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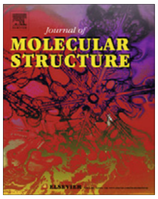

Hydrogen bonds and electrostatic interactions in the 1:1 complex of DABCO di-betaine with squaric acid: Crystallographic, theoretical and spectroscopic studies

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ABSTRACT

The molecular structure of the 1:1 complex of DABCO di-betaine (1,4-dicarboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt) with squaric acid (**1**) has been characterized by single-crystal X-ray diffraction, infrared spectroscopy and DFT calculations. Crystals **1** are monoclinic, space group $P2_1/c$. One proton of squaric acid is transferred to one of the carboxylate groups of DABCO di-betaine. The mono-protonated DABCO di-betaine cation is further engaged in the COOH···OOC hydrogen bond of 2.526(2) Å with the neighboring cations, linking them into a zigzag chain. The hydrogen squarate anion interacts with the oxygen atom of the carboxylate group of DABCO di-betaine cation, through the O—H···O═C hydrogen bonds of 2.600(2) Å. The structures of monomer **1a**, dimer **2** and cation **3** have been optimized at the B3LYP/6-31G(d,p) level of theory. The FTIR spectrum is consistent with the X-ray results. The second-derivative spectrum of **1** and calculated frequencies for the optimized structure **1a** are used to explain the frequencies in the experimental FTIR spectrum.

1. Introduction

1,4-Diazabicyclo[2.2.2]octane, $N(CH_2CH_2)_3N$, abbreviated as DABCO, in the reaction with alkylhalides forms a variety of quaternary 1,4-dialkyl-1,4-diazabicyclo[2.2.2]octane dihalides [1]. Wu and Mak synthesized and solved the crystal structures of 1,4-dicarboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt, abbreviated as DABCO di-betaine, and its hydrochloride [2]. Dissociation constant, pK_a, of DABCO di-betaine determined by the potentiometric titration of its hydrochloride is 1.79 [3].

Recently, we have studied the complex of DABCO di-betaine with *p*-hydroxybenzoic acid and two water molecules in the ratio of 1:2.5:2 [4]. In this paper we investigated the structure of the 1:1 complex of DABCO di-betaine with squaric acid (3,4-dihydroxy-3-cyclobuten-1,2-dion, H_2SQ). DABCO itself forms a hydrated complex with H_2SQ in the 1:2:1 ratio [5]. Squaric acid is a strong diprotic acid characterized by two dissociation constants, pK_1 = 1.2–1.7 and pK_2 = 3.2–3.5 [6–8]. H_2SQ by transferring one proton to a base generates a hydrogen squarate anion, HSQ^-, or by transferring two protons can generate a squarate dianion, SQ^{2-}. The molecules of H_2SQ and its anions are flat because of the full π-delocalization, and accordingly the oxygen atoms behave like planar sp^2 electron donors of one or two lone pairs [9–13]. Squaric acid and its anions have been frequently used as counter-anions in the preparation of a number of molecular crystals and their structures are stored in the Cambridge Crystallographic Database Centre [14]. Structural motifs of squarate anions include isolated monomeric and dimeric anions, single or double chains, and ribbons [9–13,15]. We would like to point out to the importance on the earlier works by Kolev and coworkers[16–23].

The aim of the present investigation is synthesis, structural and spectroscopic characterization of the complex of DABCO di-betaine with squaric acid, H_2SQ. From the point of view of material science, the crystal structure of the 1:1 complex of the mono-protonated DABCO di-betaine with hydrogen squarate anion (HSQ^-) is of interest due to its possible polar aggregation via the O—H···O═C hydrogen bond.

2. Experimental

2.1. Synthesis

1,4-Dicarboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt, DABCO di-betaine, was prepared according to the method described in Ref. [2]. The complex of DABCO di-betaine with squaric acid was prepared by mixing 0.75 g of DABCO di-betaine dissolved in 1 ml of water with 0.32 g squaric acid dissolved in 3 ml of water. The precipitate was filtered off and residue (**1**) was recrystallized from water, m.p. 298 °C with decomposition. Deuterated sample was obtained by threefold recrystallization of **1** from D_2O.

2.2. Measurements

The crystal structure of the complex of DABCO di-betaine with H_2SQ (**1**) was determined by X-ray diffraction, measured with a

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KUMA KM-4 CCD diffractometer [24,25]. The structure was solved by direct methods using SHELXS-97 and refined on F^2 by full-matrix least-squares with SHELXL-97 [26]. The crystal data, details of data collection and structure refinement are given in Table 1 and the final atomic coordinates in Table A of Supplementary material. The crystallographic and structural data in CIF format are available as an Electronic Supplementary Publication from the Cambridge Crystallographic Database Centre (CCDC 844725). Its copy can be obtained free of charge from deposit@ccdc.edu or www.ccdc.cam.ac.uk/data_request/cif.

FTIR spectra of **1** were measured in Nujol and Fluorolube suspensions between KBr plates using a Bruker IFS 66v/S instrument, with the resolution of 2 cm^{-1}. Each spectrum was measured by acquisition of 64 scans.

2.3. DFT calculations

The DFT calculations were performed with the GAUSSIAN 03 program package [27]. The calculations employed the B3LYP

Table 1
Crystal data and structure refinement for the 1:1 complex of DABCO di-betaine with squaric acid (**1**).

Empirical formula	$C_{14}H_{18}N_2O_8$
Formula weight	342.30
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
	$a = 7.0175(4)$ Å
	$b = 14.2817(7)$ Å
	$c = 14.0320(7)$ Å
	$\beta = 93.641(5)°$
Volume	1403.47(12) $Å^3$
Z	4
Calculated density	1.620 g/cm^3
Absorption coefficient	0.134 mm^{-1}
$F(000)$	720
Crystal size	0.42 × 0.15 × 0.10 mm
θ range for data collection (°)	2.04–27.72
Max/min. indices h, k, l	−9/8, −18/8, −18/15
Reflections collected/unique	5373/3042 [R(int) = 0.0219]
θ_{Max}(°)/Completeness (%)	27.72/92.5
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3042/0/289
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma_I$]	$R1 = 0.0350$, $wR2 = 0.0789$
$R1/R2$ indices (all data)	0.0564/0.0820
Largest diff. peak and hole	0.201 and −0.223 e $Å^{-3}$

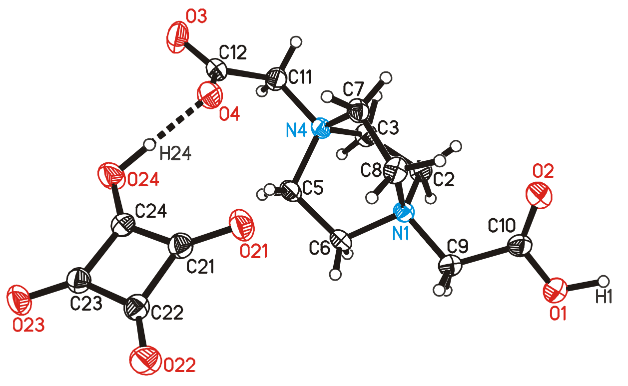

Fig. 1. The asymmetric part of the unit cell of the 1:1 complex of DABCO di-betaine with squaric acid (**1**). The thermal ellipsoids have been drawn at 50% probability level.

Table 2
Experimental and calculated by the B3LYP/6-31G(d,p) approach bond lengths (Å), bond and torsion angles (°) for the 1:1 complex of DABCO di-betaine with squaric acid.

	X-ray	*B3LYP/6-31G(d,p)*		
	1	**1a**	**2** (a)	**2** (b)
Bond lengths				
N(1)—C(2)	1.509(3)	1.513	1.513	1.519
C(2)—C(3)	1.517(3)	1.555	1.551	1.541
N(4)—C(3)	1.516(3)	1.506	1.508	1.510
N(4)—C(5)	1.513(3)	1.518	1.516	1.514
C(5)—C(6)	1.513(3)	1.523	1.530	1.531
N(1)—C(6)	1.517(3)	1.528	1.524	1.520
N(1)—C(8)	1.514(3)	1.535	1.511	1.520
C(7)—C(8)	1.522(3)	1.526	1.537	1.541
N(4)—C(7)	1.504(3)	1.517	1.514	1.514
N(1)—C(9)	1.502(3)	1.505	1.505	1.507
C(9)—C(10)	1.511(3)	1.519	1.517	1.518
C(10)—O(1)	1.301(3)	1.335	1.326	1.337
C(10)—O(2)	1.200(3)	1.213	1.214	1.213
N(4)—C(11)	1.509(3)	1.531	1.534	1.530
C(11)—C(12)	1.519(3)	1.599	1.596	1.573
C(12)—O(3)	1.250(3)	1.225	1.227	1.247
C(12)—O(4)	1.249(3)	1.265	1.264	1.257
C(21)—C(22)	1.500(3)	1.500	1.498	1.514
C(22)—C(23)	1.506(3)	1.546	1.536	1.514
C(23)—C(24)	1.424(3)	1.476	1.469	1.442
C(21)—C(24)	1.430(3)	1.411	1.419	1.447
C(21)—O(21)	1.243(3)	1.286	1.265	1.243
C(22)—O(22)	1.222(3)	1.218	1.236	1.227
C(23)—O(23)	1.241(2)	1.217	1.217	1.252
C(24)—O(24)	1.324(3)	1.334	1.335	1.329
Bond angles				
N(1)—C(2)—C(3)	108.3(2)	108.38	109.00	108.75
N(4)—C(3)—C(2)	109.2(2)	109.81	110.13	110.21
N(4)—C(5)—C(6)	108.4(2)	109.89	110.03	109.82
N(1)—C(6)—C(5)	109.0(2)	108.54	109.58	106.64
C(2)—N(1)—C(6)	107.5(2)	106.54	108.34	107.43
C(5)—N(4)—C(3)	107.8(2)	107.74	107.63	106.78
N(1)—C(8)—C(7)	108.1(2)	109.15	109.53	109.15
C(2)—N(1)—C(8)	109.1(2)	108.33	110.34	109.72
C(8)—N(1)—C(6)	107.3(2)	110.25	108.78	108.07
N(4)—C(7)—C(8)	108.9(2)	109.24	110.33	109.80
C(7)—N(4)—C(3)	107.8(2)	107.11	107.88	109.56
C(7)—N(4)—C(5)	108.1(2)	109.98	110.87	108.33
C(9)—N(1)—C(2)	111.7(2)	116.16	112.60	111.89
C(9)—N(1)—C(6)	107.3(3)	106.19	106.13	106.61
C(9)—N(1)—C(8)	113.6(2)	109.27	110.48	112.86
N(1)—C(9)—C(10)	114.7(2)	114.76	116.95	114.50
O(1)—C(10)—C(9)	109.6(2)	109.00	105.85	109.00
O(2)—C(10)—C(9)	124.9(2)	126.25	126.54	126.59
O(1)—C(10)—O(2)	125.5(2)	124.75	127.58	124.40
C(11)—N(4)—C(3)	107.1(2)	113.84	112.80	110.27
C(11)—N(4)—C(5)	113.0(2)	108.88	108.94	110.08
C(11)—N(4)—C(7)	112.8(2)	109.24	108.73	111.69
N(4)—C(11)—C(12)	116.6(2)	114.49	116.04	115.92
O(3)—C(12)—C(11)	112.9(2)	115.90	110.43	112.79
O(4)—C(12)—C(11)	120.2(2)	110.93	117.00	116.65
O(3)—C(12)—O(4)	126.9(2)	132.16	132.57	130.56
C(21)—C(22)—C(23)	88.7(2)	87.85	89.41	88.73
C(21)—C(24)—C(23)	94.8(2)	94.07	95.27	94.31
C(22)—C(21)—C(24)	88.2(2)	91.13	89.26	88.30
C(22)—C(23)—C(24)	88.2(2)	86.96	86.03	88.48
O(21)—C(21)—C(22)	134.7(2)	133.12	134.64	134.66
O(21)—C(21)—C(24)	137.1(2)	135.75	135.90	135.99
O(22)—C(22)—C(21)	135.4(2)	134.68	133.81	133.86
O(22)—C(22)—C(23)	135.9(2)	137.47	136.59	135.70
O(23)—C(23)—C(22)	135.9(2)	136.91	137.26	134.90
O(23)—C(23)—C(24)	135.9(2)	136.13	136.66	135.43
O(24)—C(24)—C(21)	135.6(2)	137.29	127.58	134.71
O(24)—C(24)—C(23)	129.6(2)	128.64	137.08	130.14
Torsion angles				
N(1)—C(2)—C(3)—N(4)	23.4(2)	16.75	7.64	16.86
C(2)—C(3)—N(4)—C(5)	−72.1(2)	−68.40	55.54	−69.38
C(3)—C(2)—N(1)—C(6)	44.7(2)	46.68	−64.29	49.91
C(2)—N(1)—C(6)—C(5)	−73.3(2)	−72.56	55.03	−68.79

(*continued on next page*)