

the square-planar one (Albano, Braga, De Felice, Panunzi & Vitagliano, 1987; Cucciolo, De Felice, Panunzi & Vitagliano, 1989). In the above case the comparable destabilization of complexes containing *meso*- and chiral  $P_4$  in a square-planar as well as a trigonal-bipyramidal coordination environment leads to the simultaneous occurrence of both configuration types. Furthermore, since tetrahedral coordinations are favoured if steric restrictions are present (Atwood, 1985), distorted tetrahedral  $P_4$  arrangements occur in  $[PtX(P_4)]Y$  species ( $X$  = various types of fifth ligands,  $Y$  = non-coordinating anion) depending on the nature of  $X$  (Brüggeller, 1989; Brüggeller, 1990).

The discussed subtle balance of (1) and (2) and corresponding five-coordinate species leads to diastereotopic interactions (Bosnich & Fryzuk, 1981; De Renzi, Di Blasio, Saporito, Scalone & Vitagliano, 1980; Brüggeller, 1989) and differences in the coordination types of five-coordinate species between those containing *meso*- $P_4$  and chiral  $P_4$ , respectively (Brüggeller, 1990). The main effect is that only in the case of *meso*- $P_4$  is a smooth transition from a planar to a distorted tetrahedral coordination observed, which facilitates the occurrence of the 'Berry' mechanism. This might be because the tetrahedral distortion in (2) reflects an already balanced configuration between electronic forces to form a  $PtP_4$  plane and the steric requirements of chiral  $P_4$ , whereas the displacement of the central atom from the  $P_4$  plane in (1) could lead to a more flexible variation of the  $P_4$  coordination.

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## Structure of Guanidinium Hydrogen Acetylenedicarboxylate, $CH_6N_3^+ \cdot C_4HO_4^-$

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**Abstract.** Guanidinium hydrogen 2-butynedioate,  $M$ , = 173.13, monoclinic,  $P2_1/c$ ,  $a = 8.837$  (1),  $b = 18.961$  (2),  $c = 9.067$  (2) Å,  $\beta = 92.09$  (1)°,  $V = 1518.2$  (4) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.515$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$

= 0.71069 Å,  $\mu = 1.24$  cm<sup>-1</sup>,  $F(000) = 720$ ,  $T = 293$  (2) K, final  $R = 0.044$  and  $wR = 0.044$  for 1622 observed reflections. The crystal structure consists of infinite chains of hydrogen acetylenedicarboxylate

residues linked together by planar guanidinium cations. There are O...H...O hydrogen bonds within the chain [2.417 (3) and 2.463 (4) Å] and N—H...O bonds [ranging from 2.809 (3) to 2.970 (4) Å] between the chains and the guanidinium cations.

**Introduction.** Acid salts of acetylenedicarboxylic acid (H<sub>2</sub>adc, HO<sub>2</sub>C—C≡C—CO<sub>2</sub>H, 2-butynedioic acid) were studied initially as part of a structural investigation of acid salts of dicarboxylic acids in a search for very short hydrogen bonds. Later, the conformation of the H<sub>2</sub>adc residue attracted our attention. The H<sub>2</sub>adc residue has been found to have various conformations in its acid salts as well as in the free acid. Each carboxylate group is planar, but twisting about the C—C bonds gives different values of the dihedral angle between the carboxylate groups. Different molecular packing seems to be the main reason for these differences in conformation. Moreover in guanidinium hydrogen malonate the hydrogen malonate ion is planar (Djinović, Golič, Hadži & Orel, 1988). This led us to the idea that the planar guanidinium cations might also stabilize a planar conformation in the acetylenedicarboxylate residue, which is the case in the structure reported here.

Acid salts of H<sub>2</sub>adc usually contain infinite chains with strong intermolecular hydrogen bonds, the only exception being the Li salt. The crystal structures of all alkali-metal (including ammonium) acid salts have been reported: LiHadc.H<sub>2</sub>O (Mattes & Plescher, 1981), NaHadc.2H<sub>2</sub>O (Leban, 1974a), KHadc (Leban, Golič & Speakman, 1973), two forms of RbHadc (Blain, Speakman, Stamp, Golič & Leban, 1973), CsHadc.H<sub>2</sub>O (Gupta & Mahata, 1976), NH<sub>4</sub>Hadc (Leban, 1974b), as well as those of free acid: H<sub>2</sub>adc.2H<sub>2</sub>O (Dunitz & Robertson, 1947).

**Experimental.** Crystals of the title compound were prepared by slow evaporation of an aqueous solution containing equimolar portions of H<sub>2</sub>adc.2H<sub>2</sub>O and guanidinium carbonate. Colourless prisms 0.22 × 0.52 × 0.24 mm. Density calculated according to Immirzi & Perini (1976) and confirmed by flotation. Space group and approximate cell parameters from Weissenberg photographs. Data collected on Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Exact cell dimensions from 25 reflections in the range 11 <  $\theta$  < 15° using Mo K $\alpha_1$  radiation (0.70930 Å).  $\omega/2\theta$  scan, max. scan time 40 s, scan width (0.8 + 0.3tan $\theta$ )°, scan aperture (2.4 + 0.9tan $\theta$ ) mm; 7047 reflections (+ $h$ ,  $\pm k$ ,  $\pm l$ ) measured to (sin $\theta/\lambda$ )<sub>max</sub> = 0.64 Å<sup>-1</sup>; orientation control monitored after every 500 reflections, standard reflections (0 $\bar{1}$ 3, 013, 14 $\bar{2}$ ) measured every 7200 s of scanning time did not show any significant change in intensity (-0.9%). After merging ( $R_{int}$  = 0.037) for  $P2_1/m$ , 3304 unique reflections

Table 1. Final fractional coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) with e.s.d.'s in parentheses

$U_{eq}$  is defined as one third of the trace of the  $U_{ij}$  tensor.

|     | <i>x</i>   | <i>y</i>   | <i>z</i>   | $U_{eq}$  |
|-----|------------|------------|------------|-----------|
| O1  | 0.8091 (3) | 0.3605 (1) | 0.4840 (3) | 0.052 (2) |
| O2  | 0.7610 (3) | 0.2488 (1) | 0.4429 (3) | 0.058 (2) |
| O3  | 0.3643 (3) | 0.2935 (1) | 0.0318 (3) | 0.054 (2) |
| O4  | 0.3446 (3) | 0.4080 (1) | 0.0850 (3) | 0.049 (2) |
| C1  | 0.7341 (4) | 0.3110 (2) | 0.4204 (3) | 0.039 (2) |
| C2  | 0.6140 (4) | 0.3299 (2) | 0.3120 (3) | 0.036 (2) |
| C3  | 0.5190 (4) | 0.3400 (2) | 0.2191 (3) | 0.036 (2) |
| C4  | 0.3997 (4) | 0.3458 (2) | 0.1009 (4) | 0.037 (2) |
| O5  | 1.1548 (3) | 0.4223 (1) | 0.8814 (2) | 0.047 (2) |
| O6  | 1.1549 (3) | 0.5383 (1) | 0.9220 (2) | 0.050 (2) |
| O7  | 0.7229 (3) | 0.4807 (1) | 0.4538 (2) | 0.043 (2) |
| O8  | 0.7448 (3) | 0.5902 (1) | 0.5312 (1) | 0.055 (2) |
| C5  | 1.1097 (4) | 0.4856 (2) | 0.8589 (3) | 0.034 (2) |
| C6  | 0.9894 (4) | 0.4936 (2) | 0.7441 (3) | 0.034 (2) |
| C7  | 0.8932 (4) | 0.5061 (2) | 0.6517 (3) | 0.036 (2) |
| C8  | 0.7792 (4) | 0.5275 (2) | 0.5395 (3) | 0.035 (2) |
| C9  | 0.9420 (4) | 0.7380 (2) | 0.7658 (3) | 0.036 (2) |
| N1  | 1.0172 (4) | 0.6900 (1) | 0.8457 (3) | 0.050 (2) |
| N2  | 0.8478 (4) | 0.7190 (1) | 0.6579 (3) | 0.048 (2) |
| N3  | 0.9629 (4) | 0.8052 (1) | 0.7966 (3) | 0.051 (2) |
| C10 | 0.4526 (4) | 0.5941 (2) | 0.2283 (3) | 0.038 (2) |
| N4  | 0.3455 (4) | 0.6134 (1) | 0.1316 (3) | 0.049 (2) |
| N5  | 0.4862 (4) | 0.5270 (1) | 0.2443 (3) | 0.045 (2) |
| N6  | 0.5240 (4) | 0.6421 (1) | 0.3104 (3) | 0.050 (2) |
| H1  | 0.765 (4)  | 0.420 (2)  | 0.473 (3)  | 0.066 (3) |
| H2  | 0.263 (4)  | 0.415 (2)  | -0.012 (4) | 0.066 (3) |

( $h - 11/10, k 0/24, l 0/11$ ) of which 1622 considered as observed [ $I > 2.5\sigma(I)$ ]. Structure solved with MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares (on  $F$ ) with SHELX76 (Sheldrick, 1976). Final  $R$  and  $wR$  values were 0.044 and 0.044 respectively with  $w = 1.27/[\sigma^2(F_o)]$  and 262 variables. H-atom positions found in final difference synthesis and included in refinement with a common isotropic temperature factor  $U$  which was refined to 0.066 (3) Å<sup>2</sup>. A constraint was imposed on the N—H distances. A final difference Fourier map showed residual electron density within +0.06 and -0.09 e Å<sup>-3</sup>. Max.  $\Delta/\sigma$  at convergence 0.033 ( $y, O2$ ). Scattering factors for C, N and O were from *International Tables for X-ray Crystallography* (1974, Vol. IV), for H from Stewart, Davidson & Simpson (1965). All calculations performed on the VAX 8550 cluster at the University Computer Centre, Ljubljana. Additionally, the GX package (Mallinson & Muir, 1985) was used for data processing and final interpretation of molecular geometry. The final atomic parameters are in Table 1.\* Bond lengths and

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, selected torsion angles and mean-planes angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54706 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

| Hydrogen acetylenedicarboxylate units |           |                                      |           |         |
|---------------------------------------|-----------|--------------------------------------|-----------|---------|
| O1—C1                                 | 1.275 (5) | O5—C5                                | 1.278 (5) |         |
| O2—C1                                 | 1.219 (5) | O6—C5                                | 1.213 (5) |         |
| O3—C4                                 | 1.208 (5) | O7—C8                                | 1.269 (4) |         |
| O4—C4                                 | 1.283 (5) | O8—C8                                | 1.228 (5) |         |
| C1—C2                                 | 1.465 (5) | C5—C6                                | 1.468 (5) |         |
| C2—C3                                 | 1.183 (5) | C6—C7                                | 1.195 (5) |         |
| C3—C4                                 | 1.479 (5) | C7—C8                                | 1.463 (5) |         |
|                                       |           |                                      |           |         |
| O1—C1—O2                              | 122.8 (3) | O5—C5—O6                             | 127.1 (3) |         |
| O1—C1—C2                              | 118.4 (3) | O5—C5—C6                             | 115.1 (3) |         |
| O2—C1—C2                              | 118.8 (3) | O6—C5—C6                             | 117.8 (3) |         |
| C1—C2—C3                              | 174.6 (4) | C5—C6—C7                             | 174.5 (4) |         |
| C2—C3—C4                              | 174.9 (4) | C6—C7—C8                             | 175.2 (4) |         |
| O3—C4—O4                              | 127.3 (3) | O7—C8—O8                             | 123.3 (3) |         |
| O3—C4—C3                              | 118.6 (3) | O7—C8—C7                             | 118.4 (3) |         |
| O4—C4—C3                              | 114.0 (3) | O8—C8—C7                             | 118.3 (3) |         |
|                                       |           |                                      |           |         |
| Guanidinium ions                      |           |                                      |           |         |
| C9—N1                                 | 1.325 (5) | C10—N4                               | 1.318 (5) |         |
| C9—N2                                 | 1.311 (5) | C10—N5                               | 1.314 (5) |         |
| C9—N3                                 | 1.317 (5) | C10—N6                               | 1.322 (5) |         |
|                                       |           |                                      |           |         |
| N1—C9—N2                              | 120.8 (3) | N4—C10—N5                            | 119.7 (3) |         |
| N1—C9—N3                              | 119.0 (3) | N4—C10—N6                            | 120.0 (3) |         |
| N2—C9—N3                              | 120.3 (3) | N5—C10—N6                            | 120.2 (3) |         |
|                                       |           |                                      |           |         |
| Hydrogen bonds                        |           |                                      |           |         |
| O···H···O                             |           |                                      |           |         |
| O1—H1                                 | 1.20 (4)  | O4—H2                                | 1.12 (3)  |         |
| O7—H1                                 | 1.22 (4)  | O5 <sup>i</sup> —H2                  | 1.34 (3)  |         |
| O1···O7                               | 2.417 (3) | O4···O5 <sup>i</sup>                 | 2.463 (4) |         |
|                                       |           |                                      |           |         |
| O1—H1—O7                              | 176 (3)   | O4—H—O5 <sup>i</sup>                 | 175 (3)   |         |
| C1—O1—O7                              | 119.1 (2) | C4—O4—O5 <sup>i</sup>                | 115.5 (2) |         |
| C8—O7—O1                              | 118.4 (2) | C5 <sup>i</sup> —O5 <sup>i</sup> —O4 | 115.0 (2) |         |
|                                       |           |                                      |           |         |
| N—H···O                               |           |                                      |           |         |
| N1—H12—O2 <sup>ii</sup>               | 2.912 (4) | 0.94 (3)                             | 2.00 (3)  | 165 (3) |
| N2—H13—O3 <sup>iii</sup>              | 2.869 (4) | 0.92 (3)                             | 1.98 (3)  | 160 (3) |
| N2—H14—O8                             | 2.834 (3) | 0.90 (3)                             | 1.98 (3)  | 158 (3) |
| N3—H15—O5 <sup>ii</sup>               | 2.915 (3) | 0.86 (3)                             | 2.07 (3)  | 162 (3) |
| N3—H16—O1 <sup>ii</sup>               | 2.970 (4) | 0.94 (3)                             | 2.04 (3)  | 173 (3) |
| N4—H21—O6 <sup>i</sup>                | 2.871 (4) | 0.95 (3)                             | 1.98 (3)  | 154 (3) |
| N4—H22—O2 <sup>iii</sup>              | 2.809 (3) | 0.92 (3)                             | 1.90 (3)  | 169 (3) |
| N5—H23—O4                             | 2.933 (3) | 0.93 (3)                             | 2.02 (3)  | 167 (3) |
| N5—H24—O7                             | 2.909 (4) | 0.90 (3)                             | 2.01 (3)  | 176 (3) |
| N6—H25—O8                             | 2.915 (4) | 0.95 (3)                             | 1.97 (3)  | 176 (3) |

Symmetry code: (i)  $x - 1, y, z - 1$ ; (ii)  $-x + 2, y + 0.5, -z + 1.5$ ; (iii)  $-x + 1, y + 0.5, -z + 0.5$ .

angles are given in Table 2. A view of the unit cell with the atomic numbering is presented in Fig. 1.

**Discussion.** There are two guanidinium cations ( $(\text{NH}_2)_3\text{C}^+$ ) and two  $\text{Hadc}^-$  residues in the asymmetric unit of the structure. The guanidinium ions are planar and the overall geometry is similar to that observed in several other crystal structures of guanidinium salts, *e.g.* in guanidinium hydrogen maleate (Golič, Leban, Detoni, Orel & Hadži, 1985).

The distances C1—C2 [1.465 (5) Å], C3—C4 [1.479 (5) Å], C5—C6 [1.468 (5) Å] and C7—C8 [1.463 (5) Å] have the character of a  $\text{C}(sp^2)\text{—C}(sp^1)$  single bond, but are larger than the mean value of 1.431 Å for this type of bond (Allen, Kennard,

Watson, Brammer, Orpen & Taylor, 1987); this is probably due to electron delocalization. Deviations from linearity of the  $\text{C—C}\equiv\text{C—C}$  group are caused by the molecular packing.

The C—O distances correspond closely to those of a  $\text{—COO}^-$  group. The distances fall into two categories; for O atoms which form hydrogen bonds to one or two N atoms they are shorter (1.21–1.23 Å) than for O atoms which are involved in the symmetric or near symmetric  $\text{O}\cdots\text{H}\cdots\text{O}$  bonds (1.27–1.28 Å).

Hydrogen acetylenedicarboxylate residues are linked into infinite zigzag chains *via* two intermolecular hydrogen bonds, O1···O7 and O4···O5. The first appears to be symmetrical, the second unsymmetrical (see Table 2); confirmation by neutron diffraction is desirable.

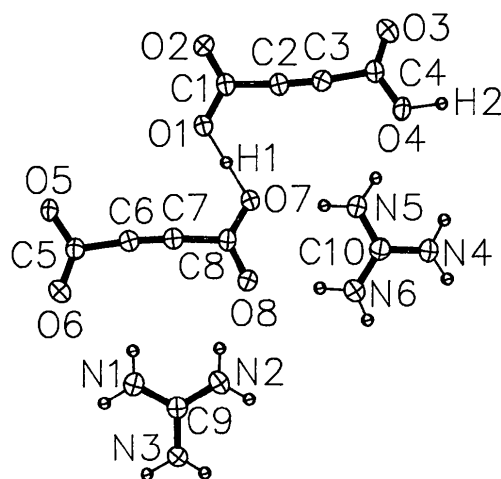


Fig. 1. ORTEP (Johnson, 1965) view of the structural units with the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

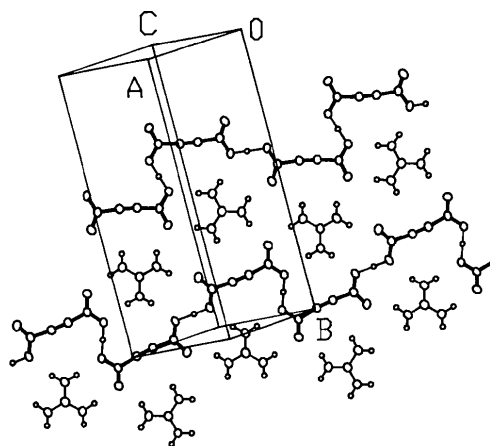


Fig. 2. A view of the planar arrangement of guanidinium ions and hydrogen acetylenedicarboxylate residues

The dihedral angles between the two carboxylate planes of Hadc residues [13.8 (7) and 3.8 (7)° respectively] differ considerably from the 62° in LiHadc.H<sub>2</sub>O, 66° in KHadc, 61° in RbHadc and 74° in NH<sub>4</sub>Hadc. Planar centrosymmetric Hadc residues were observed in NaHadc.2H<sub>2</sub>O and CsHadc.H<sub>2</sub>O. The striking feature of the structure is the nearly coplanar arrangement of the extended layers of guanidinium cations and Hadc residues (Fig. 2). The dihedral angles between separate Hadc and guanidinium entities vary from 3.5 to 13.6°, whereas in guanidinium hydrogen maleate, forms I and II, these angles are 33.2 and 16.5°, respectively (Golič, Leban, Detoni, Orel & Hadži, 1985). It seems that the planar guanidinium ions force the Hadc to assume the nearly planar conformation.

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## Bond Length and Reactivity.† Structure of the Diphenyl Phosphate Ester of 2,6-Dichlorobenzyl Alcohol

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**Abstract.** 2,6-Dichlorobenzyl diphenyl phosphate, C<sub>19</sub>H<sub>15</sub>Cl<sub>2</sub>O<sub>4</sub>P, *M<sub>r</sub>* = 409.21, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.471 (2), *b* = 12.555 (3), *c* = 13.159 (2) Å, β = 91.83 (2)°, *V* = 1894 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.435 Mg m<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 0.45 mm<sup>-1</sup>, *F*(000) = 840, *T* = 293 K. Final *R* = 0.056 for 2248 unique observed reflections. The key torsion angle, between the benzylic C—O bond and the plane of the ring (C<sub>ar</sub>—C<sub>ar</sub>—C—O), which controls the strength of the ring-π-σ<sub>C—O<sub>X</sub></sub>\* interaction is 77.3 (4)°, similar to that

found for other derivatives of this alcohol [Jones, Dölle, Kirby & Parker (1989). *Acta Cryst.* **C45**, 231–234] and this benzylic C—O bond length is 1.464 (4) Å.

**Introduction.** We recently reported (Jones, Dölle, Kirby & Parker, 1989) crystal structures for three derivatives (1) of 2,6-dichlorobenzyl alcohol, which for steric reasons adopt a conformation in which the C—OX bond is close to perpendicular (torsion angle 73 ± 5°) to the ring, and is longer for better 'leaving groups' OX. After several months in the refrigerator

† Previous paper in this series: Jones, Edwards & Kirby (1989).