Structural Characterization of *N*-(4-carboxybenzyl)pyridinium Bromide: Hydrogen Bonding between Bromide and a Carboxylic Acid

Daniel G. Shlian, James Pelaez, David A. Vaccaro and Gerard Parkin,*

Department of Chemistry,

Columbia University,

New York, New York 10027, USA.

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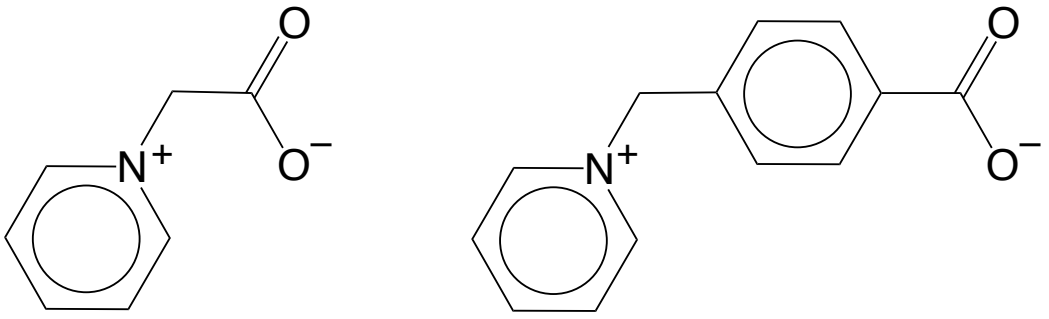
Abstract: The molecular structure of the carboxylic acid, *N*-(4-carboxybenzyl)pyridinium bromide, (CbpH)Br, has been determined by using X-ray diffraction. Significantly, (CbpH)Br does not exhibit intermolecular hydrogen bonding interactions of the type that are commonly observed between carboxylic acid moieties; instead, the O–H group participates in a hydrogen bond to the bromide anion, *i.e.* [C(O)OH•••Br], with an O•••Br distance of 3.199(5) Å and a *syn* disposition relative to the C=O group. Density functional theory calculations reproduce well the observed structure.

INTRODUCTION

Neutral zwitterionic molecules serve as interesting complements to formally anionic ligands for metal centers because the difference in charge modifies the nature of the donor according to the covalent bond classification.[1] In this regard, neutral zwitterionic versions of anionic carboxylate ligands[2-6] have found a variety of applications,[7-10] with representative examples of neutral carboxylates including deprotonated 1-(carboxymethyl)pyridinium (Cmp)[11] and *N*-(4-carboxybenzyl)pyridinium (Cbp),[12] which feature pyridinium moieties, as shown in Figure 1.[2a,3,4]

In addition to their occurrence as ligands in metal complexes, protonated forms of neutral carboxylates are also known. As such, it is of interest to both (i) compare the differential impact of coordinating a cationic metal center and a proton to a neutral carboxylate moiety, and (ii) compare the structure of the cationic carboxylic acid with neutral counterparts. Therefore, we report here the molecular structure of the carboxylic acid derivative, (CbpH)Br, and compare it to both neutral carboxylic acids and metal complexes.



Cmp **Cbp**

Figure 1. Neutral carboxylate ligands that feature pyridinium moieties.

RESULTS AND DISCUSSION

Both carboxylate and carboxylic acid groups are moieties that play important structural roles in solids.[13,14] Therefore, to complement the structural reports of metal compounds that incorporate the Cbp ligand,[4] the molecular structure of the protonated form, (CbpH)Br,[15] has been determined by using X-ray diffraction, as illustrated in Figure 2, with selected metrical data presented in Table 1.

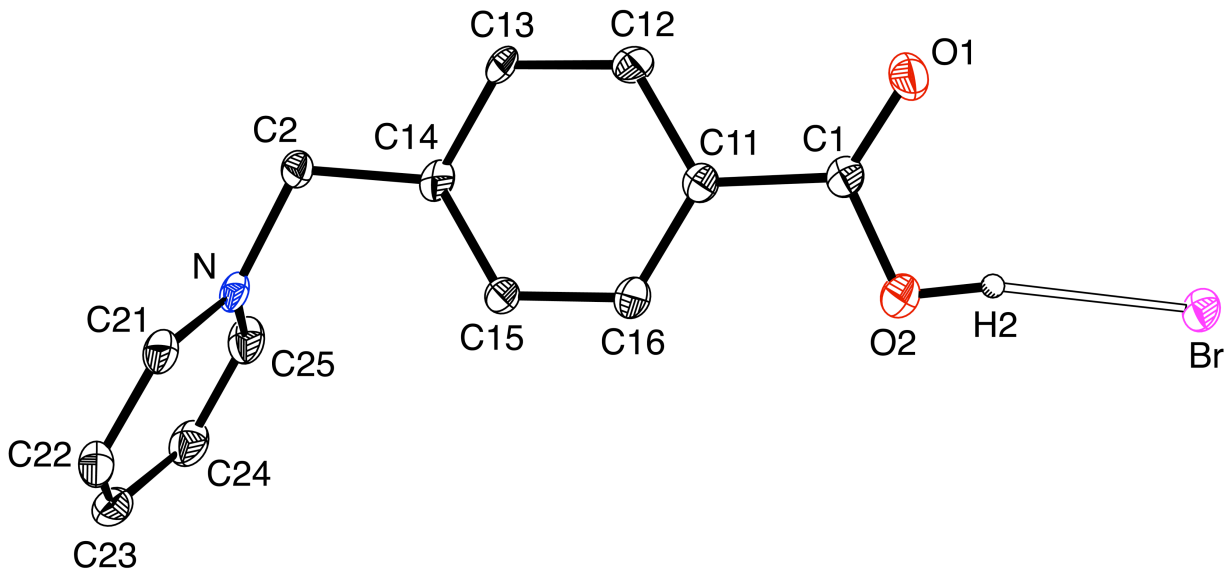


Figure 2. Molecular structure of (CbpH)Br (30 % displacement parameters).

Table 1. Selected bond lengths and angles for (CbpH)Br[a] and related compounds.

	(CbpH)Br	**(CmpH)Br**[b,c]	**Cmp**[c,d]
d(C1–O1) / Å	1.201(6)	1.195(5)	1.230
d(C1–O2) / Å	1.343(7)	1.300(5)	1.237
d(C1–C11) / Å	1.486(8)	1.504(5)	1.539
d(N–C2) / Å	1.484(7)	1.471(5)	1.477
d(O2•••Br) / Å	3.199(5)	3.116	–
O1–C1–O / °	122.8(5)	125.7(4)	128.58
N–C2–C14 / °	113.9(5)	111.4(3)	113.22

(a) Atom labeling refers to that for (CbpH)Br.

(b) reference 8.

(c) See Figure 1 for the structure of Cmp.

(d) reference 30.

The most notable aspect of (CbpH)Br is the absence of the hydrogen bonded motifs of the types illustrated in Figure 3 that are commonly observed for carboxylic acids.[13,14,16,17] Instead, the carboxylic acid group participates in a hydrogen bonding interaction with the bromide anion, which is characterized by *d*(O2–H•••Br) = 2.28(12) Å and *d*(O2•••Br) = 3.199 Å; the corresponding O•••Br distance for the carbonyl oxygen atom is 3.965 Å and so it is evident that there is no interaction between these atoms.[18] For reference, the O2•••Br hydrogen bonded distance compares favorably with that in related (CmpH)Br (Table 1 and Table 2)[19-26] and also the reported average value of 3.14 Å for such interactions.[27,28] The hydrogen bonding interaction within (CbpH)Br has also been analyzed via a Hirshfeld fingerprint plot[29] (Figure 4) which illustrates a distinct spike for the H•••Br interaction in the plots for both the $(CbpH)^+$ cation and Br^- anion.

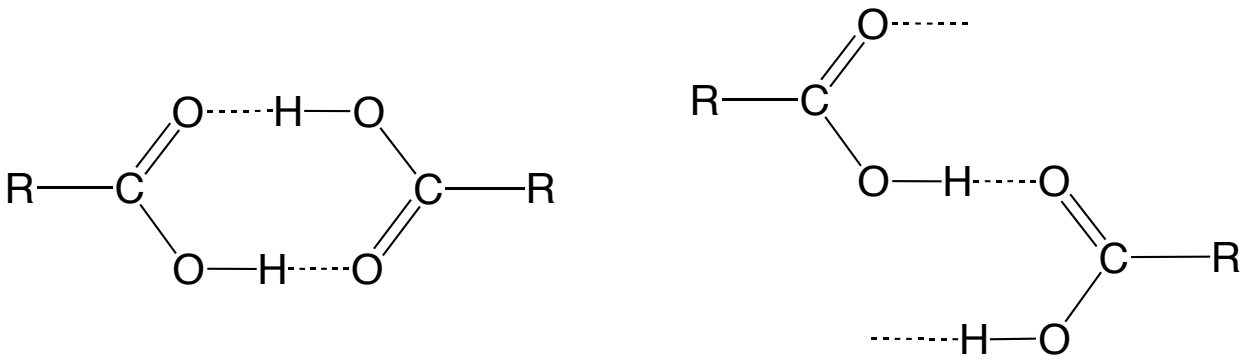


Figure 3. Common hydrogen bonding motifs for carboxylic acids.

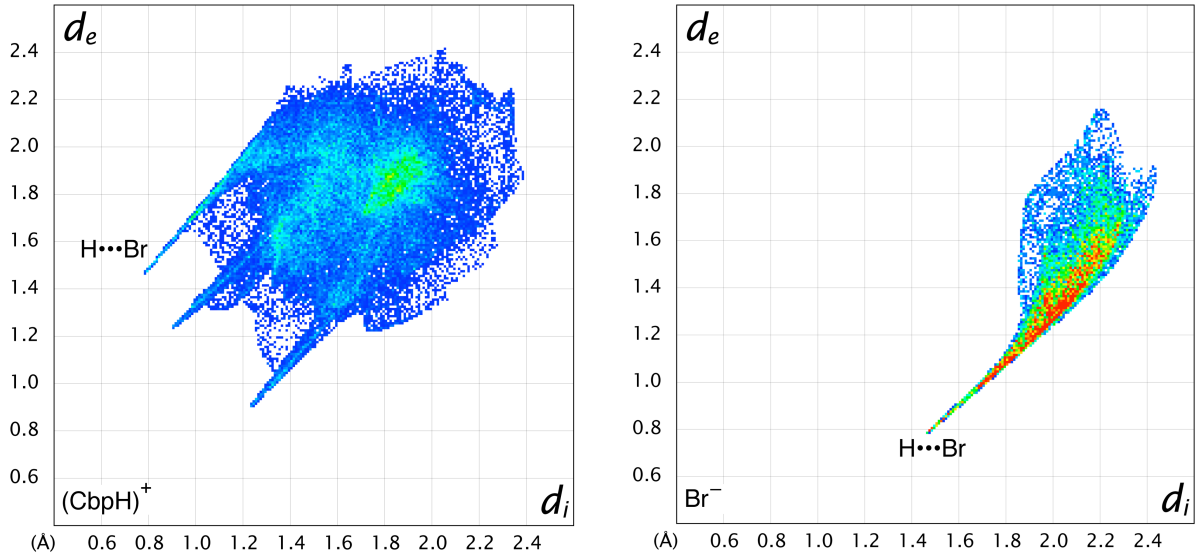


Figure 4. Hirshfeld fingerprint plots for the cation (left) and anion (right) of (CbpH)Br.

Also of note, the difference in C=O and C–O bond lengths of (CbpH)Br is 0.142 Å, which is comparable to that of 0.105 Å for (CmpH)Br; in marked contrast, however, the two C–O bonds of Cmp, which does not bear an O–H bond, differ by only 0.007 Å.[30] It is also relevant to compare the C–O bond lengths of (CbpH)Br with those in metal complexes in which there is a M–O bond rather than a O–H bond. In this regard, the difference in C=O and C–O bond lengths for Cbp-metal compounds is smaller than that for the carboxylic acid, (CbpH)Br. As an illustration, compared to a value of 0.142 Å for (CbpH)Br, Δ(C–O) for $[Zn(Cbp)(BDC)(H_2O)]_n$, is 0.055 Å,[4d] while that for $[Cu(Cbp)_2(H_2O)_2](NO_3)_2$ is 0.042 Å.[4c] For reference, Δ(C–O) for structurally

characterized unidentate metal carboxylate compounds listed in the CSD is 0.035 Å. Although the carboxylate coordination mode in $[Zn(Cbp)(BDC)(H_2O)]_n$ and $[Cu(Cbp)_2(H_2O)_2](NO_3)_2$ may be classified as unidentate since the difference in M–O bond lengths is > 0.6 Å,[6a,b] it is evident that this coordination impacts the bonding within the CO_2 moiety by both lengthening the C=O bond and shortening the C–O bond relative to that in the carboxylic acid.

Table 2. Hydrogen bonding interactions in (CbpH)Br and related compounds.

Complex	*d*(OH···X)/Å	*d*(O···X)/Å	C–O–X/°	O–C–O–X/°	Ref
(CbpH)Br	3.199	3.965	117.94	16.0	This work
(CmpH)Br [a]	3.116	3.909	118.14	11.0	8
(CmpH)Cl [a]	2.928	3.727	117.14	7.0	19
(4-NH_2CmpH)Cl [a]	2.971	3.714	115.25	1.1	20
(3-NH_2CmpH)Cl [a]	2.946	3.586	113.22	0.3	21
(2-NH_2CmpH)Cl [a]	2.975	3.872	120.49	0.8	22
(3-OHCmpH)Cl•H_2O [a]	2.993	3.735	114.82	14.7	23
(Btz$CH_2C_6H_4CO_2H$)Br [b]	3.190	3.829	114.48	7.6	24
($H_3NC_2H_4CO_2H$)F	2.403	3.277	116.20	4.4	25
($Me_3NCH_2CO_2H$)I	3.383	4.160	119.16	1.0	26

(a) See Figure 1 for the structure of Cmp.

(b) Btz = benzothiazole.

The presence of the O–H•••Br interaction clearly indicates that the bromide anion effectively interrupts the hydrogen bonding motifs that are commonly observed for carboxylic acids. The ability of Br^-, rather than the carboxylic acid moiety, to serve as a hydrogen bond acceptor in (CbpH)Br, nevertheless, has precedent. Indeed, an analysis of relevant structures that are listed in the CSD has demonstrated that halide ions are very effective hydrogen bond acceptors for carboxylic acids,[31] such that Br^- has been assigned a "relative success" factor, *succ*(A), of 0.81 for forming hydrogen bond interactions with carboxylic acid moieties; for reference, a relative success of 1.0 for a

given acceptor would indicate that all structures that feature carboxylic acids and an acceptor (A) possess only OH•••A hydrogen bonds, whereas a value 0.0 would indicate that there are no occurrences of OH•••A hydrogen bonds.[32,33]

Despite the precedence for O–H•••X (X = F, Cl, Br, I) interactions in related carboxylic acid-halide systems, however, there are examples in which the halide ions do not participate in hydrogen bonding interactions with the carboxylic acid group. For example, some structures exhibit hydrogen bonding of the carboxylic acid moiety to *(i)* another carboxylic group[34] and *(ii)* a water molecule.[35-37]

The molecular structure of (CbpH)Br is also in accord with that determined by density functional theory geometry optimization calculations, as illustrated in Figure 5 and Table 3, which also includes the geometry optimized structures for $(CbpH)^+$ and Cbp for additional comparison. Of note, the calculations reproduce well the [C(O)OH•••Br] moiety, and indicate that the hydrogen bonding interaction to the bromide anion does not significantly perturb the C–O bonds, in contrast to deprotonation that results in them becoming equivalent.

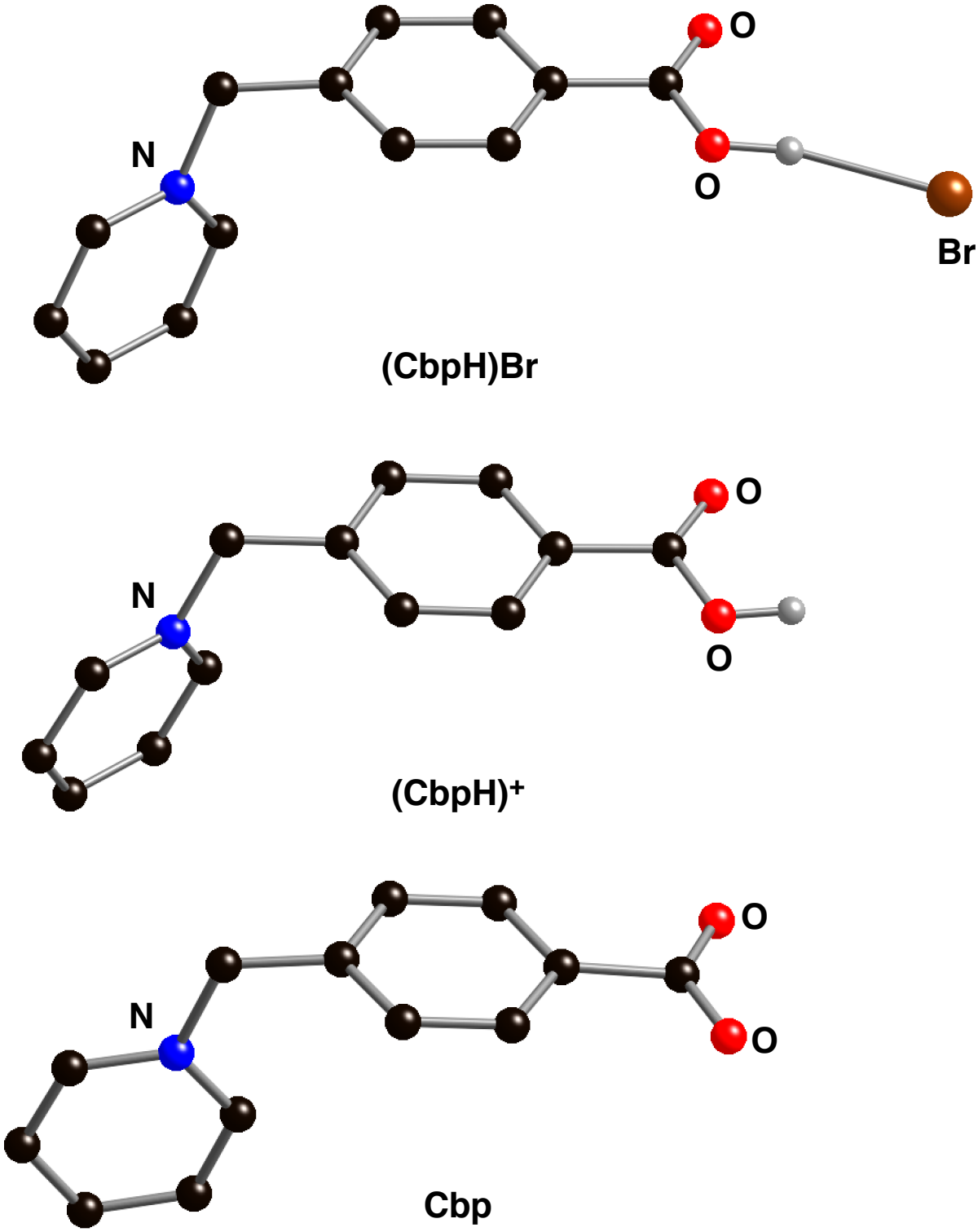


Figure 5. Geometry optimized structures of (CbpH)Br, $(CbpH)^{+}$ and Cbp.

Table 3. Comparison of the experimental structure of (CbpH)Br with those of the geometry optimized structures of (CbpH)Br, $(CbpH)^+$ and Cbp.

	(CbpH)Br (exptl)	**(CbpH)Br (DFT)**	**$(CbpH)^+$ (DFT)**	**Cbp (DFT)**
d(O1—C1)/Å	1.201(6)	1.218	1.212	1.253
d(O2—C1)/Å	1.343(7)	1.319	1.348	1.253
d(C1—C11)/Å	1.486(8)	1.513	1.498	1.549
d(N—C2) /Å	1.484(7)	1.508	1.517	1.535
d(O2•••Br) /Å	3.199(5)	3.150	–	–
O1—C1—O/°	122.8(5)	127.57	123.74	130.22
N—C2—C14/°	113.9(5)	112.56	113.02	113.08

Another relevant feature of the structure of (CbpH)Br is that the O–C–O–Br torsion angle is 16.0°, which indicates that the group is close to planar and that the H•••Br moiety is located *syn* to the carbonyl group (Figure 6).[13] Analysis of the O–C–O–Br torsion angles for [(RCO_2H)Br] compounds listed in the CSD indicates that the vast majority adopt *syn* conformations, with only two[38] exhibiting an *anti* conformation (Figure 7). A similar trend is observed for hydrogen bonding of carboxylic acids to other halides, with there also being only few occurrences of *anti* configurations for fluoride,[39] chloride,[40] and iodide[26] derivatives (see the Supplementary Information). With respect to the *syn*/*anti* conformational preferences of [(RCO_2H)X] species, it is pertinent to note that carboxylic acids exhibit the same preference, such that the *syn* conformers are more common.[13,41-44] It has also been noted that while the *syn* conformers are generally more stable, hydrogen bonding with the O–H group reduces this preference;[41] despite this stabilization, however, it is evident that hydrogen bonding to halide ions is insufficient to have a pronounced effect on the stability of these conformers.

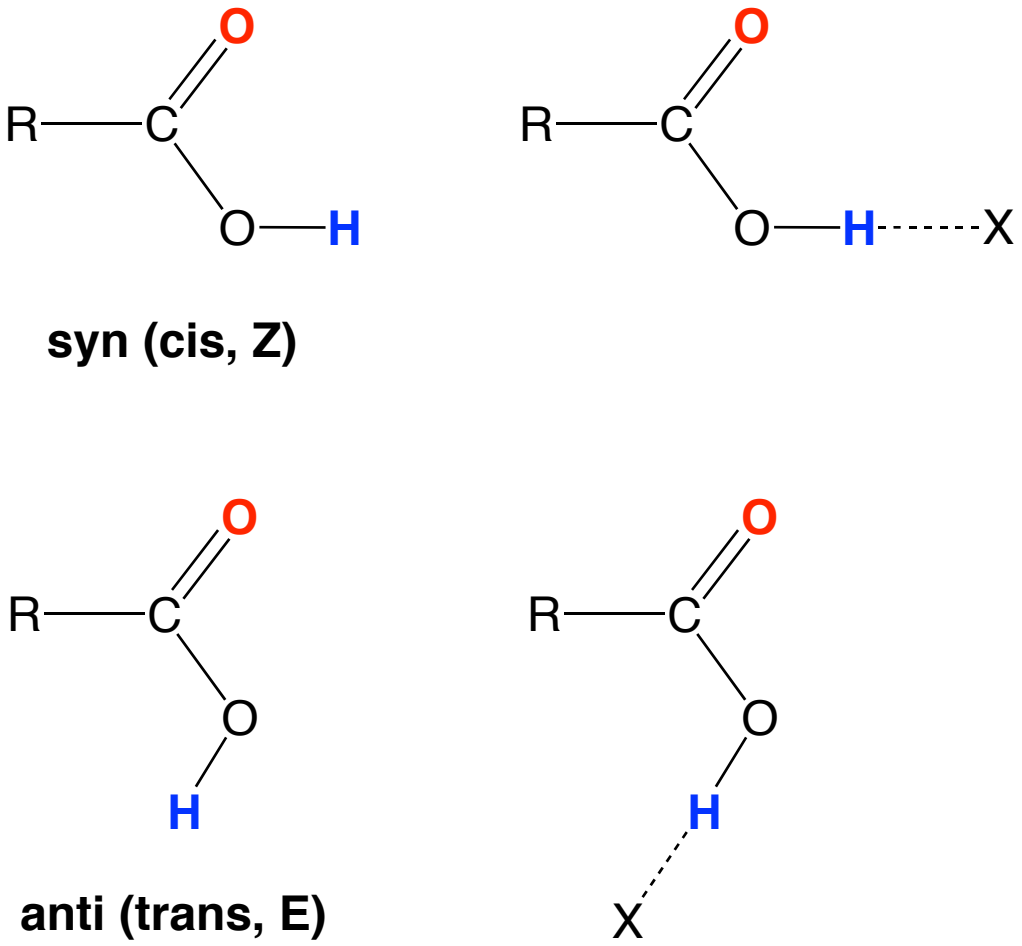


Figure 6. *Syn* and *anti* conformations of carboxylic acids and halide adducts.

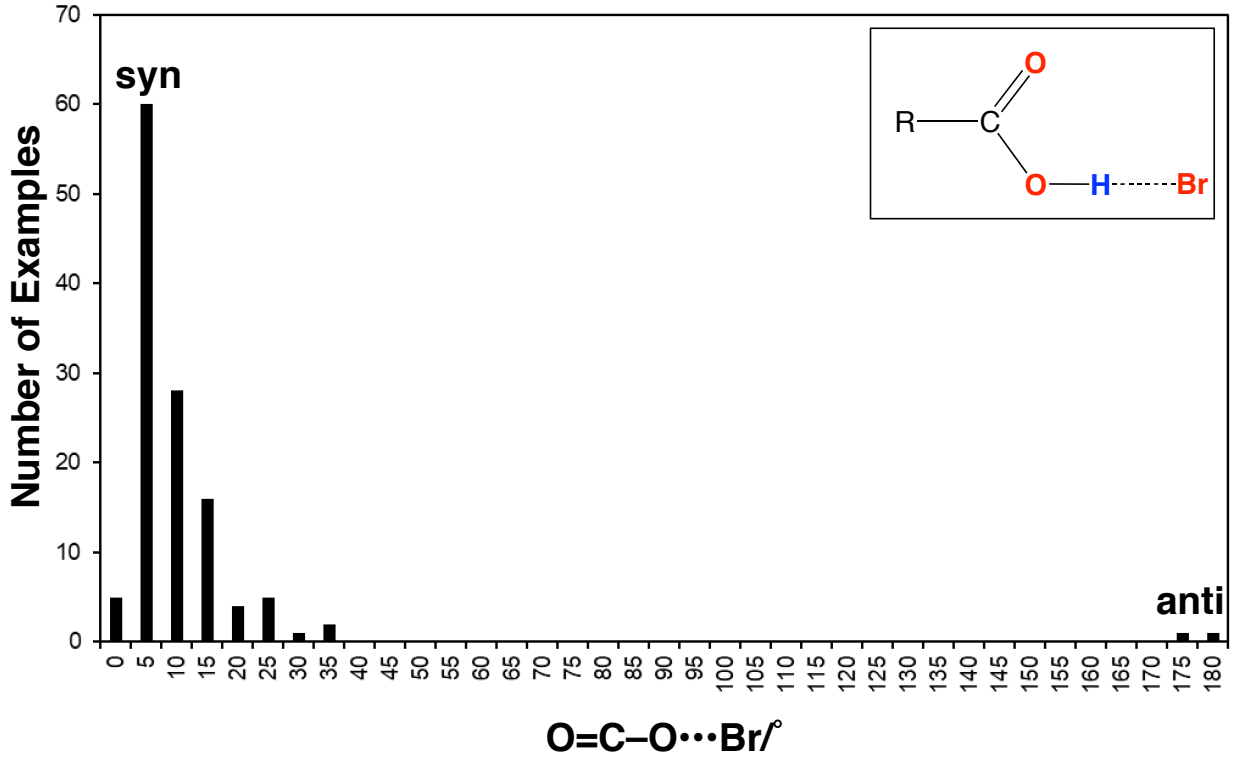


Figure 7. Distribution of O–C–O•••Br torsion angles for (RCO_2H)Br compounds listed in the CSD.

CONCLUSIONS

In summary, the molecular structure of (CbpH)Br has been determined by using X-ray diffraction and reveals a hydrogen bonding motif that is distinct from those commonly observed for carboxylic acids. Specifically, rather than exhibit intermolecular interactions between carboxylic acid groups, the structure possesses a [C(O)OH•••Br] hydrogen bonding interaction, with an O•••Br distance of 3.199 Å. The C=O and C–O bonds differ by 0.142 Å, which is distinctly larger than observed in Cbp-metal complexes. As such, it indicates that, relative to a hydrogen, coordination of a metal center impacts the CO_2 moiety by both lengthening the C=O bond and shortening the C–O bond. The structures of (CbpH)Br, $(CbpH)^+$ and Cbp have also been evaluated by performing density functional theory geometry optimization calculations which, as expected, indicate that the two C–O bonds become equivalent in the deprotonated form.

EXPERIMENTAL SECTION

X-ray Structure Determinations

(CbpH)Br was prepared by the literature method[15] and crystals (melting point 254 – 257 ˚C) suitable for X-ray diffraction were obtained from acetone. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are provided in the Supplementary Data. X-ray diffraction data (Table 4) were collected on a Bruker Apex II diffractometer. The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).[45] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC #2203540). Hirshfeld fingerprint plots were obtained by using *CrystalExplorer21*.[29e]

Table 4. Crystallographic data for (CbpH)Br.

	(CbpH)Br
lattice	Monoclinic
formula	$C_{13}H_{12}BrNO_2$
formula weight	294.15
space group	$P2_1/c$
a / Å	11.851(5)
b / Å	8.389(3)
c / Å	12.950(5)
α / °	90
β / °	107.968(6)
γ / °	90
V / Å^3	1224.6(8)
Z	4
temperature (K)	180(2)
radiation (λ, Å)	0.71073
ρ (calcd.), g cm^{-3}	1.595
μ (Mo Kα), mm^{-1}	3.345
θ max, deg.	26.239
no. of data collected	14521
no. of data	2505
no. of parameters	158
R_1 $[I > 2\sigma(I)]$	0.0597
wR_2 $[I > 2\sigma(I)]$	0.1358
R_1 [all data]	0.0992
wR_2 [all data]	0.1567
GOF	1.036
R_{int}	0.1278

Computational Details

Calculations were carried out by using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[46] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets. The starting geometries for the geometry optimizations were based on that corresponding to the structure of (CbpH)Br as determined by X-ray diffraction. Cartesian coordinates are provided in the Supplementary Data.

APPENDIX A. Supplementary Data

Crystallographic data in CIF format (CCDC #2203540); Cartesian coordinates for geometry optimized structures; NMR spectroscopic data; Figures illustrating the distribution of O–C–O•••X torsion angles for (RCO_2H)X compounds (X = F, Cl, I). The crystallographic data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/xxxxx

Acknowledgments

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