A Simple new route of the reaction of 2-dicyanomethyleneindane-1,3-dione with morpholine, piperidine and pyrrolidine. Structural confirmation based on x-ray crystallography

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Abstract: Reaction 2-(dicyanomethyleneindane)-1,3-dione with some cyclic secondary amines are reported herein. The reaction of 2- (dicyanomethyleneindane)-1,3-dione with morpholine and piperidine in acetone yielded 2-(di-morpholinomethylene)-1H-indene-1,3(2H)-dione and 2-(di(piperidin-1-yl)methylene)-1H-indene-1,3(2H)-dione. It also reacted with molar ratio of pyrrolidine in acetone to yield 2-(1,3-dioxo-1H-inden-2(3H)-ylidene)-2-(pyrrolidin-1-yl)acetonitrile and with two moles yielded beside above product the compound 1-acetyl-4-(pyrrolidin-1-yl)-5H-indeno[1,2 c]pyridin-5-one. The 1:2 adduct 2-(di(pyrrolidin-1-yl) methylene)-1H-indene-1,3(2H)-dione and cyclic product formed from addition excess of pyrrolidine in acetone. On the other hand, the reaction of two moles of pyrrolidine with the same dione in 2-butanone gave 2-(1,3-dioxo-1H-inden-2(3H)-ylidene)-2-(pyrrolidin-1-yl)acetonitrile and 1-propionyl-4-(pyrrolidin-1-yl)-5H-indeno[1,2 c]pyridin-5-one.

Keywords: 2-dicyanomethyleneindane-1,3-dione, morpholine, piperidine, pyrrolidine, Structural confirmation, x-ray crystallography.

Introduction

Recently, It has been found that the reaction of 2-(dicyanomethyleneindane)-1,3-dione (1) as an selected π-acceptor with 1,8-diaminonaphthaline (2) to form 2-(1H,3H)perimidin-2-ylidaneindane)-1,3-dione (3) which aiming to produce some heterocyclic compounds which might have biological and/or pharmaceutical applications (Scheme 1).
In literature, Harusawa and his co-worker reported that diethyl phosphorocyanidate (4) can be easily reacted with pyrrolidine (5) in tetrahydrofuran to give the corresponding o,ɔ-diethyl N-pyrrolidino phosphoramidate (6) in quantitative yields (Scheme 2).

The morpholine and piperidine skeleton containing species important in the synthesis of organic compounds including pharmaceuticals has selective enzyme inhibition, antimicrobial and antifungal activities. Antioxidant and hypocholesterolemic activities of 2-biphenylmorpholine derivatives have also been reported.

Experimental

Melting points were determined on an Electrothermal Digital Melting Point Apparatus and were uncorrected. Elemental analytical data were obtained at the analytical laboratory of the National Research Centre. The IR spectra were recorded in KBr disks on a Jasco Fourier Transform Infrared Spectrophotometer model FT/IR-300E. The 1H NMR spectra were recorded in deuterated chloroform (CDCl3) or in deuterated dimethylsulphoxide (DMSO-d6) on JOEL 500 AS (at 500 MHz) or on Varian Mercury VX-300 (at 300 MHz) Spectrometer using tetramethylsilane (TMS) as an internal reference. 13C NMR spectra were recorded on JOEL 500 AS (at 125 MHz) or on Varian Mercury VX-300 (at 75.46 MHz). Mass spectra (EI-MS) were determined at 70 eV on a Finnigan MAT SSQ 7000 spectrometer.

X-ray structure determination

The crystal data were measured at T = 298 K on a Kappa CCD Enraf Nonius FR 590 diffractometer. The crystal structure was solved and refined, using maXus (Bruker Nonius, Delft and MacScience, Japan). Mo-Kα radiation (λ= 0.71073 Å) and a graphite monochromator were used for data collection.

Compound 8a:

C18H20N2O4, M_r = 328.368, Monoclinic, crystallizes in space group C 2/c, a = 14.4615(6), b = 12.7573(7), c = 9.8740(4) Å, v = 1787.25 (14) Å³, z = 4, Dc = 1.220 cm⁻³, 2θ range 2.910-25.028°, absorption coefficient μ (Mo-Kα) = 0.09 nm⁻¹, F (000) = 696. The unique reflections measured 1713, of which 1077 reflections with threshold expression I > 3σ(I) were used in the structural analysis. Convergence for 104 variable parameters by least- squares refinement on F² with w = 1/ [σ²(Fo²) + 0.10000 Fo²]. The final agreement factors were R = 0.082 and wR = 0.153 with a goodness- of- fit of 2.543.

Further details of the structure determination (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, United Kingdom. Any request should be accompanied by the full literature citation and the CCDC reference numbers 1409433 (8a)

General procedure for the preparation of compounds 8a and 8b

The solution of 2-(dicyanomethyleneindane)-1,3-dione (1) (0.62 g, 3 mmol) in acetone (20 mL) was
stirred at room temperature, then cyclic amine (7) (2 mL) was added. Progress of reaction was monitored on TLC. After completion of reaction (5 h), the mixture was concentrated on rotary-evaporator under reduced pressure, to obtain the yellow crystals, which filtered off and crystallized from chloroform-n-hexane to give 8 (0.32 g). The filtrate was evaporated and the residue was chromatographed on silica gel, using petroleum ether (b.p. 60-80 °C) containing increasing amounts of acetone to give an additional amount of 8.

2-(Dimorpholinomethylene)-1H-indene-1,3(2H)-dione (8a)

Eluent: petroleum ether (60-80 °C) / acetone (60/40, v/v). Yellow crystals (0.66 g, 67% yield), mp 273-275 °C; Anal. Calcd for C₁₇H₁₅N₂O₄: C, 65.84; H, 6.14; N, 8.53; O, 19.49. Found: C, 65.81; H, 6.17; N, 8.50; O, 19.52%. ¹H NMR (300 MHz, DMSO): δ = 3.49 (m, 8H, 2 -CH₂NCH₂- of mopholine rings), 3.87 (m, 8H, 2-CH₂OCH₂- of mopholine rings); 7.49-7.64 (m, 4H, ArH) ppm; ¹³C NMR: δ = 50.9 (C2, C6 of mopholine rings), 66.1 (C3, C5 of of mopholine rings), 96.7, 139.8 and 163.1 (quaternary carbons), 120.1, 132.2 (CH aromatic), 189.2 (C=O) ppm; IR (KBr): ν = 1663 (C=O) cm⁻¹. MS (70 eV): m/z = 328 ( M⁺, 100%), 283 (12), 243 (31), 214 (37), 198 (23), 186 (54), 172 (35), 158 (35), 144 (17), 102 (32), 85 (37).

2-(di(piperidin-1-yl)methylene)-1H-indene-1,3(2H)-dione (8b)

Eluent: petroleum ether (60-80 °C) / acetone (80/20, v/v) gave yellow crystalline product (0.72 g, 74%) 8b. M.p.: 121-123°C; Anal. Calcd for C₂₀H₂₁N₂O₂: C, 74.04; H, 7.46; N, 8.64; O, 9.86. Found: C, 74.07; H, 7.48; N, 8.60; O, 9.89%; ¹H NMR (300 MHz, DMSO): δ = 1.72 (m, 12H, 2 CH₂ at 4 position and 2 CH₂ at 3, 5 positions of piperidine rings), 3.43 (m, 8H, 4 CH₂ at 2, 6 positions of piperidine rings), 7.28 – 7.60 (m, 4ArH) ppm; ¹³C NMR: δ = 24.4 (C4 of piperidine rings), 51.7, 52.1 (C2, C6 of piperidine rings), 97.7, 139.9 and 164.3 (quaternary carbons), 120.1, 132.2 (CH aromatic), 189.0 (C=O) ppm; IR (KBr): ν = 1663 (C=O) cm⁻¹. MS (70 eV): m/z = 324 ( M⁺, 100%), 307 (3), 267 (5), 241 (98), 226 (10), 213 (28), 198 (32), 186 (52), 172 (15), 158 (15), 144 (13), 130 (8), 115 (8), 102 (12), 96 (9), 84 (66), 69 (12), 55 (15).

2-(1,3-Dioxo-1H-inden-2(3H)-ylidene)-2-(pyrrolidin-1-yl)acetonitrile (9)

To a stirred solution of 1 (0.62 g, 3 mmol) in acetone (20 mL), the pyrrolidine (5) (3 mmol) in acetone (10 mL) was added dropwise during 15 min at room temperature. The mixture continues stirred for about 2 h, and then the solvent was concentrated on rotary-evaporator under reduced pressure till dryness. The residue was purified by column chromatography on silica gel using n-hexane and ethyl acetate as eluent. From (30% ethyl acetate) gave yellow crystals recrystallized from ethyl acetate-petroleum ether (b.p. 60-80 °C) to give (0.45 g, 60%) 9, m.p. 188-190°C; Anal. Calcd for C₁₈H₁₅N₂O₄: C, 71.42; H, 4.79; N, 11.10; O, 12.68. Found: C, 71.45; H, 4.75; N, 11.08; O, 12.73%; ¹H NMR (300 MHz, CDCl₃): δ = 2.07-2.14 (m, 4H, 2 CH₂ at 3, 4 position of pyrrolidine ring); 3.99-4.03 (m, 4H, 2 CH₂ at 2, 5 positions of pyrrolidine ring); 7.62 – 7.75 (m, 4ArH) ppm; ¹³C NMR (CDCl₃): δ = 24.8, 26.4 (C3, C4 of pyrrolidine ring), 54.56, 57.29 (C2, C5 of pyrrolidine ring), 97.7, 120.0, 122.10, 132.2, 133.99 and 139.90, 164.3 and 189.1 (C=O) ppm. IR (KBr): ν = 2201 (CN), 1667 (C=O) cm⁻¹; MS (70 eV): m/z = 252 ( M⁺, 100%), 235 (8), 224 (18), 207 (5), 197 (20), 184 (17), 169 (11), 146 (10), 127 (25), 114 (8), 104 (14), 76 (18), 69 (25), 51 (8).

1-Acetyl-4-(pyrrolidin-1-yl)-5H-indeno[1,2-c]pyridin-5-one (10)

To a stirred solution of 1 (0.62 g, 3 mmol) in acetone (20 mL), the pyrrolidine (5) (6 mmol) in acetone (15 mL) was added dropwise during 15 min at room temperature. After 10 min the red crystals began to appear and the mixture continues stirred for about 1 h. The solid was collected and recrystallized from acetonitrile to give (0.60 g, 67% yield) 10. M.p.: 248-250 °C; Anal. Calcd for C₁₈H₁₂N₂O₅: C, 73.95; H, 5.52; N, 9.58; O, 10.95. Found: C, 73.91; H, 5.55; N, 9.54; O, 10.98%; ¹H NMR (300 MHz, DMSO): δ = 2.02-2.09 (m, 4H, 2 CH₂ at 3, 4 position of pyrrolidine ring), 2.67 (s, 3H, COMe), 3.68 – 3.81 (2 m, 4H, 2 CH₂ at 2, 5 positions of pyrrolidine ring); 7.55 – 7.73 (m, 4ArH), 7.96 (s, 1H, =CH-) ppm; ¹³C NMR (DMSO): 24.1, 26.1, 28.9, 50.8, 98.7, 119.1, 120.0, 124.0, 126.4, 128.9, 131.1, 136.9, 139.3, 146.0, 158.1, 187.1, 197.8. IR (KBr): ν = 1682, (C=O) cm⁻¹; MS (70 eV): m/z = 292 ( M⁺, 25%), 274 (100), 252 (15), 222 (8), 218 (20), 190 (10), 176 (14), 159(8), 147 (47), 118 (7), 104 (28), 90 (10), 85 (17), 76 (16). The filtrate was evaporated and the residue was chromatographed on silica gel, using petroleum ether (b.p. 60-80 °C) containing increasing amounts of ethyl acetate. The first fraction (20% ethyl acetate) gave the compound 9 (10% yield). The second fraction (40% ethyl acetate) afforded an additional amount of 10 (10%), total yield (77%).
2-(di(pyrrolidin-1-yl)methylene)-1H-indene-1,3(2H)-dione (11)

Repetition the above reaction between 1 (0.62 g, 3 mmol) and 5 (10 mmol) in acetone (40 mL) at room temperature gave the compounds 10 and 11 after about 3 h. The solvent was evaporated under reduced pressure and the residue was separated on column chromatography on silica gel using petroleum ether (60-80°C)/ethyl acetate as eluent. The first fraction (40% ethyl acetate) gave red crystals of 10 (15% yields). The second fraction petroleum ether (60-80°C)/ethyl acetate (40/60, v/v) gave yellow crystalline product of 2-(di(pyrrolidin-1-yl)methylene)-1H-indene-1,3(2H)-dione (11) (0.44 g, 50% yield) as yellow crystals, m.p. 185-187°C. Anal. Calcd for: C19H20N2O2; C, 72.95; H, 6.80; N, 9.45; O, 10.80. Found: C, 72.91; H, 6.84; N, 9.42; O, 10.84%. 1H NMR (300 MHz, DMSO): δ = 1.91, 3.53 ppm (2m, 16H, pyrrolidine rings), 7.34-7.47 (m, 4H, ArH) ppm; 13C NMR: δ = 24.2, 26.1, 50.8, 98.7, 119.1, 131.1, 139.3, 158.0 and 187.1 (C=O) ppm; IR (KBr): ν = 1620 (C=O) cm⁻¹; MS (70 eV): m/z = 296 (M⁺, 100%), 252 (22), 226 (25), 199 (13), 171 (15), 154 (9), 104 (10), 70 (34).

1-propionyl-4-(pyrrolidin-1-yl)-5H-indeno[1,2-c]pyridin-5-one (12)

To a stirred solution of 1 (0.62 g, 3 mmol) in 2-butanone (20 mL), the pyrrolidine (5) (6 mmol) in 2-butanone (15 mL) was added dropwise during 15 min at room temperature. After 10 min the solution becomes red and the mixture continues stirred for about 2 h. The solvent was evaporated under reduced pressure and the residue was separated on column chromatography using n-hexane/ethyl acetate as eluent. The first fraction (30% ethyl acetate) gave yellow crystals of 11 (0.12 g, 80% yield), mp 210-212°C; Anal. Calcd for: C19H20N2O2; C, 72.95; H, 6.80; N, 9.45; O, 10.80. Found: C, 72.91; H, 6.84; N, 9.42; O, 10.84%. 1H NMR (300 MHz, DMSO): δ = 1.41, 1.83 ppm (2m, 10H, 4H of pyrrolidine ring and 6H of piperidine ring), 2.29 (m, 4H, -CH₂NCH₂- of pyrrolidine ring), 3.55 (m, 4H, -CH₂NCH₂- of piperidine ring); 7.31-7.41 (m, 4 ArH) ppm; IR (KBr): ν = 1649 (C=O) cm⁻¹; MS (70 eV): m/z = 310 (M⁺, 100%), 296 (12), 281 (12), 237 (85), 195 (10), 181 (45), 154 (17), 127 (25), 77 (15).

General Procedure to prepare 13a and 13b

To a stirred solution of 1 (0.62 g, 3 mmol) in 2-butanone (20 mL), the pyrrolidine (5) (6 mmol) in 2-butanone (15 mL) was added dropwise during 15 min at room temperature. After 10 min the solution becomes red and the mixture continues stirred for about 2 h. The solvent was evaporated under reduced pressure and the residue was separated on column chromatography using n-hexane/ethyl acetate as eluent. The first fraction (30% ethyl acetate) gave yellow crystals of 11 (0.12 g, 80% yield), mp 210-212°C; Anal. Calcd for: C19H20N2O2; C, 72.95; H, 6.80; N, 9.45; O, 10.80. Found: C, 72.91; H, 6.84; N, 9.42; O, 10.84%. 1H NMR (300 MHz, DMSO): δ = 1.41, 1.83 ppm (2m, 10H, 4H of pyrrolidine ring and 6H of piperidine ring), 2.29 (m, 4H, -CH₂NCH₂- of pyrrolidine ring), 3.55 (m, 4H, -CH₂NCH₂- of piperidine ring); 7.31-7.41 (m, 4 ArH) ppm; IR (KBr): ν = 1649 (C=O) cm⁻¹; MS (70 eV): m/z = 310 (M⁺, 100%), 296 (12), 281 (12), 237 (85), 195 (10), 181 (45), 154 (17), 127 (25), 77 (15).

2-(piperidin-1-yl)(pyrrolidin-1-yl)methylene)-1H-indene-1,3(2H)-dione (13a)

Yellow crystals (0.11 g, 73% yield), mp 223-225°C; Anal. Calcd for: C19H20N2O2; C, 72.95; H, 6.80; N, 9.45; O, 10.80. Found: C, 72.91; H, 6.84; N, 9.42; O, 10.84%. 1H NMR (300 MHz, DMSO): δ = 2.00, 3.99 ppm (2m, 8H, pyrrolidine ring), 3.29, 3.73 (2m, 8H, morpholine ring), 7.46-7.55 (m, 4H, ArH) ppm; IR (KBr): ν = 1668 (C=O) cm⁻¹; MS (70 eV): m/z = 312 (M⁺, 27%), 242 (25), 196 (100), 170 (61), 140 (42), 114 (23), 70 (15).

2-(piperidin-1-yl)(pyrrolidin-1-yl)methylene)-1H-indene-1,3(2H)-dione (13b)

Yellow crystals (0.12 g, 80% yield), mp 210-212°C; Anal. Calcd for: C19H20N2O2; C, 73.52; H, 7.14; N, 9.03; O, 10.31. Found: C, 73.56; H, 7.10; N, 9.07; O, 10.34%. 1H NMR (300 MHz, DMSO): δ = 1.41, 1.83 ppm (2m, 10H, 4H of pyrrolidine ring and 6H of piperidine ring), 2.29 (m, 4H, -CH₂NCH₂- of pyrrolidine ring), 3.55 (m, 4H, -CH₂NCH₂- of piperidine ring); 7.31-7.41 (m, 4 ArH) ppm; IR (KBr): ν = 1649 (C=O) cm⁻¹; MS (70 eV): m/z = 310 (M⁺, 100%), 296 (12), 281 (12), 237 (85), 195 (10), 181 (45), 154 (17), 127 (25), 77 (15).
Results and Discussion

The reaction of 2-(dicyanomethyleneindane)-1,3-dione (1) was readily added N-nucleophiles of cyclic secondary aliphatic amines such as morpholine, piperidine and pyrrolidine at dicyanomethylene carbon atom with release of hydrogen cyanide. The reaction of indanetrione 1 with two molar ratio of morpholine (7a) in dry acetone at room temperature gave the corresponding product 2-(dimorpholinomethylene)-1H-indene-1,3(2H)-dione (8a) (Scheme 3) as yellow crystalline substance in 67% yields. The structure of 8a was deduced from their spectroscopic measurements. The $^1$H NMR spectrum shows signals of methylene protons of morpholine rings as two triplets at $\delta = 3.49, 3.87$ ppm with coupling constant $= 7.2$ Hz (2 – CH$_2$NCH$_2$ –, 2 – CH$_2$OCH$_2$ –, respectively). Also, the signals of aromatic protons were appeared as a multiblets in the region 7.49-7.64 ppm. The $^{13}$C NMR spectrum of compound 8a displayed the carbon atoms of morpholine rings at $\delta = 50.9$ and 66.1 ppm, respectively. Furthermore, it also shows quaternary carbons at $\delta = 96.7$, 139.8 and 163.1 with CH aromatic 120.3 and 132.5 189.2 ppm. The mass spectrum of 8a recorded a highest ion peak at $m/z$ 328 (M$^+$) (Scheme 3). Moreover, a single crystal x-ray diffraction analysis of 8a (Fig. 1) confirms the established configuration.
In a similar manner, indanedione 1 reacted with 2 mole equivalents of piperidine in acetone at room temperature to give the corresponding yellow crystalline product of 2-(di(pyrrolidin-1-yl)methylene)-1H-indene-1,3(2H)-dione (8b). Correct elementary and molecular weight determination for 8b corresponded to C_{20}H_{24}N_{2}O_{2}, MS: m/z = 324 (M^+, 100%). The $^1$H NMR spectrum of 8b (CDCl$_3$, $\delta$ ppm) showed signals at $\delta$ = 1.72 (m, 12H, 2 CH$_2$ at 4 position and 4 CH$_2$ at 3,5 positions of piperidine rings); 3.43 (m, 8H, 4 CH$_2$ at 2, 6 positions of piperidine rings); 7.28 – 7.60 (m, 4ArH) ppm. $^{13}$C NMR: $\delta$ = 24.38 (C4 of piperidine rings), 25.47 (C3, C5 of piperidine rings), 51.70, 52.11 (C2, C6 of piperidine rings), 97.69, 139.94 and 164.27 (quaternary carbons), 120.10, 132.20 (CH aromatic), 189.03 (C=O) ppm.

Upon treatment of compound 1 with a molar ratio of pyrrolidine 5, under the reaction conditions mentioned before, the reaction afforded a yellow crystals of 2-(1,3-dioxo-1H-inden-2(3H)-ylidene)-2-(pyrrolidin-1-yl)acetonitrile (9) in 60% yield (Scheme 4). The structural proof of 9 was based upon the mass, $^1$H NMR, $^{13}$C NMR and IR spectra as well as elemental analysis. The gross formula C$_{18}$H$_{16}$N$_2$O$_2$ is confirmed by its mass spectrum (M$^+$ at m/z 252, 100%). The IR spectrum of 9 revealed absorption bands at $\nu$ = 2201 (CN), 1667 (CO) cm$^{-1}$. Another point of concern is the fact that in 9 pyrrolidine ring is attached to the isindole skeleton with release of one molecule of HCN and the $^1$H NMR spectrum is in accordance with the suggested structure which is showed two multiplets (8H) at $\delta$ = 2.07, 3.99 ppm for 4 CH$_2$ of pyrrolidine ring. The $^{13}$C NMR spectrum of 9 showed four signals at $\delta$ = 24.8, 26.36 (C3, C4 of pyrrolidine ring), 54.56, 57.29 (C2, C5 of pyrrolidine ring), 108.38, 111.93, 131.55 and 139.90 (quaternary carbons), 122.10, 133.99 (CH aromatic), 188.11 (C=O) ppm.

Surprisingly, the reaction of 1 with two molar ratios of 5 at the same experimental conditions afforded beside the 1:1 adduct 9 (15% yield), the cyclic 1-acetyl-4-(pyrrolidin-1-yl)-5H-indeno[1,2-c]pyridin-5-one (10) in 67% yield (Scheme 4). The latter cyclic compound 10 was formed by the condensation reaction of acetone and 9 with elimination of a molecule of water and molecular rearrangement in presence of pyrrolidine as a strong base than morpholine and piperidine. The molecular formula of 10 was elucidated by mass spectroscopy and correct elemental values as C$_{18}$H$_{16}$N$_{2}$O$_{2}$. The $^1$H NMR spectrum of 10 is in accordance with the suggested structure which showed three multiplets (8H) at $\delta$ = 2.02 (4H), 3.68 (2H) and 3.81(2H) for pyrrolidine ring and also gave two singlets at 2.67 (COCH$_3$) and 7.96 (=CH) ppm. When the same reaction was carried out using excess of pyrrolidine (5) at room temperature, the 1:2 adduct 2-(di(pyrrolidin-1-yl)methylene)-1H-indene-1,3(2H)-dione (11) as yellow crystals was obtained along with compound 10. The structure of compound 11 was elucidated by correct elemental analyses, molecular weight determination (MS) and compatible spectroscopic results. Its $^1$H NMR revealed the presence of two multiplats at $\delta$ = 1.85 and 1.92 and a triplet at 3.53 ppm with coupling constant 6.6 Hz attributed to 16 H of pyrrolidine rings. The multiplet in the region $\delta$ = 7.34-7.46 ppm corresponds to aromatic protons. Moreover, the $^{13}$C NMR spectrum of 11 showed three signals at $\delta$ = 24.2, 26.1 and 50.8 ppm attributable to the carbon atoms of pyrrolidine rings.

Repetition the same reaction of 1 with two molar ratios of pyrrolidine (5) in 2-butane at room temperature for 2 h followed by column chromatography led to the formation of 1:1 adduct 9 (30%) with cyclic product 12 (40%). The identity of compound 12 was supported by correct elemental analyses and molecular weight determinations (MS) as well as the IR and $^1$H NMR spectra which were compatible with the assigned structure. The IR spectra of 12 disclosed the presence of strong absorption band at 1720 cm$^{-1}$ due to the carbonyl group (COE). Moreover, the $^1$H NMR spectrum of 12 showed a triplet at $\delta$ = 0.87 (J$_{HH}$= 7.0 Hz, 3H, -CH$_3$CH$_3$) ppm and two multiplets at $\delta$ = 1.40 and 3.70 attributable to 8H of pyrrolidine ring. The methylene protons of ethyl group appear as a quartet at $\delta$ = 4.15 ppm (J$_{HH}$ = 7.0 Hz),. The multiplet in the region $\delta$ = 7.47 – 7.70 ppm corresponds to 4 aromatic protons.

The reaction of 1 with excess of 5 in 2- butanone at room temperature afforded the compounds 9 (20%), 11 (50%) and 12 (10%). The mixture was separated on column chromatography on silica gel using ethyl acetate and petroleum ether b.p. 60-80°C as eluent.
On the other hand, the reaction of compound 9 with morpholine (7a) and piperidine (7b) in acetone at room temperature afforded yellow crystalline products 13 in which the cyanide group was replaced by morpholinyl or piperidinyl group (Scheme 5). The structure of 13a as an example was formulated for the following reasons: a) Its microanalyses and its molecular weight determination corresponded to C_{19}H_{20}N_{2}O_3; MS: m/z 312 (M^+, 27%). b) Its IR spectrum showed the absence of cyanide band at 2201 cm\(^{-1}\). c) The \(^1\)H NMR spectrum of 13a (DMSO, \(\delta\) ppm) disclosed the presence of pyrrolidine protons as two multiplies at 2.00 and 3.99 ppm, while the protons of morpholine ring occurred as two multiplies at 3.29 and 3.73 ppm. The phenyl protons resonated in the range 7.46–7.55 ppm.

These conclusion let us to produce from the reaction of 2-(dicyanomethylene indane)-1,3 -dione (1) with morpholine and piperidine (7) in acetone at room temperature gave the 1:2 adducts 8. The reaction of 1 with different molar ratio of pyrrolidine (5) in acetone or 2-butanone was studied. The 1:1 adduct 9 formed from reaction of 1 with molar ratio of 5 and it also produced beside cyclic product 10 and 12 when we add two molar ratios in acetone or 2-butanone, respectively. The addition of excess of pyrrolidine (5) to 1 in acetone afforded beside 10 the product 11 and in 2-butanone yielded compounds 9, 11 and 12. The replacement of cyano group in compound 9 with morpholine and piperidine in acetone led to the formation of 13. These compounds were separated by column chromatography on silica gel and identified by spectroscopic tools.

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