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The Crystal Structure of Phenylmalondialdehyde at —162 °C

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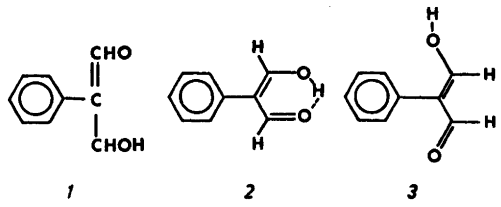
The crystal structure of 2-phenylmalondialdehyde (2-phenyl-2-propen-3-ol-1-one, $C_9H_8O_2$) has been determined at −162 °C. The crystals are orthorhombic with space group $Pna2_1$, cell dimensions $a=7.523(2)$, $b=17.165(3)$, $c=5.552(2)$ Å, and four molecules in the unit cell. The structure was solved by direct methods and refined by the full-matrix least-squares methods to $R=0.032$ ($R_w=0.035$) for 1012 reflections with sin $\theta/\lambda>0.5$ Å^{-1}. The compound crystallizes in the *trans*-enol form. The crystal packing consists of asymmetrically hydrogen bonded chains of molecules in a pseudo *Pnab* cell. The polar axis of the space group may therefore be reversible and the crystals may show ferroelectric properties.

Phenyl malondialdehyde was first prepared by reduction of hydroxymethylenebenzyl cyanide followed by mild acidic hydrolysis of the intermediate aldimine.[1] More recently it has been prepared in high yield by hydrolysis of 2-phenyl-3-(dimethylamino)acrolein.[2] It was originally assigned the structure (*1*) but NMR studies in solution suggest the presence of an intramolecular hydrogen bond (*2*).[2,3] Since no structural analysis has so far been reported for pure β-dialdehyde compounds, it was considered of interest to perform a structural analysis of phenylmalondialdehyde. During the structure analysis it turned out that the compound in the solid state assumes a *trans* enol arrangement (*3*), similar to that found in dimedone (5,5-cyclohexane-1,3-dione) [4] and triose reductone (2-propene-2,3-diol-1-one).[5]

EXPERIMENTAL

A sample of the compound was kindly provided by Dr. G. M. Coppola and Dr. G. E. Hardtmann. White, transparent crystals suitable for X-ray work were grown by slow sublimation at 50 °C and 0.1 mmHg. The identity of the sublimed sample was confirmed by infrared spectroscopy (KBr). X-Ray photographs showed the following systematic absences ($0kl$): $k+l=2n+1$ and ($h0l$): $h=2n$ indicating the space group to be either $Pna2_1$ or *Pnam*. However, it was noted that in addition, most $hk0$ for $k=2n+1$ were weak or absent, suggesting that the space group might be pseudo *Pnab*. Data collection was carried out with a crystal of approximate dimensions 0.3 × 0.4 × 0.35 mm on a SYNTEX P$\bar{1}$ diffractometer with graphite monochromatized Mo$K\alpha$ radiation ($\lambda=0.71069$ Å) equipped with an Enraf-Nonius liquid nitrogen gas-flow cooling device (modified by H. Hope). The temperature at the crystal position was −162 °C. The cell parameters (at −162 °C) were determined by least squares refinements from 20 high angle reflections. One octant of the reciprocal lattice was examined for which $2\theta<70°$, and data were collected in the $\omega-2\theta$ scanning mode. For 2θ below 45° a constant scan speed of 4°/min in 2θ was used, while for $45<2\theta\leq 70°$ a variable scan speed (2−4°/min) and a rejection level were applied. A symmetrical scan range of 1.8° corrected for spectral dispersion was specified and the ratio of background time to time of integration was 0.6. Three reference reflections were monitored every 50 measurement cycles and showed no significant variation. A total of 1559 reciprocal lattice points including all space group absences were examined, of which 1430 had intensities larger than $2\sigma(I)$. The remainder, including all symmetry absent reflections for $Pna2_1$ were rejected, while most reflections for $hk0$ for k odd



1 *2* *3*

were found to be observable at −162 °C. Corrections for Lorentz and polarization effects were applied to the intensities and their standard deviations and a 2 % uncertainty due to instrument instability was included in the latter.

CRYSTAL DATA (AT −162 °C)

Phenylmalondialdehyde $C_9H_8O_2$
Space group $Pna2_1$, orthorhombic
$a = 7.523(2)$, $b = 17.165(3)$, $c = 5.552(2)$ Å
$V = 716.9$ Å^3; $F.W. = 148.16$; $F(000) = 312$; $Z = 4$.
D_{obs}(flotation 20 °C) = 1.36 g cm^{-3}; $D_{calc} = 1.373$ g cm^{-3}.

STRUCTURE SOLUTION AND REFINEMENTS

Statistical tests strongly indicated a centric distribution. The space group *Pnam* was, however, considered unlikely for chemical reasons since it requires either a mirror plane or a centre of inversion in the molecule. Direct methods [6] were therefore applied to $Pna2_1$ and positions of all non-hydrogen atoms in a non-planar, chemically reasonable arrangement were obtained. Least-squares refinements [7]* of these positions resulted in divergence. However, preliminary refinement by the minimum residual method [8] resulted in a model which was then successfully refined by conventional least-squares procedure to $R = 0.09$ and $R_w = 0.12$ (hydrogen atoms and anisotropic parameters included). Unfortunately the resulting model was found to contain a number of unreasonable bond lengths in both the benzene ring and the enol moiety. Least-squares refinements with unit weights and only reflections with $\sin\theta/\lambda < 0.5$ did not improve the model, but reduced the residuals to 0.08. An acceptable model for the structure was obtained from the initial coordinates after several cycles of Fourier refinements followed by least-squares refinements yielding the residuals $R = 0.040$, $R_w = 0.045$ and $S = 2.27$.** All hydrogen atoms were located in a difference Fourier map, which did not contain other density fluctuations larger than ±0.3 e Å^{-3}. A comparison of the atomic positions finally arrived at and those of the former false minimum showed that the average shift in the x coordinates was about 0.3 Å, while only small changes in the y and z coordinates were found. Refinements of the heavy atoms parameters with 1012 reflections for which $\sin\theta/\lambda > 0.5$ were also performed, resulting in the residuals $R = 0.032$, $R_w = 0.035$ and $S = 1.38$. Positional parameters were shifted by amounts up to 4 estimated standard deviations (e.s.d.), the average shift being of the order of one e.s.d., while all U_{ij} were reduced by amounts ranging between 0.5 to 4 e.s.d.'s by exclusion of the low angle data. Atomic parameters for non-hydrogen atoms obtained in the latter refinement are listed in Table 1 along with the parameters for the hydrogen

* Descriptions of all programs used (except those for the phase determination) are included in this reference.

** Standard deviations of unit weight $S = [\sum W(F_o^2 - F_c^2)^2/(m-n)]^{\frac{1}{2}}$

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations, from the final refinement of high angle data. Expression for anisotropic vibration is exp $[-2\pi^2(h^2a^{*2}U11 + \cdots + 2klb^*c^*U23)]$. Hn is bonded to Cn and HO to O2.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O1	.41117(15)	.78881(7)	0.88888(8)	.0224(4)	.0219(4)	.0149(5)	-.0066(3)	.0050(4)	-.0001(4)
O2	.85582(14)	.69734(6)	.69528(25)	.0188(4)	.0191(4)	.0143(4)	.0035(3)	.0049(4)	.0007(4)
C1	.32362(18)	.73617(7)	.16698(41)	.0173(4)	.0164(5)	.0126(6)	-.0036(4)	.0002(4)	.0018(4)
C2	.14788(16)	.73164(7)	.52388(42)	.0157(4)	.0142(4)	.0138(6)	.0022(3)	-.0002(4)	-.0004(5)
C3	.23727(16)	.69847(6)	.35888(45)	.0137(4)	.0133(3)	.0116(3)	-.0005(3)	.0002(3)	.0011(6)
C4	.24588(16)	.66481(5)	.34986(48)	.0122(3)	.0136(3)	.0101(3)	-.0006(4)	.0003(3)	-.0005(6)
C5	.32366(19)	.64484(8)	.54882(42)	.0151(4)	.0156(5)	.0132(7)	.0015(3)	-.0014(4)	.0002(4)
C6	.33271(18)	.68271(8)	.53786(45)	.0197(5)	.0155(5)	.0156(8)	.0031(3)	.0006(5)	.0020(5)
C7	.25866(22)	.44132(6)	.34677(55)	.0216(5)	.0142(4)	.0171(4)	.0000(4)	.0038(4)	.0006(6)
C8	.17687(20)	.48878(8)	.15734(46)	.0214(5)	.0165(5)	.0154(8)	-.0038(4)	-.0005(5)	-.0027(5)
C9	.17245(17)	.86286(8)	.15641(42)	.0162(4)	.0169(5)	.0184(6)	-.0013(4)	-.0014(4)	-.0002(4)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1	.3896(27)	.7922(11)	.1715(52)	2.1(4)	H2	.1445(26)	.7887(10)	.4974(53)	2.9(3)
H6	.3745(25)	.6933(11)	.6759(56)	2.1(3)	H6	.3948(27)	.4571(11)	.6758(54)	2.2(4)
H7	.2662(27)	.3846(12)	.3689(77)	3.2(4)	H8	.1225(29)	.4519(11)	.0281(70)	2.7(4)
H9	.1184(27)	.5876(11)	.9279(62)	2.4(4)	HO	.8102(34)	.7388(14)	.7944(58)	4.1(6)

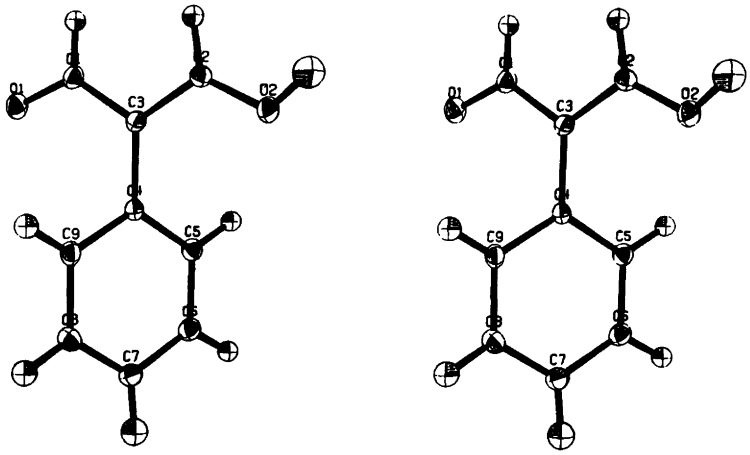


Fig. 1. Stereoscopic illustration of the molecule with atom numbering as indicated. Ellipsoids indicate amplitudes of vibration and enclose 50 % of the probability.[9]

atoms from the refinements including all observed reflections. The average and maximum parameter shifts as fractions of the e.s.d.'s in the final cycle of computation were 0.15 and 0.3, respectively. The function minimized during refinements was $\sum w(F_o - F_c)^2$, $w = \sigma(F_o)^2$. The atomic form factors were those of Doyle and Turner[9] except for hydrogen.[10] Lists of observed and calculated structure factors are available from the author upon request.

DISCUSSION

Bond lengths and angles are given in Table 2, and Fig. 1 shows a drawing of the molecule indicating the atom numbering scheme. The compound crystallizes in the *trans*-enol form (3) as previously has been found for other derivatives of malondialdehyde in the solid state.[5,11] The stability of the *trans*-form (*3*) relative to the *cis*-form in these compounds is mainly due to the small size of the terminal substituents (H1 and H2), facilitating an essentially planar conjugated system with intermolecular hydrogen bonds in the solid state. The non-bonded intra-molecular distance between H1 and H2 is 2.2(1) Å in phenylmalonaldehyde and longer than the sum of the van der Waals radii (2.0 Å) between these atoms.[12,13] A *trans*-enol arrangement corresponding to that observed in the crystal structure of phenylmalondialdehyde has not been found for any of the acyclic β-diketones so far investigated by diffraction methods.[14] This is no surprise in view of the increase in steric hindrance to a planar structure where larger substituents are incorporated at the β-positions. The *trans* arrangement does, however, occur in cyclic homologues as has been demonstrated in the structure investigation of dimedone.[14]

The average C–C bond length in the benzene ring is 1.396 Å in perfect agreement with the r_α^0 value of benzene [1.396(2) Å] obtained from spectroscopic measurements.[15] The largest

Table 2. Interatomic distances, bond angles and hydrogen bond parameters, with estimated standard deviations, from the final refinement of high angle data.

Distance	(Å)	Distance	(Å)
O1 - O2	2.577(1)	O1 - C1	1.238(2)
O2 - C2	1.316(2)	C1 - C3	1.431(2)
C2 - C3	1.372(2)	C3 - C4	1.465(1)
C4 - C5	1.398(2)	C5 - C6	1.398(2)
C6 - C7	1.395(3)	C7 - C8	1.392(3)
C8 - C9	1.396(2)	C4 - C9	1.400(2)
C1 - H1	.968(0)	C2 - H2	.990(0)
C5 - H5	.980(0)	C6 - H6	.996(0)
C7 - H7	.978(0)	C8 - H8	.964(0)
C9 - H9	.931(0)	O2 - HO	.867(0)
O1 - HO	1.712(0)		

Angle	(°)	Angle	(°)
C1 - O1 - O2	119.0(1)	C2 - O2 - O1	114.7(1)
O1 - HO - O2	175.6(0)	C1 - O1 - HO	120.4(0)
C2 - O2 - HO	111.8(0)	O1 - C1 - C3	124.4(1)
O2 - C2 - C3	122.4(1)	C1 - C3 - C2	115.7(1)
C1 - C3 - C4	121.8(1)	C2 - C3 - C4	122.4(1)
C3 - C4 - C5	120.3(1)	C3 - C4 - C9	120.1(1)
C4 - C5 - C6	120.1(1)	C5 - C6 - C7	119.9(1)
C6 - C7 - C8	120.2(1)	C7 - C8 - C9	120.0(2)
C4 - C9 - C8	120.1(1)	C5 - C4 - C9	119.6(1)

Table 3. Deviations (Å) of atoms from least-squares planes through the benzene ring (I) and enol arrangement (II). Atoms in parenthesis are not included in the calculations.

I		II	
C4	0.001	O1	−0.006
C5	−0.011	O2	−0.014
C6	0.010	C1	−0.008
C7	0.006	C2	0.015
C8	−0.010	C3	0.019
C9	0.009	(C4)	0.044
(C3)	0.003	(C7)	0.082
		(HO)	0.024
		(H1)	−0.074
		(H2)	−0.069

discrepancy from the mean value is about 0.004 Å, only slightly more than the average combined standard deviation in these bonds (0.003 Å). The agreement is taken to indicate that the bond lengths derived for the other heavy atoms are physically meaningful. The bond lengths found in the enol arrangement show considerable conjugation, although single and double bonds are clearly recognizable. This is in qualitative agreement with the findings in the previous study of dimedone. However, the C−C bonds in the enol fragment in the present study appear to be somewhat longer than those determined in dimedone [1.418(2) and 1.351(2) Å], whereas the C−O bonds are slightly shorter [1.246(2) and 1.326(2) Å in dimedone]. It is tempting to correlate these small changes with the negative inductive effect exerted by the phenyl ring. Since the phenyl ring makes an angle of 63.2° with the enol system, it seems unlikely that the enol system is influenced through conjugation across the central bond C3−C4. The length of this bond [1.485(1) Å] compares well with other carbon sp^2-sp^2 single bonds determined in similar systems.[14]

Deviations of the atoms from least-squares planes through the enol system and the benzene ring planes are given in Table 3. Although the benzene ring and enol system separately are essentially planar, the deviations are significant in terms of the estimated standard deviations in atomic positions. These deviations are, however, not considered to be of chemical origin.

The O---O distance [2.575(2) Å] shows the presence of a strong asymmetric hydrogen bond, similar to those found in dimedone [2.593(2) Å] and α-methyltetronic acid [2.600(3) Å].[16] The hydrogen bond formed by the *trans*-enol arrangement thus appear to be somewhat stronger than those formed by carboxylic acids (2.63−2.64 Å).[17] The hydrogen atom (HO) is

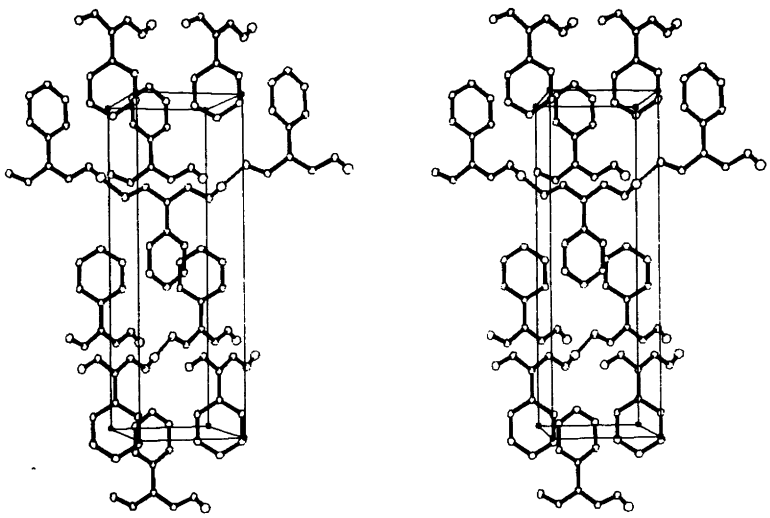


Fig. 2. Stereoscopic illustration of the crystal structure of phenylmalondialdehyde, as viewed along the *a* axis.

close to the mean squares planes through the donor and acceptor groups at distances 0.87 and 1.71 Å from O2 and O1, respectively. The bond is nearly linear (O−H···O = 175.6°) and the observed asymmetries in the heavy atom arrangement and the proton position form a consistent chemical pattern. No evidence of disorder in the HO proton could be seen from the final difference Fourier map.

The packing of the molecules is shown in Fig. 2. The hydrogen bonds link the molecules together along the [102] and [10$\bar{2}$] directions into infinite chains. The long dimension of the molecule nearly coincides with the [010] direction, and the structure is built up from alternating regions containing phenyl rings and hydrogen bonded enol arrangements around the twofold screw axes and *a* glides, respectively.

Crystallographically the structure of phenylmalondialdehyde is very interesting. Referring to the origin at the twofold screw axis there is a pseudo twofold axis through the molecule at $y \simeq 0.25$, and a pseudo centre of inversion at the centre of the hydrogen bond (0,0.25,0.15). The crystal structure is therefore pseudo *Pnab*, in agreement with the observed pseudo extinctions in the *hk*0 zone for $k = 2n+1$. The space group $Pna2_1$ is polar, and the structure arrived at may possibly show cooperative properties such as reversibility of the sense of the polar axis and a phase-transition to *Pnab*. However, no ferroelectric twinning was observed in the crystalline material utilized for this investigation, nor could any phase-transition be inferred from difference scanning calorimetric measurements in the temperature region from 25 to 95 °C (the melting point of the substance). The entropy of such a transition may, however, be so small that it is not detectable in a routine measurement of this kind.

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