J Chem Crystallogr (2010) 40:1142–1145
DOI 10.1007/s10870-010-9810-y

ORIGINAL PAPER

Synthesis and Crystal Structure of 1,3-Bis[2-(pyrrol-2-carbonyloxy)ethoxy]Benzene

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Received: 30 November 2009 / Accepted: 20 May 2010 / Published online: 15 June 2010

Abstract A new compound, 1,3-bis[2-(pyrrol-2-carbonyloxy)ethoxy]benzene (**1**), was synthesized and characterized by X-ray diffraction. The crystal is monoclinic, space group $P2_1/c$ with $a = 6.3571(7)$, $b = 11.0416(11)$, $c = 28.156(3)$ Å, $b = 92.821(2)$, $V = 1974.0(4)$ Å^3, $Z = 4$, $Dc = 1.293$ g/cm^3, $F(000) = 808$, $\mu = 0.097$ mm^{-1}. The final $R = 0.0395$ and $wR = 0.0927$ for 3478 observed reflections with $I > 2\ \sigma(I)$, and $R = 0.0660$ and $wR = 0.1058$ for all reflections. The title compound assembles into 2-D structure through a catemer type N–H···O hydrogen bonding motif and further forms 3-D structure through C–H···O hydrogen bonds.

Keywords 1,3-Bis[2-(pyrrol-2-carbonyloxy)ethoxy] benzene · Synthesis · Crystal structure · Hydrogen bonding motif

Introduction

Pyrrole-based compounds are frequently observed as hosts for neutral molecules [1–3] and anionic species [4–9] for its ability to form hydrogen bonds. 2-Carbonyl substituted pyrrole possesses one hydrogen bond donor (N–H$_{\text{pyrrole}}$) and one acceptor (C=O), which was found preferring to form centrosymmetric dimers with a pair of N–H···O hydrogen bonds (Scheme 1) [10]. Thus, using α-carbonyl-functionalized pyrrole moieties as building blocks to create hydrogen bonded aggregates has received some attention recently [11, 12]. For instance, Sessler et al. [13] have reported that some ferrocene-based pyrrole-2-carboxylates form one-dimensional chain via pair of N–H···O hydrogen bonds. Branda and coworkers [14] found that 2,2′-dipyrrolyl ketone self-assembles via hydrogen bonding into supramolecular helices. Lightner and cowokers [15] later reported that 2,2′-dipyrrylethanedione self-assembles via hydrogen bonding into supramolecular ribbons. Recently Maeda et al. [16] have fabricated micro- and nanometer-scale porous, fibrous, and sheet architectures from supramolecular assemblies of dipyrrolyl diketones through hydrogen bonds. We have studied the solid state structures of some pyrrole-2-carboxylate compounds in our earlier works [17, 18], and demonstrated that the pyrrole-2-carboxylate has good perspective on application to crystal engineering. In the present study, we report the synthesis and crystal structure of a new compound, 1,3-bis[2-(pyrrol-2-carbonyloxy)ethoxy]benzene (**1**), which forms a two-dimensional structure through helical catemeric hydrogen bonding motif rather than the frequently observed dimeric hydrogen bonding motif.

Experimental

General

^{1}H NMR spectra were recorded in DMSO-d_6, with TMS as internal standard, on a BRUKER AV-400 MHz spectrometer. Mass spectra were obtained on an AEIMS-50/PS 30 mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. Melting points (mp) were recorded on an electro-thermal digital melting point apparatus and uncorrected. 2-Trichloroacetylpyrrole was prepared according to literature procedures [19].

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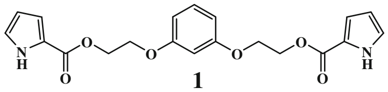

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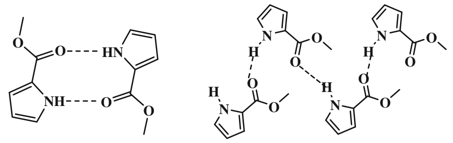

Scheme 1 Diagram of dimeric R_2^2 (10) hydrogen bonding motif (*left*) and catemeric type motif (*right*) of pyrrole-2-carboxylate

1,3-bis(hydroxyethoxy)benzene were commercial available and used without further purification.

Synthesis of Compound 1

A mixture of 1,3-Bis(hydroxyethoxy)benzene (198 mg, 1 mmol), 2-trichloroacetylpyrrole (633 mg, 3 mmol), triethylamine (0.5 mL), and acetonitrile (20 mL) was stirred at the refluxing temperature for 20 h. After the solution was allowed to cool to room temperature, the solvent was removed under the reduced pressure and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (v:v = 1:2) as eluent, affording 242 mg compounds **1**, white powder, yield 63%, m.p. = 124 °C. ^{1}H NMR (400 MHz, Methanol-*d*$_4$): δ 4.27 (t, 4H, $J = 4.2$ Hz, –CH$_2$–), 4.56 (t, 4H, $J = 4.2$ Hz, –CH$_2$–), 6.20 (s, 2H, PyCH), 6.55 −6.62(m, 3H, PhCH), 6.90 (s, 2H, PyCH), 6.98 (s, 2H, PyCH), 7.17–9.20 (m, 1H, PhCH) ppm; ^{13}C NMR (100 MHz, Methanol-*d*$_4$): δ 63.7, 67.3, 102.8, 108.4, 110.8, 117.0, 123.2, 124.9, 131.1, 161.4, 162.6 ppm; ESI–MS: 385(M + 1$^+$). Elemental analysis: $C_{20}H_{21}N_3O_4$: Calcd: C, 62.49; H, 5.24; N, 7.29. Found: C, 62.21; H, 5.44; N, 7.05.

X-Ray Crystallography

The single crystal of compound **1** suitable for X-ray crystallography study was grown by slowly evaporating its MeOH solution. The diffraction data were measured on a BRUKER SMART APEX II CCD diffractometer with Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) by ω scan mode at 293(2) K. All data were corrected by semi-empirical method using SADABS program. The program SAINT [20] was used for integration of the diffraction profiles. The structure was solved by the direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL [21]. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. Crystallographic data and refinement parameters of the three crystals were summarized in Table 1.

Table 1 Crystal data of compounds **1**

CCDC deposit no.	756384
Empirical formula	$C_{20}H_{20}N_2O_6$
Formula weight	384.38
Temperature (K)	293
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2$_1$/c
Crystal size (mm)	0.24 × 0.20 × 0.18
a (Å)	6.3571(7)
b (Å)	11.0416(11)
c (Å)	28.156(3)
α (°)	90
β (°)	92.821(2)
γ (°)	90
V (Å^3)	1974.0(4)
Z	4
D$_{\text{calc.}}$ (g/cm^3)	1.293
Absorption coefficient (mm^{-1})	0.097
F(000)	808
Range for data collection	1.98 to 25.03
Limiting indices	$-7 \le h \le 7$, $-13 \le k \le 11$, $-33 \le l \le 33$
Reflections collected/unique	10486/3478 [*R*(int) = 0.0326]
Refinement method	Full-matrix least-squares on F^2
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0395$, $wR_2 = 0.0927$
R indices (all data)	$R_1 = 0.0660$, $wR_2 = 0.1058$
Goodness of fit F^2	1.042
Extinction coefficient	0.0075 (11)
Largest different peak and hole (e Å^{-3})	0.141 and −0.138

DFT Calculation

The catemer hydrogen bonding motif linked **1·1** dimer and its two monomers units were cut out as the calculation models from the crystal of **1**. All hydrogen atoms were included in the models. Single point energies of the monomers and dimer were calculated at the B3LYP/6-31G* level by using the Gaussian 98 program [22]. The energies of the hydrogen bonds was computed as the difference in the single point energies between the **1·1** dimer and its two monomers [23].

Results and Discussion

The molecular structure of compound **1** is shown in Fig. 1 which shows a C type conformation. In the structure, both the pyrrole-2-carboxylate moieties adopt *syn* conformation, with the carbonyl group arranged *syn* to its adjacent pyrrole NH. The angles between the benzene ring and the two pyrrole rings are 57.6° and 76.7°, respectively. The angle

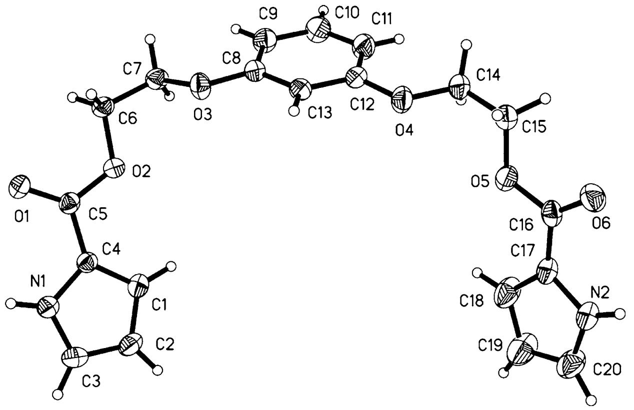

Fig. 1 ORTEP view of compound **1**; showing 30% probability displacement ellipsoids with atom numbering

Table 2 Hydrogen bonds parameters in crystals of **1**

D–H···A	D–H	H···A (Å)	D···A (Å)	∠D–H···A (°)
N1–H1···O6^{i}	0.86	2.06	2.843 (2)	152
N2–H2···O1^{ii}	0.86	2.11	2.947 (2)	164
C3–H3···O3^{iii}	0.93	2.56	3.494 (2)	177

Symmetry code: (i) x, −y + 3/2, z − 1/2; (ii) x + 1, −y + 3/2, z + 1/2; (iii) 2 − x, 1/2 + y, ½ − z

between the two pyrrole rings is 71.6°. The torsion angles of O2–C6–C7–O3 and O4–C14–C15–O5 are 69.4° and 79.6°, respectively.

Molecules of **1** formed 2-D structure through a helical catemeric hydrogen bonding motif which consists of alternate N1–H1···O6 and N2–H2···O1 hydrogen bonds (Fig. 2b). In terms of Etter's graph-set formalism, this kind of hydrogen bonds motif can be described as an $C_2^2(10)$ system [24]. This kind of hydrogen bonding motif is quite different with previous results in which the dimeric $R_2^2(10)$ type motif is frequently observed (Scheme 1) [16, 25–28]. Few case of the catemeric hydrogen bonding motif has been reported in crystals of pyrrole-2-carboxylate compounds. However, they belong to C(5) system [17, 29]. The 2-D layer structures were held together to form 3-D structure through C3–H3···O3 hydrogen bonds (Fig. 2a, c). The parameters of the hydrogen bonds were listed in Table 2.

DFT calculation reveals that the energies of the hydrogen bonds N1–H1···O6 and N2–H2···O1 are 7.1 and 5.7 kcal/mol, respectively. It is a well agreement with previous result that the N–H···O hydrogen bonds in the catemeric motif is more stable than that in the $R_2^2(10)$ type motif. Calculations with PLATON [30] revealed that the available volume for solvent is 4.5% of per unit cell in the crystal of compound **1**. It is also consistent with previous presumption that the catemeric hydrogen bonding motif of pyrrole-2-carboxylate always companies with loose crystal packing.

Conclusions

In conclusion, a new bis-pyrrole-2-carboxylate compound was synthesized and its crystal structure was characterized by X-ray crystallography. In the crystal, the pyrrole-2-carboxylate moieties involve into a new helical catemeric

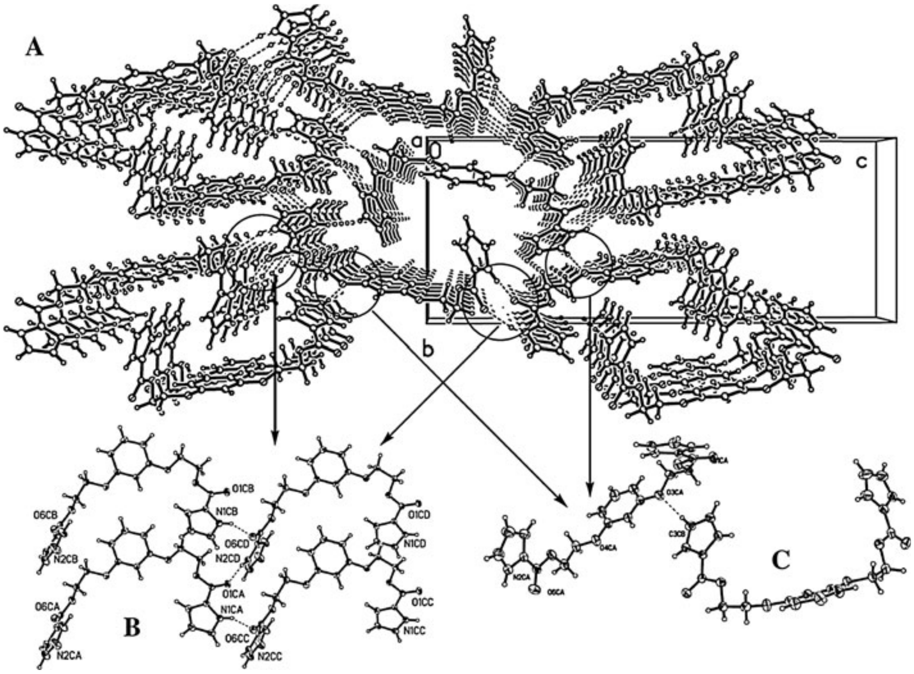

Fig. 2 Crystal packing diagram (**b**), catemer N–H···O hydrogen bonding motif (**b**) and C–H···O hydrogen bonding (**c**) in the crystal of compound 1

hydrogen bonding motif. DFT calculation rationalized that the catemer synthon is energy more stable but is geometry disadvantaged. This observation will help us make clear the intermolecular interaction of pyrrole-2-carboxylate.

Supplementary Material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 756384. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements We are indebted to Professor Jin-Pei Cheng, Department of Chemistry, Nankai University, for calculation. We sincerely thank the financial supports from the Natural Science Foundation of China (NSFC No. 20702038).

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