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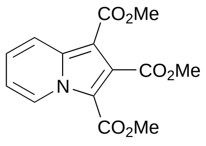
Reaction between 1,10-Phenanthroline and Dialkyl Acetylenedicarboxylates. A Facile Synthetic Route to Helical Dipyrrolophenanthrolines†

Issa Yavari,* Malek Taher Maghsoodlou and Ali Pourmossavi

Chemistry Department, Tarbiat Modarres University, P.O. Box 14155-4838, Tehran, Iran

1,10-Phenanthroline and its 5-substituted derivatives react with dialkyl acetylenedicarboxylates to give dipyrrolo[1,2-*a*:2′,1′-*k*][1,10]phenanthroline derivatives, which exhibit nonplanarity enforced by the crowding of the ester groups.

Many diverse products can be prepared from the addition of acetylenic esters to nitrogen-containing heterocycles.[1] An example is the interesting reaction between pyridine and dimethyl acetylenedicarboxylate in methanol, in which the indolizine-1,2,3-tricarboxylate (**1**) is isolated.[2–5] However, there appears to be no report of a reaction product formed from 1,10-phenanthroline (**2a**)[6] and acetylenic esters. We have found that 1,10-phenanthrolines **2a–d** undergo reaction with dialkyl acetylenedicarboxylates **3a**,**b** to give hitherto unknown dipyrrolo[1,2-*a*:2′,1′-*k*][1,10]phenanthroline derivatives **4a–e** in moderate yields.



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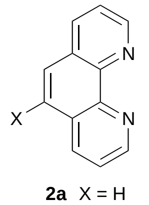
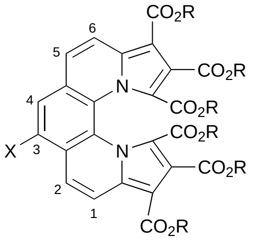


2a X = H
b X = Me
c X = Cl
d X = NO$_2$

$RO_2C{-}C{\equiv}C{-}CO_2R$

3a R = Me
b R = Et



4a X = H, R = Me
b X = H, R = Et
c X = Me, R = Me
d X = Cl, R = Me
e X = NO$_2$, R = Me

The essential structures of compounds **4a–e** were deduced from their elemental analyses and their ^{1}H and ^{13}C NMR spectra as well as from the IR spectra which exhibited strong C═O signals. The mass spectra of these compounds displayed molecular ion peaks at *m*/*z* 604, 688, 618, 638 and 649 for **4a–e**, respectively. Initial fragmentations involve loss of the side chains.

The ^{1}H NMR spectrum of **4a** exhibited three single sharp lines at δ 3.37, 3.99 and 4.03, readily recognizable as arising from methoxy protons, along with two superimposed AB systems and an A_2 system for the 1,10-phenanthroline residue in **4a**. The ^{13}C NMR spectrum of **4a** displayed three signals for the methoxy (δ 51.48, 51.95 and 52.78) groups, along with nine signals for the dipyrrolophenanthroline nucleus. The chemical shifts of the ester carbonyl groups at δ 158.16, 163.64 and 166.26 are consistent with the symmetrical structure of **4a**.

The ^{1}H NMR spectrum of compound **4b** is analogous to that obtained for **4a**, except for the ester groups which exhibited three ABX_3 systems (see Table 1) as a result of nonplanarity enforced by the crowding of the ester groups.[7]

Table 1 ^{1}H and ^{13}C NMR data for compounds **4a–e**

Compound	^{1}H/^{13}C	δ (ppm) ($CDCl_3$–Me_4Si)
4a	^{1}H	3.37, 3.99 and 4.03(18 H, 3 s, 6 OCH$_3$), 8.06 (2 H, d, *J* 9.2 Hz, C2-H and C5-H), 8.10 (2 H, s, C3-H and C4-H), 8.66 (2 H, d, *J* 9.2 Hz, C1-H and C6-H)
	^{13}C	51.48, 51.95 and 52.78 (6 OCH$_3$), 106.44 (2 C), 118.14 (2 CH), 120.07 and 124.82 (4 C), 126.58 (2 CH), 126.92 (2 C), 127.56 (2 CH), 131.08 and 137.62 (4 C), 158.16, 163.64 and 166.26 (6 C═O)
4b	^{1}H	1.166 (6 H, t, *J* 7.2 Hz, 2 CH$_3$), 1.440 (6 H, t, *J* 7.2 Hz, 2 CH$_3$), 1.474 (6 H, *J* 7.2 Hz, 2 CH$_3$), 3.73 and 3.79 (4 H, q of AB system, J_{AB} −10.8, *J* 7.2 Hz, 2 CH$_2$), 4.434 and 4.468 (4 H, q of AB system, J_{AB} −10.8, *J* 7.2 Hz, 2 CH$_2$), 4.441 and 4.480 (4 H, q of AB system, J_{AB} −10.7, *J* 7.2 Hz, CH$_2$), 8.040 (2 H, d, *J* 9.2 Hz, C2-H and C5-H), 8.070 (2 H, s, C3-H and C4-H), 8.67 (2 H, d, *J* 9.2 Hz, C1-H and C6-H)
	^{13}C	13.80, 14.23 and 14.42 (6 CH$_3$), 60.67, 60.70 and 61.62 (6 CH$_2$), 107.76 (2 C), 118.02 (2 CH), 120.58 and 125.45 (4 C), 126.56 and 127.08 (4 CH), 127.52, 131.25 and 138.12 (6 C), 157.65, 164.10 and 166.06 (6 C═O)
4c	^{1}H	2.95 (3 H, s, CH$_3$), 3.35, 3.38, 3.98, 4.00, 4.04 and 4.05 (18 H, 6 s, 6 OCH$_3$), 7.94 (1 H, s, C4-H), 8.02 and 8.62 (2 H, AB system, *J* 9.0 Hz, CHCH), 8.24 and 8.68 (2 H, AB system, *J* 9.2 Hz, CHCH)
	^{13}C	19.46 (CH$_3$), 51.35, 51.40, 51.98, 52.00, 52.65 and 52.70 (6 OCH$_3$), 106.50, 106.57, 117.56, 118.09, 119.35, 121.59, 123.18, 123.79, 124.65, 126.19, 126.64, 127.05, 130.07, 130.39, 132.95, 136.82, 136.93, and 138.33 (18 C), 157.43, 157.45, 163.45, 163.48, 165.77 and 165.82 (6 C═O)
4d	^{1}H	3.36, 3.38, 4.00, 4.03, 4.06 and 4.07 (18 H, 6 s, 6 OCH$_3$), 7.97 and 8.67 (2 H, AB system, *J* 9 Hz, C1-H and C2-H), 8.20 (1 H, s, C4-H), 8.52 and 8.73 (2 H, AB system, *J* 9.2 Hz, C5-H and C6-H)
	^{13}C	51.46, 51.50, 52.02, 52.10, 52.65 and 52.70 (6 OCH$_3$), 107.01, 107.18, 118.62, 118.86, 119.39, 119.56, 123.14, 123.75, 124.93, 125.20, 125.28, 126.19, 125.56, 129.41, 130.43, 130.84, 136.75 and 136.86 (18 C), 157.35, 157.45, 163.16, 163.22, 165.49 and 165.62 (6 C═O)
4e	^{1}H	3.36, 3.39, 4.00, 4.02, 4.05, and 4.06 (18 H, 6 s, 6 OCH$_3$), 8.15 and 8.78 (2 H, AB system, *J* 9.0 Hz, C1-H and C2-H), 8.82 (1 H, s, C4-H), 8.81 and 8.88 (2 H, AB system, *J* 9.1 Hz, C1-H and C3-H)
	^{13}C	51.46, 51.55, 52.20, 52.25, 52.74 and 52.82 (6 OCH$_3$), 107.67, 107.72, 119.72, 120.00, 120.29, 121.55, 122.49, 122.94, 124.52, 124.89, 126.45, 126.60, 130.12, 131.12, 133.49, 136.21, 137.43 and 143.13 (18 C), 157.06, 157.20, 162.76, 162.84, 164.92 and 165.00 (6 C═O).

Compounds **4c–e** are unsymmetrical and exhibit more complicated, but resolved, ^{1}H and ^{13}C spectra (see Table 1).

The structural assignments made on the basis of the NMR spectra of compounds **4a–e** were supported by measure-

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*To receive any correspondence.

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ments of their IR and UV spectra. Of special interest is the carbonyl absorption (1698–1748 cm^{-1}) for these compounds. Conjugation with the heterocyclic ring appears to be a plausible factor in the reduction of the wave numbers of the carbonyl absorption bands.[8] The electronic spectra of compounds **4a**,**b** each exhibited bands at 237–340 nm owing to the dipyrrolophenanthroline nucleus.

The reactions described herein represent a simple and efficient synthesis of functionalized dipyrrolophenanthrolines.

Experimental

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyser. IR spectra were measured on a Shimadzu IR-460 spectrometer. UV spectra were measured using solutions in ethanol (95%) on a Shimadzu UV-2100 spectrometer. ^1H and ^{13}C NMR spectra were measured with a JEOL EX-90A spectrometer at 90 and 22.6 MHz, respectively. The ^1H NMR spectrum of **4b** was recorded at 400 MHz using a Varian Unity Plus NMR spectrometer. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. 1,10-Phenanthrolines **2a–d** and dialkyl acetylenedicarboxylates **3a**,**b** were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

Typical preparation of hexamethyl dipyrrolo[1,2-a:2′,1′-k][1,10] *phenanthroline*-7,8,9,12,13,14-*hexacarboxylate (***4a***)*.—To a magnetically stirred solution of 1,10-phenanthroline (0.18 g, 1 mmol) in methanol (10 ml) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.71 g, 5 mmol) in methanol (2 ml) at room temperature and the mixture refluxed for 24 h. After 24 h in a refrigerator at 5 °C, a yellow solid (0.31 g, yield 52%, mp 205–207 °C) was collected by filtration. Recrystallization from methanol yielded **4a** as pale yellow *crystals* (0.28 g), mp 209–211 °C; ν_{max} (KBr)/cm^{-1} 1745, 1720 and 1698 (C═O); 1240 and 1174 (C—O); λ_{max}/nm (log ε) 237 (4.7), 2.8), 289 (3.1), 336 (2.2); MS (*m*/*z*, %): 604 (M^+, 2), 430 (25), 415 (56), 353 (100), 149 (45), 105 (60) (Found: C, 59.7; H, 4.1; N, 4.7. $C_{30}H_{24}N_2O_{12}$ requires C, 59.61; H, 4.00; N, 4.63%).

Selected data for **4b**.—Yellow *crystals*, 0.4 g, yield 58%, mp 183–185 °C; ν_{max} (KBr)/cm^{-1} 1748, 1741 and 1703 (C═O); 1231 and 1180 (C—O); λ_{max}/nm (log ε) 238 (4.5), 270 (2.6), 285 (3.0), 340 (2.5); MS (*m*/*z*, %): 688 (M^+, 1), 387 (10), 368 (25), 324 (22), 282 (33), 150 (42), 57 (100) (Found: C, 62.6; H, 5.3; N, 4.1. $C_{36}H_{36}N_2O_{12}$ requires C, 62.83; H, 5.27; N, 4.07%).

Selected data for **4c**.—Dark-yellow *powder*, 0.27 g, yield 44%, mp 265 (decomp.); ν_{max} (KBr)/cm^{-1} 1741, 1735 and 1699 (C═O); 1213 and 1195 (C—O); MS (*m*/*z*, %): 619 (M^+ + 1, 8), 560 (40), 516 (35), 501 (100), 470 (28), 457 (18), 267 (35) (Found: C, 59.9; H, 4.3; N, 4.7. $C_{31}H_{26}N_2O_{12}$ requires C, 60.20; H, 4.24; N, 4.53%).

Selected data for **4d**.—Pale yellow *powder*, 0.26 gm, yield 40%, mp 256 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1746, 1738 and 1700 (C═O); 1221 and 1174 (C—O); MS (*m*/*z*, %): 638 (M^+, 15), 579 (25), 535 (38), 520 (100), 489 (35), 286 (82), 149 (42), 144 (76) (Found: C, 56.4; H, 3.7; N, 4.2. $C_{30}H_{23}N_2O_{12}Cl$ requires C, 56.39; H, 3.63; N, 4.38%).

Selected data for **4e**.—Yellow *powder*, 0.21 g, yield 32%, mp 280 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1745, 1731 and 1702 (C═O); 1212 and 1168 (C—O); MS (*m*/*z*,%): 649 (M^+, 5), 590 (12), 546 (55), 531 (100), 485 (26), 310 (38), 251 (42), 149 (90) (Found: C, 55.6; H, 3.6, N, 6.5. $C_{30}H_{23}N_3O_{14}$ requires C, 55.48; H, 3.57; N, 6.47%).

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References

1 R. M. Acheson and N. F. Elmore, *Adv. Heterocycl. Chem.*, 1978, **23**, 263.
2 R. M. Acheson and J. M. Woollard, *J. Chem. Soc. C*, 1971, 3296; R. M. Acheson and G. A. Taylor, *J. Chem. Soc.*, 1960, 1691.
3 A. Crabtree, A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 1961, 3497.
4 F. J. Swinbourne, J. H. Hunt and G. Klinkert, *Adv. Heterocycl. Chem.*, 1978, **23**, 103.
5 W. Flitsh, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon, London, 1984, vol. 3, pp. 443–470.
6 L. A. Summers, *Adv. Heterocycl. Chem.*, 1977, **22**, 1.
7 E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994, pp. 1163–1166.
8 R. M. Silverstein, G. C. Bassler and T. C. Morril, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 5th edn., 1991, p. 111.