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The crystal structure, supramolecular interplay and theoretical studies of helical dipyrrolophenanthroline

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Abstract: The crystal structure of the hexamethyldipyrrolo [1, 2-a:2, 1–k][1,10] phenanthroline 7, 8, 9, 12, 13, 14-hexacarboxylate (helical) compound has been determined by single X-ray diffraction analysis, confirming the chiral and helical nature previously established by ^{1}H and ^{13}C NMR studies[6]. The compound crystallizes in the triclinic space group $P\bar{1}$ with the following unit-cell parameters: a = 7.7457 (7) Å, b = 11.7194 (7) Å, c = 15.5427 (9) Å, α= 103.315 (5)°, β= 90.583 (6)°, γ = 101.659 (6)°, Z = 2 and V = 1342.25 (16) Å3. The final R value is 0.0541 for 7821 measured reflections. In addition quantum mechanical calculation has been preferment for confirmation of some experimental data.

Keywords: Dipyrrolophenanthroline, ^{13}C NMR, X-ray diffraction, Chirality.

Introduction

In the chiral molecule described so far, helicity was due to some form of restricted rotation about a chiral axis, due to a high bond order, a rigid framework, on steric factors, combined with an appropriate substitution pattern. In this paper we consider molecules whose helicity is inherent in the molecular frame work [1]. Diverse chiral supramolecular tectons can be prepared from the addition of acetylenic esters to nitrogen-containing heterocycles [2]. Bridge-head nitrogen heterocycles have been the subject of great consideration because they constitute an important class of compounds which exhibit useful biological activity [3]. Recently, di-components condensation reactions between 1, 10-Phenanthroline and dialkyl acetylenedicarboxylates have been reported for preparation of helical dipyrrolophenanthrolines [4]. 1,10-Phenanthroline undergoes a smooth reaction with dimethyl acetylenedicarboxylate to give hexamethyldipyrrolo[1,2-a:2,1–k][1,10] phenanthroline 7,8,9,12,13,14-hexacarboxylate(helical compound) in

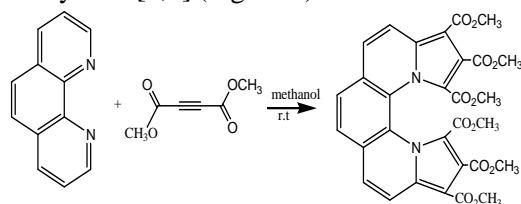moderate ylides [5,6] (Figure **1**).

Figure 1: Synthesis of hexamethyldipyrrolo[1,2-a:2,1–k][1,10] phenanthroline 7,8,9,12,13,14-hexacarboxylate.

The structure of the helical hexamethyldipyrrolo [1,2-a:2,1–k][1,10] phenanthroline 7,8,9,12,13,14-hexacarboxylate compound have been previously deduced from elemental analyses, mass, IR, ^{1}HNMR and ^{13}CNMR spectroscopies [6]. Herein we report the single X-ray diffraction studies of the compound that crystallized from mixture of CH_2Cl_2-hexane to give pale yellow crystals. We determined the torsion angle theoretically and compared it with the structural information obtained from X-ray analysis and NMR studies.

Results and discussion

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Pale yellow studies of triclinic crystal of hexamethyldipyrrolo[1,2-a:2,1–k][1,10]phenanthroline 7,8,9,12,13,14-hexacarboxylate having approximate dimensions 0.26 x 0.22 x 0.16 mm^3 was sealed in a glass capillary, and then intensity data were measured at 100 (2) K on an oxford Diffraction Xcalibur diffractometer fitted with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The structure was obtained by direct methods using SHELXS-97 [7] ,and refinement by full matrix least square on F^2 (SHELXS-97) [7]. All H-atoms were added at calculated positions and refined by using a riding model with isotropic displacement parameters based on the isotropic displacement parameters of the parent atom. Anisotropic displacement parameters were employed for all non-H atoms. The ORTEP representation of the crystal structure of hexamethyldipyrrolo [1, 2-a: 2, 1–k] [1, 10] phenanthroline 7, 8, 9, 12, 13, 14-hexacarboxylate and the molecular packing diagram of this compound are shown in Figures **2** and **3**, respectively.
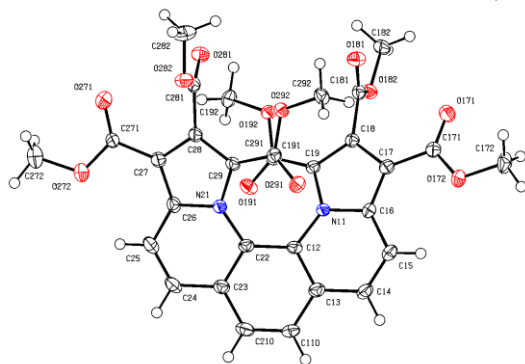

Figure 2: ORTEP representation of the structure of hexamethyldipyrrolo[1,2-a:2,1–k][1,10] phenanthroline 7,8,9,12,13,14-hexacarboxylate(helical compound).
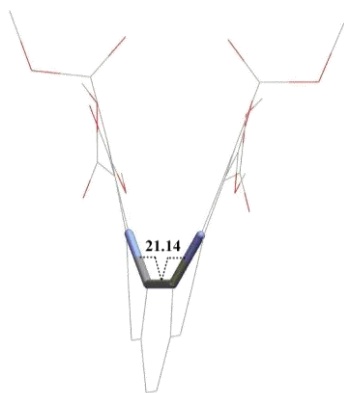

Figure 3: Asymmetric unit in the structure of hexamethyldipyrrolo [1, 2-a: 2, 1–k] [1, 10] phenanthroline 7, 8, 9, 12, 13, 14-hexacarboxylate, torsion angle derived of (-21.14°), hydrogen atoms omitted for clarity.

The chiral compound has a C$_2$ axis of symmetry, thus ^{1}H and ^{13}C NMR spectra were simple with the ester groups and carbons of the aromatic ring were not diastrotopic. The ^{1}H NMR spectrum of the compound exhibited three signals for the methoxy protons along with two superimposed AB systems and an A$_2$ system for the 1,10-Phenanthroline residue [5]. The ^{13}C NMR spectrum of the compound displayed three signals for the carbons of the methoxy groups, nine signals for the dipyrrolophenanthroline, The torsion angle of the helical structure of the compound was optimized at HF/6-31g(d,p) level of theory [8] using Gaussian 03 program package [9] and theoretically calculated at HF/6-31g(d,p) level. The calculated value of the torsion angle (-19.97°) is in good agreement with the experimental value (-21.14°) derived from the ORTEP view in the structural study. The solid state structure obtained by the X-ray diffraction for the compound is also in consistent with the observed data from NMR solution studies. The crystal data are listed in Table **1**.

Table 1. Crystal data and structure refinement details for hexamethyldipyrrolo[1,2-a:2,1–k][1,10] phenanthroline 7,8,9,12,13,14-hexacarboxylate(helical compound).

Formula	C$_{30}$H$_{24}$N$_2$O$_{12}$
Formula weight	604.51
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	Pī
	a = 7.7457(7) Å
	b = 11.7194(7) Å
Unit cell dimensions	c = 15.5427(9) Å
	α = 103.315(5)°
	β = 90.583(6)°
	γ = 101.659(6)°
Volume	1342.25(16) Å^3
Z	2
D$_{calc}$	1.496 Mg/m^3
Absorption coefficient	0.118 mm^{-1}
F(000)	628
Crystal size	0.26 × 0.22 × 0.16 mm^3
θ range for data collection	2.88 to 30.00º
Index ranges	-10≤h≤10, -11≤k≤16, -21≤l≤21
Reflection collected, N$_{total}$	21383
Independent reflections, N	7821 [R(int)=0.0337]
N$_o$, [I>2σ(I)]	5501
Max./min. transmission	0.98/0.93
Goodness-of-fit on F^2	1.132
Final R indices [I>2σ(I)]	R$_1$=0.0541, w R$_2$=0.1559
R indices (all data)	R$_1$=0.0742, w R$_2$=0.1632

Extensive hydrogen bondings were identified within the structure that include phenanthroline aromatic CH…carbonyl of the methyl ester (ArCH…O=C, 2.46A$^°$) and the methyl groups interactions with the carbonyl of the methyl esters (CH…O=C, 2.46A$^°$). These hydrogen bondings in

optimized structure of helical compound at HF/6-31G (d, p) level of theory are 2.35 and 2.36A° respectively. Within the overall structure, the molecules take on a linear arrangement in alternating fashion to optimize the hydrogen bonding interactions. The association of these arrays via hydrogen bonding forms sheets that in turn pack in the layered arrangement.
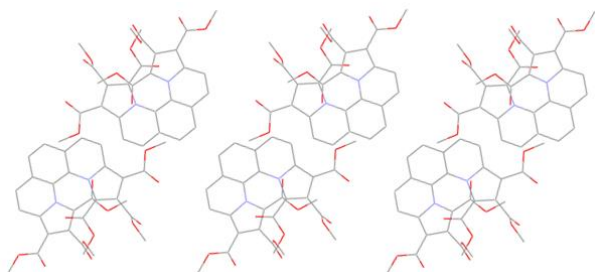

Figure 4: Partial molecular packing diagram of hexamethyl-dipyrrolo phenanthroline hexacarboxylate showing the layered arrangement motif, hydrogen atoms omitted for clarity.

Calculation:

Quantum mechanical calculation has been performed for determination of the values of proton and carbon coupling constants and also chemical shifts (δ^C_{iso}, δ^H_{iso}) using SPINSPIN keyword. First the structure of helical hexamethyl dipyrrolo phenanthroline hexacarboxylate was optimized at HF/6-31G (d, p) level of theory [8] by Gaussian 03 package program [9]. The individual chemical shifts have been characterized by NMR calculations at mentioned level. The total spin–spin coupling constant is the sum of four components: the paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC), and spin-dipole (SD) terms. The value of chemical shifts (δ) and coupling constants (J_{x-y}) are reported in (Tables **2-3**) for helical dipyrrolophenanthroline compound. As can be seen there is good agreement between both the experimental[10] and theoretical values of chemical shifts (δ) and coupling constants (J_{x-y}). In the present work, molecular structures of Helical dipyrrolophenanthroline involving large atoms such as twelve oxygen atoms and two nitrogen are huge with the large numbers of other atoms, for this reason, employment of basis set higher than HF/6-31G(d,p) is impossible for performance of more accurate calculations. This limitation causes a small difference between both the experimental and theoretical values of coupling constants in some functional groups.

X-ray crystallography:

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 729596 for this compound, Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/data_request/cif.

Table 2: Selected ^{13}C NMR chemical shift (δ in ppm) for some functional groups in the helical dipyrrolophenanthroline.

groups	δ^C/ppm
2C^{3,8}	106.44[a](121.40)[b]
2C^{4,7}	127.56(123.80)
2C$^{(1,12)}$H	118.14(113.20)
2C$^{(6,9)}$H	126.58(118.90)
2C$^{(2,10)}$H	127.56(125.20)
4C$^{(13,20,21,22)}$	120.07(116.40) 124.82(120.66)
4C$^{(5,45,46,47)}$	131.08(131.91) 137.62(142.27)
6C, C=O	158.16(153.94) 163.64(155.1) 166.26(156.59)

[a] Experimental data in accord with the results reported in the literature.[6]
[b] Theoretical data**.**

Table 3: Selected ^{1}H NMR chemical shift (δ in ppm) and coupling constants (J in Hz) for some functional groups in the helical dipyrrolophenanthroline.

groups	δ_E^H/ppm	J_{PH}/Hz
6H, 2s, 2CO$_2$Me	3.37[a] (3.20)[b] 3.99[a] (3.55)[b] 4.03[a] (3.83)[b]	
2H$^{(11,16)}$, d, $^3J_{HH}$, 2CH	8.06(7.88)	9.2(11.45)
2H^{14,17}, s, 2CH	8.10(7.86)	
2H$^{(15,18)}$, d, $^3J_{HH}$, 2CH	8.66(8.74)	9.2(11.45)

[a] Experimental data in accord with the results reported in the literature.[6]
[b] Theoretical data.

Conclusion

In briefly, the structure of the compound is unequivocally elucidated by the X-ray crystallography, confirming the chiral and helical nature previously established by ^{1}H and ^{13}C NMR studies [6]**.** In

optimized structure of hexamethyl dipyrrolo phenanthroline hexacarboxylate of HF/6-31G (d, p) level of theory there was a good agreement between experimental and calculated values of torgen angle. In addition, experimental data from NMR spectroscopy involving chemical shift (δ in ppm) and coupling constants (J_{x-y} in HZ) were consistent with those that obtained by mechanical calculations at HF/6-31G (d, p) level of theory.

Acknowledgement

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