(18)—C(13)—N(1)—C(1) | 29.75(16) | C(8)—C(7)—N(1)—C(1) | 21.9(4) |
| C(14)—C(13)—N(1)—C(7) | 27.92(17) | C(16)—C(19)—C(28)—C(30) | –47.2(3) |

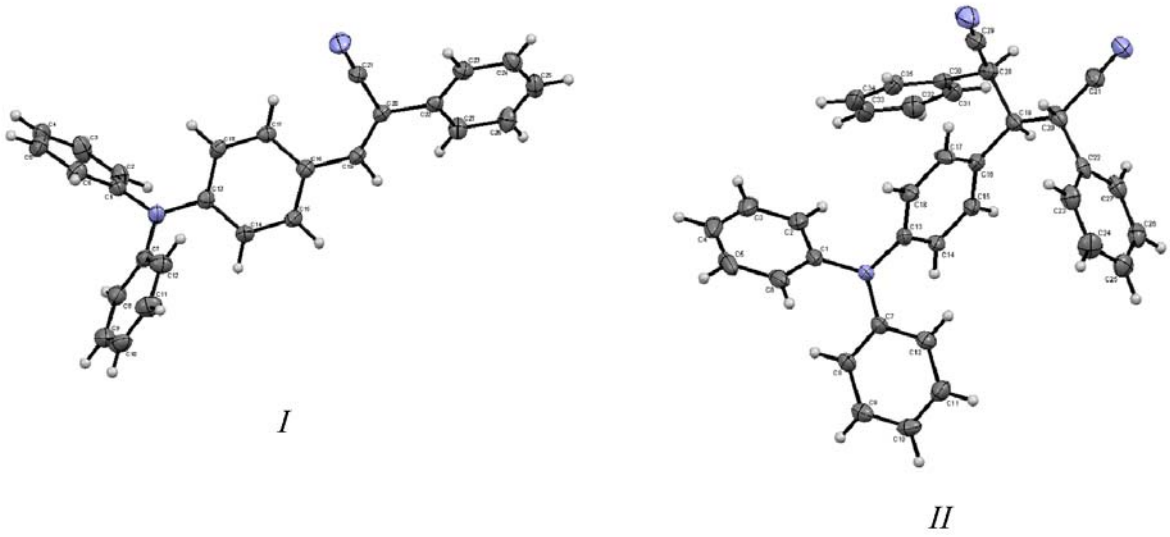


**Fig. 6.** Molecular structure of compounds *I* and *II*; displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radii.

phenyl ring and with the *p*-diphenylaminophenyl moiety.

From the molecular structure of *I*, it was observed that the phenyl ring was *Z*-located to the diphenylaminophenyl ring in relation to the double bond. The C($sp^2$)—C($sp^2$) conjugated bond length between

C(19)—C(20) was 1.3495(6) Å, which is slightly longer than a typical bond length for $C(sp^2)$—$C(sp^2)^2$ conjugated (C═C—C═C, subst.), usually found to be 1.330 Å (Allen et al., 1987). The $C(sp^2)$—$C(sp^2)$ C(16)—C(19) was 1.4557(15) Å and C(20)—C(22) was 1.4839(15) Å, lengths that deviated slightly from the standard values for $C(sp^2)$—C(Ar) of 1.470 Å (Table 3), indicating a delocalisation of the $\pi$-electrons at the junction of the two rings through the C(20)—C(19) bond. Also, the distances of C(15)—C(16) equal to 1.410(16) and C(16)—C(17) equal to 1.4011(15) Å were slightly longer than for typical C(Ar)≈≈C(Ar) C═C (overall), generally reported to be 1.384 Å. This value was closer to that for the bond lengths of C(15)—C(14), C(17)—C(18), C(18)—C(13) and C(14)—C(13) which were 1.379(16) Å, 1.3797(16) Å, 1.3980(16) Å and 1.3973(16) Å, respectively.

It was also observed that the C(13)—N(1) bond length was 1.3997(15) Å which is larger higher than a standard bond for $C(sp^2)$—N(3) with $N(sp^2)$ planar, at 1.355 Å. The information accords well with the variation of the resonance structure depicted in Fig. 7.

The 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile electron density is appropriately delocalised through the $\pi$-conjugated units, as they provide an effective pathway for the efficient push–pull charge transfer for the donor and acceptor groups. The molecular packing does not present non-planar molecules for the phenyl, double bond and diphenylamine moieties (Fig. 8). The diphenylamino group forms a dihedral angle of C(14)—C(13)—N(1)—C(7) = –27.92(17)°

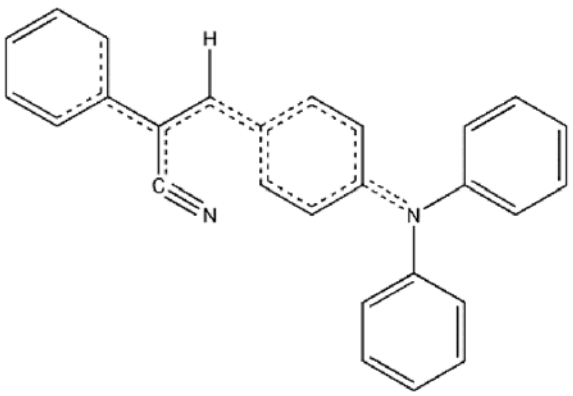


**Fig. 7.** Resonance structure of 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (*I*).

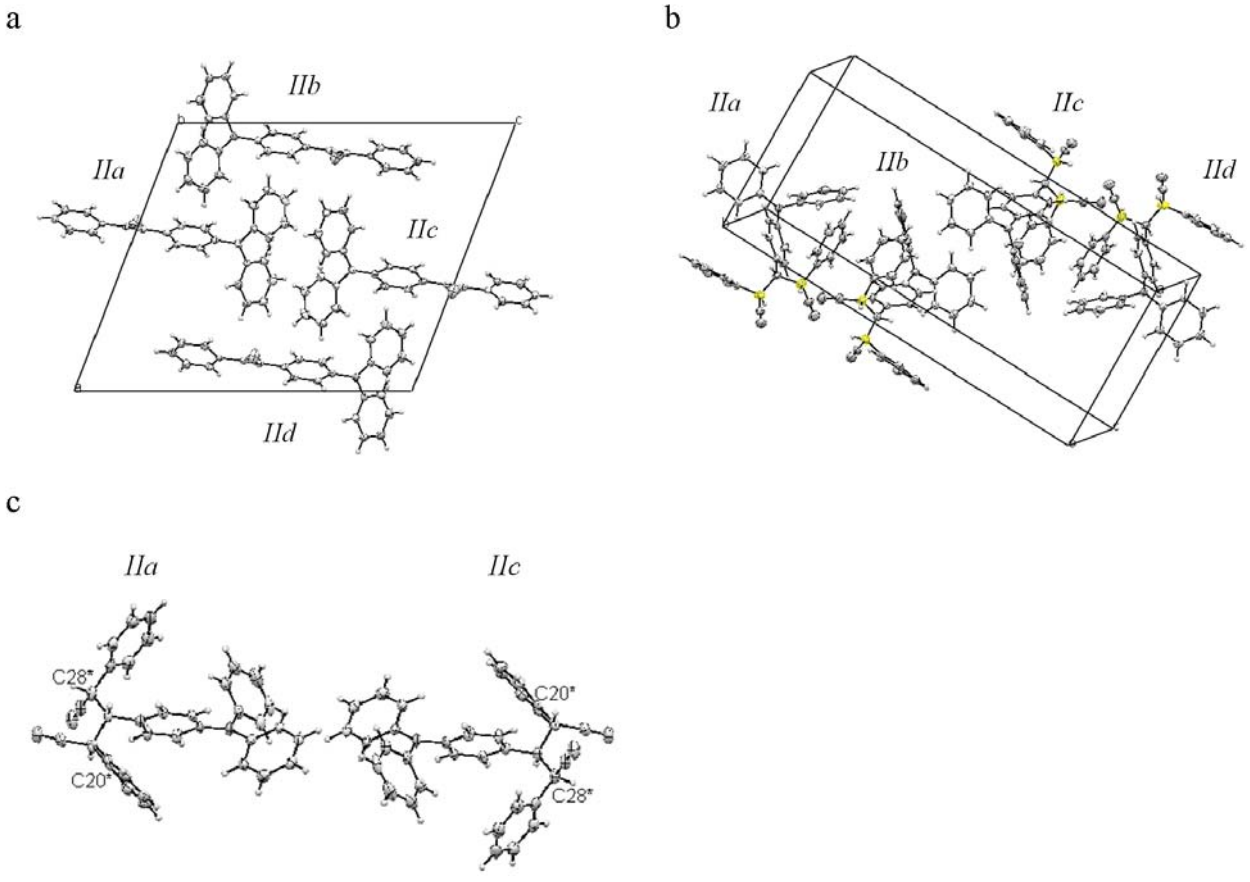


**Fig. 8.** Projection of crystal packing of *I* along *b* axis (a), *II* along *a* axis (b) and diastereoisomers (2*R*,4*R*) and (2*S*,4*S*) with stereocentric atoms (c).

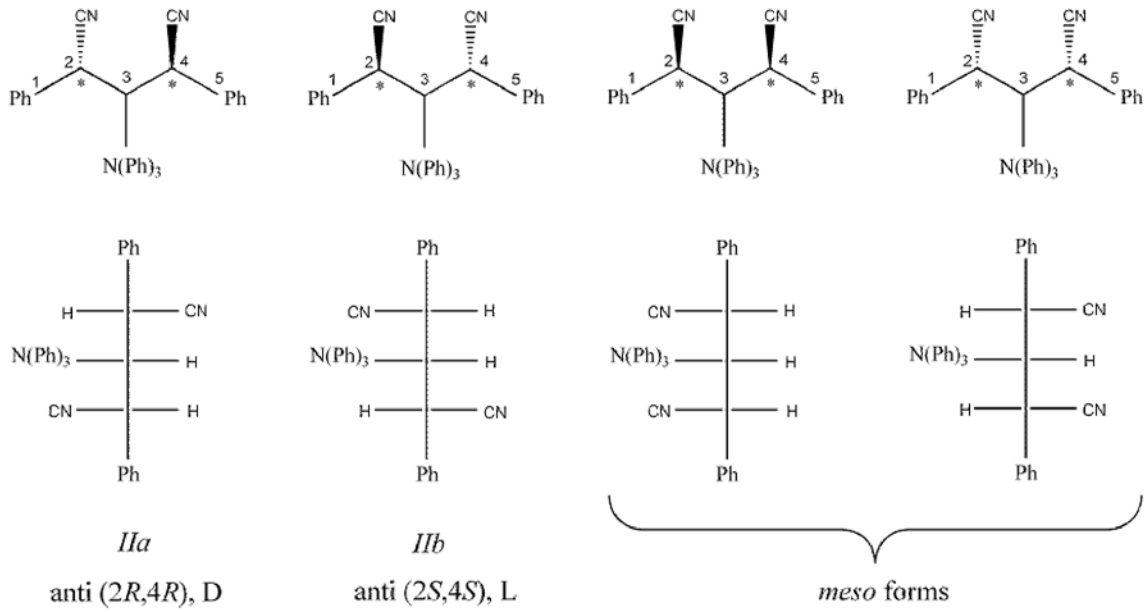


**Fig. 9.** Stereoisomers of 3-((4-diphenylamino)phenyl)-2,4-diphenylpentanedinitrile (*II*).

and C(18)—C(13)—N(1)—C(1) = 29.75(16)° in respect of its phenyl rings. The phenyl rings are twisted out of the ethylene bond plane of C(17)—C(16)—C(19)═C(20) for 29.69(17) Å, C(19)═C(20)—C(22)—C(23) for –154.21(11); the —C≡N group is not co-planar with the aromatic ring, with a torsion angle C(16)—C(19)═C(20)—C(21) of 6.53(17)°. Also, the area between the planes of the rings is defined by the torsion angle for molecule *I*, showing a torsion angle of C(19)═C(20)—C(22)—C(27) = 26.45(16)°. Deviations from the ideal bond-angle geometry for C($sp^2$) atoms of the double bond are lower for C(16)—C(19)═C(20) = 129.59(10)° while C(19)═C(20)—C(22) = 123.96(10)° is closer to 120°, indicating a small repulsion between the aromatic rings.

The X-ray structural refinement showed that molecule *II* possessed two stereogenic carbon atoms, C(20)* and C(28)*, indicating four possible stereoisomers of (*II*), two enantiomers and two equivalent diastereoisomers of a *meso* form: see Fig. 9. In this case, the crystal structure belongs to a centrosymmetric space group, $P2_1/c$, revealing that it is a racemic mixture, as was expected for stereomeric racemates. The assignment of relative configurations to the racemates (2*R*,4*R*) and (2*S*,4*S*), as enantiomeric forms, was performed by X-ray diffraction of monocrystal, while *meso* forms of *II* were not found in the crystalline structure. Figs. 8a and 8b show that the crystal packing containing four molecules of *II*, denoted as *IIa*–*IId*, *IIa* and *IIc* corresponds to the (2*R*,4*R*) relative configuration, while *IIb* and *IId* have (2*S*,4*S*) relative configuration. Fig. 8c displays a view of the molecules with stereocentric atomic numbering, which are a couple of enantiomers (2*R*,4*R*) and (2*S*,4*S*) in their *anti* forms, which can also be identified as D and L forms, respectively: see Fig. 9.

Selected bond lengths, bond angles and torsion angles are given in Table 3. All lengths and angles have normal values. The molecule consists of a central chain of five C atoms including two phenyl rings, with two cyano groups attached to positions 2 and 4 and the diphenylaminophenyl attached to the central atom in position 3 of the —PhCH—CH—CHPh— moiety: see Fig. 9. The —PhCH—CH—CHPh— moiety of the molecule revealed bond lengths for C(20)—C(22) = 1.517(4) Å, C(19)—C(20) = 1.556(4) Å; C(19)—C(28) = 1.560(4) Å and C(28)—C(30) = 1.518(4) Å. The typical distance for a single C(Ar)—C($sp^3$), C*—C(Ar) (overall) bond is 1.513 Å and for C($sp^3$)—C($sp^3$) C*—C* (overall) is 1.530, as previously reported in the literature (Nakanishi & Solomon, 1977). For C($sp^3$)—C($sp^1$), C*—C≡N, a bond length of 1.470 Å has been reported while for C═C—C≡N = 1.427 Å, as observed for molecule (*I*). The distances of C(21)—N(2) = 1.151(3) Å and C(29)—N(3) = 1.161(4) Å, as well as, C(28)—C(29) = 1.469(4) Å and C(20)—C(21) = 1.479(4) Å were values closer to those reported for $Csp^1$*N(1) and C*—C≡N.

On the other hand, the benzene ring composed of atoms C(13)—C(14)—C(15)—C(16)—C(17)—C(18) is co-planar with the carbon C(19) and with the N(1) with bond angles between C(1)—N(1)—C(13) = 118.2(2)° and C(7)—N(1)—C(13) = 118.25(19)°. In addition, C(15)—C(16)—C(19) = 119.0(2)° and C(17)—C(16)—C(19) = 122.6(2)° are angles with values of almost 120°. For torsion angles around C(28)—C(19)—C(20) are C(16)—C(19)—C(20)—C(22) = 55.8(3)° while C(16)—C(19)—C(28)—C(30) = –47.2(3)°. For the rest of the molecule, the planes de-

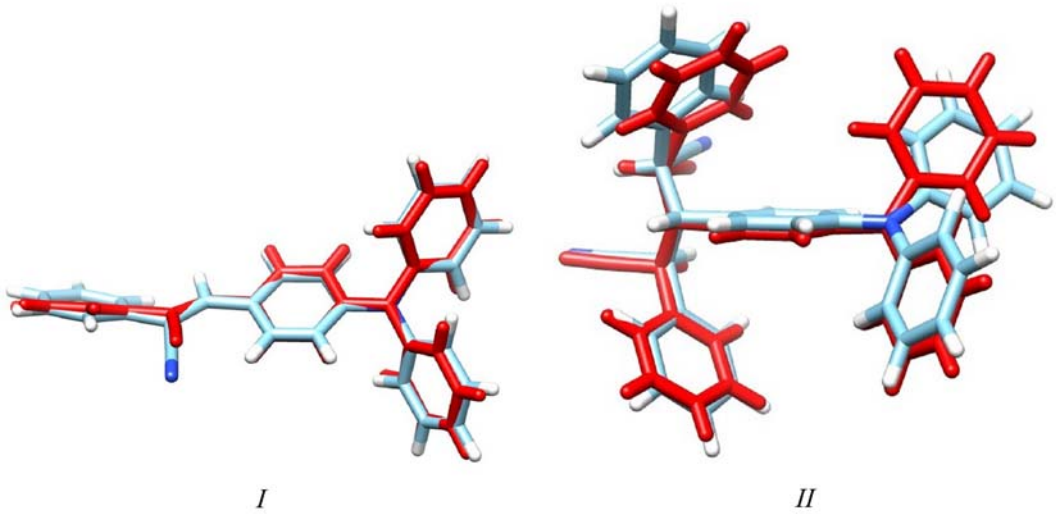


**Fig. 10.** Comparison between geometrical structures of X-ray (red) and optimised structures (blue) calculated at B3LYP/6-31+G(d) level for compounds *I* and *II*.

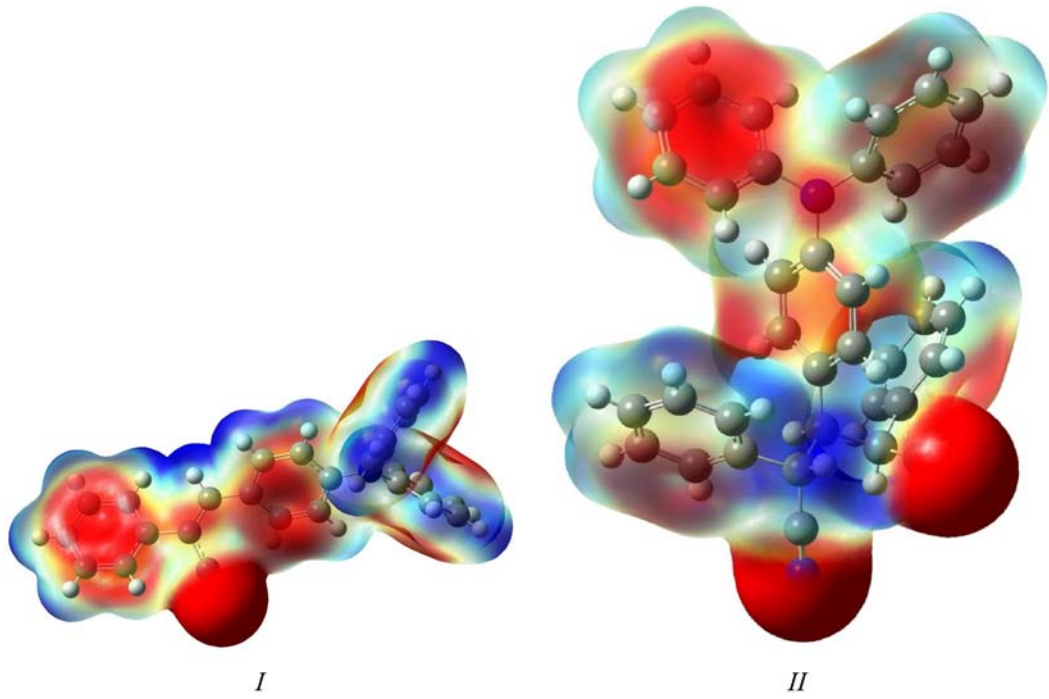


**Fig. 11.** Total electronic density distribution was mapped onto the electrostatic potential surface throughout compounds *I* and *II* calculated at B3LYP/6-31+G(d) level. Red regions indicate negative charge and blue regions indicate positive charge. Yellow regions correspond to an intermediate value between extremes of red and blue.

fined by C(6)—C(1)—N(1), C(2)—C(1)—N(1), C(12)—C(7)—N(1) and C(8)—C(7)—N(1) were related to the amine geometry and were all perfectly planar, indicating that the nitrogen atoms are of $sp^2$ hybridisation. The ring systems were non-co-planar. The dihedral angles between the planes of three substituted groups attached to the atoms of N1 are C(12)—C(7)—N(1)—C(13) = 41.1(3)°, C(8)—C(7)—N(1)—C(1) = 21.9(4)°, C(6)—C(1)—N(1)—C(13) = 147.2(2)° and C(2)—C(1)—N(1)—C(13) = 32.4(4)°. Accordingly, such arrangements have little steric crowding. All bond lengths in the compound are within the normal range. In the cell projection along the *c* axis, the connected molecular units of *I* are located along the border and for units *II* at the centre. The two molecular units differed substantially in their packing.

### *Theoretical calculations*

On the other hand, theoretical calculations of the

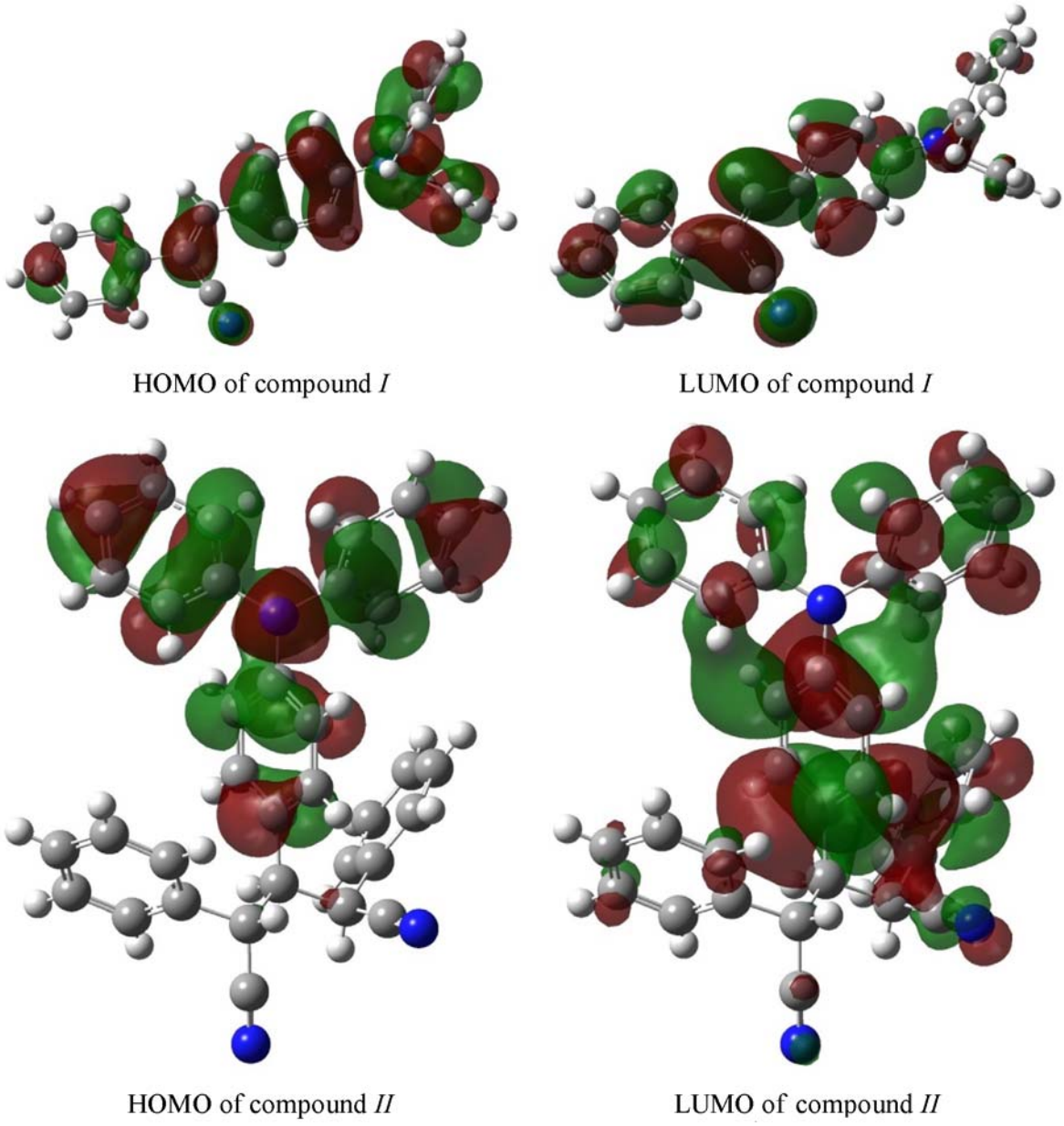


**Fig. 12.** Isosurfaces of frontier molecular orbitals HOMO and LUMO of compounds *I* and *II* calculated at B3LYP/6-31+G(d) level. Red regions correspond to regions of high electron density.

fully optimised compounds *I* and *II* were carried out using the B3LYP hybrid functional (Becke, 1993) with 6-31+G(d) basis set (Ditchfield et al., 1971) in the Gaussian 09 package (Frisch et al., 2009). For modelling, the initial designs of the molecules were obtained from X-ray coordinate data and transformed using the Mercury program (The Cambridge Crystallographic Data Centre, 2012) into the Gaussian *Z*-matrix format. Fig. 10 shows that the optimised geometries (shown in blue) for compounds *I* and *II* did not differ significantly from the X-ray structures (shown in red).

It was observed that, for compound *I*, the maximum variation was located on the part of the phenyl ring and the acrylonitrile linkage. The variation calculated for the torsion of the phenyl ring in respect of the acrylonitrile moiety was 7.4° with regard to the X-ray data. The dihedral angle formed by C(21)—C(20)—C(22)—C(23) was 21.51(14)° while the optimised structure of the angle was calculated as having a value of 28.87°. For compound *II*, the maximum structural variations were located in one of the phenyl rings bonded to the acrylonitrile moiety at the chiral carbon C(20) and in one of the phenyl rings of the diphenylaminophenyl group. These variations are best evaluated by the dihedral values of C(16)—C(19)—C(20)—C(22) of 55.8(3)° and 56.36° and for C(12)—C(7)—N(1)—C(13), 41.1(3)° and 43.96° for the X-ray and the optimised structures, respectively. Hence, the results of the structural analysis of the theoretical cal-

culations on these compounds were consistent with those observed in the crystal diffraction analysis.

The total electron density distribution was mapped onto the electrostatic potential surface through the whole molecules (isoval = 0.003) in Fig. 11. In compound *I*, the distribution of the electron density indicated a charge distribution delocalised for the $\pi$-electrons throughout the phenyl rings and the central bond substituted with the cyano group. A high electron density on the cyano group was clearly observed. The continuous distribution throughout the molecule is lost in the N-atom of the diphenylamine moiety due to a twist of the phenyl rings. A similar delocalised distribution was observed in previous studies, even though the structure was not completely planar (Improta & Santoro, 2005; Mabrouk et al., 2010; Lin et al., 2010). In stilbene-like compounds, a range of 0–60° for the torsion angle of the phenyl rings in the photoisomerisation process was evaluated (Mabrouk et al., 2010). The dihedral angles of the ethylenic bridge of the *trans* isomers were closer to planarity than the *cis* isomers. In benzothiazole derivatives, non-planar structures were found with dihedral angles with significant twists between the bonds linking aromatic rings, with the average angles being circa 37° and 47° (Mabrouk et al., 2010). In naphthylacrylonitrile derivatives, the electronic resonances were evaluated according to the electronic nature of the amino group (Lin et al., 2010). In these compounds, the phenyl rings are twisted out of the plane with dihedral angles of 30° and 55°.

Fig. 12 shows the isosurfaces of the frontier molecular orbitals HOMO and LUMO for both molecules. For compound *I*, the orbital HOMO was localised over the entire molecule while the orbital LUMO was not localised on the phenyl rings of the diphenylamine group, but only on the N-atom. On the other hand, for compound *II*, the distribution of the electron density did not show the distribution delocalised as for compound *I*. This outcome was expected due to the change in the $sp^2$ to $sp^3$ configuration of C(3) accepting another phenylacetonitrile for the formation of 2,4-diphenylpentanedinitrile. Fig. 12 shows the regions with high electronic density (in red) for the cyano group, phenyl rings and the N-atom of the diphenylamine group. The isosurfaces of the orbitals HOMO and LUMO show that the distributions for both orbitals are localised mainly in the diphenylamine group and the phenyl ring attached to it. In the case of orbital LUMO, its distribution is extended to the phenylacetonitrile substituted in the $\alpha$ position.

## Conclusions

It has been shown that, under piperidine conditions, the condensation reaction of 4-diphenylaminophenylacetonitrile with phenylacetonitrile under conventional heating afforded 3-(4-diphenylamino)phenyl)-2,4-diphenylpentanedinitrile (*II*), resulting from the Michael addition of phenylacetonitrile to the expected $\alpha,\beta$-unsaturated nitrile. The reaction conducted at ambient temperature using neat powdered KOH afforded 2-(phenyl)-3-(4-diphenylaminophenyl) acrylonitrile (*I*) with a yield of almost 100 %. This outcome is an indication that the reaction depends on the strong base used to avoid side reactions such as the Michael addition or the Baylis–Hillman reaction.

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## Supplementary data

The crystallographic data (excluding structure factors) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 920122 CCDC and no. 920123 CCDC. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road. Cambridge CB2 IEZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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