

디프로파질디페닐메탄의 결정 및 분자구조

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The Crystal and Molecular Structure of Dipropargyldiphenylmethane

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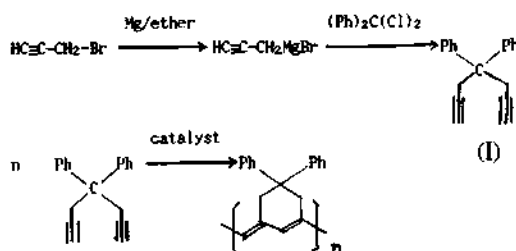
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요약. 디프로파질디페닐메탄($C_{19}H_{16}$)은 단사정계의 공간군 $C2/c$ 에 속하며 $a=11.304(3)$, $b=20.779(5)$, $c=6.622(2)\text{\AA}$, $\beta=112.8(3)^\circ$, $Z=4$, $V=1435.3\text{\AA}^3$, $F(000)=520$, $D_c=1.14\text{ g}\cdot\text{cm}^{-3}$, $\mu=0.32\text{ cm}^{-1}$ 이며 $I\geq 1.0\sigma(I)$ 인 1328개의 회절반점에 대한 최종 R 값은 0.055였다. 직접법에 의하여 구조를 풀었으며 수소를 제외한 모든 원자는 E-map에서 찾았다. 한 분자는 단위세포내에 있는 결정학적 2-회전축과 일치하는 대칭축을 분자내의 메탄의 탄소원자에 가짐으로서 C_2 점군에 속한다. 직선인 프로파질 부분은 벤젠기의 분자평면과 거의 수직(94.2°)을 이루고 있으며, 메탄의 탄소원자의 내부각은 $108.1(1)^\circ$ 으로 벤젠기와의 $1.530(2)\text{\AA}$, 프로파질기와의 $1.560(2)\text{\AA}$ 의 길이로 결합하고 있다. 분자사이의 가장 짧은 접촉은 $C(9)$ 과 $C(9)(-x, y, -1/2-z)$ 사이의 $3.538(2)\text{\AA}$ 이다.

ABSTRACT. Dipropargyldiphenylmethane, $C_{19}H_{16}$, crystallizes in a monoclinic space group $C2/c$ with $a=11.304(3)$, $b=20.779(5)$, $c=6.622(2)\text{\AA}$, $\beta=112.8(3)^\circ$, $Z=4$, $V=1435.3\text{\AA}^3$, $F(000)=520$, $D_c=1.14\text{ g}\cdot\text{cm}^{-3}$ and $\mu=0.32\text{ cm}^{-1}$. The structure was solved by direct methods and all non-H atoms were identified in the E-map. The final refinement gave $R=0.055$ from 1328 unique observed reflections with $I\geq 1.0\sigma(I)$. The molecule belongs to the point group C_2 of symmetry by possessing the 2-fold axis which coincides with the crystallographic symmetry axis in the unit cell. The linear propargyl moiety is nearly perpendicular(94.2°) to the molecular plane of the benzene ring. The internal angle of methane carbon atoms in $108.1(1)^\circ$, bonding to the benzene and the propargyl moiety with the bond lengths of $1.530(2)$ and $1.560(2)\text{\AA}$, respectively. The shortest contact between the molecules is $3.538(2)\text{\AA}$ between $C(9)$ and $C(9)(-x, y, -1/2-z)$.

INTRODUCTION

In the course of studies of the cyclopolymerization¹ of terminal diacetylenes by transition-metal catalysts, the title compound (I) was prepared by Grignard reaction according to the literature² and single crystals were grown up to investigate its conformational arrangement in the crystalline state.



We describe here the structure of dipropargyl-diphenylmethane.

EXPERIMENTAL

The title compound was prepared by standard procedure and needle-like single crystals were obtained by slow evaporation of chloroform at room temperature. The X-ray data were collected using a Nicolet R3m/E diffractometer with graphite-mo-
nochromatized Mo-K α radiation ($\lambda=0.71069 \text{ \AA}$).

The cell constants were determined by least-squares refinement from 25 reflections within the ranges ($25 \leq 2\theta \leq 35^\circ$). The space group was determined to be C2/c on the basis of the systematic absences (hkl ; $h+k=2n$, $h0l$; $l=2n$, $0k0$; $k=2n$). The data collections were performed by the $\theta-2\theta$ scan technique at variable scan rates of 4.9 to $29.3^\circ/\text{min}$ with $2\theta_{\text{max}}=45^\circ$ in the ranges $0 \leq h \leq 13$, $0 \leq k \leq 24$, $-7 \leq l \leq 7$. Three standard reflections monitored every 97 reflections and there were no significant intensity variations during measurement. The 1328 unique observed reflections with $I \geq 1.0\sigma(I)$ were used in structure determination. Corrections for Lorentz and polarization effects were applied to the intensity data, while no absorption or extinction correction was carried out.

Structure was solved by direct methods using 200 reflections with $E > 1.26$. All the carbon atoms were identified in the E-map. The subsequent dif-

ference Fourier syntheses were done by fixing the methane carbon atom C(7) at the special posi-

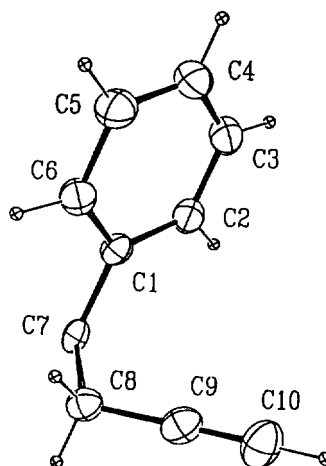


Fig. 1. A molecular conformation with the thermal ellipsoids and atomic labelling scheme of dipropargyl-diphenylmethane.

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) of dipropargyl-diphenylmethane. The e.s.d.'s are in parentheses

Atom	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
C(1)	1096(1)	1287(1)	2446(2)	42(3)
C(2)	837(2)	851(1)	723(2)	54(4)
C(3)	1800(2)	468(1)	545(3)	63(4)
C(4)	3033(2)	516(1)	2076(4)	58(4)
C(5)	3305(2)	935(1)	3798(4)	43(4)
C(6)	2355(1)	1318(1)	3989(3)	43(3)
C(7)	0000(0)	1709(1)	2500(0)	45(5)
C(8)	-445(2)	2154(1)	444(2)	53(3)
C(9)	558(2)	2587(1)	392(2)	46(5)
C(10)	1345(2)	2940(1)	314(3)	77(5)
H(2)	-55(17)	766(9)	-308(33)	80(6)
H(3)	1578(24)	165(11)	-716(41)	86(6)
H(4)	3685(20)	258(10)	1903(30)	81(6)
H(5)	4051(28)	988(13)	4736(43)	104(8)
H(6)	2623(15)	1596(8)	5224(30)	68(5)
H(8a)	-667(17)	1867(9)	-812(29)	62(4)
H(8b)	-1179(17)	2427(8)	439(27)	62(4)
H(10)	1953(24)	3207(12)	107(36)	103(7)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalised U tensor. ^bAnisotropic thermal parameters of the non-H atoms are available from the first author.

Table 1. Crystal data

Chemical formula; $\text{C}_{10}\text{H}_{16}$
Molecular weight; 244.34
Unit cell parameters; $a=11.304(3)\text{\AA}$
$b=20.799(5)$ $\beta=112.8(3)^\circ$
$c=6.622(2)$
$V=1435.3 \text{ \AA}^3$
$Z=4$
Crystal system; monoclinic
Space group; C2/c
Crystal size; $0.22 \times 0.31 \times 0.33 \text{ mm}$
$F(000)=520$
$\lambda(\text{Mo-K}\alpha)=0.71069 \text{ \AA}$
$D_c=1.14 \text{ g}\cdot\text{cm}^{-3}$
$\mu=0.32 \text{ cm}^{-1}$
$T=298 \text{ K}$

tion ($x=0.00$, $z=0.25$), assigning carbon atoms to anisotropic temperature factor and hydrogen atoms to isotropic. The final cycle of least-squared refinement with 121 parameters gave R and R_w values of 0.055 and 0.065, where $w=1/(\sigma^2(F)+0.04364 F^2)$. The maximum and minimum peaks were 0.46 and 0.80 eA⁻³, respectively.

All atomic scattering factors used were from the "International Tables for X-ray Crystallography" and all calculations were performed using the SHELX-76⁴ and SHELXS-86⁵ programs.

RESULTS AND DISCUSSION

Crystal data of dipropargyldiphenylmethane is listed in Table 1. The molecular conformation of the asymmetric unit with atomic labelling scheme is shown in Fig. 1. The final atomic coordinates and thermal parameters are listed in Table 2. Bond lengths and bond angles are given in Table 3, and torsion angles and least-squares planes in Table 4. The bond lengths of the benzene⁶⁻⁸ ring are 1.372(3)~1.397(3)Å and the bond angles are

Table 3. Bond lengths (Å) and bond angles (°) of dipropargyldiphenylmethane. The e.s.d.'s are in parentheses

(1) Bond lengths			
C(1)-C(2)	1.397(2)	C(2)-C(3)	1.391(2)
C(3)-C(4)	1.373(3)	C(4)-C(5)	1.371(3)
C(5)-C(6)	1.382(2)	C(6)-C(1)	1.395(2)
C(1)-C(7)	1.530(2)	C(7)-C(8)	1.559(2)
C(8)-C(9)	1.459(2)	C(9)-C(10)	1.171(3)
C(2)-H(2)	0.99(2)	C(3)-H(3)	0.10(3)
C(4)-H(4)	0.95(2)	C(5)-H(5)	0.84(3)
C(6)-H(6)	0.95(2)	C(8)-H(8a)	0.97(2)
C(8)-H(8b)	1.01(2)	C(10)-H(10)	0.93(3)
(2) Bond angles			
C(2)-C(1)-C(6)	117.4(1)	C(1)-C(2)-C(3)	121.2(2)
C(2)-C(3)-C(4)	120.0(2)	C(3)-C(4)-C(5)	119.8(2)
C(4)-C(5)-C(6)	120.7(2)	C(5)-C(6)-C(1)	121.0(2)
C(6)-C(1)-C(7)	124.2(1)	C(2)-C(1)-C(7)	118.4(1)
C(1)-C(7)-C(8)	108.1(1)	C(7)-C(8)-C(9)	113.3(1)
C(8)-C(9)-C(10)	178.6(1)	C(7)-C(8)-H(8a)	106(1)
C(7)-C(8)-H(8a)	109(1)	C(9)-C(8)-H(8a)	108(1)
C(9)-C(8)-H(8b)	107(1)	H(8a)-C(8)-H(8b)	114(2)
C(9)-C(10)-H(10)	174(1)		

117.4(2)~121.2(2)°. Its molecular plane is nearly planar with the deviations of 0.003~0.008 Å. The propargyl moiety, -C(8)H₂-C(9)≡C(10)-, which has the single bond length of 1.459(3)Å and the triple bond length of 1.170(3)Å is nearly linear with the angle of 178.2(1)°. The methane carbon atom C(7) has a approximate tetrahedral angle of 108.1(1)° and linked to the benzene and the propargyl moieties with the C-C bond lengths of 1.530(2) and 1.560(2)Å, respectively. The linear propargyl moiety is declined perpendicularly(94.2°) to the plane of the benzene ring.

The molecule belongs to the point group C₂ by possessing a 2-fold axis of symmetry on the C(7) methane atom, which coincides with the crystallo-

Table 4. Torsion angles and least-squares planes of the molecule

(1) Torsion angles (°)			
C(6)-C(1)-C(2)-C(3)	-0.6(2)		
C(1)-C(2)-C(3)-C(4)	-0.2(2)		
C(3)-C(4)-C(5)-C(6)	-1.1(2)		
C(7)-C(1)-C(2)-C(3)	178.0(3)		
C(2)-C(1)-C(7)-C(8)	-63.7(2)		
C(1)-C(7)-C(8)-C(9)	-61.8(2)		
C(2)-C(1)-C(6)-C(5)	0.6(2)		
C(2)-C(3)-C(4)-C(5)	1.1(2)		
C(4)-C(5)-C(6)-C(1)	0.3(2)		
C(7)-C(1)-C(6)-C(5)	-178.0(3)		
C(6)-C(1)-C(7)-C(8)	114.8(2)		
C(7)-C(8)-C(9)-C(10)	-174.4(6.7)		
(2) The least-squares planes and deviations of each atom from the planes. The equation of the plane is expressed in the form Ax+By+Cz=D, where x, y and z are in Å			
Atoms in plan	Atoms out of plane	Distances(Å) from best plane	Given constants
C(1)		-0.004	A = -0.4471
C(2)		0.003	B = -0.7109
C(3)		0.003	C = 0.5429
C(4)		-0.008	D = -1.3618
C(5)		0.004	
C(6)		0.003	
	C(7)	-0.050	
	C(8)	-1.400	
	C(9)	-2.570	
	C(10)	-3.525	

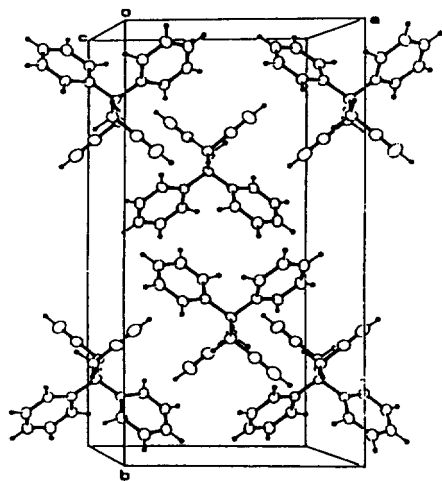


Fig. 2. The unit cell packing diagram of molecules.

graphic 2-fold axis parallel to the b-axis in the unit cell.

The molecular packing diagram in the unit cell is given in Fig. 2. The shortest intermolecular contact is $3.538(2)\text{\AA}$ between C(9) and C(9)($-x, y, -1/2-z$).

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