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Structural, spectroscopic and theoretical studies of dimethylphenyl betaine complex with two molecules of 2,6-dichloro-4-nitro-phenol



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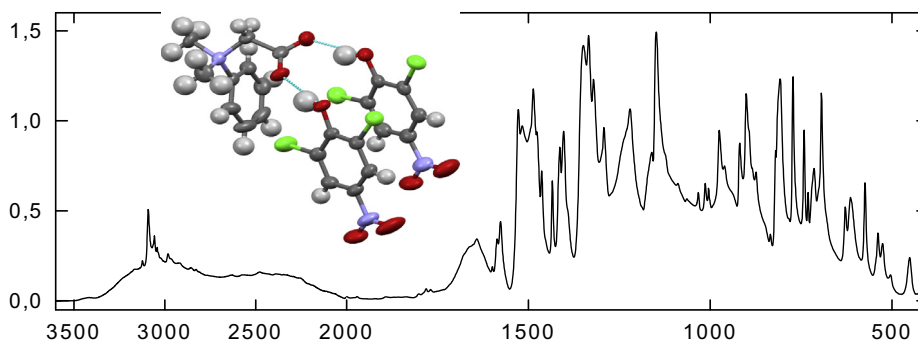
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HIGHLIGHTS

- Dimethylphenyl betaine crystallizes with two molecules of 2,6-dichloro-4-nitro-phenol.
- Molecules are linked by two different O—H...O hydrogen bonds without the proton transfer.
- The structures in crystal, gas phase and DMSO solution are analyzed.
- The experimental and calculated frequencies have been assigned.
- The magnetic isotropic shielding constants reproduce the experimental chemical shifts.

GRAPHICAL ABSTRACT

The 1:2 complex of dimethylphenyl betaine with two molecules of 2,6-dichloro-4-nitro-phenol was prepared and investigated by X-ray diffraction, B3LYP/6-311++G(d,p) and B3LYP-D3/6-311++G(d,p) calculations, FTIR and NMR spectroscopies. Phenols are bonded to each oxygen atoms of COO⁻ group of the betaine by two nonequivalent O...H—O hydrogen bonds of 2.473(5) and 2.688(4) Å.



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ABSTRACT

The 1:2 complex (**1**) of dimethylphenyl betaine (DMPB) with two molecules of 2,6-dichloro-4-nitro-phenol (DCNP) was prepared and characterized by X-ray diffraction, B3LYP/6-311++G(d,p) and B3LYP-D3/6-311++G(d,p) calculations, FTIR and NMR spectroscopies. The crystal is monoclinic, space group $P2_1/c$ with $Z = 4$. The protons at the oxygen atoms of phenols are bonded to each oxygen atoms of the DMPB carboxylate group by two nonequivalent H-bonds with the O—H...O distances of 2.473(5) and 2.688(4) Å. Both H-bonds in the optimized structures **2** (in vacuum), **3** (in DMSO solution) and dispersion-correlated functional (D3) **4** (in vacuum) are comparable and are slightly shorter than O(6)—H(O6)...O(2) in the crystal. The FTIR spectrum of **1** shows a broad absorption in the 3400–2000 cm⁻¹ region corresponding to a longer hydrogen bond and a broad absorption in the 1800–500 cm⁻¹ region caused by the shorter H-bond. The relations between the experimental ¹³C and ¹H chemical shifts (δ_{exp}) of the investigated compound **1** in DMSO solution and GIAO/B3LYP/6-311++G(d,p) magnetic isotropic shielding constants (σ_{calc}) obtained by using the screening solvation model (COSMO) for **3** are linear and reproduce well the experimental chemical shifts described by the equation: $\delta_{\text{exp}} = a + b \sigma_{\text{calc}}$.

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Introduction

Among many various kinds of molecular interactions, the hydrogen bond has a special position. The hydrogen bond is of great importance in natural sciences, chemistry, physics and biochemical processes. Hence, its nature is often the subject of investigation and polemics [1–9]. Interesting hydrogen bonds are in complexes of betaines with mineral and organic acids [10].

Betaines are compounds with oppositely charged centers and are often referred to as zwitterions, inner salts, dipolar ions or salt-bridged-containing molecules. This diverse nomenclature reflects the extraordinary importance of these species in biological transformations, organic synthesis, preparation of novel materials and as chromatographic supports [10–12]. Betaine $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-]$ is distributed in animals, plants, microorganisms and is a significant component of many food products [13]. In betaines $[(\text{R}_3\text{N}^+\text{CH}_2\text{COO}^-)]$ the quaternary nitrogen atom is inert as a hydrogen-bond center, whereas the carboxylate group is basic and can interact with different proton donors. The nitrogen atom can be surrounded by alkyl groups or be involved in heteroaliphatic or heteroaromatic rings [10].

Betaines form 1:1 and 2:1 complexes with mineral and organic acids [14,15] and phenols [16]. Recently, we have described a third type of complex (1:2) of pyridine betaine with two molecules of 2,6-dichloro-4-nitro-phenol (DCNP) [17] and pentachlorophenol [18]. In this study, we have synthesized another 1:2 complex of dimethylphenyl betaine with two molecules of 2,6-dichloro-4-nitro-phenol.

Experimental and calculations

Dimethylphenyl betaine (DMPB) was prepared according to the method described in Ref. [19]. When mixing stoichiometric amount of DMPB with 2,6-dichloro-4-nitro-phenol (DCNP) in methanol only the 1:2 complex, $\text{DMPB}(\text{DCNP})_2$, is formed. Thus the best method of synthesis is mixing the components at the 1:2 ratio. The obtained complex was recrystallized from methanol, m.p. 138 °C. Analysis for $\text{C}_{22}\text{H}_{19}\text{Cl}_4\text{N}_3\text{O}_8$; calculated: C, 44.39%; H, 3.22%; N, 7.06%; found: C, 44.37%; H, 3.25%; N, 7.08%. The deuterated complex was prepared by a twofold dissolution in D_2O with subsequent removal of the solvent under reduced pressure. The residue was recrystallized from CH_3OD .

FTIR spectra were recorded in Nujol and Fluorolube mulls on Bruker IFS 66v/S spectrometer, evacuated to avoid water and CO_2 absorptions at 2 cm^{-1} resolution. Each FTIR spectrum was accumulated by acquisition of 64 scans. The Raman spectrum of crystalline sample was measured on a Bruker FRA-106/S instrument operating at the 1064 nm exciting line of Nd:YAG laser with the resolution of 1 cm^{-1} . The spectrum was accumulated by acquisition of 200 scans.

NMR spectra were recorded using a Varian VNMRS-400 spectrometer operating at 402.6435 and 101.2440 MHz for ^1H and ^{13}C , respectively. The ^1H and ^{13}C chemical shifts were measured in DMSO-d_6 solution relative to TMS. The chemical shifts were confirmed by COSY and HETCOR experiments.

The X-ray diffraction measurements on the crystal of **1** were carried out on an Oxford Diffraction Excalibur EOS-CCD diffractometer. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares with SHELXL-97 [20]. The H-atoms were located on the basis of geometry (methyl C–H 0.97 Å, phenyl 0.93 Å, methylene 0.96 Å). The anisotropic thermal parameters were refined for the non-H-atoms, and isotropic U_{iso} parameters for H atoms were linked to U_{eq} of their carriers. The crystal data, together with the details concerning the data collection and structure refinement are given in Table 1 and the atomic

coordinates are in Table S1 in Supplementary Material. The crystal data have been deposited in the Cambridge Crystallographic Database Centre as a Supplementary publication CCDC 992834. Molecular illustrations were prepared using ORTEPII [21] and XP [22] packages.

The calculations were performed using the Gaussian 09 program package [23] and the B3LYP and B3LYP-D3 [24–26] approaches in conjunction with 6-311++G(d,p) basis set [27]. B3LYP-D3 [26] denotes a calculation with the usual B3LYP functional plus a D3 dispersion correlation energy term. The dispersion correlation energy term is a function of interatomic distances and contains adjustable parameters that are fitted to conformational and interaction energies computed using CCSD(T)/CBS. The vibrational FTIR spectra (harmonic wavenumbers and absolute intensities) were calculated at the B3LYP/6-311++G(d,p) level of theory. The calculated IR frequencies were positive and confirmed that the optimized structures were in the states of minimum energies. The magnetic isotropic shielding constants were calculated using the standard GIAO/B3LYP/6-311++G(d,p) (Gauge-Independent Atomic Orbital) approach with the Gaussian 09 program package using the conductor-like screening solvation model (COSMO) [28–32].

Results and discussion

Crystal structure

The crystals of the 1:2 complex of dimethylphenyl betaine (DMPB) with 2,6-dichloro-4-nitro-phenol (DCNP) (**1**) belong to monoclinic system, space group $P2_1/c$. The selected bond lengths, bond and torsion angles are listed in Table 2. The molecular structure and labeling scheme are shown in Fig. 1, while the crystal packing is presented in Fig. 2. In the investigated complex both phenol molecules (DCNP) form two nonequivalent hydrogen bonds with the DMPB carboxylate group with the O–H...O distances of 2.473(5) and 2.688(4) Å without proton transfer (Table 3). The O...O distances are comparable with those found in the 1:2 complex of pyridine betaine with DCNP [17], however in this complex pyridine betaine is protonated and the O...H–O distances are

Table 1

Crystal data and structure refinement of the 1:2 complex of dimethylphenyl betaine with 2,6-dichloro-4-nitro-phenol.

Empirical formula	$\text{C}_{22}\text{H}_{19}\text{Cl}_4\text{N}_3\text{O}_8$
Formula weight	595.20
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 16.6511(5)$ Å $b = 11.6487(5)$ Å $c = 13.3614(6)$ Å $\beta = 105.864(4)^\circ$
Volume	$2492.92(17)$ Å ³
Z	4
Calculated density	1.586 g cm^{-3}
Absorption coefficient	0.529 mm^{-1}
$F(000)$	1216
Crystal size	$0.30 \times 0.30 \times 0.10\text{ mm}$
θ range for data collection	$3.48\text{--}27.58^\circ$
Max/min. indices h, k, l	$-12 \leq h \leq 21, -14 \leq k \leq 15, -16 \leq l \leq 19$
Reflections collected/unique	10,547/5267 $R_{int} = 0.0334$
Completeness to $\theta_{max} = 29.9^\circ$	91.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5267/0/341
Goodness-of-fit on F^2	1.004
Final R indices [$I > 2\sigma_I$]	$R_1 = 0.0641, wR_2 = 0.1243$
R indices (all data)	$R_1 = 0.0960, wR_2 = 0.1555$
Largest diff. peak and hole	0.362 and -0.351 e Å^{-3}

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