

A ladder type structure: Rubidium diphenylacetate diphenylacetic acid

Manuela Ramos Silva,⁽¹⁾ Ana Matos Beja,^{(1)*} José A. Paixão,⁽¹⁾ Sérgio R. Domingos,⁽¹⁾
and Jesús Martín-Gil⁽²⁾

Received April 13, 2006; accepted August 14, 2006
Published Online November 7, 2006

A new rubidium complex, rubidium diphenylacetate diphenylacetic acid has been synthesised and characterised by single-crystal X-ray diffraction: triclinic, $P\bar{1}$ with $a = 7.437(3)$ Å, $b = 12.377(4)$ Å, $c = 14.384(3)$ Å, $\alpha = 107.08(2)^\circ$, $\beta = 103.67(2)^\circ$, $\gamma = 96.95(3)^\circ$, $Mr = 508.93$, $V = 1203.6(6)$ Å³, $Z = 2$. The diphenylacetic molecules bridge the metallic ions forming an infinite ladder structure. Two strong hydrogen bonds link the organic moieties.

KEY WORDS: Ladder structure; hydrogen bonds; flexible molecule; diphenylacetic acid; rubidium complex.

Introduction

The formation of enantiomerically enriched products from achiral precursors without the intervention of chiral chemical reagents or catalysts is known as absolute asymmetric synthesis. This can be achieved if a molecular torsion causes a chiral conformation in an achiral molecule subsequently inducing crystallization into a chiral crystal structure. A common example is benzophenone that crystallizes in the chiral $P2_12_12_1$ space group¹ and exhibits non-linear optical behaviour.² It is the propeller like arrangement of the phenyl rings of benzophenone that promotes such chiral crystallization. Diphenylacetic acid is another molecule that can assemble in helical conformations. It has been used in absolute asymmetric

synthesis to provide chiral cocrystals namely with acridines.^{3,4} Searching for other compounds with the same features we have engaged in a structural study of diphenylacetic acid salts or adducts, such as the title compound, rubidium diphenylacetate diphenylacetic acid. The organic molecules of this compound assume a helical conformation with the two phenyl rings oriented like the blades of a propeller but they crystallize in the centrosymmetric $P\bar{1}$ group therefore with both enantiomers of the helical conformation in the crystal.

Experimental

Preparation of Rubidium diphenylacetate diphenylacetic acid

The title compound was prepared by neutralising an ethanolic solution of diphenylacetic acid (98%, Aldrich) with rubidium hydroxide. Clear transparent single crystals of prismatic form grew from the solution by slow evaporation over a period of a few weeks, from which one was selected

⁽¹⁾CEMDRX, Departamento de Física, FCT, Universidade de Coimbra, 3004-516 Coimbra, Portugal.

⁽²⁾ETSIA, Universidad de Valladolid, Avda Madrid 57, 34004 Palencia, Spain.

* To whom correspondence should be addressed; e-mail: ana@pollux.fis.uc.pt.

and used for the X-ray analysis. Before data collection, the quality of the crystal was checked by photographic methods (Lauegrams).

Crystal structure determination

A crystal of the title compound having approximate dimensions of 0.39 mm × 0.34 mm × 0.16 mm was placed in a glass fiber and mounted on a Enraf-Nonius CAD4 diffractometer. Diffraction data were collected at room temperature 293(2) K using graphite monochromated Mo K α ($\lambda = 0.71073$ Å). The unit cell parameters were determined by least-squares refinement of diffractometer angles ($8.7^\circ < \theta < 13.72^\circ$) for 24 automatically centered reflections.

Data were processed using PLATON⁵ and an absorption correction (psi scan) was applied which resulted in transmission factors ranging from 0.869 to 0.944. The data were corrected for Lorentz and Polarization effects. Reflections with $2\theta \leq 50^\circ$ were used for structure solution and refinement.

The structure was solved by direct methods using SHELXS-97⁶ and refined anisotropically (non-H atoms) by full-matrix least-squares on F^2 using the SHELXL-97⁶ program. All the hydrogen atoms with exception of those of the carboxylic groups (H21 and H22) were placed at calculated positions and allowed to ride on their parent atoms using SHELXL-97 defaults. H21 and H22 were placed at special positions with an isotropic displacement parameter multiple of the parent atom O2A and O2B, respectively. The final least-squares cycle based on 2683 observed reflections [$I > 2\sigma(I)$] and 283 variable parameters, converged with $R = 0.034$ and $wR = 0.066$. The crystallographic details and selected interatomic distances and angles are given in Tables 1 and 2.

Results and discussion

Crystal structure of the complex

The structure of the title compound together with the atom-numbering scheme, is illustrated in Fig. 1. The formation of ladders is shown on

Table 1. Summary of Crystallographic Results

Temperature (K)	293(2)
Empirical formula	C ₂₈ H ₂₃ O ₄ Rb
Formula weight	508.93
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.437(3)
b (Å)	12.377(4)
c (Å)	14.384(3)
α (°)	107.08(2)
β (°)	103.67(2)
γ (°)	96.95(3)
Volume (Å ³)	1203.6(6)
Z	2
Calculated density (g/cm ³)	1.404
Absorption coefficient (mm ⁻¹)	2.088
$F(000)$	520
Crystal size (mm ³)	0.39 × 0.34 × 0.16
θ range for data collection (deg.)	3.0–25.0
Index ranges	$-8 \leq h \leq 8$ $-14 \leq k \leq 14$ $-17 \leq l \leq 0$
Reflections collected/unique	4504/4211
Completeness to $\theta = 50^\circ$	99.7%
Transmission factors (min/max)	0.869/0.944
Data/restraints/parameters	2683/0/283
Goodness-of-fit on F^2	0.990
Final R indices [$I > 2\sigma(I)$]	0.034/0.066
R indices (all data)	0.109/0.078
Largest diff. peak and hole (eÅ ⁻³)	– 0.467/0.248
CCDC Number	602647

Fig. 2, and Fig. 3 shows the packing diagram. Selected bond lengths and angles are listed in Table 2.

The diphenylacetic molecules bridge the metallic ions forming an infinite ladder struc-

Table 2. Selected Bond Lengths (Å) and angles (°)

C1A–C2A	1.533(5)
C2A–C3A	1.519(5)
C2A–C9A	1.517(4)
C1A–O1A	1.221(4)
C1A–O2A	1.278(4)
C1B–C2B	1.532(5)
C2B–C3B	1.526(3)
C2B–C9B	1.512(4)
C1B–O1B	1.220(4)
C1B–O2B	1.289(4)
O1B–C1B–O2B	125.1(3)
O1A–C1A–O2A	124.4(3)

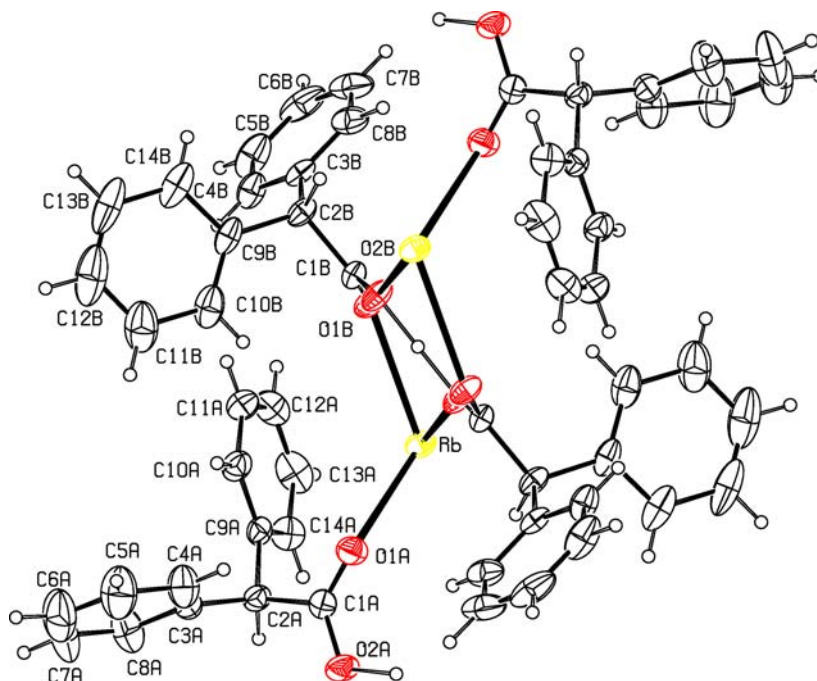
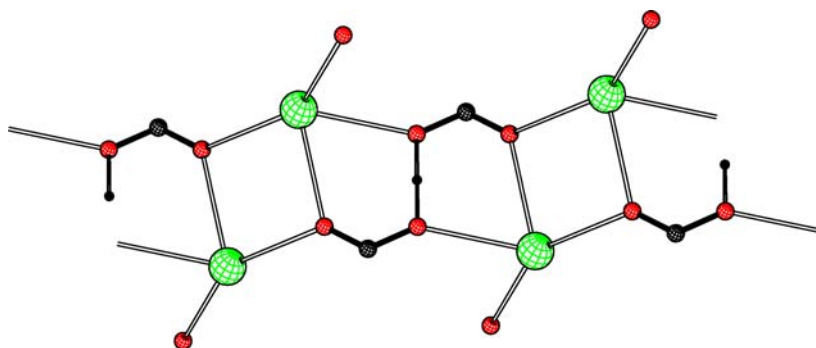


Fig. 1. ORTEPII plot of the title compound. Displacement ellipsoids are drawn at the 30% level.

ture similar to that seen in sodium diphenylacetate.⁷ In the previously reported structure, the carboxylate oxygen atoms and the Na⁺ ions alternate at the vertices of a distorted cube centered at the origin of the $\bar{4}$ axis, forming an infinite columnar structure. At the present structure the rotoinversion axis is lost and the ladder climbs along an $\bar{1}$ axis. Each Rb⁺ ion is coordinated with 4 oxygen atoms, 3 of those atoms belonging to

the diphenylacetic B molecule and its symmetry relatives, and the remaining (O1A) belongs to the A molecule. The B molecules, together with the alkali ions form the ladder which is a sequence of two wider steps (O1B...Rb) and one narrower O2B...O2Bⁱ ($i: -x+1, -y+1, -z+1$), with widths 2.8640(18) and 2.452(5) Å, respectively (Fig. 2). The heights of the steps follow the sequence one larger (Rb...O1Bⁱⁱ, $ii: -x+2,$



Scheme

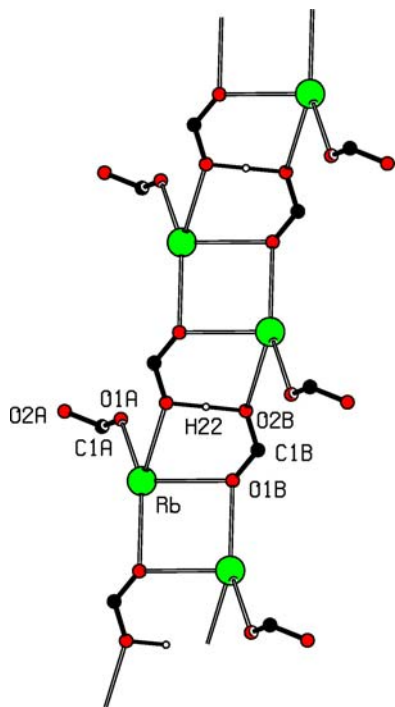


Fig. 2. Stacking of the Rb/O core along the a axis showing the ladder structure. The phenyl groups have been omitted for clarity.

$-y + 1, -z + 1$) and two shorter ($\text{Rb} \cdots \text{O2B}^i$) of 2.8946(18) and 2.8639(18) Å.

The A molecules just complete the alkali coordination without composing the ladder with a Rb-O distance of 2.809(3) Å. The diago-

nal Rb-Rbⁱⁱ (ii: $2 - x, 1 - y, 1 - z$) distance is 4.1726(18) Å.

The carboxylate skeleton defined by atoms C1, C2, O1 and O2 is planar to within 0.003 Å for molecule A and 0.009 Å for B. The dihedral angle between the least-squares plane of the two phenyl rings is 80.98(13)° and 79.94(13)° for A and B, respectively. In the A molecule the carboxylate group makes an angle of 83.89(15)° and 76.11(13)° with rings C3A-C8A and C9A-C14A, respectively. In the B molecule the carboxylate group makes angles of 85.67(7)° and 80.66(11)° with rings C3B-C8B and C9B-C14B, respectively. Both molecules have the phenyl rings and the carboxylate planes with torsions around the single bonds to C2 in the same direction mimicking the blades of a propeller. The common sign of the torsion angles around C2, H2-C2-C1-O1 148.49°, H2-C2-C3-C4 144.0°, H2-C2-C9-C10 159.82 [for A] confirms this orientation [-141.16, -151.13, -125.74° for B, respectively]. There are interactions between the Rubidium ion and the π electron clouds of the phenyl rings, the shortest Rb-centroid distances are 3.173(2) Å for ring C3B-C8Bⁱⁱ and 3.292(2) for ring C9A-C14A.

There are two strong hydrogen bonds joining the organic moieties in this crystal. In each case a hydrogen atom is shared between a carboxylic group and its inverted counterpart. The highest peaks of the difference fourier synthesis

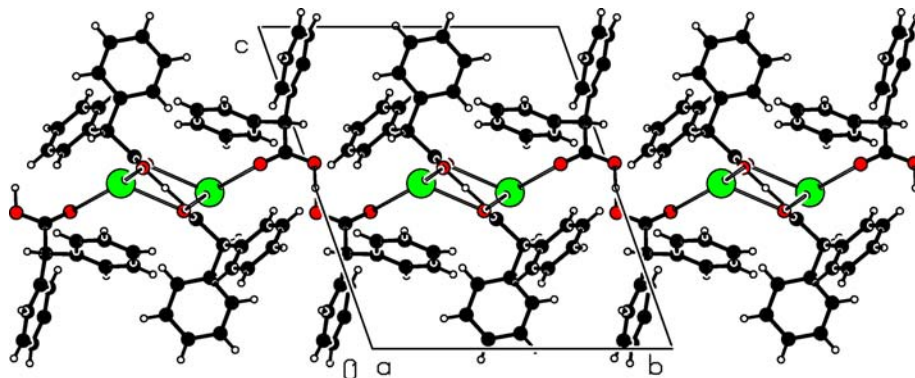


Fig. 3. Packing diagram of the complexes in the unit cell.

at final stage of the refinement locate at the origins of the inversion axis, middle points of the bonds $O2A \cdots O2A^{iii}$ (bond length 2.455(5) Å, bond angle 180.00(11)°, $iii: -x + 1, -y, -z + 1$) and $O2B \cdots O2B^i$ (bond length 2.452(5) Å, bond angle 180.00(11)°, $i: -x + 1, -y + 1, -z + 1$). This might correspond to a highly symmetric situation with the shared hydrogen exactly midway between donor and acceptor or most likely, the shared hydrogen atom is statistically disordered being either close to one oxygen or to its symmetric counterpart.

Anyway the overall counting of the atoms shows that one of the protons was lost, so the negative charge of the organic moiety compensates the positive charge of Rb^+ . While one of the H-bonds forms one of the ladder steps, the other ($O2A \cdots O2A^{iii}$) joins the ladders together, forming layers parallel to the *ab* plane, as seen in Fig. 3.

Supplementary materials Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic

Data Center, CCDC No. 602647. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgement

This work was supported by Fundação para a Ciência e a Tecnologia under project POCI/FIS/57876/2004.

References

1. Fleisher, E.B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1969**, *72*, 4311.
2. Sankaranarayanan, K.; Ramasamy, P. *Cryst. Res. Technol.* **2006**, *41*, 225.
3. Koshima, H.; Ding, K.; Chisaka, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1996**, *118*, 12059.
4. Koshima, H. *Mol. Cryst. Liq. Cryst.* **2005**, *440*, 207.
5. Spek, A.L. *J. Appl. Cryst.* **2003**, *36*, 7.
6. Sheldrick, G.M. *SHELXS97 and SHELXL-97*; University of Göttingen: Germany, 1997.
7. Paixão, J.A.; Nascimento, F.V.; Matos Beja, A.; Ramos Silva, M. *Acta Crystallogr. C* **2000**, *56*, 168.