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Hydrogen Bonding in the 2,2′-Bipyridinium Salt of 1,2,4,5-Benzenetetracarboxylic Acid (Pyromellitic Acid)

DRAGINJA MRVOŠ-SERMEK, ZORA POPOVIĆ AND DUBRAVKA MATKOVIĆ-ČALOGOVIĆ

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia. E-mail: mrvos@olimp.irb.hr

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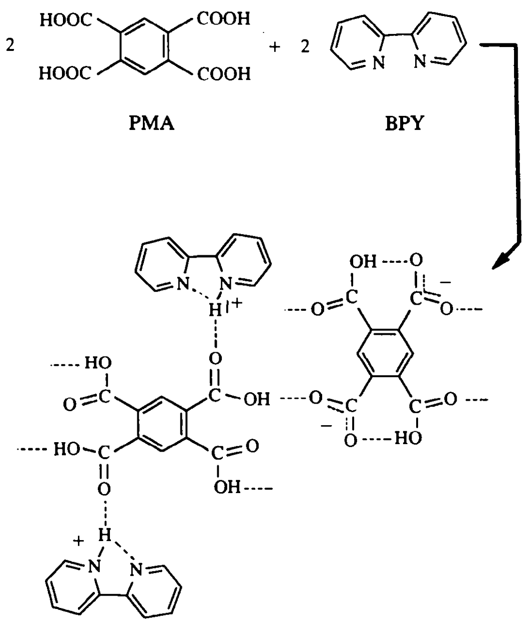
Abstract

The 2,2′-bipyridinium salt of pyromellitic acid (PMA, 1,2,4,5-benzenetetracarboxylic acid), 2,2′-bipyridinium hemi[1,2,4,5-benzenetetracarboxylate(2−)] hemi(1,2,4,5-benzenetetracarboxylic acid), $C_{10}H_8N_2H^+.\frac{1}{2}[C_6H_2(COO)_4H_2]^{2-}.\frac{1}{2}[C_6H_2(COO)_4H_4]$, has been prepared and studied by X-ray diffraction and IR spectroscopy. 2,2′-Bipyridine acts as a proton sponge by accepting a proton from pyromellitic acid. The transfer of protons results in strong asymmetric intramolecular hydrogen bonds; H(N)···N 2.603 (2) Å in the bipyridinium cation, which has a *syn* conformation, and H(O)···O 2.396 (2) Å in the pyromellitate anion. The N—H···N hydrogen bond is part of a three-centre hydrogen bond with a carbonyl group of the neutral pyromellitic acid; N—H···N/O with an N···O distance of 2.805 (2) Å. Each neutral PMA molecule is connected by hydrogen bonds to two cations and four anions forming a two-dimensional network with plane indices (112). The IR spectrum also suggests the presence of strong hydrogen bonds.

Comment

We decided to combine a hydrogen-bond donor molecule (pyromellitic acid, PMA) and a hydrogen-bond acceptor molecule having two basic N atoms (2,2′-bipyridine, BPY), (I), in order to explore the influence of weak forces such as hydrogen bonds and electrostatic interactions on the potential self-organization of molecules (Reetz, Höger & Harms, 1994). Also, in the course of a systematic investigation of compounds with short intramolecular hydrogen bonds (Jeffrey, 1995), acid salts of pyromellitic acid were of special interest.



(I)

One of the two crystallographically independent molecules of pyromellitic acid in (I) is deprotonated, with the two protons transferred to the N atoms of two bipyridine groups. The pyromellitate anion, PMA^{2-}, and the neutral PMA molecule lie on crystallographic centres of symmetry $(0,\frac{1}{2},0)$ and $(0,\frac{1}{2},\frac{1}{2})$, respectively. They are connected by H(O3)···O5 2.569 (2) (Fig. 1) and H(O1)···$O7^{i}$ 2.636 (2) Å hydrogen bonds [symmetry code: (i) $1-x$, $2-y$, $-z$]. The bond distances in the neutral PMA molecule and the PMA^{2-} anion are consistent with those usually found (Jessen, Küppers & Luehrs, 1992). The structure of the pyromellitate anion differs from that of the neutral acid. The ring of the neutral PMA molecule is planar, with the carboxyl groups rotated out of plane by 11.96 (8) and 75.6 (1)°, values which are similar to those found in PMA dihydrate (18 and 75°; Takusagawa, Hirotsu & Shimada, 1971). The carboxyl groups of the PMA^{2-} anion are twisted by 18.0 (1) and 6.9 (1)° with respect to the benzene ring, and the two neighbouring carboxylic acid groups are connected by a very short intramolecular hydrogen bond [O6···O8 2.396 (2) Å] which is clearly asymmet-

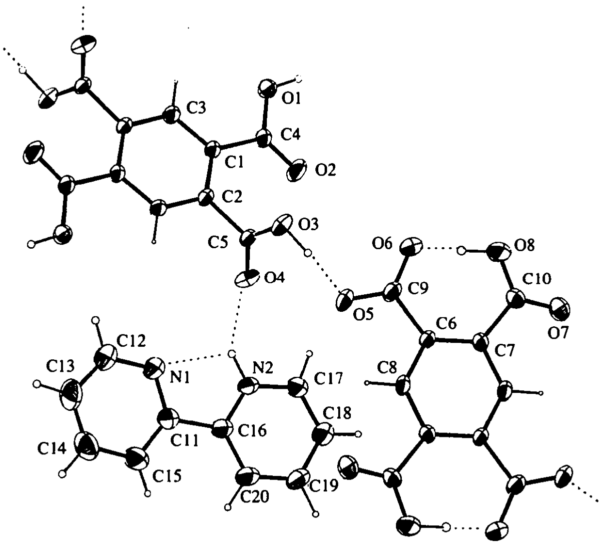


Fig. 1. *ORTEP*92 (Vicković, 1994) view of the molecules of (I), showing the atom-labelling scheme and the hydrogen-bond in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

ric [O8—H8 1.07 (2) and O6· · ·H8 1.34 (2) Å]. The formation of this extremely short hydrogen bond and the resulting repulsion of the carboxylic acid groups leads to a considerable deformation of the PMA^{2-} anion.

Attention shall be focused on the angles inside and around the benzene rings which usually have values *ca.* 120°. The angles formed by the carboxylic acid groups and the benzene ring, C6—C7—C10 and C7—C6—C9, show values of 128.13 (12) and 127.65 (12)°, respectively. Furthermore, the hexagon of the benzene ring is considerably deformed. The internal angles at C6 and C7 are reduced to below 118° and the angle at C8 between them is 124.85 (12)°. The distance between the C6 and C7 ring atoms bearing the carboxylic acid groups is increased [1.410 (2) Å]. Monoprotonated 2,2′-bipyridinium cations have been identified in many earlier crystal structure studies (Khan, Kumar & Tuck, 1984). The present work, as with those of earlier authors, shows that in the crystal lattice, the cation adopts a configuration in which the two N atoms are *syn*, in contrast to the *anti* stereochemistry found in the neutral molecule (Merritt & Schroeder, 1956) and in the diprotonated cation (Chantler & Maslen, 1989). The geometry of the monopositive cation is generally close to that of the neutral compound. The *syn* conformation is not stablized by a slight twisting about the C—C axis (Khan *et al.*, 1984) but by a strong asymmetric intramolecular hydrogen bond, N^+—H· · ·N (Decurtins, Schmalle, Schneuwly & Oswald, 1993). There are some significant differences between the protonated C_5H_4N moiety of the cation and the non-protonated ring, as noted previously (Khan *et al.*, 1984). The most significant point is an increase of the C—N—C angle at the protonated N2 atom [123.64 (13)°] and a corresponding decrease of the angles at the adjacent C16 and C17 atoms [117.82 (14) and 119.83 (15)°, respectively].

The geometry of the intramolecular N2—H· · ·N1 hydrogen bond [N· · ·N, N—H and N—H· · ·N are 2.603 (2), 0.92 (2) Å and 106 (2)°, respectively] establishes this bridge as truly asymmetric. The $BPYH^+$ cation is involved in a three-centre hydrogen bond with a carbonyl group of neutral pyromellitic acid; N2—H· · ·N1/O4 with an N· · ·O distance of 2.805 (2) Å and an N—H· · ·O angle of 138 (2)°. The four-atom configuration is planar as follows from the sum of the angles around the H atom [360 (2)°].

The absorption bands at 2500 and 1940 cm^{-1} are indicative of strong hydrogen bonding between the pyromellitic acid, its anions and the bipyridinium cations (Odinokov, Mashkovsky, Glazunov, Ioganson & Rassadin, 1976; Lee, Painter & Coleman, 1988; Kato, Kihara, Uryu, Fujishima & Fréchet, 1992; Kato, Uryu, Kaneuchi, Jin & Fréchet, 1993). The cations and anions are stacked along the *a* axis, forming 'sandwiches' of PMA^{2-}, $BPYH^+$, $BPYH^+$ and PMA^{2-} ions with only van der Waals contacts between them. Each neutral PMA molecule is connected by hydrogen bonds to two $BPYH^+$ and four PMA^{2-} ions, forming a two-dimensional network with plane indices (112) (Fig. 2 and Table 3).

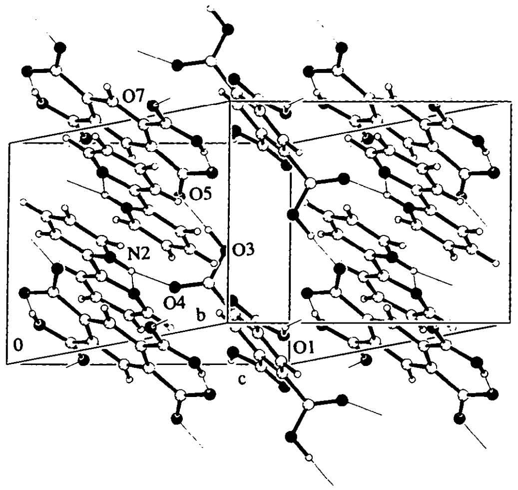


Fig. 2. Packing of the molecules in the unit cell. The pyromellitate anion, PMA^{2-}, and neutral PMA molecule lie on crystallographic centres of symmetry $(0,\frac{1}{2},0)$ and $(0,\frac{1}{2},\frac{1}{2})$, respectively. Each neutral PMA molecule is connected by hydrogen bonds (thin lines) to two $BPYH^+$ cations (O4· · ·H—N2) and four PMA^{2-} anions (O3—H· · ·O5 and O1—H· · ·O7).

Experimental

The reaction mixture was prepared by accurate weighing of pyromellitic acid and 2,2′-bipyridine in a 1:1 stoichiometry and by dissolving them in ethanol. Slow evaporation of the solvent at room temperature yielded crystals suitable for X-ray structure determination. The compound was characterized by IR spectroscopy and elemental analysis. Found: C 58.81, H 3.32%; calculated for $C_{20}H_{14}N_2O_8$: C 58.54, H 3.44%. The IR spectrum in the region 4000–450 cm^{-1} was recorded on a Perkin–Elmer FT–IR spectrophotometer Model 1600 using a KBr disk.

Crystal data

$C_{10}H_9N_2^+.\frac{1}{2}C_{10}H_4O_8^{2-}.\frac{1}{2}C_{10}H_6O_8$
$M_r = 410.33$
Triclinic
$P\bar{1}$
$a = 7.912\ (4)$ Å
$b = 10.307\ (5)$ Å
$c = 11.533\ (9)$ Å
$\alpha = 69.09\ (4)°$
$\beta = 87.72\ (3)°$
$\gamma = 84.06\ (6)°$
$V = 873.8\ (9)$ Å^3
$Z = 2$
$D_x = 1.559$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 8.60–16.83°$
$\mu = 0.123$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.55 × 0.30 × 0.20 mm
Transparent

Data collection

Philips PW1100 diffractometer updated by Stoe
ω/θ scans
Absorption correction: none
8255 measured reflections
5135 independent reflections
3010 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0253$
$\theta_{\rm max} = 30.09°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 14$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 100 min
intensity decay: 5%

Refinement

Refinement on F^2
$R(F) = 0.0434$
$wR(F^2) = 0.1032$
$S = 1.140$
5134 reflections
327 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.0338P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.124$
$\Delta\rho_{\rm max} = 0.360$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.188$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.0276 (2)	0.62280 (12)	0.40103 (12)	0.0255 (3)
C2	0.1299 (2)	0.49917 (13)	0.41489 (12)	0.0255 (3)
C3	−0.1015 (2)	0.62203 (13)	0.48657 (13)	0.0284 (3)
C4	0.0551 (2)	0.75264 (13)	0.29338 (13)	0.0290 (3)
C5	0.2758 (2)	0.48896 (13)	0.32964 (13)	0.0292 (3)
O1	−0.0287 (2)	0.86506 (10)	0.30435 (11)	0.0424 (3)
O2	0.1459 (2)	0.75279 (11)	0.20732 (10)	0.0455 (3)
O3	0.41073 (14)	0.53972 (11)	0.35046 (11)	0.0397 (3)
O4	0.2677 (2)	0.43037 (12)	0.25633 (11)	0.0469 (3)
C6	0.8823 (2)	0.55003 (13)	0.07401 (12)	0.0248 (3)
C7	0.9622 (2)	0.64554 (12)	−0.02758 (13)	0.0248 (3)
C8	0.9239 (2)	0.40887 (13)	0.09747 (13)	0.0279 (3)
C9	0.7521 (2)	0.58270 (14)	0.16282 (13)	0.0301 (3)
C10	0.9376 (2)	0.80409 (13)	−0.07402 (14)	0.0314 (3)
O5	0.66599 (15)	0.48694 (11)	0.22418 (11)	0.0477 (3)
O6	0.7345 (2)	0.70153 (11)	0.17194 (11)	0.0443 (3)
O7	1.0042 (2)	0.86988 (10)	−0.17144 (11)	0.0499 (3)
O8	0.8470 (2)	0.86584 (11)	−0.01146 (13)	0.0527 (4)
C11	0.4017 (2)	−0.0148 (2)	0.34354 (14)	0.0343 (3)
N1	0.3085 (2)	0.05731 (14)	0.40365 (13)	0.0431 (4)
C12	0.2344 (3)	−0.0162 (2)	0.5088 (2)	0.0535 (5)
C13	0.2501 (3)	−0.1596 (2)	0.5568 (2)	0.0559 (5)
C14	0.3468 (3)	−0.2318 (2)	0.4951 (2)	0.0499 (5)
C15	0.4251 (2)	−0.1589 (2)	0.3858 (2)	0.0422 (4)
C16	0.4782 (2)	0.07304 (14)	0.22683 (14)	0.0311 (3)
N2	0.4422 (2)	0.21122 (12)	0.19672 (12)	0.0339 (3)
C17	0.5000 (2)	0.3058 (2)	0.09424 (15)	0.0381 (4)
C18	0.6020 (2)	0.2631 (2)	0.0134 (2)	0.0391 (4)
C19	0.6441 (2)	0.1220 (2)	0.0411 (2)	0.0422 (4)
C20	0.5822 (2)	0.0269 (2)	0.1473 (2)	0.0410 (4)
H1O	−0.009 (3)	0.949 (2)	0.2441 (19)	0.061 (6)
H3O	0.508 (3)	0.526 (2)	0.298 (2)	0.064 (6)
H8O	0.811 (3)	0.790 (2)	0.074 (2)	0.070 (7)
HN2	0.375 (3)	0.243 (2)	0.2496 (18)	0.056 (6)

Table 2. *Selected geometric parameters (Å, °)*

C1—C3	1.390 (2)	C10—O7	1.218 (2)
C1—C2	1.399 (2)	C10—O8	1.277 (2)
C1—C4	1.494 (2)	C11—N1	1.339 (2)
C2—C3^{i}	1.388 (2)	C11—C15	1.382 (2)
C2—C5	1.506 (2)	C11—C16	1.475 (2)
C4—O2	1.201 (2)	N1—C12	1.329 (2)
C4—O1	1.318 (2)	C12—C13	1.374 (3)
C5—O4	1.208 (2)	C13—C14	1.365 (3)
C5—O3	1.302 (2)	C14—C15	1.377 (3)
C6—C8	1.388 (2)	C16—N2	1.342 (2)
C6—C7	1.410 (2)	C16—C20	1.384 (2)
C6—C9	1.521 (2)	N2—C17	1.335 (2)
C7—C8^{ii}	1.391 (2)	C17—C18	1.369 (2)
C7—C10	1.521 (2)	C18—C19	1.380 (2)
C9—O5	1.241 (2)	C19—C20	1.377 (2)
C9—O6	1.259 (2)		
C3—C1—C2	119.21 (12)	O5—C9—C6	116.52 (13)
C3—C1—C4	120.85 (12)	O6—C9—C6	120.70 (13)
C2—C1—C4	119.92 (11)	O7—C10—O8	121.20 (14)
C3^{i}—C2—C1	119.76 (11)	O7—C10—C7	118.91 (13)
C3^{i}—C2—C5	116.57 (12)	O8—C10—C7	119.89 (13)
C1—C2—C5	123.64 (12)	N1—C11—C15	123.56 (15)
C2^{i}—C3—C1	121.02 (12)	N1—C11—C16	114.07 (14)
O2—C4—O1	124.39 (13)	C15—C11—C16	122.37 (14)
O2—C4—C1	122.75 (13)	C12—N1—C11	116.9 (2)
O1—C4—C1	112.86 (12)	N1—C12—C13	123.2 (2)
O4—C5—O3	125.04 (13)	C14—C13—C12	119.3 (2)
O4—C5—C2	121.71 (15)	C13—C14—C15	119.0 (2)
O3—C5—C2	113.06 (13)	C14—C15—C11	118.0 (2)
C8—C6—C7	117.64 (11)	N2—C16—C20	117.82 (14)
C8—C6—C9	114.71 (12)	N2—C16—C11	115.69 (13)
C7—C6—C9	127.65 (12)	C20—C16—C11	126.49 (14)
C8^{ii}—C7—C6	117.51 (12)	C17—N2—C16	123.64 (13)
C8^{ii}—C7—C10	114.35 (12)	N2—C17—C18	119.83 (15)
C6—C7—C10	128.13 (12)	C17—C18—C19	118.65 (15)
C6—C8—C7^{ii}	124.85 (12)	C20—C19—C18	120.21 (14)
O5—C9—O6	122.78 (13)	C19—C20—C16	119.84 (15)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $2-x, 1-y, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8O···O6	1.07 (2)	1.34 (2)	2.396 (2)	169 (2)
N2—HN2···N1	0.92 (2)	2.19 (2)	2.603 (2)	106 (2)
O1—H1O···O7^{i}	0.92 (2)	1.76 (2)	2.636 (2)	159 (2)
O3—H3O···O5	0.99 (2)	1.58 (2)	2.569 (2)	174 (2)
N2—HN2···O4	0.92 (2)	2.05 (2)	2.805 (2)	138 (2)

Symmetry code: (i) $1-x, 2-y, -z$.

All non-H atoms in the structure were found by direct methods. All H atoms were located by subsequent isotropic refinement and difference electron-density synthesis. Final full-matrix least-squares refinement of the coordinates and anisotropic displacement parameters for the non-H atoms, and of the coordinates and isotropic temperature factors for the H atoms, reduced R to 0.0434.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*92 (Vicković, 1994) and *PLUTON* (Spek, 1993). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *CSU* (Vicković, 1988).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,4-Bis(1,3-benzothiazol-2-yl)furan

DRAGINJA MRVOŠ-SERMEK,[a]* VESNA TRALIĆ-KULENOVIĆ,[b]
ANTE NAGL[b] AND LELJA FIŠER-JAKIĆ[b]

[a]*Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia, and* [b]*Faculty of Textile Technology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia. E-mail: mrvos@olimp.irb.hr*

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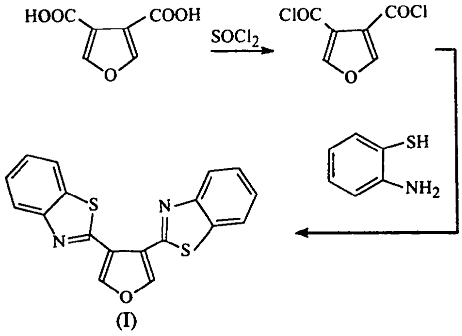
Abstract

The title compound, $C_{18}H_{10}N_2OS_2$, was prepared and characterized on the basis of its ^{1}H NMR and UV spectra, and X-ray diffraction analysis. The five-membered heterocyclic rings are flat and coplanar with their fused benzene rings. The furan ring is planar, with the 2-benzothiazolyl groups rotated out of plane by 6.3 (1) and 32.7 (1)°. The S atoms of the 2-benzothiazolyl groups are positioned *anti* with respect to one another.

Comment

In the course of our previous studies, we have paid attention on the synthesis and spectroscopic properties of some aryl- and heteroaryl-substituted benzothiazoles (Fišer-Jakić, Karaman & Jakopčić, 1980; Fišer-Jakić & Jakopčić, 1981; Tralić-Kulenović, Fišer-Jakić & Lazarević, 1993, 1994; Racané, Tralić-Kulenović, Karminski-Zamola & Fišer-Jakić, 1995). Similar substances are known and used as plant protectors and pharmaceuticals (Papenfuhs, 1987), growth-regulating substances (Chulák, Sutoris, Gáplovský & Sekerka, 1990), pesticides (Lácová, Chovancová, Hýblová & Varkonda, 1991), intermediates for dyes (Barni, Savarino, Larovere & Viscardi, 1986) and optical brighteners (Allen, 1971). Continuing the earlier investigations of furylbenzothiazoles, the title compound, 3,4-bis(1,3-benzothiazol-2-yl)furan, (I), was prepared.

The bond distances in both five-membered heterocyclic rings are consistent with those usually found



(I)