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# Structure of complex of *N*-methylpiperidine betaine with *p*-hydroxybenzoic acid studied by X-ray, FT-IR and DFT methods

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## Abstract

Crystal structure of the complex of *N*-methylpiperidine betaine (*N*-carboxymethyl-*N*-methylpiperidinium inner salt, MPB) with *p*-hydroxybenzoic acid (HBA) has been determined by X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, with $a = 6.1156(5)$, $b = 10.6869(10)$, $c = 12.0320(10)$ Å, $\alpha = 109.55(1)°$, $\beta = 95.25(1)°$, $\gamma = 99.22(1)°$, $Z = 2$, $R = 0.034$. Two molecules of *p*-hydroxybenzoic acid and two molecules of *N*-methylpiperidine betaine are linked together forming a centrosymmetric dimer, $(\mathrm{MPB \cdot HBA})_2$, by four O–H···O hydrogen bonds of lengths 2.622(1) and 2.617(1) Å, between the carboxylic and hydroxy groups of HBA and both oxygen atoms of the carboxylate group of MPB, respectively. The piperidine ring has a chair conformation with the $CH_2COO^-$ substituent in the axial position and the $CH_3$ group in the equatorial one. Two parallel aromatic rings in $(\mathrm{MPB \cdot HBA})_2$ are distanced by 3.457 Å. In the crystals the complexes form "islands" related to the neighboring complexes by the inversion centers, weak C–H···O bonds and van der Waals forces. A broad band in the 3100–2400 cm$^{-1}$ region and two bands attributed to the $\nu$C=O (1689 cm$^{-1}$) and $\nu_{as}$COO (1607 cm$^{-1}$) vibrations in the FT-IR spectrum confirm the structure of the title complex. The two structures of MPB·HBA, denoted as **A** and **B**, have been optimized by the B3LYP/6-31G(d,p) method. In **A**, MPB forms a O–H···O hydrogen bond (2.562 Å) with the carboxylic group of HBA shorter than in the crystals, while in **B** it interacts with the phenolic group of HBA by a longer O–H···O hydrogen bond (2.661 Å) than in the crystals. Complex **A** is slightly more stable than **B** (0.15 kcal/mol).

*Keywords:* *N*-Methylpiperidine betaine; *p*-Hydroxybenzoic acid; Hydrogen bond; X-ray diffraction; FT-IR; DFT calculations

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## 1. Introduction

Carboxybetaines are inner salts (zwitterionic compounds) consisting of an anionic carboxylate group and the oppositely charged quaternary ammonium moiety. The charged groups can be either coupled via π-electrons or are separated by a neutral skeleton and they are not conjugated [1–3].

In previous studies, we have determined the crystal structures of complexes of *p*-hydroxybenzoic acid with *N*-methylmorpholine betaine, *N*,*N*′-dimethylpiperazine mono- and di-betaines and nipecotic acid [4–7]. To get more details on the role of the hydroxyl group in the proton-donor molecules and the pattern of their hydrogen bonds, in this paper we present the molecular structure and spectroscopic properties of the complex of *N*-methylpiperidine betaine, MPB (p$K_a = 2.01$ [8]) with *p*-hydroxybenzoic acid, HBA, which has two different proton-donor groups, COOH (p$K_{a1} = 4.67$) and OH (p$K_{a2} = 9.37$) [9].

## 2. Experimental

*N*-Methylpiperidine betaine (*N*-carboxymethyl-*N*-methylpiperidinium inner salt, MPB) was obtained as described in Ref. [10]. Complex with *p*-hydroxybenzoic acid (HBA) was prepared by mixing one equivalent of MPB with one equivalent of HBA in methanol. The crude product was recrystallized from methanol, m.p. 178 °C. Analysis for $C_{15}H_{18}NO_5$: calcd: %C, 61.64; %H, 6.21; %N, 4.79; found:

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%C, 61.41; %H, 6.30; %N, 4.77. $^1$H NMR (DMSO-$d_6$, ppm): 1.51 (m, 2H, H-4), 1.79 (m, 4H, H-3, H-5), 3.20 (s, 3H, $CH_3$), 3.40 (m, 2H, H-2 ax, H-6 ax), 3.63 (m, 2H, H-2 eq, H-6 eq), 3.72 (s, 2H, $N^+CH_2$), 6.86 (d, 2H, H-13, H-15), 8.26 (d, 2H, H-12, H-16). $^{13}$C NMR (DMSO-$d_6$, ppm): 19.49 (C-3, C-5), 21.07 (C-4), 47.28 ($CH_3$), 59.81 (C-2, C-6), 63.28 ($N^+CH_2$), 115.12 (C-13, C-15), 121.26 (C-11), 131.36 (C-12, C-16), 161.77 (C-14), 164.71 (COO), 167.17 (C=O). The deuterated analogue was prepared by threefold crystallization form $CH_3OD$.

Crystals of (MPB·HBA)$_2$ for diffraction measurements were grown from methanol. Diffraction measurements were carried out at ambient temperature on a KUMA-KM4 diffractometer equipped with CCD detector, using CuKα radiation [11]. Data reduction was carried out with the KM4 CCD software [12]. The structure was solved with direct methods SHELXS-97 program [13]. All atom positions were found from E-map, non-hydrogen atoms were refined with anisotropic displacement parameters and the parameters of hydrogen atoms were refined by isotropic methods, using the SHELXL-97 program [14]. The final *R* factor equals 0.0344 for 3777 reflections and 275 refined parameters. The crystal data and details of data processing are given in Table 1, and the final fractional atomic coordinates are in Table 2. The supplementary information in the CIF form is available from Cambridge Crystallographic Data Base Center, No CCDC 642346.

Table 1
Crystal data and structure refinement for the complex of *N*-methylpiperidine betaine with *p*-hydroxybenzoic acid, (MPB·HBA)$_2$

| | |
|---|---|
| Empirical formula | $C_{15}H_{21}NO_5$ |
| Formula weight | 295.33 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | $a = 6.1156(5)$ Å |
| | $b = 10.6869(10)$ Å |
| | $c = 12.0320(10)$ Å |
| | $\alpha = 109.545(8)°$ |
| | $\beta = 95.249(7)°$ |
| | $\gamma = 99.223(7)°$ |
| Volume | 722.53(11) Å$^3$ |
| *Z* | 2 |
| Calculated density | 1.357 g/cm$^3$ |
| Absorption coefficient | 0.102 mm$^{-1}$ |
| *F*(000) | 316 |
| Crystal size | 0.2 × 0.2 × 0.55 mm |
| θ range for data collection | 2.07–29.76° |
| Limiting indices | $-8 \leqslant h \leqslant 8$ |
| | $-14 \leqslant k \leqslant 12$ |
| | $-14 \leqslant l \leqslant 16$ |
| Reflections collected/unique | 10274/3777 [$R_{int} = 0.0126$] |
| Completeness to θ = 25.00 | 99.3% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3777/0/275 |
| Goodness-of-fit on $F^2$ | 1.091 |
| Final *R* indices [$I>2\sigma(I)$] | $R1 = 0.0344$, $wR2 = 0.1035$ |
| *R* indices (all data) | $R1 = 0.0414$, $wR2 = 0.1102$ |
| Extinction coefficient | 0.075(8) |
| Largest diff. peak and hole | 0.315 and −0.179 e Å$^{-3}$ |

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for the complex of *N*-methylpiperidine betaine with *p*-hydroxybenzoic acid

| Atom | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|
| N(1) | 0.9324(1) | 0.2604(1) | 0.5942(1) | 28(1) |
| C(2) | 1.1092(2) | 0.2264(1) | 0.6702(1) | 32(1) |
| C(3) | 1.2401(2) | 0.3511(1) | 0.7713(1) | 38(1) |
| C(4) | 1.0859(2) | 0.4212(1) | 0.8523(1) | 46(1) |
| C(5) | 0.9032(2) | 0.4554(1) | 0.7798(1) | 40(1) |
| C(6) | 0.7790(2) | 0.3339(1) | 0.6741(1) | 36(1) |
| C(7) | 0.7885(2) | 0.1319(1) | 0.5056(1) | 45(1) |
| C(8) | 1.0334(2) | 0.3480(1) | 0.5288(1) | 29(1) |
| C(9) | 1.1934(2) | 0.2923(1) | 0.4426(1) | 32(1) |
| O(1) | 1.2376(2) | 0.1782(1) | 0.4278(1) | 46(1) |
| O(2) | 1.2649(1) | 0.3715(1) | 0.3920(1) | 45(1) |
| C(10) | 0.6113(2) | 0.0567(1) | 0.8157(1) | 33(1) |
| O(3) | 0.7746(1) | −0.0112(1) | 0.7905(1) | 46(1) |
| O(4) | 0.4717(2) | 0.0605(1) | 0.7395(1) | 51(1) |
| C(11) | 0.6203(2) | 0.1291(1) | 0.9452(1) | 29(1) |
| C(12) | 0.8024(2) | 0.1397(1) | 1.0284(1) | 33(1) |
| C(13) | 0.8046(2) | 0.2048(1) | 1.1490(1) | 35(1) |
| C(14) | 0.6230(2) | 0.2610(1) | 1.1885(1) | 31(1) |
| C(15) | 0.4389(2) | 0.2497(1) | 1.1062(1) | 33(1) |
| C(16) | 0.4382(2) | 0.1841(1) | 0.9857(1) | 32(1) |
| O(5) | 0.6355(1) | 0.3265(1) | 1.3075(1) | 44(1) |
| H(2A) | 1.0270(20) | 0.1612(13) | 0.6995(11) | 40(3) |
| H(2B) | 1.2020(20) | 0.1809(12) | 0.6163(11) | 35(3) |
| H(3B) | 1.3250(20) | 0.4172(13) | 0.7407(11) | 38(3) |
| H(3A) | 1.3490(20) | 0.3221(14) | 0.8158(12) | 44(3) |
| H(4A) | 1.0190(30) | 0.3590(15) | 0.8895(13) | 55(4) |
| H(4B) | 1.1750(30) | 0.5085(17) | 0.9188(15) | 63(4) |
| H(5A) | 0.7880(20) | 0.4894(14) | 0.8280(13) | 51(4) |
| H(5B) | 0.9680(20) | 0.5295(14) | 0.7522(12) | 44(3) |
| H(6A) | 0.6990(20) | 0.2669(12) | 0.7013(11) | 37(3) |
| H(6B) | 0.6760(20) | 0.3586(13) | 0.6193(11) | 43(3) |
| H(7A) | 0.7220(30) | 0.0765(16) | 0.5509(14) | 61(4) |
| H(7B) | 0.8860(30) | 0.0848(15) | 0.4520(14) | 55(4) |
| H(7C) | 0.6730(30) | 0.1554(15) | 0.4645(14) | 55(4) |
| H(8A) | 0.9120(20) | 0.3630(13) | 0.4835(11) | 38(3) |
| H(8B) | 1.1140(20) | 0.4344(12) | 0.5893(11) | 35(3) |
| H(12) | 0.9260(20) | 0.1005(14) | 1.0016(13) | 48(4) |
| H(13) | 0.9290(20) | 0.2101(14) | 1.2069(12) | 45(3) |
| H(15) | 0.3120(20) | 0.2872(14) | 1.1362(12) | 45(3) |
| H(16) | 0.3070(20) | 0.1720(14) | 0.9275(13) | 48(3) |
| H(3) | 0.7560(30) | −0.0699(18) | 0.7107(16) | 71(5) |
| H(5) | 0.5010(30) | 0.3374(18) | 1.3259(16) | 69(5) |

*U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

FT-IR spectra were measured on a Bruker IFS 66v/S instrument, evacuated to avoid water and $CO_2$ absorptions. Solid state spectra were recorded in Nujol and Fluorolube suspension using KBr plates. Each spectrum consisted of 64 scans. The Raman spectrum was measured on a Bruker IFS 66 instrument.

The NMR spectra were recorded on a Varian Gemini 300 VT spectrometer operating at 300.07 and 75.46 MHz for $^1$H and $^{13}$C, respectively. The spectra were measured in DMSO-$d_6$ relative to TMS as internal reference. The 2D (COSY, HETCOR) spectra were obtained with standard Varian software.