0·88 Å from S atom. Final refinement converged to $R = 0·069$, $wR = 0·071$, five reflections omitted from the last cycle. Scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1,* bond distances, bond angles and selected torsion angles in Table 2.

The molecule (see Fig. 1) is practically planar; the weighted least-squares plane through the thiazole ring gives $\sum(\Delta/\sigma)^2 = 0·834$. C(6) and S(8) also lie in this plane while C(7) shows a small but significant out-of-plane deviation of 0·72 (16) Å.

Bond distances and bond angles clearly show a localized π interaction between C(4)—C(5), according to the distance S(1)—C(5) = 1·745 (17) Å which is close to the expected value for an S—C(sp^2) = 1·74 Å bond (Pauling, 1967).

Other C—S bond distances, C(2)—S(1) = 1·694 (14) and C(2)—S(8) = 1·708 (16) Å, are significantly shorter than the corresponding distances observed in benzothiazoles (Hinrichs, Mandak & Klar, 1982; Zingaro & Meyers, 1980). This seems to be related to the lengthening of the distance N(3)—C(2) = 1·349 (23) Å which is significantly greater than the corresponding ones, 1·317 (17) and 1·277 (5) Å, given by these authors. Other bond distances and bond angles are mainly as expected.

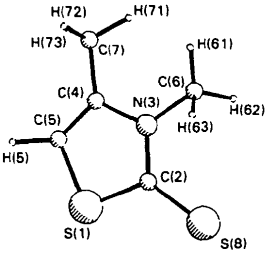


Fig. 1. View of the molecule projected along [100].

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43338 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo* 220. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma. Internal reports 1–3/79.

Dondoni, A., Galliani, G. & Mastellari, A. (1985). *Tetrahedron Lett.* **26**, 2917–2920.

Hinrichs, W., Mandak, D. & Klar, G. (1982). *Cryst. Struct. Commun.* **11**, 1781–1786.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–589.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J.-P. (1974). *MULTAN74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Pauling, L. (1967). *The Nature of the Chemical Bond.* Cornell Univ. Press.

Sheldrick, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Zingaro, R. A. & Meyers, E. A. (1980). *Cryst. Struct. Commun.* **9**, 1167–1172.

Acta Cryst. (1987). C**43**, 260–263

A New Polymorph of Dibenzoylmethane

By Margaret C. Etter,* Donald A. Jahn and Zofia Urbańczyk-Lipkowska†

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

(*Received* 17 *April* 1986; *accepted* 26 *August* 1986)

Abstract. 1,3-Diphenyl-1,3-propanedione (dibenzoylmethane), $C_{15}H_{12}O_2$, $M_r = 224·3$, orthorhombic, *Pbca*, $a = 11·706$ (5), $b = 7·668$ (4), $c = 25·572$ (8) Å, $V = 2295$ (3) Å^3, $Z = 8$, $D_x = 1·298$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu(\text{Mo } K\alpha) = 0·79$ cm^{-1}, $F(000) = 944$, $T = 298$ K, $R = 0·049$ for 915 observed reflections, $wR = 0·048$. This polymorph of dibenzoylmethane (DBM) is a metastable kinetically favored crystal form in which the molecules are enolic and contain a slightly asymmetric intramolecular hydrogen bond. The molecular structure is nearly identical to that of DBM molecules in the stable crystal form, but the packing patterns of the two different polymorphs are markedly different.

---

* To whom correspondence should be addressed.

† Present address: Polish Academy of Sciences, Warsaw, Poland.

0108-2701/87/020260-04$01.50

Introduction. The structures of β-diketomethanes (DKM) have been of long-standing interest because of the role of the intramolecular hydrogen bond in determining the conformational and electronic properties of these compounds. For symmetrically substituted DKM compounds, the proton can exist in a symmetrical double minimum potential energy well such that rapid exchange or tunnelling occurs between the two minima (Emsley, 1984). In the solid state, whenever the molecule is on a general crystallographic position the proton will exist in an asymmetric double minimum with the solid-state environment influencing the positions of the protons involved in DKM intramolecular hydrogen bonds. In order to probe the relationships between crystal packing properties and hydrogen-bond geometry we have solved the crystal structure of a metastable crystal form of dibenzoylmethane (DBM), (II), and have compared its structure with that of previously reported structures of the stable form of DBM, (I) (Williams, 1966; Hollander, Templeton & Zalkin, 1973; Jones, 1976). This is the first example in the literature of crystal structure analyses being reported for two different crystal forms of a DKM compound.

We also report here the observation of a solid-state phase transformation from the metastable to the stable form of DBM.

Experimental. *Crystal growth and characterization.* Single, 1–2 mm long, rod-shaped crystals of (II) are grown by rapidly cooling a hot ethanol solution of DBM to 243 K. In order to prevent the transformation of (II) to (I), it is necessary to remove the crystals of (II) from solution immediately and under a vigorous stream of dry nitrogen. If the solvent is not removed rapidly enough the crystals become opaque within a few minutes, but when properly isolated they are indefinitely stable. A phase front, corresponding to the opaque phase, can be seen moving along the long (*b*) axis of the crystals. Crystals of (II) will transform to polycrystalline (I) when heated to 323 K on a hot stage, or when exposed to solvent vapors. When the crystals are left in the mother liquor for more than a few minutes they transform by an induction mechanism whereby each single rod of (II) is converted to a rock-candy-like array of rhombic crystals of (I).

Differential scanning calorimetry analyses (Perkin–Elmer Model DSC-2) of (I) and (II) were carried out. (I), the stable form, melts at 349–351 K. (II), the metastable form, melts either at 341–344 K or at 349–351 K. ΔH_{fusion} for either transition is 4·9 (1) kcal mol^{-1}.* When (I) or (II) is melted, then cooled and remelted, either the low or the high melt transition is seen, but we could not correlate the occurrence of the low or high melting transition with heating rate. Thus (II) can be thermally transformed into (I), and melt recrystallization can give rise to either (I) or (II). The observed melting points correspond to previously reported values for dibenzoylmethane (Eistert, Weygard & Csendes, 1952; Beilstein, 1969).

Crystal structure solution. Crystal dimensions 0·27 × 0·22 × 0·45 mm, CAD-4 diffractometer, graphite-monochromatized Mo$K\alpha$ radiation. Cell parameters by least-squares fit of 25 reflections, $8 < \theta < 18°$, θ–2θ scan technique. Three standard reflections showed no significant loss in intensity during data collection. Absorption corrections were not applied, μ(Mo $K\alpha$) = 0·79 cm^{-1}. 2064 unique reflctions measured, $\theta_{\max} = 25°$, $h,k,l = 0\to13, 0\to8, 0\to29$. Of these, 915 used in structure analysis $[I > 1\sigma(I)]$. Structure solved by direct methods using the *SDP* software package (Frenz, 1982). Difference map indicated all H atoms clearly. Refinement performed on F_{obs} using full-matrix least-squares methods. All non-H atoms refined anisotropically; H atoms refined isotropically. $R = 0{\cdot}049$, $wR = 0{\cdot}048$, $S = 1{\cdot}408$, max. shift/e.s.d. 0·05 (0·32 for hydrogens). The weights, $w = 1/\sigma^2(F_o)$, were calculated from $\sigma^2(I) = \sigma^2(I_c) + (0{\cdot}04I)^2$ where $\sigma(I_c)$ is the standard deviation in I based on counting statistics. $R = 0{\cdot}20$ including all nonobserved reflections. Largest peak on the difference map = 0·16 e Å^{-3}, and the deepest hollow = 0·15 e Å^{-3}. An isotropic secondary-extinction coefficient of 3·2 (6) × 10^{-7} was included in the final refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Several possible H-atom positions for the enol hydrogen in the intramolecular hydrogen bond were evaluated. A difference map revealed a single electron density peak (0·33 e Å^{-3}) located closer to O(2) than to O(1). Isotropic refinement of the proton at this position gave satisfactory convergence. Attempts to refine the occupancies of a proton at an alternative position nearer to O(1) were not successful, so a proton with occupancy 1, located in an asymmetric hydrogen bond nearer to O(2), was used for final refinements.

Atomic fractional coordinates are shown in Table 1.*

Discussion. The existence of at least four polymorphic forms of DBM has been reported in the literature (Beilstein, 1948), yet the only crystal structures reported to date have been for the stable form. From our crystal growth experiments we were able to isolate one metastable form whose crystal structure is reported here. We have been unable to confirm the presence of additional crystal forms growing from ethanol solution.

---

* 1 kcal mol^{-1} ≡ 4·2 kJ mol^{-1}.

* Tables of F_{obs} and F_{calc}, thermal parameters, and inter- and intramolecular bond lengths, angles, and estimated standard deviations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43352 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecular structures of DBM in the stable form, (I), and in the metastable form, (II), are nearly identical. The hydrogen-bond geometries are shown for the present structure, (II), and for the X-ray-determined structure of (I), in Fig 1. A neutron structure determination of (I) showed the presence of a somewhat less symmetrical hydrogen bond than that shown in Fig. 1 (Jones, 1976). Thus, the enol proton in (I) and in (II) appears from the X-ray data to be static and

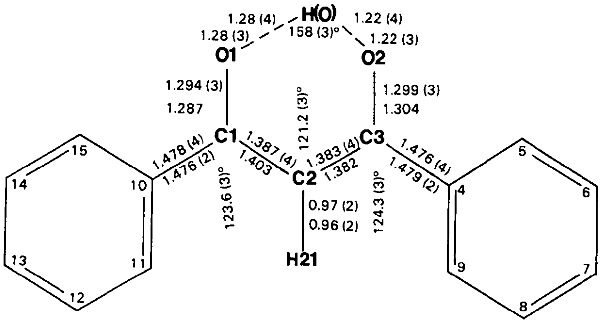
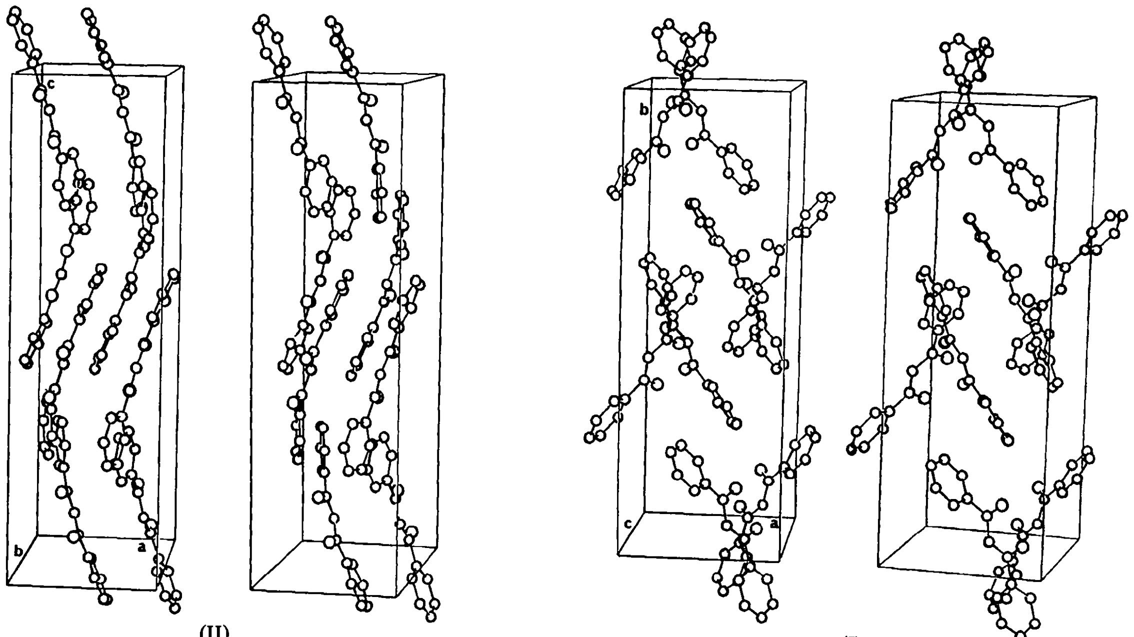


Fig. 1. Hydrogen-bond geometry for the enol ring of dibenzoylmethane. The bond angles and the upper values of the pairs of bond lengths (Å) refer to the metastable crystal form, (II), as reported in this paper. The lower bond-length values refer to the X-ray. data reported for the stable form, (I) (Hollander, Templeton & Zalkin, 1973).

Table 1. *Fractional coordinates and equivalent isotropic temperature factors for the unstable polymorph of DBM with e.s.d.'s in parentheses (starred atoms were refined isotropically)*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B(Å^2)
C1	0·2603 (2)	0·2411 (5)	0·6239 (1)	4·31 (7)
C2	0·2186 (2)	0·1932 (5)	0·5752 (1)	4·24 (7)
C3	0·2916 (2)	0·1498 (4)	0·5347 (1)	4·10 (7)
C4	0·2539 (3)	0·0832 (4)	0·4834 (1)	3·99 (7)
C5	0·1400 (3)	0·0799 (5)	0·4689 (1)	4·61 (8)
C6	0·1083 (3)	0·0124 (5)	0·4208 (1)	5·16 (9)
C7	0·1894 (3)	−0·0474 (5)	0·3864 (1)	5·31 (9)
C8	0·3028 (3)	−0·0417 (5)	0·4003 (1)	5·52 (9)
C9	0·3349 (3)	0·0234 (5)	0·4482 (1)	4·64 (8)
C10	0·1864 (2)	0·2787 (4)	0·6694 (1)	4·21 (7)
C11	0·2295 (3)	0·2630 (5)	0·7192 (1)	5·43 (9)
C12	0·1632 (3)	0·2984 (5)	0·7622 (1)	6·2 (1)
C13	0·0544 (3)	0·3507 (6)	0·7562 (1)	6·4 (1)
C14	0·0078 (3)	0·3673 (6)	0·7068 (1)	6·1 (1)
C15	0·0739 (3)	0·3312 (5)	0·6638 (1)	5·12 (8)
O1	0·3689 (2)	0·2576 (3)	0·63175 (8)	5·79 (6)
O2	0·4013 (2)	0·1618 (3)	0·54146 (8)	6·07 (6)
H(O)	0·402 (3)	0·306 (4)	0·088 (1)	9 (1)*
H21	0·137 (2)	0·328 (3)	0·0712 (8)	4·1 (6)*
H51	0·079	0·124	0·492	4·8 (6)*
H61	0·025	0·031	0·410	5·5 (7)*
H71	0·170	−0·091	0·351	7·9 (9)*
H81	0·359	−0·075	0·378	8·6 (9)*
H91	0·414	0·024	0·459	3·8 (6)*
H111	0·306	0·230	0·720	5·8 (7)*
H121	0·199	0·285	0·798	7·6 (9)*
H131	0·006	0·376	0·787	5·1 (7)*
H141	−0·069	0·400	0·701	7·3 (8)*
H151	0·039	0·345	0·629	5·9 (7)*



(II)

(I)

Fig. 2. Stereoviews of the unit cells of the metastable crystal form of DBM, (II), and of the stable crystal form, (I) [calculated from the data given in the reference by Hollander, Templeton & Zalkin (1973)]. The unit cells are viewed along the b axis of (II) and the c axis of (I) for comparison. These axes are the short (~8 Å) axes of the two structures. No unusually close intermolecular contacts were observed for (II), while a possible CH···O stabilizing interaction has been proposed for (I) (D. Y. Curtin, private communication). The close approach of C(2) and O(1) can be seen between pairs of molecules in (I).

located in an asymmetrical potential energy well. A recently published high resolution solid-state ^{13}C CP-MAS NMR spectrum of (I) lends support to this claim since two clearly resolved ^{13}C peaks ($\Delta\sigma_i = 5{\cdot}3$ p.p.m.) are seen for the carbonyl carbon and the enol carbon (Imashiro, Maeda, Takegoshi, Terao & Saika, 1982), indicating that these atoms are not being dynamically averaged. If the proton were rapidly exchanging between two equivalent positions, a single averaged isotropic chemical shift would be seen. Attempts to obtain a ^{13}C CP-MAS NMR spectrum of (II) have been unsuccessful owing to the facile phase change to (I) during sample preparation.

A small difference between the structures of (I) and (II) is found in the torsion angles between the least-squares planes of the central hydrogen-bonded ring and the phenyl rings. In (I), the two phenyl torsion angles are 4 and 17° (Hollander, Templeton & Zalkin, 1973), but in (II) they are 8 (3) and 24 (3)°.

The unit-cell packing patterns of (I) and (II) are shown viewed along their short axes, *c* and *b* respectively, in Fig. 2. Despite the strikingly similar unit-cell parameters and identical space groups [(I), *Pbca*, $Z = 8$, $a = 10{\cdot}853$ (1), $b = 24{\cdot}441$ (1), $c = 8{\cdot}7559$ (1) Å; Jones (1976)] the packing patterns show no significant similarities. There are no unusually short intermolecular contacts in (II) and no evidence for any intermolecular hydrogen bonds. It has been suggested that form (I) may be stabilized by a weak intermolecular hydrogen bond between C(2)—H and O(1) on neighboring *a*-glide-related molecules (D. Y. Curtin, private communication). The C(2)···O(1) distance in (I) is 3·70 Å (C—H···O angle, 141°), and no such contact is found in (II).

This crystal structure and the previously reported structures of (I) provide the first opportunity to study the effect of two different solid-state environments on the structure of a DKM compound. For DBM, we have found that for room-temperature X-ray data, the solid-state packing patterns are markedly different but the intramolecular geometries, including the position of the enol H atom, are virtually identical. These results are in contrast to those of Herbstein, Kapon, Reisner, Duesler, Paul & Curtin (1985) who found that in the multiple polymorphs of naphthazarin the properties of the enolized proton and of its hydrogen bonds are very sensitive to differences in crystal packing patterns.

Facile solvent-assisted (Cardew & Davey, 1985) and solid-state phase changes from (II) to (I) were observed. A detailed study of these transformation mechanisms is in progress.

Helpful discussions with Professor Doyle Britton, University of Minnesota, are gratefully acknowledged.

References

BEILSTEIN (1948). *Handbuch der Organischen Chemie*, II, B7, 689–690.

BEILSTEIN (1969). *Handbuch der Organischen Chemie*, III, B7, S3838–S3840.

CARDEW, P. T. & DAVEY, R. G. (1985). *Proc. R. Soc. London Ser. A*, **398**, 415–428.

EISTERT, B., WEYGARD, F. & CSENDES, E. (1952). *Chem. Ber.* **85**, 164–168.

EMSLEY, J. (1984). *Struct. Bonding (Berlin)*, **57**, 147–191.

FRENZ, B. A. (1982). *Enraf–Nonius Structure Determination Package*. College Station, Texas.

HERBSTEIN, F. H., KAPON, M., REISNER, G. M., DUESLER, E. N., PAUL, I. C. & CURTIN, D. Y. (1985). *Proc. R. Soc. London Ser. A*, **399**, 295–319.

HOLLANDER, F. J., TEMPLETON, D. H. & ZALKIN, A. (1973). *Acta Cryst.* B**29**, 1552–1553.

IMASHIRO, F., MAEDA, S., TAKEGOSHI, K., TERAO, T. & SAIKA, A. (1982). *Chem. Phys. Lett.* **92**, 642–645.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JONES, R. D. G. (1976). *Acta Cryst.* B**32**, 1807–1811.

WILLIAMS, D. E. (1966). *Acta Cryst.* **21**, 340–349.

Acta Cryst. (1987). C**43**, 263–266

Structures of (+)-(*R*)-α-Methylbenzylammonium (+)-(1*S*,6*R*,7*S*)-Bicyclo[4.1.0]hept-2-ene-7-carboxylate (I) and (+)-(*R*)-α-Methylbenzylammonium (+)-(1*R*,8*S*,9*R*)-Bicyclo[6.1.0]non-2-ene-9-carboxylate (II)

BY KAZUNORI YANAGI AND TADATOSHI ARATANI

Takatsuki Research Laboratory, Sumitomo Chemical Co. Ltd, 2-10-1, *Tsukahara, Takatsuki, Osaka* 569, *Japan*

(*Received* 2 *July* 1986; *accepted* 28 *August* 1986)

Abstract. (I): $C_8H_{12}N^+.C_8H_9O_2^-$, $M_r = 259{\cdot}35$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}582$ (1), $b = 19{\cdot}537$ (2), $c = 6{\cdot}159$ (1) Å, $V = 1513{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}14$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu(\text{Cu } K\alpha) = 0{\cdot}56$ mm^{-1}, $T = 295$ K, $F(000) = 560$, $R = 0{\cdot}045$ for 1218 observed reflections. (II): $C_8H_{12}N^+.C_{10}H_{13}O_2^-$,

0108-2701/87/020263-04$01.50