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α,β-Diphenylsuccinic Acid의 構造

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Structure of α,β-Diphenylsuccinic Acid

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요 약

$C_{19}H_{20}O_5$, Mr=314.337, 三斜晶系, $P\bar{1}$, a=10.291(2)Å, b=11.218(3)Å, c=9.059(1)Å, α=74.54(2)°, β=114.84(1)°, γ=109.84(2)°, V=883.283(2)Å^3, λ(Mo kα)=0.71069Å, μ=0.47 mm^{-1}, F(000)=324, 296K, Z=2, D_x=1.18Mgm^{-3}. 1637[$F_o>3\sigma(F_o)$]個 獨立 反射面에 對한 最終 R=0.0580 이다.

α,β-diphenylsuccinic acid, $C_{16}H_{14}O_4$, 分子들은 O(4)-H···O(5) 水素結合에 依하여 溶劑인 acetone과 結合되어 있고 中心對稱關係에 있는 dimer는 分子間의 carboxylic 水素結合 O(1)-H···O(2)(-x, -y, -z)에 依하여 結合되어 있다. Dimer間의 가장 가까운 距離 3.288Å [O(2)···O(2) (-x, -y, -z)]은 分子들의 packing이 van der Waals 力으로 이루워졌음을 보인다.

Abstract

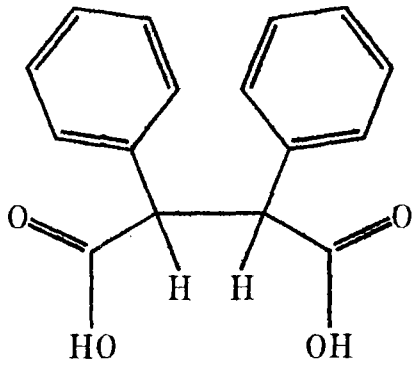
$C_{19}H_{20}O_5$, Mr=314.337, triclinic, $P\bar{1}$, a=10.291(2)Å, b=11.218(3)Å, c=9.059(1)Å, α=74.54(2)°, β=114.84(1)°, γ=109.84(2)°, V=883.283(2)Å^3, λ(Mokα)=0.71069Å, μ=0.47 mm^{-1}, F(000)=324, 296K, Z=2, D_x=1.18Mgm^{-3}. Final R=0.058 for 1637 [$F_o>3\sigma(F_o)$] unique reflections.

The molecules of α,β-diphenylsuccinic acid, $C_{16}H_{14}O_4$, are connected with the solvent acetone by hydrogen bond O(4)-H···O(5), forming a dimer related by centrosymmetry through intermolecular carboxylic hydrogen bond O(1)-H···O(2) (-x,-y,-z). The nearest distance 3.288Å[O(2)···O(2) (-x,-y,-z) between the dimers shows that the packing of the dimers is governed by van der Waals' force.

1. Introduction

The title compound(I) was newly synthesized in the course of studies carried out on 2,3-diphenylmaleic anhydride, a new analogue of cis-stilbene[1]. Since many succinic acid derivatives have been used for food, dyes and photography[2], it is expcted that the title compound would be also of interest in the practical application.

In this work, we determined the X-ray crystal structure of the title compound as no crystallographic data are available in the literature. The present results would bring some materials for comparison with those reported for other succinic acid derivatives[3].



2. Experimental

The title compound was synthesized by refluxing α,β-diphenylsuccinonitrile in the mixed solution of sulfuric and glacial acetic acids as in the literature[4]. The compound was further purified by extraction once from dry diethyl ether. The final single crystals were obtained by recrystallization from acetone(m.p. 219-221℃).

Preliminary photography[5] established the space groups as P1 or $\bar{P}1$ for the title compound. A platelet white crystal of size 0.03×0.4×0.5mm was used for all X-ray intensity measurements on an Enraf-Nonius CAD-4 diffractometer[6]. The lattice parameters were determined by a least-squares fit to 25 automatically centered reflections in the range $10.04^\circ < \theta < 13.75^\circ$. Three standard reflections (5 -4 -4), (-4 1 -1) and (-4 4 -1) were measured every 3 hours of X-ray exposure and showed maximum variation of 2.4%. One orientation reflection (5 -4 -4) was monitored every 200 reflections. 2753 independent reflections with $-11 \le h \le 10$, $0 \le k \le 12$, $-9 \le l \le 10$[7] were collected using graphite-monochromated MoKα radiation and $\omega/2\theta$ scan mode, ω-scan width=$(0.8 + 0.34 \tan\theta)^\circ$, $\theta_{max}=24^\circ$. Lorentz and polarization corrections were applied but no absorption correction.

3. Structure Determination and Refinements

The structure was solved by direct methods using SHELXS86[8] with the space group $\bar{P}1$, and refined by full-matrix least squares using SHELX76[9]. Function minimized was $\Sigma\omega(|F_o|)-(|F_c|)^2$, where ω is unit weight. 1637 reflections with $F_o > 3\sigma(F_o)$ were used in refinement.

All of the non-H atoms were refined with anisotropic temperature factors. Some hydrogen atoms were found by difference Fourier syntheses and others were located by geometrical calculation (C-H distance 1.08Å). Hydrogen atoms were refined isotropically. Number of parameters refined was 279.

Final reliability factors were R=0.058, ωR=0.058 and S=0.79 with $(\triangle/\sigma)_{max}=0.739$ for the isotropic thermal parameter of one of H-atoms and $\triangle\rho_{max}/\triangle\rho_{min}=0.220/-0.204$ eÅ^{-3} in final difference map. Atomic scattering factors were provided in

SHELX76. Geometric calculations on the molecular structure were done using GEOM program[10]. All computations were performed using the Micro VAX/VMS 3400 computer at Chungnam National University.

4. Results and Discussion

Fractional atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, bond distances, bond angles, torsion angles and hydrogen bonds in Table 2, least-square planes in Table 3. An ORTEP[11] drawing of a molecule with the numbering scheme of atoms is depicted in Fig. 1, which shows details of the hydrogen bondings, and a stereoview of the unit cell packing is provided in Fig. 2.

As shown in Table 2, the C-C mean bond length of benzene ring is 1.377 Å, and, in the two carboxyl groups, the bond distances C(1)-O(1) [1.311(6) Å] and C(2)-O(4) [1.321(6) Å] show single bond character while C(1)-O(2) [1.210(6) Å] and C(2)-O(3) [1.201(6) Å] double bond one. The C=O bond lengths agree well with the accepted value of 1.215 Å[12] and the similar distances were found in 3,5-dichloro -2-hydroxy-4-methoxy-6-n-propylbenzoic acid[13].

The carbon atoms around C(10) and C(20) atoms have the tetrahedral angles with mean value 110.72° and their average bond length is 1.517 Å indicating single bond

The dihedral angle of two benzene rings is 66.6(3)° and the one of the two carboxyl groups is 67.7(2)° (see Table 3) with the torsion angle 60.7(4)° for C(11)-C(10)-C(20)-C(21) as shown in Table 2.

α,β-diphenylsuccinic acid, $C_{16}H_{14}O_4$, and solvent acetone, OC_3H_6, molecules in an asymmetric unit are linked by hydrogen bond O(4)-H(8)···O(5) of 2.695(7) Å

Table 1. Fractional atomic coordinates($\times10^4$) and equivalent isotropic temperature factors($Å^2\times10^3$) with e.s.d's in parentheses.

atoms	x	y	z	$^*U_{eq}$
O(1)	-100(4)	1074(4)	1113(5)	63
O(2)	1444(4)	-112(4)	1704(4)	63
O(3)	788(4)	-1349(3)	5004(5)	68
O(4)	2945(4)	-1785(4)	5728(5)	67
O(5)	1714(6)	-4315(5)	6316(7)	110
C(1)	1062(5)	640(5)	2073(6)	48
C(2)	2082(6)	-999(5)	5200(5)	49
C(10)	1884(5)	1186(4)	3658(5)	41
C(20)	2928(5)	401(5)	4933(6)	44
C(11)	2723(5)	2569(5)	3310(5)	53
C(12)	3748(6)	2857(6)	2566(7)	69
C(13)	4494(8)	4120(10)	2251(10)	102
C(14)	4247(11)	5086(9)	2641(12)	120
C(15)	3254(11)	4823(7)	3377(11)	104
C(16)	2464(8)	3551(6)	3707(8)	72
C(21)	3725(5)	892(4)	6574(5)	44
C(22)	5248(6)	1214(5)	7280(6)	51
C(23)	5966(7)	1602(5)	8821(7)	66
C(24)	5155(7)	1684(5)	9654(7)	65
C(25)	3655(7)	1381(6)	8958(6)	64
C(26)	2926(6)	981(5)	7430(6)	59
C(27)	1257(8)	-4936(8)	7407(9)	96
C(28)	1128(10)	-4236(10)	8493(11)	139
C(29)	895(16)	-6351(8)	7665(13)	181

$$^*U_{eq} = [1/3(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)] \times(U_{11}\sin^2\alpha+U_{22}\sin^2\beta+U_{33}\sin^2\gamma+2U_{12}\sin\alpha\cos\gamma + 2U_{13}\sin\alpha\sin\gamma\cos\beta+2U_{33}\sin\beta\sin\gamma\cos\alpha)$$

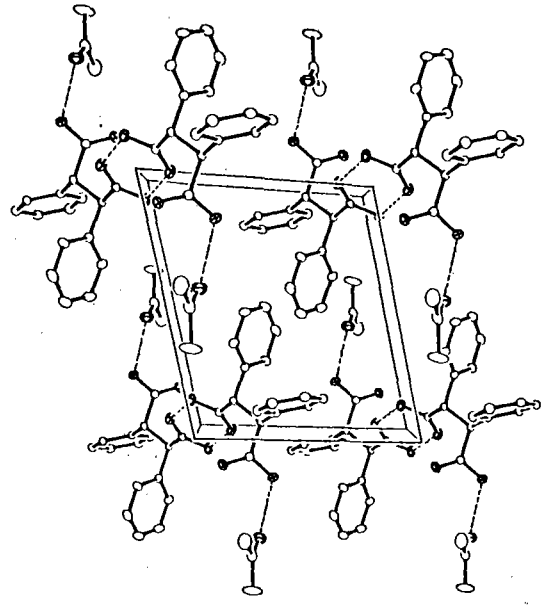


Fig. 1. Stereoview of the title compound indicating the atom-numbering scheme. Hydrogen bonds are indicated by dotted lines.

Table 2. Interatomic distances(Å), angles(°), selected torsion angles(°) and hydrogen bonds(Å, °) with e.s.d.'s in parentheses.

α,β-diphenylsuccinic, $C_{16}H_{14}O_4$, molecule

O(1) -C(1)	1.311(6)	O(3)-C(2) -C(20)	124.1(5)
O(2) -C(1)	1.210(6)	O(4)-C(2) -C(20)	112.4(5)
O(3) -C(2)	1.201(6)	C(1)-C(10)-C(11)	108.9(4)
O(4) -C(2)	1.321(6)	C(1)-C(10)-C(20)	111.8(4)
C(1) -C(10)	1.501(6)	C(2)-C(20)-C(10)	110.4(4)
C(2) -C(20)	1.527(7)	C(2)-C(20)-C(21)	108.9(4)
C(10)-C(20)	1.523(6)	C(10)-C(11)-C(12)	120.0(5)
C(10)-C(11)	1.519(7)	C(10)-C(11)-C(16)	120.8(5)
C(11)-C(12)	1.386(7)	C(10)-C(20)-C(21)	113.2(4)
C(11)-C(16)	1.380(7)	C(11)-C(12)-C(13)	119.2(8)
C(12)-C(13)	1.381(9)	C(12)-C(13)-C(14)	121.8(9)
C(13)-C(14)	1.353(12)	C(13)-C(14)-C(15)	119.9(9)
C(14)-C(15)	1.356(12)	C(14)-C(15)-C(16)	120.0(9)
C(15)-C(16)	1.405(10)	C(15)-C(16)-C(11)	119.9(8)
C(20)-C(21)	1.514(6)	C(16)-C(11)-C(12)	119.2(6)
C(21)-C(22)	1.376(6)	C(20)-C(10)-C(11)	111.1(4)
C(21)-C(26)	1.386(6)	C(20)-C(21)-C(22)	121.3(4)
C(22)-C(23)	1.387(7)	C(20)-C(21)-C(26)	120.3(4)
C(23)-C(24)	1.377(8)	C(21)-C(22)-C(23)	118.4(5)
C(24)-C(25)	1.354(8)	C(22)-C(23)-C(24)	120.0(6)
C(25)-C(26)	1.383(7)	C(23)-C(24)-C(25)	119.5(6)
O(1)-C(1)-O(2)	123.2(5)	C(24)-C(25)-C(26)	121.1(6)
O(1)-C(1)-C(10)	113.3(5)	C(25)-C(26)-C(21)	120.2(5)
O(2)-C(1)-C(10)	123.4(4)	C(26)-C(21)-C(22)	118.4(5)
O(3)-C(2)-O(4)	123.5(5)		

Acetone, C_3H_6O, molecule

O(5) -C(27)	1.217(8)	C(28)-C(27)-O(5)	118.2(8)
C(27)-C(28)	1.483(10)	C(29)-C(27)-O(5)	120.4(9)
C(27)-C(29)	1.478(10)	C(29)-C(27)-C(28)	121.3(9)

Table 2. (cont.)

Selected torsion angles

O(1) -C(1) -C(10)-C(11)	-73.4(4)
O(1) -C(1) -C(10)-C(20)	163.4(5)
O(2) -C(1) -C(10)-C(11)	105.6(6)
O(2) -C(1) -C(10)-C(20)	-17.6(4)
O(3) -C(2) -C(20)-C(10)	-27.9(5)
O(3) -C(2) -C(20)-C(21)	97.0(6)
O(4) -C(2) -C(20)-C(10)	154.3(5)
O(4) -C(2) -C(20)-C(21)	-80.8(5)
C(1) -C(10)-C(11)-C(12)	-57.8(5)
C(1) -C(10)-C(11)-C(16)	121.4(6)
C(1) -C(10)-C(20)-C(2)	-55.1(4)
C(1) -C(10)-C(20)-C(21)	-177.4(5)
C(2) -C(20)-C(21)-C(22)	112.6(5)
C(2) -C(20)-C(21)-C(26)	-64.9(5)
C(10)-C(20)-C(21)-C(22)	-124.2(6)
C(10)-C(20)-C(21)-C(26)	58.3(5)
C(11)-C(10)-C(20)-C(2)	-177.0(5)
C(11)-C(10)-C(20)-C(21)	60.7(4)
C(20)-C(10)-C(11)-C(12)	65.8(5)
C(20)-C(10)-C(11)-C(16)	-115.0(6)

Hydrogen bonds

D — H ··· A	D — H	H ··· A	D ··· A	∠D — H···A
O(1)-H(7)···O(2')[a]	0.91(6)	1.76(6)	2.661(5)	170.4(60)
O(1')[a]-H(7')[a]···O(2)	0.91(6)	1.76(6)	2.661(5)	170.4(60)
O(4)-H(8)···O(5)	0.96(6)	1.74(6)	2.695(7)	172.4(47)

Symmetry code (a) -x,-y,-z

Table 3. Least-square planes and dihedral angles. Starred atoms not included in the plane definition

Atom	Dev, Å	Atom	Dev, Å	Atom	Dev, Å
Phenyl ring 1 : 4.46607X - 1.19984Y + 5.72289Z = 2.80049					
C(11)	0.001(3)	C(12)	-0.001(4)	C(13)	0.000(9)
C(14)	-0.003(8)	C(15)	0.007(9)	C(16)	-0.005(6)
*C(10)	-0.008(11)	*C(1)	-1.217(12)	*C(20)	1.282(13)
Phenyl ring2 : 1.09614X - 9.85974Y + 2.02802Z = 0.85827					
C(21)	0.002(3)	C(22)	-0.005(4)	C(23)	0.003(5)
C(24)	0.002(5)	C(25)	-0.004(5)	C(26)	0.001(4)
*C(20)	0.067(9)	*C(2)	1.408(11)	*C(10)	-1.080(10)
Plane 3 : -5.86377X - 5.23955Y + 4.80116Z = 0.03150					
O(1)	-0.001(1)	O(2)	-0.001(1)	C(1)	0.006(5)
C(10)	-0.001(1)	*C(11)	-1.385(8)	*C(20)	0.410(10)
Plane 4 : -2.32301X + 3.20078Y + 8.84158Z = 3.80680					
O(3)	0.003(1)	O(4)	0.002(1)	C(2)	-0.013(6)
C(20)	0.003(1)	*C(21)	1.426(9)	*C(10)	-0.631(10)
Plane 5 : -7.99100X + 1.77961Y - 2.22887Z = -3.54351					
O(5)	-0.001(1)	C(27)	0.097(7)	C(28)	-0.005(3)
C(29)	-0.010(8)	*O(4)	-0.404(24)	*O(3)	1.558(27)
*C(2)	0.543(30)				

Dihedral angles

Planes	Angles(°)	Planes	Angles(°)
1 - 2	66.6(3)	2 - 4	79.3(2)
1 - 3	83.8(3)	2 - 5	104.5(5)
1 - 4	40.1(3)	3 - 4	67.7(2)
1 - 5	154.1(4)	3 - 5	75.2(4)
2 - 3	41.2(2)	4 - 5	116.0(4)

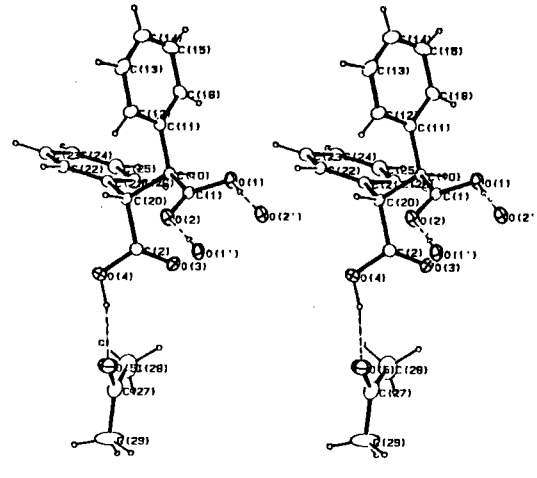


Figure 2. The unit cell packing for the molecules: origin, lower left : a-axis, horizontal; b-axis, vertical. Hydrogen bonds are indicated by dotted lines and hydrogen atoms are omitted for clarity..

The crystal structure projected along the c-axis is shown in Figure 2. It consists of controsymmetric dimers linked by hydrogen bonds between carboxylic groups. As can be seen in Table 2, the intermolecular hydrogen-bond distance O(1)...O(2′) = O(2)...O(1′) is 2.661(5) Å. The similar distance 2.655 Å was found in the structure of 3,5-ichloro-2-hydroxy--methoxy-6-n-propylbenzoic acid[13]. The dimers are stacked by van der Waals′ contact with the shortest distance 3.288 Å for O(2)···O(2) at -x, -y, -z.

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