Acta Cryst. (1993). C**49**, 1523–1525

Structure of a New Crystal Modification of 1,3-Diphenyl-1,3-propanedione

Branko Kaitner and Ernest Meštrović

Laboratory of General and Inorganic Chemistry,
Faculty of Science, University of Zagreb,
41001 Zagreb PO Box 153, Croatia

(*Received* 8 *December* 1992; *accepted* 15 *February* 1993)

Abstract

The crystal structure of the enolic form of 1,3-diphenyl-1,3-propanedione consists of discrete molecules containing slightly asymmetric strong intramolecular hydrogen bonds. The molecule is almost identical to the dibenzoylmethane molecules in the stable and metastable crystal polymorphs determined previously. The crystal packing pattern is nearly identical to that found in the metastable crystal form.

Comment

1,3-Diphenyl-1,3-propanedione (DMB, dibenzoylmethane) is a typical example of a symmetrical β-diketone. The interest in structural chemistry of β-diketones arises from their ability to form strong intra- and intermolecular hydrogen bonds (Bertolasi, Gilli, Ferretti & Gilli, 1991). DBM and various substituted β-diketones have been used for many years in the synthesis of different transition-metal complexes (Mehrotra, Bohra & Gaur, 1978; Kawaguchi, 1986). The existence of at least four polymorphic forms of DBM has been reported in the literature (Beilstein, 1948). The crystal structures of a stable orthorhombic polymorph (I) (Williams, 1966; Hollander, Templeton & Zalkin, 1973; Jones, 1976) and a metastable orthorhombic polymorph (II) (Etter, Jahn, Urbańczyk-Lipkowska, 1987) have been determined. Both crystallize in the space group *Pbca*, but with different crystal-packing patterns. In the present paper the structure of a new monoclinic modification (III), crystallizing with the space group $P2_1/c$, is reported. Three different crystal modifications of any diketomethane compound have not been reported in the literature previously.

The crystal structure of (III) consists of discrete enolic molecules separated by normal van der Waals interactions. There are no significant differences in the bond lengths and bond angles between (I), (II) and (III). Our molecule contains a nearly symmetric strong intramolecular hydrogen bond O1—HO···O2 [O1···O2 2.461 (4), O1—HO 1.287, O2···HO 1.257 Å; corresponding values are 2.461, 1.22 and 1.28 Å, respectively, in (I), and 2.452, 1.22 and 1.28 Å, respectively, in (II)]. The values of these intramolecular hydrogen interactions are the essential difference between (I)/(II) and (III). Another difference appears in the twisting angle of the terminal phenyl rings (C4-C9 and C10-C15) in relation to the β-diketone enol fragment (O1—C1—C2—C3—O2—HO). While the values of two dihedral angles in (I) and (II) between these three best planes differ [(I) 16.98 and 4.24°; (II) 8.27 and 24.33°] our molecule is almost planar with corresponding angles 7.60 and 6.91°, respectively. The C3—C4 and C1—C10 bond lengths of 1.480 and 1.481 Å can be considered as single C(sp^2)—C(sp^2) bond distances (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), but the position of the H atom HO, which is nearly equidistant to O1 and O2, suggests that the phenyl rings with their low twisting angles participate in the π delocalization of the β-diketone enol ring.

The difference in crystal packing was pointed out as the substantial distinction between (I) and (II) (Etter, Jahn & Urbańczyk-Lipkowska, 1987). Comparing the unit-cell packing diagrams of (II) and (III), we established that the stacking of the molecules is almost identical in the **y** viewing direction (*x*,*z* projection) in (II) and in the **z** viewing direction (*x*,*y* projection) in (III).

The correlation of molecular geometry for all three structures was performed. To avoid any error we labelled our molecule in the same way as Etter, Jahn & Urbańczyk-Lipkowska (1987) labelled form (II), and relabelled the molecule of the form (I) to be consistent with the labelling scheme in (II). We are not convinced

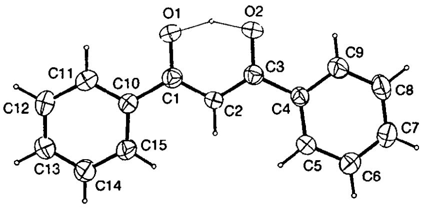


Fig. 1. An *ORTEP*II perspective view of the molecule. Thermal ellipsoids are drawn at the 30% probability level. H atoms are shown as spheres of arbitrary size.

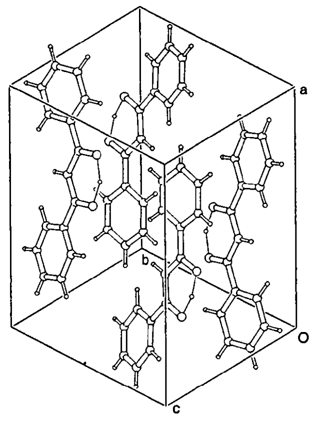


Fig. 2. A *PLUTON* unit-cell packing diagram.

Acta Crystallographica Section C
ISSN 0108-2701 ©1993

by the statement that a carbon-to-oxygen intermolecular contact of 3.70 Å is a very good explanation for the stabilization of the orthorhombic form (I) (Etter, Jahn & Urbańczyk-Lipkowska, 1987; D. Y. Curtin, private communication), when shorter carbon-to-oxygen (O1 and O2) contacts (< 3.5 Å) are present simultaneously in the structure (3.411 and 3.436 Å, respectively). We found nearly identical intermolecular C· · ·O1 and C· · ·O2 contacts in (II) (3.409 and 3.437 Å) and in our structure (3.420 and 3.487 Å, respectively).

Experimental

Crystal data

$C_{15}H_{12}O_2$
$M_r = 224.3$
Monoclinic
$P2_1/c$
$a = 12.491$ (8) Å
$b = 11.850$ (4) Å
$c = 8.068$ (3) Å
$\beta = 103.41$ (5)°
$V = 1161$ (1) Å^3
$Z = 4$
$D_x = 1.28$ Mg m^{-3}
$D_m = 1.26$ Mg m^{-3}
Density measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.7093$ Å
Cell parameters from 25 reflections
$\theta = 7$-18°
$\mu = 0.787$ mm^{-1}
$T = 293$ K
Prism
0.53 × 0.28 × 0.21 mm
Colourless
Crystal source: evaporation from MeOH at room temperature

Data collection

Philips PW1100 four-circle diffractometer (Stoe upgrade)
ω-2θ scans
Absorption correction: none
3169 measured reflections
3169 independent reflections
2291 observed reflections $[F_o > 2.5\sigma(F_o)]$

$R_{\rm int} = 0.015$
$\theta_{\rm max} = 27°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity variation: ±2%

Refinement

Refinement on F
Final $R = 0.042$
$wR = 0.045$
$S = 0.967$
898 reflections
155 parameters
$w = 1/[\sigma^2(F_o)+0.004625F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.2401 (2)	0.3695 (2)	0.2253 (3)	0.081 (1)
O2	0.4163 (2)	0.4047 (2)	0.1474 (3)	0.085 (1)
C1	0.2570 (2)	0.2632 (2)	0.2147 (3)	0.059 (1)
C2	0.3529 (2)	0.2238 (2)	0.1757 (3)	0.060 (1)
C3	0.4315 (2)	0.2970 (2)	0.1426 (3)	0.060 (1)
C4	0.5349 (2)	0.2608 (2)	0.0986 (3)	0.056 (1)
C5	0.5656 (2)	0.1483 (2)	0.0988 (4)	0.071 (1)
C6	0.6630 (3)	0.1180 (3)	0.0599 (4)	0.081 (1)
C7	0.7313 (3)	0.1980 (3)	0.0197 (4)	0.081 (1)
C8	0.7026 (3)	0.3090 (3)	0.0196 (4)	0.085 (2)
C9	0.6051 (3)	0.3411 (3)	0.0585 (4)	0.073 (1)
C10	0.1688 (2)	0.1877 (2)	0.2443 (3)	0.057 (1)
C11	0.0824 (2)	0.2312 (3)	0.3031 (4)	0.076 (1)
C12	−0.0024 (3)	0.1641 (3)	0.3270 (4)	0.089 (2)
C13	−0.0031 (3)	0.0523 (3)	0.2929 (4)	0.085 (2)
C14	0.0819 (3)	0.0078 (3)	0.2355 (6)	0.116 (2)
C15	0.1669 (3)	0.0742 (3)	0.2121 (5)	0.101 (2)

Table 2. *Geometric parameters* (Å, °)

O1—C1	1.284 (3)	C7—C8	1.363 (5)
O2—C3	1.292 (3)	C8—C9	1.380 (5)
C1—C2	1.389 (4)	C10—C11	1.376 (4)
C1—C10	1.481 (4)	C10—C15	1.369 (4)
C2—C3	1.383 (4)	C11—C12	1.373 (5)
C3—C4	1.480 (4)	C12—C13	1.353 (5)
C4—C5	1.386 (4)	C13—C14	1.359 (6)
C4—C9	1.382 (4)	C14—C15	1.370 (5)
C5—C6	1.373 (5)	O1—HO	1.287
C6—C7	1.364 (5)	O2—HO	1.257
O1—C1—C10	116.3 (3)	C6—C7—C8	119.5 (4)
O1—C1—C2	120.6 (3)	C7—C8—C9	120.8 (3)
C2—C1—C10	123.1 (3)	C4—C9—C8	120.3 (3)
C1—C2—C3	121.4 (3)	C1—C10—C15	122.9 (3)
O2—C3—C2	119.9 (3)	C1—C10—C11	120.1 (2)
C2—C3—C4	124.2 (2)	C11—C10—C15	117.0 (3)
O2—C3—C4	115.9 (3)	C10—C11—C12	121.6 (3)
C3—C4—C9	119.5 (3)	C11—C12—C13	120.5 (4)
C3—C4—C5	122.4 (3)	C12—C13—C14	118.7 (4)
C5—C4—C9	118.2 (3)	C13—C14—C15	121.0 (3)
C4—C5—C6	120.7 (3)	C10—C15—C14	121.2 (3)
C5—C6—C7	120.5 (3)	O1—HO—O2	150.7

Data collection and reduction: Stoe software (Stoe & Cie, 1992). Program(s) used to solve and refine structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989); *SHELX*76 (Sheldrick, 1976). The H atoms attached to the C atoms were positioned geometrically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations. The HO enolic H atom was found in a difference Fourier synthesis calculated at $R = 0.046$ as a low (0.23 e Å^{-3}) but well defined maximum. The coordinates of HO were refreshed every two cycles of refinement by ΔF map calculation. A check was made for crystal system and cell parameters by *CREDUC* and a search for higher symmetries was performed using *MISSYM* (both programs are part of the *NRCVAX* suite of programs). Software used to prepare molecular graphics and material for publication: *ORTEP*II (Johnson, 1976); *PLUTON* (Spek, 1982); *PARST* (Nardelli, 1983).

We thank the Scientific Research Foundation, Croatia, for financial support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data, as well as an electron-density contour map have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71123 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1028]

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1—S19.

Beilstein, X. (1948). *Beilsteins Handbuch der Organischen Chemie*, 4th ed., Vol. 7, edited by F. Richter, pp. 689-690. Berlin: Springer-Verlag.
Bertolasi, V., Gilli, P., Ferretti, V. & Gilli, G. (1991). *J. Am. Chem. Soc.* **113**, 4917-4925.
Etter, M. C., Jahn, D. A. & Urbańczyk-Lipkowska, Z. (1987). *Acta Cryst.* C**43**, 260-263.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384-387.
Hollander, F. J., Templeton, D. H. & Zalkin, A. (1973). *Acta Cryst.* B**29**, 1552-1553.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Jones, R. D. G. (1976). *Acta Cryst.* B**32**, 1807-1811.
Kawaguchi, S. (1986). *Coord. Chem. Rev.* **70**, 51-84.
Mehrotra, R. C., Bohra, R. & Gaur, D. P. (1978). *Metal β-Diketonates and Allied Derivatives*. New York: Academic Press.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95-98.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
Stoe & Cie (1992). Diffractometer control programs. Stoe & Cie, Darmstadt, Germany.
Williams, D. E. (1966). *Acta Cryst.* **21**, 340-349.

Acta Cryst. (1993). C**49**, 1525–1528

Symmetrically H-Bridged Dimer of 2-Carboxylatobenzenediazonium. The 1:1 Complex Between 2-Carboxybenzenediazonium Chloride and Benzenediazonium-2-carboxylate

Christopher J. Horan,† Paul E. Haney, Charles L. Barnes* and Rainer Glaser*

Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, USA

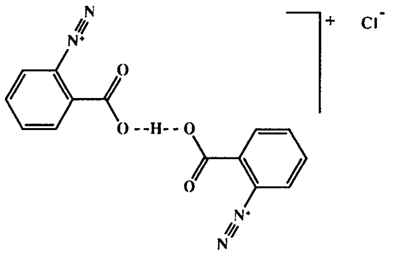
(*Received* 29 *April* 1992; *accepted* 27 *January* 1993)

Abstract

The two zwitterions in the H-bridged dimer of 2-carboxylatobenzenediazonium (1) are linked by a crystallographically symmetric O···H···O hydrogen bond with an O···O distance of 2.436 (3) Å. Comparison of (1) with other benzenediazonium salts shows that the phenyl ring distortions in (1) are determined primarily by the diazonium substituent with only modest additional effects by the carboxylate group. Intramolecular neighboring group interactions between the N_2 group and the *ortho* COO(H) group are indicated and are discussed. The terminal N atom of the diazonium group is bent away from the neighboring carboxylato group. The N_2 and the caboxylato group are on *opposite* sides of the best plane of the aromatic ring. Importantly, the carboxylato group is not fully conjugated with the aromatic ring but instead is rotated 6.5 (2)° around the C—CO_2 axis in a fashion that suggests minimization of *intra*molecular repulsion between N_α and the proximate O atom and optimization of the *inter*molecular hydrogen bonding.

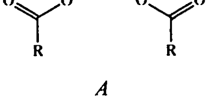
Comment

The crystal structure of the H-bridged dimer of the 2-carboxylatobenzenediazonium system, (1), was determined as part of our studies of the incipient nucleophilic attack in diazonium ions. These studies of the incipient nucleophilic attack serve as a probe for the electronic structures of diazonium ions (Glaser, Horan, Nelson & Hall, 1992) which we have been studying with *ab initio* methods.

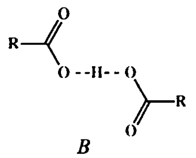


(I)

The crystal structure is characterized by aggregates of two 2-carboxylatobenzenediazonium zwitterions, (1). An H atom, located on a center of symmetry, hydrogen bonds between the carboxylato O atoms of two neighboring zwitterions. In general, unsymmetrical hydrogen bonds between two O atoms lead to O···O distances within the range 2.6–2.7 Å, while symmetrical hydrogen bonds have shorter O···O distances of about 2.5 Å (Cupertino, Harding, Cole-Hamilton, Dawes & Hursthouse, 1986). In (1), the observed intermolecular distance O(2)···O(2) of 2.436 (3) Å is thus consistent with a *symmetric* hydrogen bond. While there have been several reports of intramolecular hydrogen bonding between proximate carboxylate groups of the type *A* (*e.g.* Hsu



A



B

---

* Part of the projected PhD dissertation of CJH; presented in part at the 26th American Chemical Society Midwest Regional Meeting, Omaha, Nebraska, November 7, 1991.