Crystal Structure of 2,6-Dimethylpyridinium Hydrogen Fumarate: Hydrogen Bonds of C(sp^3)–H···O, C(sp^2)–H···O and N$^+$–H···O$^-$(sp^3)

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X-ray diffraction study on 2,6-dimethylpyridinium hydrogen fumarate reveals that the same site of O$^-$(sp^3) is confined by hydrogen bonds not only of N$^+$–H···O$^-$, but also those of C(sp^3)–H···O and C(sp^2)–H···O.

Since reports of separate case of C(sp^3)–H···O and C(sp^2)–H···O hydrogen bonds are accelerated, it come to be known that they play important roles in supramolecular packing. However, objections to the existence of such hydrogen bond are still present in resent journal.[1] Normal hydrogen bonds such as N$^+$–H···O$^-$ are frequently observed in various salts,[2,3] and C(sp^2)–H···O hydrogen bonds are observed in some cases to appear with those normal ones.[4,5] However, C(sp^3)–H···O hydrogen bonds, which have been found in dimethyl oxalate[6] and in acetamide–barbital adduct[7] previously, are not so often discussed. At present, the structure of the title salt has been determined by X-ray diffraction, and it is observed that three kinds of hydrogen bonds such as N$^+$–H···O$^-$(sp^3), C(sp^3)–H···O and C(sp^2)–H···O are involved concurrently in the same site of O$^-$(sp^3). Of interesting is that extra energy consumed for the unique conformation of the title salt is compensated by C(sp^3)–H···O and C(sp^2)–H···O.

A single crystal used on the diffractometer for X-ray data collection was obtained in the following procedure. Being heated to a threshold temperature, the mixture of fumaric acid (FA) and 2,6-dimethylpyridine (DMP) in the molar ratios of 1:2 was solved. Crystals of the title salt were formed in the resulting solutions by standing overnight at 20 °C. The structure[8] of the title salt was solved by direct methods SHELXS-97, and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. While the hydrogen atoms involved in hydrogen bonding were deduced from difference Fourier maps, the others were placed in calculated positions.

Figure 1 shows the unit of FA and DMP with atom labels. The FA entity is linked with DMP by intermolecular hydrogen bond of [N···O (2) 2.619(2) Å, H(0)···O(2) 1.77 Å, N–H(0)···O(2) 166.9°] to result the title salt. And, by intermolecular hydrogen bond of [O(3)···O(1) (x, y, 1+z) 2.5527(18) Å, H(3)···O(1) 1.75 Å, O(3)–H(3)···O(1) 166.2°], the cell unit of FA and DMP is linked with each other.

Figure 2 shows the packing of cell unit viewed down along *c* axis. The O(2) atoms are confined by hydrogen bonds of [C(1)···O(2) (x, –y+3/2, z+1/2) 3.248(3) Å, H(1A)···O(2) 2.42 Å, C(1)–H(1A)···O(2) 143.9°] and [C(9)···O(2) (x, –y+3/2, z+1/2) 3.415(2) Å, H(9)···O(2) 2.51 Å, C(9)–H(9)···O(2) 163.6°]. Thus, all the unshared lone pair electron of the O(2) atoms, and the hydrogen atom originally attaching to O(2) are involved in hydrogen bonding. In addition, other hydrogen bonds of C(sp^3)–H···O, and C(sp^2)–H···O, i.e., [C(7)···O(1) (–x, 2–y, –z) 3.286(3) Å, H(7C)···O(1) 2.52 Å, C(7)–H(7C)···O(1) 137.0°] and [C(10)···O(4) (1–x, 2–y, 1–z) 3.568(3) Å, H(10)···O(4) 2.68 Å, C(10)–H(10)···O(4) 160.3°] are observed in the title salt.

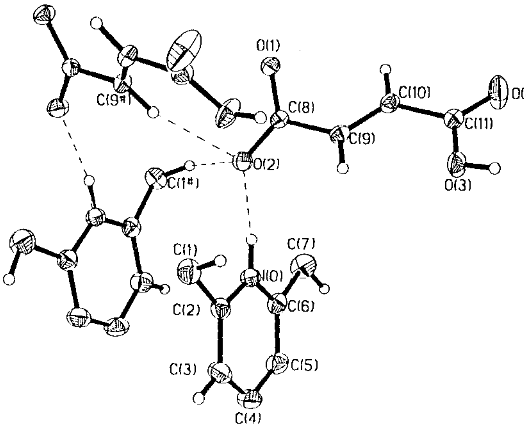


Figure 1. The FA and DMP units with atom labels, showing 50% probability displacement ellipsoids. H atoms are omitted for clarity, save those involved in hydrogen bonding, and selections of hydrogen bonding are illustrated as thin lines. # Symmetry code of (x, –y + 3/2, z + 1/2).

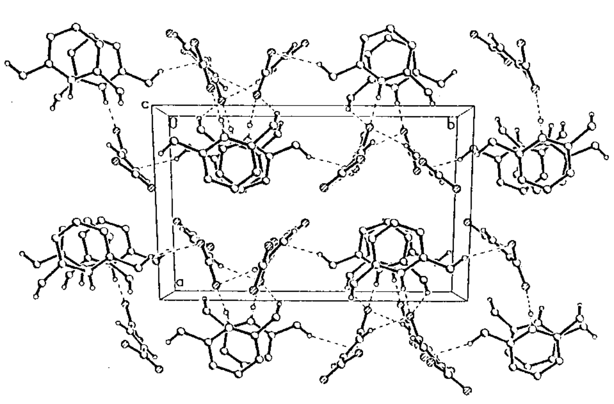
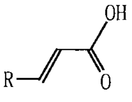
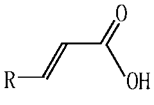


Figure 2. An illustration of the unit-cell packing of the title salt viewed down along the *c* axis. H atoms are omitted for clarity, saving those involved in hydrogen bonding.

Among the known structure of carboxylic acid with chain, there exist two types of conformers, the *syn*-planar and the *anti*-planar, as shown in followings.



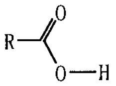
syn-planar (a)



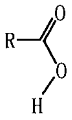
anti-planar (b)

In the title salt, the *syn*-planar and the *anti*-planar conformer for C(8)–C(9)–C(10)=O(1) and C(9)–C(10)–C(11)=O(4) concur respectively. Survey of several carboxylic acid shows that, while saturated acid and α,β-unsaturated esters always show the *syn*-planar conformation, the situation is not so clear for the case of α,β-unsaturated acid.[4] The *anti*-planar is always stablized because of lateral C–H···O hydrogen bond, for example as α-*trans*-cinnamic acid[4] the C···O distance is of 3.66 Å. In the title salt, the *anti*planar motif C(9)–C(10)–C(11)=O(4) is stablized by hydrogen bond of C(10)–H(10)···O(4).

Carboxylic groups may appear in two forms: *syn*-planar and *anti*-planar.



syn-planar (c)



anti-planar (d)

While carboxylic group of O(4)=C–O(3)–H adopts a *syn*-planar comformer, that of O(1)=C–O(2)–H demonstrate an *anti*-planar comformer. According to experimental[9] and theoretical results[10], the *syn*-planar is at least 2 kcal/mol more stable than the *anti*-planar. Theoretical calculation has been published for weakly polarized C–H groups, estimating C–H···O hydrogen bond energy to be around 0.5 to 1 kcal/mol.[11] In the title salt, the extra energy consumed for the *anti*-planar O(1)=C–O(2)–H is offset by hydrogen bond of C(1)–H(1A)···O(2) and C(9)–H(9)···O(2).

The average C–O distances of carboxylic groups that form intermolecular hydrogen bonds are given by Borthwiek[12] as 1.32(2) Å for the hydroxy C–OH, and 1.21(3) Å for the carbonyl C=O bond. The bond length of O(4)–C(11) [1.200(2) Å], O(3)–C(11) [1.299(2) Å] fall in the category of the normal COOH group.

The average C–O distance in the carboxylate anion is reported[12] as 1.25Å. In comparison by bond length of the normal carboxylate anion, while, the distance of O(1)–C(8) [1.249(2)Å] falls in the normal one, that of O(2)–C(8) [1.263(2)Å] is a little larger than the normal one, indicating a carboxylate motif with slight deviation. The deprotonation of O(1)–C(8)–O(2) results a group as a whole with extra electron, deloctation of which favors the formation of C(10)–H(10)···O(4) and C(9)–H(9)···O(2) hydrogen bonding.

The C–N–C angle of pyridines is very sensitive to protonation.[13,14] In the title salt, protonation of the heterocycle is indicated by the enlarged angle of C(2)–N–C(6) [123.92(17)°], and the reduced angle of N–C(2)–C(3) [117.82(19)°] and N–C(2)–C(1) [117.76(18)°]. In comparison of the geometry of DMP in the title salt and that of unprotonated DMP[15] in the 1:1 adduct of DMP and urea, the angle of C(10)–N(1)–C(14) is enlarged by 3.92°, consequently, the angle of N–C(2)–C(3) and N–C(2)–C(1) reduced by 2.24° respectively. These deviations are the indication of protonated DMP. Theoretical studies had revealed that the protonation of pyridine result more acidic of C–H group.[16,17] To same extension, it may account for the formation of hydrogen bonds of C(1)–H(1A)···O(2) and C(7)–H(7C)···O(1) in this case.

The carboxylate group of O(1)–C(8)–O(2) and the ring of pyridinium cation are not coplanar, but are skewed at a dihedral angle of 96.4°. As shown by the torsion angles of C(9)–C(10)–C(11)–O(3) [8.0(3)°] and O(1)–C(8)–C(9)–C(10) [25.8(3)°], the FA shown in the title salt is not coplanar.

References and Notes

1 F. A. Cotton, L. M. Daniels, G. T. Jordan IV, and C. A. Murillo, *Chem. Commun.*, 1673 (1997).
2 K. Kinbara, Y. Hashimoto, M. Sukegawa, H. Nohira, and K. Saigo, *J. Am. Chem. Soc.*, **118**, 3441 (1996).
3 A. Matsumoto, T. Odani, M. Chikada, K. Sada, and M. Miyata, *J. Am. Chem. Soc.*, **121**, 11122 (1999).
4 L. Leiserowitz, *Acta Crystallogr.*, *Sect. B*, **32**, 775 (1976).
5 I. L. Karle, D. Ranganathan, and V. Haridas, *J. Am. Chem. Soc.*, **118**, 7128 (1996).
6 M. W. Dougill and G. A. Jeffrey, *Acta Crystallogr.*, **6**, 831 (1953).
7 Z. Berkovitch-Yellin and L. Leiserowitz, *Acta Crystallogr.*, *Sect. B*, **40**, 159 (1984).
8 Crystal data: $C_{11}H_{13}NO_4$, fw 223.22, dimensions of 0.56 × 0.40 × 0.36 mm., monoclinic space group of $P2(1)/c$, a = 9.898(2) Å, b = 15.347(2) Å, c = 7.4970(10) Å, β = 107.810(10)°, V = 1084.3(3) Å^3, Z = 4, D_c = 1.367 g/cm^3, F(71073 Å, T = 292(2) K, ω–2θ scan, $2.16° < \theta < 25.00°$, 2233 reflections measured ($-11 \le h \le 11$, $-18 \le k \le 0$, $0 \le l \le 8$), 1913 unique with $I/\sigma(I) > 2.0$, $R_1 = 0.0405$, wR_2 = 0.1066.
9 T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.*, **30**, 1076 (1959).
10 D. R. Lide and Jr., *Annu. Rev. Phys. Chem.*, **15**, 225 (1964).
11 T. Van Mourik and F. B. Van Duijineveldt, *J. Mol. Struct.*, *THEOCHEM.*, **63**, 341 (1995).
12 P. W. Borthwick, *Acta Crystallogr.*, *Sect. B*, **36**, 628 (1980).
13 Z. M. Jin, Y. J. Pan, D. J. Xun, and Y. Z. Xu, *Acta Crystallogr. Sect. C*, **56**, e69(2000).
14 D. Boenigk and D. Mootz, *J. Am. Chem. Soc.*, **110**, 2135 (1988).
15 J. D. Lee and S. C. Wallwork, *Acta Crystallogr.*, **19**, 311 (1965).
16 J. W. Emsley and Inorg., *J. Chem. Soc.*, *Sect. A*, 1387 (1968).
17 Z. Dega-Szafran, A. Kania, B. Nowak-Wydra, and M. Szafran, *J. Mol. Struct.*, **322**, 223 (1994).