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Structures of 1,2,3,4-Benzenetetracarboxylic Acid and 1,2,3,5-Benzenetetracarboxylic Acid Dihydrate

By C. Barrio

Departamento de Filosofía y Psicología, Facultad de Filosofía, Psicología y C. Educación, Aniceto Sela s/n, 33005 Oviedo, Spain

and 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

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Abstract. 1,2,3,4-Benzenetetracarboxylic acid (compound *A*), $C_{10}H_6O_8$, $M_r = 254.2$, triclinic, $P\overline{1}$, $a = 9.5616\,(1)$, $b = 8.4696\,(1)$, $c = 7.0568\,(1)$ Å, $\alpha = 106.806\,(1)$, $\beta = 100.192\,(1)$, $\gamma = 69.557\,(1)°$, $V = 510.77\,(1)$ Å^3, $Z = 2$, $D_x = 1.65$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.39$ cm^{-1}, $F(000) = 260$, $T = 293$ K, final conventional $R = 0.036$, $wR = 0.039$ for 1699 'observed' reflections and 187 variables. 1,2,3,5-Benzenetetracarboxylic acid dihydrate (compound *B*), $C_{10}H_6O_8.2H_2O$, $M_r = 290.2$, triclinic, $P\overline{1}$, $a = 5.845\,(4)$, $b = 7.828\,(6)$, $c = 13.31\,(1)$ Å, $\alpha = 94.8\,(1)$, $\beta = 100.6\,(1)$, $\gamma = 93.63\,(9)°$, $V = 594.6\,(9)$ Å^3, $Z = 2$, $D_x = 1.62$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.41$ cm^{-1}, $F(000) = 300$, $T = 293$K, final conventional $R = 0.070$, $wR = 0.072$ for 2354 'observed' reflections and 221 variables. The molecules in both structures are associated through their carboxylic groups forming a network of hydrogen bonds including water molecules in *B*. The molecules, O atoms excluded, are essentially planar in both compounds. The benzene rings show a week distortion towards a half-chair conformation for compound *A* and towards a slightly twisted boat conformation for *B*. The angles between the planes of the carboxyl groups and the least-squares plane of the C atoms of the ring are respectively 2.5 (2), 82.8 (1), 72.7 (1) and 14.7 (1)° for compound *A*, and 6.6 (3), 85.6 (3), 4.0 (3) and 5.8 (3)° for *B*.

Introduction. Benzenecarboxylic acids form a complete 'group' (12 members) of compounds whose physicochemical properties must depend on the

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* To whom correspondence should be addressed.

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number and the preferred spatial disposition of their carboxyl groups. Seeking inferences about changes in physicochemical properties correlated with the number and spatial disposition around the benzene ring of the carboxyl groups present in the 12 members of the group we began, a couple of years ago, to solve the remaining 'unknown' crystal structures of the 'group'. We have published the structure of the benzenepentacarboxylic acid (Barrio, García-Granda & Gómez-Beltrán, 1990) and now we report the structures of the 1,2,3,4-benzenetetracarboxylic acid (prehnitic acid) and 1,2,3,5-benzenetetracarboxylic acid. Knowledge of these two crystal structures completes the X-ray structural analysis of the group.

Table 1. *Experimental data*

	Compound *A*	Compound *B*
Crystal colour	Colourless	Colourless
Crystal shape	Prismatic	Prismatic
Crystal size (mm)	0.33 × 0.17 × 0.17	0.53 × 0.30 × 0.13
Drift corrections range	0.99–1.08	0.96–1.00
θ limits (°)	0–30	0–30
h, *k*, *l* range	$-13, -11, -9$ to 13, 11, 9	$0, -10, -18$ to 8, 10, 18
Number of measured reflections	5984	6844
Number of unique reflections	2972	3422
R_{int} (for some measured twice)	0.051	0.024
Number of observed reflections $I > 3\sigma(I)$	1699	2354
Number of refined parameters	187	221
R, *wR*	0.036, 0.039	0.070, 0.072
g value	0.0004	0.0012
Maximum shift/σ	0.02	0.02
Final difference Fourier synthesis maximum/minium (e Å^{-3})	0.2 −0.2	0.4 −0.6

Experimental. The benzenecarboxylic acids employed for growing crystals of the two subject compounds were prepared by slow oxidation at room temperature of the corresponding tetramethylbenzenes (prehnitene and isodurene) with aqueous potassium permanganate. After three months of reaction, the aqueous solution was extracted with methyl ethyl ketone (Gómez-Aranda, Gómez-Beltrán & Usón-Lacal, 1962). Evaporation of the organic solvent rendered crude white solids which were purified by successive crystallizations in water. The final products were characterized by chemical analysis and infrared spectroscopy. Infrared spectra of prehnitic and 1,2,3,5-benzenetetracarboxylic acid are known (González-Sánchez, 1955) and also their X-ray powder diagrams (Gómez-Beltrán & Fornies-Marquina, 1964).

Crystallographic data for both structures *A* and *B* are collected in Table 1. Mo $K\alpha$ radiation was used with a graphite-crystal monochromator and Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions were determined from the angular settings of 25 reflections; $20° < \theta < 25°$. The space group, $P\bar{1}$, for both compounds was established from the structure determinations. Data were collected using ω–2θ scans with a variable scan rate and a maximum scan time of 60 s per reflection. On all reflections, profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Symmetry-equivalent reflections were averaged (compound *A*) and some measured twice (compound *B*); $R_{\text{int}} = \sum(I - \langle I \rangle)/\sum I$. Semi-empirical absorption corrections were applied (North, Phillips & Mathews, 1968), with minimum and maximum transmission factors of 0.96 and 1.00 for compound *A*, and 0.98 and 1.00 for compound *B*. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Isotropic least-squares refinement, using *SHELX*76 (Sheldrick, 1976), converged to $R = 0.13$ (compound *A*), 0.15 (compound *B*). At this stage empirical absorption corrections were applied (Walker & Stuart, 1983), resulting in a further decrease of *R* to 0.11 (compound *A*), and 0.14 (compound *B*). Maximum and minimum absorption corrections were 1.43 and 0.74 for compound *A*, and 1.64 and 0.55 for compound *B*. Further anisotropic refinements followed by a difference Fourier synthesis allowed the location of all the H atoms. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. H atoms were isotropically refined. Final conventional agreement factors were $R = 0.036$, $wR = 0.039$ for 1699 observed reflections and 187 variables for compound *A*, and $R = 0.070$, $wR = 0.072$ for 2354 observed reflections and 221 variables for compound *B*. The function minimized was $\sum w(F_o - F_c)^2$, where $w = 1/[\sigma^2(F_o) + gF_o^2]$, with $\sigma(F_o)$ from counting statistics. Maximum shift over e.s.d. ratios in the last full-matrix least-squares cycles were less than 0.02 for both compounds. Final difference Fourier maps showed no peaks higher nor deeper than 0.2 e Å^{-3} for compound *A*, and none higher than 0.4 or deeper than 0.6 e Å^{-3} for compound *B*. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Plots were made with *ORTEP* (Johnson, 1965). Geometrical calculations were made with *PARST* (Nardelli, 1983). All calculations were made on an DEC MicroVAX 3400 of the Scientific Computer Centre of the University of Oviedo.

Discussion. Final positional and thermal parameters are given in Table 2.* Molecular geometry data are collected in Tables 3 and 4. Plots of the molecules,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55493 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1002]

Table 2. *Fractional positional parameters and equivalent isotropic thermal parameters* (Å^2 × 10^2)

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

	x	y	z	$U_{\rm eq}$
Compound *A*				
C(1)	0.4135 (2)	0.6967 (2)	0.4168 (2)	2.27 (5)
C(2)	0.3353 (2)	0.7883 (2)	0.5865 (2)	2.18 (5)
C(3)	0.1902 (2)	0.7861 (2)	0.5883 (2)	2.14 (5)
C(4)	0.1229 (2)	0.6957 (2)	0.4198 (2)	2.33 (6)
C(5)	0.2010 (2)	0.6062 (2)	0.2527 (2)	2.71 (6)
C(6)	0.3459 (2)	0.6064 (2)	0.2511 (3)	2.75 (6)
C(11)	0.5714 (2)	0.6895 (2)	0.4147 (3)	2.54 (6)
C(21)	0.4044 (2)	0.8853 (2)	0.7716 (2)	2.43 (6)
C(31)	0.1114 (2)	0.8808 (2)	0.7755 (2)	2.43 (6)
C(41)	−0.0351 (2)	0.6978 (2)	0.4124 (3)	2.64 (6)
O(11)	0.6366 (2)	0.6005 (2)	0.2581 (2)	3.81 (5)
O(12)	0.6314 (2)	0.7697 (2)	0.5651 (2)	4.71 (6)
O(21)	0.3957 (2)	1.0395 (2)	0.7772 (2)	4.16 (6)
O(22)	0.4582 (2)	0.8121 (2)	0.9090 (2)	3.92 (6)
O(31)	0.1023 (2)	0.7801 (2)	0.8761 (2)	3.74 (5)
O(32)	0.0685 (2)	1.0389 (2)	0.8257 (2)	4.05 (6)
O(41)	−0.1146 (2)	0.8120 (2)	0.5461 (2)	4.45 (6)
O(42)	−0.0817 (2)	0.5930 (2)	0.2753 (2)	4.70 (6)
Compound *B*				
C(1)	0.3983 (4)	0.796 (3)	0.1929 (2)	2.13 (6)
C(2)	0.5709 (3)	0.7619 (3)	0.2756 (2)	2.12 (6)
C(3)	0.5525 (4)	0.6031 (3)	0.3169 (2)	2.36 (6)
C(4)	0.3594 (4)	0.4856 (3)	0.2804 (2)	2.62 (7)
C(5)	0.1853 (4)	0.5242 (3)	0.2007 (2)	2.28 (6)
C(6)	0.2080 (4)	0.6769 (3)	0.1561 (2)	2.35 (6)
C(11)	0.4122 (4)	0.9626 (3)	0.1467 (2)	2.52 (7)
C(21)	0.7655 (4)	0.8973 (3)	0.3247 (2)	2.35 (6)
C(31)	0.7433 (4)	0.5570 (3)	0.3993 (2)	2.93 (7)
C(51)	−0.0307 (4)	0.4072 (3)	0.1648 (2)	2.83 (7)
O(11)	0.2486 (3)	0.9728 (2)	0.0656 (1)	3.99 (6)
O(12)	0.5606 (3)	1.0786 (3)	0.1806 (2)	4.46 (6)
O(21)	0.9476 (3)	0.8986 (3)	0.2817 (2)	3.51 (6)
O(22)	0.7442 (3)	0.9946 (2)	0.3983 (1)	3.32 (6)
O(31)	0.7069 (4)	0.4073 (3)	0.4311 (2)	6.47 (9)
O(32)	0.9175 (4)	0.6513 (3)	0.4320 (2)	6.10 (8)
O(51)	−0.0288 (4)	0.2644 (3)	0.2090 (2)	5.86 (8)
O(52)	−0.1940 (3)	0.4416 (2)	0.1008 (2)	4.00 (6)
O(7)	0.3460 (4)	0.2770 (3)	0.0078 (2)	4.30 (7)
O(8)	0.2822 (3)	0.0990 (3)	0.3960 (2)	4.01 (7)

Table 3. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond geometries* (Å, °) *for compound A*

C(1)—C(2)	1.403 (2)	C(4)—C(41)	1.497 (2)
C(1)—C(6)	1.389 (2)	C(11)—O(11)	1.270 (2)
C(2)—C(3)	1.397 (2)	C(11)—O(12)	1.247 (2)
C(3)—C(4)	1.400 (2)	C(21)—O(21)	1.268 (2)
C(4)—C(5)	1.386 (2)	C(21)—O(22)	1.240 (2)
C(5)—C(6)	1.388 (2)	C(31)—O(31)	1.289 (2)
C(1)—C(11)	1.492 (2)	C(31)—O(32)	1.217 (2)
C(2)—C(21)	1.507 (2)	C(41)—O(41)	1.272 (2)
C(3)—C(31)	1.507 (2)	C(41)—O(42)	1.244 (2)

C(1)—C(2)—C(3)	119.6 (1)	C(6)—C(1)—C(11)	119.3 (1)
C(1)—C(6)—C(5)	120.2 (1)	C(1)—C(11)—O(11)	117.2 (1)
C(2)—C(1)—C(6)	120.0 (1)	C(1)—C(11)—O(12)	118.7 (1)
C(2)—C(3)—C(4)	119.8 (1)	C(2)—C(21)—O(21)	116.7 (2)
C(3)—C(4)—C(5)	120.2 (1)	C(2)—C(21)—O(22)	117.8 (2)
C(4)—C(5)—C(6)	120.2 (1)	C(3)—C(31)—C(31)	114.1 (1)
C(1)—C(2)—C(21)	122.2 (1)	C(3)—C(31)—O(32)	120.6 (2)
C(2)—C(1)—C(11)	120.6 (1)	C(4)—C(41)—O(41)	116.7 (1)
C(2)—C(3)—C(31)	118.1 (1)	C(4)—C(41)—O(42)	119.0 (1)
C(3)—C(2)—C(21)	118.2 (1)	O(11)—C(11)—O(12)	124.0 (1)
C(3)—C(4)—C(41)	121.4 (1)	O(21)—C(21)—O(22)	125.3 (2)
C(4)—C(3)—C(31)	122.1 (1)	O(31)—C(31)—C(32)	125.2 (1)
C(5)—C(4)—C(41)	118.5 (1)	O(41)—C(41)—O(42)	124.2 (2)

D—H···*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
O(11)—H(11)···O(41$^{\rm i}$)	1.16 (4)	3.487 (2)	2.67 (4)	127 (3)
O(11)—H(11)···O(42$^{\rm i}$)	1.16 (4)	2.654 (2)	1.50 (4)	177 (3)
O(41)—H(41)···O(11$^{\rm ii}$)	1.18 (5)	3.487 (2)	2.64 (4)	128 (3)
O(41)—H(41)···O(12$^{\rm ii}$)	1.18 (5)	2.607 (2)	1.44 (5)	174 (4)

Symmetry code: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.

Table 4. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond geometries* (Å, °) *for compound B*

C(1)—C(2)	1.405 (3)	C(5)—C(51)	1.489 (3)
C(1)—C(6)	1.393 (3)	C(11)—O(11)	1.315 (3)
C(2)—C(3)	1.407 (3)	C(11)—O(12)	1.211 (3)
C(3)—C(4)	1.395 (3)	C(21)—O(21)	1.298 (3)
C(4)—C(5)	1.395 (3)	C(21)—O(22)	1.219 (3)
C(5)—C(6)	1.388 (3)	C(31)—O(31)	1.297 (3)
C(1)—C(11)	1.491 (3)	C(31)—O(32)	1.208 (3)
C(2)—C(21)	1.517 (3)	C(51)—O(51)	1.306 (3)
C(3)—C(31)	1.498 (3)	C(51)—O(52)	1.217 (3)

C(1)—C(2)—C(3)	118.9 (2)	C(6)—C(5)—C(51)	118.9 (2)
C(1)—C(6)—C(5)	120.7 (2)	C(1)—C(11)—O(11)	114.1 (2)
C(2)—C(1)—C(6)	120.0 (2)	C(1)—C(11)—O(12)	123.2 (2)
C(2)—C(3)—C(4)	120.6 (2)	C(2)—C(21)—O(21)	114.5 (2)
C(3)—C(4)—C(5)	119.8 (2)	C(2)—C(21)—O(22)	120.6 (2)
C(4)—C(5)—C(6)	119.9 (2)	C(3)—C(31)—O(31)	114.5 (2)
C(1)—C(2)—C(21)	121.0 (2)	C(3)—C(31)—O(32)	122.3 (2)
C(2)—C(1)—C(11)	120.5 (2)	C(5)—C(51)—O(51)	113.6 (2)
C(2)—C(3)—C(31)	120.2 (2)	C(5)—C(51)—O(52)	123.3 (2)
C(3)—C(2)—C(21)	120.0 (2)	O(11)—C(11)—O(12)	122.8 (2)
C(4)—C(3)—C(31)	119.3 (2)	O(21)—C(21)—O(22)	125.0 (2)
C(4)—C(5)—C(51)	121.1 (2)	O(31)—C(31)—O(32)	123.2 (2)
C(6)—C(1)—C(11)	119.5 (2)	O(51)—C(51)—O(52)	123.1 (2)

D—H···*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
O(11)—H(11)···O(7$^{\rm i}$)	1.03 (5)	2.625 (4)	1.60 (5)	172 (4)
O(21)···H(21)···O(8$^{\rm ii}$)	0.92 (4)	2.591 (4)	1.67 (4)	174 (4)
O(51)—H(51)···O(12$^{\rm iii}$)	0.98 (4)	2.674 (4)	1.73 (4)	161 (4)

Symmetry code: (i) $x, y + 1, z$; (ii) $x + 1, y + 1, z$; (iii) $x - 1, y - 1, z$.

showing the molecular configuration and crystallographic labelling schemes, are given in Figs. 1 and 2. Geometrical features of the hydrogen bonds are also shown in Tables 3 and 4. The molecules are almost planar, O atoms excluded, fitting to a least-squares ideal plane defined by all C atoms. The benzene ring shows a weak distortion from the ideal least-squares plane towards a half-chair conformation for compound *A*, and towards a slightly twisted boat conformation for *B*. The puckering parameters (Cremer & Pople, 1975) are $QT = 0.010$ (1), $\varphi = -80$ (10)° and $\theta = 130$ (10)° for compound *A*, and $QT = 0.035$ (4), $\varphi = -104.0$ (7)° and $\theta = 96.0$ (7)° for compound *B*. The molecules are associated through their carboxylic groups forming network of hydrogen bonds. For compound *A* there are two hydrogen bonds linking the O atoms of every 'outer' carboxyl group [C(11) and C(41)] and the O atom of the carboxyl group in *para* position on the symmetry related molecule [C(41) and C(11)]. These hydrogen-bonding linkages lead to the formation of chains of molecules parallel to the *ab* plane. For compound *B*, two water molecules are linked as hydrogen acceptors to contiguous carboxyl groups; there are also hydrogen bridges relating carboxyl groups C(11) and C(51) on symmetry related molecules (see Table 4). The angles between the planes of the carboxyl groups and the least-squares plane of the C atoms of the ring are respectively 2.5 (2), 82.8 (1), 72.7 (1) and 14.7 (1)° for compound *A*, and 6.6 (3), 85.6 (3), 4.0 (3) and 5.8 (3)° for *B*, showing, as in other benzenecarboxylic acids (see Table 5), the tendency of 'lone' or 'outer' carboxyl groups to be arranged in a coplanar fashion and of the 'inner' to be arranged perpendicularly to the aromatic ring in order to minimize electronic repulsion and steric hindrance.

Table 5. *Conformational angles (°) of the carboxylic groups in the benzenecarboxylic acids*

Each compound is identified by the locants of its carboxylic acid groups, as well as by any hydration. For each carboxylic acid group, identified by its locant, its conformational angle is given followed by its type, *i.e.* *l* = 'lone', *i* = 'inner' and *o* = 'outer', where known.

Compound	Carboxylic acid group	Angle	Type	Comments
1	1	0.00	*l*	Sim, Robertson & Goodwin (1954) (*R* = 0.088)
	1	1.5 (4)	*l*	Bruno & Randaccio, (1980) (*R* = 0.038)
	1	1.0	*l*	Feld, Lehmann, Muir & Speakman (1981) (*R* = 0.0497)
1,2	1	20.3 (1)	*o*	Ermer (1981) (*R* = 0.040). Positions 1 and 2 related by a twofold axis
	1	34.3	*o*	Küppers (1981) (*R* = 0.037)
1,3	1	2.8	*l*	Alcala & Martínez-Carrera (1972) (*R* = 0.050)
	3	4.7	*l*	
1,4	1	5.25	*l*	Bailey & Brown (1967) (*R* = 0.075). Centrosymmetric molecule
1,2,3–$2H_2O$	1	4.3	*o*	Average values from Fornies-Marquina, Courseille, Buesetta & Hospital (1972) (*R* = 0.057), Takusagawa & Shimada (1973) (*R* = 0.093) and Mo & Adman (1975) (*R* = 0.039)
	2	87.0	*i*	
	3	9.8	*o*	
1,2,4	1	88.0	*o*	Takusagawa, Hirotsu & Shimada (1973) (*R* = 0.136)
	2	9.0	*o*	
	4	8.0	*l*	
1,3,5	1		*l*	Duchamp & Marsh (1967) (*R* = 0.068). Six molecules in the asymmetric unit with several twist angles, up to 27°
	3		*l*	
	5		*l*	
1,3,5–$\frac{5}{6}H_2O$	1	3.7	*l*	Herbstein & Marsh (1977) (*R* = 0.112)
	3	3.0	*l*	
	5	6.2	*l*	
1,2,3,4	1	2.5 (2)	*o*	This work (*R* = 0.036)
	2	82.8 (1)	*i*	
	3	72.7 (1)	*i*	
	4	14.7 (1)	*o*	
1,2,3,5–$2H_2O$	1	6.6 (3)	*o*	This work (*R* = 0.070)
	2	85.6 (3)	*i*	
	3	4.0 (3)	*o*	
	5	5.8 (3)	*l*	
1,2,4,5–$2H_2O$	1	17.9	*o*	Takusagawa, Hirotsu & Shimada (1971) (*R* = 0.074). Centrosymmetric molecule
	2	74.4	*o*	
1,2,3,4,5	1	26.5 (2)	*o*	Barrio, García-Granda & Gómez-Beltrán (1990) (*R* = 0.037)
	2	76.4 (1)	*i*	
	3	29.8 (1)	*i*	
	4	79.7 (1)	*i*	
	5	3.0 (2)	*o*	
1,2,3,4,5,6	1	66.8		Darlow (1961) (*R* = 0.095). Two independent sets of molecules. Positions 2,3 and 5,6 are symmetry related
	2	25.7		
	3	80.7		
	4	24.6		
	1′	55.5		
	2′	44.0		
	3′	66.0		
	4′	51.5		

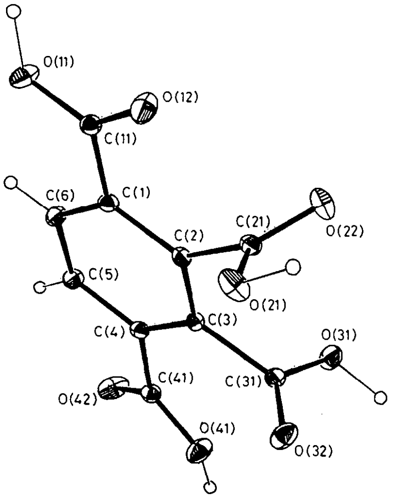

Fig. 1. *ORTEP* (Johnson, 1965) plot of the atomic arrangement and labelling for compound *A*.

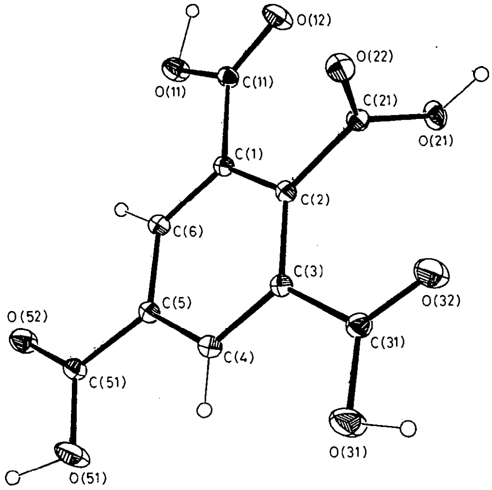

Fig. 2. *ORTEP* (Johnson, 1965) plot of the atomic arrangement and labelling for compound *B*.

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Ketone Pyramidalization in a Tetracyclic Perpendicular Enone Derivative

BY BARRY A. LLOYD* AND CLAYTON ERICSON

Department of Chemistry, Weber State University, Ogden, Utah 84408, *USA*

AND ATTA M. ARIF AND EVAN L. ALLRED†

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, *USA*

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Abstract. *endo,exo*-11,11-Dimethoxytetracyclo-$[6.2.1.1^{3,6}.0^{2,7}]$dodeca-9-en-12-one (1), $C_{14}H_{18}O_3$, $M_r = 234.30$, monoclinic, $P2_1/n$, $a = 14.113\,(2)$, $b = 10.032\,(1)$, $c = 17.086\,(2)$ Å, $\beta = 103.55\,(1)°$, $V = 2351.74$ Å^3, $Z = 8$, $D_x = 1.323$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54056$ Å, $\mu = 7.038$ cm^{-1}, $F(000) = 1008$, $T = 133$ K, $R = 0.0433$ and $wR = 0.0435$ for 4255 unique reflections. The molecule contains a norbornanone unit fused to a substituted norbornene. The ring C atom of the ketone is significantly pyramidalized. Possible factors contributing to this deformation include incipient nucleophilic attack by the π electrons at the carbonyl C atom, polarization of the π system, relief of bond-angle compression, and steric effects.

Introduction. Structural deformations of C═C double bonds have received considerable attention in recent years (Luef & Keese, 1991; Borden, 1989). Although experimental structures are known of many compounds containing C═N and C═O double bonds, few authors have focused on pyramidalization in these groups. X-ray diffraction data show that pyramidalization in C═N double bonds (Hollenstein & Laube, 1990; Carrupt, Vogel, Mison, Eddaïf, Pellissier, Faure & Loiseleur, 1986) is small (less than 5°). Similarly, neutron diffraction data for amides, amino acids or dipeptides (Jeffrey, Houk, Paddon-Row, Rondan & Mitra, 1985) show that carbonyl pyramidalization in these functional groups is no larger than 5°. Significant carbonyl pyramidalizations have been observed in cyclic structures containing nucleophilic functional groups (Bürgi & Dunitz, 1983; Cossu, Bachmann, N'Guessan, Viani,

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* Author to whom correspondence should be addressed.

† Deceased 8 July 1991.

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