

## Structure of Benzenepentacarboxylic Acid

BY C. BARRIO, S. GARCÍA-GRANDA AND F. GÓMEZ-BELTRÁN

*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julián Clavería s/n, 33006 Oviedo, Spain*

(Received 7 February 1989; accepted 2 March 1990)

**Abstract.**  $C_{11}H_6O_{10}$ ,  $M_r = 298.2$ , monoclinic,  $P2_1/n$ ,  $a = 8.1104$  (2),  $b = 8.8737$  (2),  $c = 16.5061$  (5) Å,  $\beta = 102.068$  (4)°,  $V = 1161.68$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.70$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 1.47$  cm<sup>-1</sup>,  $F(000) = 608$ ,  $T = 293$  K, final conventional  $R$  factor = 0.037,  $wR = 0.039$  for 1589 observed reflections and 214 variables. The molecules are associated through their carboxylic groups forming a network of hydrogen bonds. The molecule, O atoms excluded, is essentially planar.

**Introduction.** As far as we know, the structures of nine of the twelve benzenecarboxylic acids have been determined by X-rays. Thus the structures of benzoic acid (Sim, Robertson & Goodwin, 1955; Bruno & Randaccio, 1980; Feld, Lehmann, Muir & Speakman, 1981), 1,2-benzenedicarboxylic acid (Nowacki & Jaggi, 1957; Küppers, 1981; Ermer, 1981), 1,3-benzenedicarboxylic acid (Alcalá & Martínez-Carrera, 1972; Derissen, 1974), 1,4-benzenedicarboxylic acid (Bailey & Brown, 1967; Colapietro, Domenicano, Marciante & Portalone, 1984), 1,2,3-benzenetricarboxylic acid (Fornies-Marquina, Courseille, Busetta & Hospital, 1972; Takusagawa & Shimada, 1973; Mo & Adman, 1975), 1,2,4-benzenetricarboxylic acid (Takusagawa, Hirotsu & Shimada, 1973), 1,3,5-benzenetricarboxylic acid (Duchamp & Marsh, 1969; Herbststein & Marsh, 1977; Herbststein & Kapon, 1978), 1,2,4,5-benzenetetracarboxylic acid (Takusagawa, Hirotsu & Shimada, 1971) and mellitic acid (Darlow, 1961) have been reported. The corresponding structures of 1,2,3,5-benzenetetracarboxylic, 1,2,3,4-benzenetetracarboxylic and benzenepentacarboxylic acids have not been determined by X-rays. The present paper reports the crystal and molecular structure of benzenepentacarboxylic acid. This investigation has been undertaken in order to determine the preferred solid-state conformation of the carboxyl groups.

**Experimental.** The title compound was prepared by oxidation of pentamethylbenzene with potassium permanganate at room temperature. The recovered crude material was crystallized several times from concentrated nitric acid. The crystalline compound

was analyzed (quantitative carbon and hydrogen analysis) showing it free of water of crystallization. The material was hygroscopic when exposed to the atmosphere. When the anhydrous compound was recrystallized from 3M HCl, very fine needles of a trihydrated variety (stable to the atmosphere) were obtained. An X-ray powder diagram of this hydrated compound has been published (Gómez-Beltrán & Fornies-Marquina, 1964).

Colorless crystals of the anhydrous compound, dimensions  $0.40 \times 0.23 \times 0.17$  mm. Because of instability, the data collection was performed using a crystal coated with an araldite film. Despite protection, data collection had to be stopped before planned owing to crystal destruction. Mo  $K\alpha$  radiation used with a graphite-crystal monochromator, Nonius CAD-4 single-crystal diffractometer ( $\lambda = 0.71073$  Å). Unit-cell dimensions determined from the angular settings of 25 reflections,  $20 < \theta < 30^\circ$ . Space group  $P2_1/n$  from the systematic absences. 5255 reflections measured,  $hkl$  range  $(-11, -12, 0)$  to  $(3, 12, 23)$ ,  $\theta$  limits  $(0 < \theta < 30^\circ)$ ;  $\omega$ - $2\theta$  scan technique with a variable scan rate and a maximum scan time of 60 s per reflection. Intensity of the primary beam checked by monitoring three standard reflections every 60 min. Drift correction factors between 0.99 and 1.35. Profile analysis performed on all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Symmetry-equivalent reflections averaged,  $R_{int} = 0.054$ , 2587 unique reflections, 1598 observed with  $I > 3\sigma(I)$ . Lorentz and polarization corrections applied and data reduced to  $|F_o|$  values. Structure solved by direct methods using MITHRIL (Gilmore, 1984). The electron-density map showed all non-H atoms. Isotropic least-squares refinement, using SHELX76 (Sheldrick, 1976), converged to  $R = 0.099$ . At this stage, an empirical absorption correction (Walker & Stuart, 1983) was applied, resulting in a further decrease of  $R$  to 0.090. Maximum and minimum absorption corrections 1.26 and 0.64. Further anisotropic refinements followed by a difference Fourier synthesis resulted in the location of all the H atoms.

During the final stages of the refinement the positional parameters and the anisotropic thermal

Table 1. Fractional positional and thermal parameters with e.s.d.'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq} (\times 10^3)$
C(1)	0.3142 (3)	0.0770 (2)	0.5830 (1)	2.12 (6)
C(2)	0.3617 (3)	-0.0741 (2)	0.5814 (1)	2.06 (6)
C(3)	0.3127 (3)	-0.1582 (2)	0.5081 (1)	2.07 (6)
C(4)	0.2115 (3)	-0.0923 (2)	0.4386 (1)	2.09 (6)
C(5)	0.1659 (3)	0.0605 (2)	0.4403 (1)	2.19 (6)
C(6)	0.2200 (3)	0.1432 (2)	0.5126 (1)	2.22 (6)
C(11)	0.3635 (3)	0.1650 (2)	0.6616 (1)	2.42 (7)
C(21)	0.4549 (3)	-0.1492 (2)	0.6594 (1)	2.28 (6)
C(31)	0.3816 (3)	-0.3149 (2)	0.5068 (1)	2.41 (7)
C(41)	0.1450 (3)	-0.1835 (2)	0.3614 (1)	2.34 (6)
C(51)	0.0662 (3)	0.1353 (2)	0.3648 (1)	2.43 (6)
O(11)	0.3901 (2)	0.1034 (2)	0.7287 (1)	3.10 (5)
O(12)	0.3724 (3)	0.3106 (2)	0.6499 (1)	3.30 (6)
O(21)	0.6073 (2)	-0.1281 (2)	0.6851 (1)	2.78 (5)
O(22)	0.3586 (2)	-0.2309 (2)	0.6938 (1)	3.44 (6)
O(31)	0.5174 (2)	-0.3471 (2)	0.5503 (1)	3.95 (6)
O(32)	0.2889 (3)	-0.4080 (2)	0.4557 (1)	4.41 (7)
O(41)	-0.0010 (2)	-0.2307 (2)	0.3504 (1)	3.03 (5)
O(42)	0.2492 (2)	-0.2077 (2)	0.3142 (1)	3.26 (5)
O(51)	0.0205 (2)	0.0698 (2)	0.2993 (1)	3.35 (6)
O(52)	0.0363 (3)	0.2782 (2)	0.3759 (1)	4.48 (8)

Table 2. Bond lengths (Å), angles (°) and hydrogen-bond parameters (Å, °) with e.s.d.'s in parentheses

C(1)—C(2)	1.397 (2)	C(11)—O(11)	1.214 (2)
C(1)—C(6)	1.381 (3)	C(11)—O(12)	1.310 (2)
C(1)—C(11)	1.494 (3)	C(21)—O(21)	1.235 (3)
C(2)—C(3)	1.406 (3)		
C(2)—C(21)	1.505 (3)	C(21)—O(22)	1.282 (2)
C(3)—C(4)	1.393 (3)	C(31)—O(31)	1.217 (3)
C(3)—C(31)	1.501 (3)	C(31)—O(32)	1.301 (3)
C(4)—C(5)	1.408 (2)	C(41)—O(41)	1.233 (3)
C(4)—C(41)	1.510 (3)	C(41)—O(42)	1.282 (2)
C(5)—C(6)	1.392 (3)	C(51)—O(51)	1.214 (3)
C(5)—C(51)	1.493 (3)	C(51)—O(52)	1.311 (2)
C(1)—C(11)—O(11)	121.4 (2)	C(4)—C(3)—C(31)	122.3 (2)
C(1)—C(11)—O(12)	113.6 (2)	C(4)—C(41)—O(41)	118.0 (2)
C(1)—C(2)—C(21)	120.0 (2)	C(4)—C(41)—O(42)	116.0 (2)
C(1)—C(2)—C(3)	119.8 (2)	C(4)—C(5)—C(51)	120.7 (2)
C(1)—C(6)—C(5)	121.1 (2)	C(4)—C(5)—C(6)	119.3 (2)
C(2)—C(1)—C(11)	119.6 (2)	C(5)—C(4)—C(41)	119.0 (2)
C(2)—C(1)—C(6)	119.9 (2)	C(5)—C(51)—O(51)	122.8 (2)
C(2)—C(21)—O(21)	121.0 (2)	C(5)—C(51)—O(52)	113.4 (2)
C(2)—C(21)—O(22)	112.7 (2)	C(6)—C(1)—C(11)	120.5 (2)
C(2)—C(3)—C(31)	117.7 (2)	C(6)—C(5)—C(51)	120.0 (2)
C(2)—C(3)—C(4)	119.9 (2)	O(11)—C(11)—O(12)	125.0 (2)
C(3)—C(2)—C(21)	120.1 (2)	O(21)—C(21)—O(22)	126.3 (2)
C(3)—C(31)—O(31)	120.2 (2)	O(31)—C(31)—O(32)	124.3 (2)
C(3)—C(31)—O(32)	115.5 (2)	O(41)—C(41)—O(42)	126.0 (2)
C(3)—C(4)—C(41)	121.0 (2)	O(51)—C(51)—O(52)	123.9 (2)
C(3)—C(4)—C(5)	120.0 (2)		
D—H	D...A	H...A	D—H...A
O(12)—H(12)	O(12)...O(51)	H(12)...O(51)	O(12)—H(12)...O(51 <sup>ii</sup> )
0.95 (5)	2.723 (2)	1.78 (5)	170 (5)
O(22)—H(22)	O(22)...O(41)	H(22)...O(41)	O(22)—H(22)...O(41 <sup>iv</sup> )
1.17 (4)	2.620 (2)	1.46 (4)	169 (4)
O(32)—H(32)	O(32)...O(31)	H(32)...O(31)	O(32)—H(32)...O(31 <sup>iv</sup> )
0.95 (5)	2.696 (3)	1.74 (5)	176 (4)
O(42)—H(42)	O(42)...O(21)	H(42)...O(21)	O(42)—H(42)...O(21 <sup>iv</sup> )
1.04 (3)	2.639 (2)	1.62 (3)	168 (3)
O(52)—H(52)	O(52)...O(11)	H(52)...O(11)	O(52)—H(52)...O(11 <sup>v</sup> )
0.89 (4)	2.685 (2)	1.80 (4)	174 (4)

Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $-x + 1, -y - 1, -z + 1$ ; (iv)  $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$ ; (v)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

parameters of the non-H atoms were refined. H atoms refined isotropically. Final conventional agreement factors were  $R = 0.037$ ,  $wR = 0.039$  for 1589 observed reflections and 214 variables. Function minimized  $\sum w(F_o - F_c)^2$ ,  $w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$ ,  $\sigma(F_o)$  from counting statistics. Maximum shift/e.s.d. in the last full-matrix least-squares cycle less than 0.06. Final difference Fourier map showed no fluctuations higher than  $\pm 0.2 \text{ e } \text{Å}^{-3}$ . Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Plots made with *PLUTO* (Motherwell, 1976). Geometrical calculations made with *PARST* (Nardelli, 1983).

**Discussion.** Final positional and thermal parameters are given in Table 1.\* Molecular-geometry data are collected in Table 2. A plot of the molecule, showing the molecular configuration and crystallographic numbering scheme is given in Fig. 1.

The molecule, O atoms excluded, is almost planar, fitting to a least-squares ideal plane defined by all C atoms. Carboxylic groups connected to C(2) and C(4) are related approximately by a twofold axis through the atoms C(3), C(6) and C(31). The rest of the carboxylic groups are not related by this symmetry as can be seen from the dihedral angles given below. The benzene ring shows a weak distortion from the ideal least-squares plane. The puckering parameters (Cremer & Pople, 1975) are  $Q = 0.030 (2)$ ,  $\varphi = -44. (4)^\circ$  and  $\theta = 100. (4)^\circ$ .

It was found that like other benzenecarboxylic acids with adjacent carboxyl groups, these have

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, least-squares-planes data, and principal torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53110 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

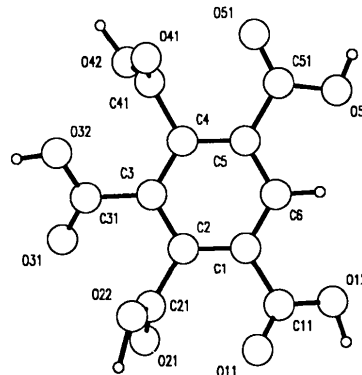


Fig. 1. A *PLUTO* (Motherwell, 1976) plot showing the atomic arrangement and numbering.

several orientations referred to the C-atom plane, namely 26.5 (2), 76.4 (1), 29.8 (1), 79.7 (1) and 3.0 (2)° showing, alternately, low and high-angle values owing to steric hindrance and repulsion between O atoms. This molecular conformation is similar to the conformation found for benzenehexacarboxylic acid (Darlow, 1961) and differs from 1,2,4,5-benzenetetracarboxylic acid (Takusagawa, Hirotsu & Shimada, 1973) which shows a center of symmetry. The distances and angles are as expected for this type of compound.

Geometrical features of the hydrogen bonds are shown in Table 2. The molecules are associated through their carboxylic groups forming a network of hydrogen bonds. There are centrosymmetric hydrogen bonds connecting related molecules by a double hydrogen-bond link through the carboxylic group attached to C(3). The rest of the carboxyl groups are also doubly hydrogen bonded as donor and acceptor to different molecules, related by glide-plane symmetry. The effect of this hydrogen-bonding network on the packing seems to be too weak to protect the anhydrous material against the attack of water in the atmosphere, this probably being responsible for the observed instability of the crystal employed.

#### References

- ALCALÁ, R. & MARTÍNEZ-CARRERA, S. (1972). *Acta Cryst.* **B28**, 1671–1677.  
 BAILEY, M. & BROWN, C. J. (1967). *Acta Cryst.* **22**, 387–391.  
 BRUNO, G. & RANDACCIO, L. (1980). *Acta Cryst.* **B36**, 1711–1712.  
 COLAPIETRO, M., DOMENICANO, A., MARCIANTE, C. & PORTALONE, G. (1984). *Acta Cryst.* **A40**, C98–C99.  
 CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **95**(6), 1354–1358.  
 DARLOW, S. F. (1961). *Acta Cryst.* **14**, 159–166.  
 DERISSEN, J. L. (1974). *Acta Cryst.* **B30**, 2764–2765.  
 DUCHAMP, D. J. & MARSH, R. E. (1969). *Acta Cryst.* **B25**, 5–19.  
 ERMER, O. (1981). *Helv. Chim. Acta*, **64**, 1902–1909.  
 FELD, R., LEHMANN, M. S., MUTR, K. W. & SPEAKMAN, J. C. (1981). *Z. Kristallogr.* **157**, 215–231.  
 FORNIES-MARQUINA, J. M., COURSEILLE, C., BUSETTA, B. & HOSPITAL, M. (1972). *Cryst. Struct. Commun.* **1**, 47–50.  
 GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.  
 GÓMEZ-BELTRÁN, F. & FORNIES-MARQUINA, J. M. (1964). *Combustibles*, **24**(135–136), 77–86.  
 GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.  
 HERBSTSTEIN, F. H. & KAPON, M. (1978). *Acta Cryst.* **B34**, 1608–1612.  
 HERBSTSTEIN, F. H. & MARSH, R. E. (1977). *Acta Cryst.* **B33**, 2358–2367.  
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.  
 KÜPPERS, H. (1981). *Cryst. Struct. Commun.* **10**, 989–991.  
 MO, F. & ADMAN, E. (1975). *Acta Cryst.* **B31**, 192–198.  
 MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.  
 NOWACKI, W. & JAGGI, H. (1957). *Z. Kristallogr.* **109**, 272–283.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* **8**, 157–164.  
 TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1971). *Bull. Chem. Soc. Jpn*, **44**, 1274–1278.  
 TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2960–2965.  
 TAKUSAGAWA, F. & SHIMADA, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2998–3004.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1990). **C46**, 2401–2405

## Structures of a Spiro[3.3]heptane and a Related Dispiro[3.1.3.]decane Derivative

BY JOSEPH A. POTENZA, PAIVI J. KUKKOLA, SPENCER KNAPP AND HARVEY J. SCHUGAR  
*Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick,  
 New Jersey 08903, USA*

(Received 4 August 1989; accepted 26 February 1990)

**Abstract.** 2,2,6,6-Tetrakis(mesyloxymethyl)spiro[3.3]heptane (1),  $C_{15}H_{28}O_{12}S_4$ ,  $M_r = 528.64$ , triclinic,  $P\bar{1}$ ,  $a = 10.319$  (1),  $b = 14.233$  (2),  $c = 8.5187$  (9) Å,  $\alpha = 97.87$  (1),  $\beta = 104.08$  (1),  $\gamma = 98.86$  (1)°,  $V = 1179.0$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.46$  (1),  $D_x = 1.489$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 0.44$  mm<sup>-1</sup>,  $F(000) = 556$ ,  $T = 298$  (1) K,  $R = 0.036$  for 2411 reflections. Diethyl 8,8-bis(mesyloxymethyl)dispiro[3.1.3.]decane-2,2-dicarboxylate (2),  $C_{20}H_{32}O_{10}S_2$ ,  $M_r = 496.60$ , triclinic,  $P\bar{1}$ ,  $a = 12.168$  (1),  $b = 16.789$  (2),  $c = 5.9411$  (6) Å,  $\alpha =$

$90.416$  (8),  $\beta = 94.294$  (9),  $\gamma = 87.590$  (9)°,  $V = 1209.2$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.35$  (1),  $D_x = 1.364$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 0.26$  mm<sup>-1</sup>,  $F(000) = 528$ ,  $T = 292$  (1) K,  $R = 0.037$  for 2530 reflections. The cyclobutane rings in both structures are puckered. Dihedral angles of these rings in the spiroheptane derivative (1) [12.9 (7) and 21.2 (5)°], and in the end rings of the dispirodecane derivative (2) [18.9 (5) and -18.5 (4)°], are significantly smaller than that for the central cyclobutane ring in (2) [29.0 (3)°]. Ring puckering in (2) gives the