Crystal structure of 9,10-bis(phenylethynyl)anthracene

Masahiko Maekawa,[a,*] Yusaku Suenaga,[b] Takayoshi Kuroda-Sowa[b] and Megumu Munakata[b]

[a]Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan
[b]Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

(Received, November 25, 1999)

Abstract

Single crystals of 9,10-bis(phenyletynyl)anthracene (**1**) were prepared and the structure was crystallographically determined. Crystal data: Formula $C_{15}H_9$; Formula weight, 189.24; Crystal system, Monoclinic; Space group, *C*2/c; a=22.855(5), b=5.359(5), c=16.939(3)Å, β=99.98(2)°, U=2043(1)Å^3, Z=8, D_{calc}=1.230cm^{-3}, $R1$=0.060 and $wR2$=0.207.

Key words: Anthracenes, Alkynes, Crystal structures

1. Introduction

The cross-coupling of terminal alkynes and aryl halides catalyzed by palladium and copper[1] has been used widely to prepare ethynylarenes[2] and their derivatives.[3] Many organic and polymeric new materials[4] have been prepared in recent years via this method. In particular, 9,10-bis(*p*-R-phenylethynyl)-anthracenes (R=H,[5] and OMe[6]) are highly emissive with quantum yields approaching unity,[6b,7] suggesting their use as laser dyes, scintillation agents and elecrochemiluminescence fluorescers.[8]

In this study orange single crystals of 9,10-bis-(phenylethynyl)anthracene (**1**) were by chance obtained from THF reaction solution of $AgClO_4$ and **1**, and the structure was crystallographically characterized.

2. Experimental

An orange prism crystal of **1** having approximate dimensions of 0.20 x 0.20 x 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC-7R diffractometer with a graphite mono-chromated Mo Kα radiation and a rotating anode generator. The details of measurement conditions and crystal data are listed in Table 1. The intensity data were collected at a temperature of 23℃ using the ω-2θ scan technique to a maximum 2θ of value of 55.0°. Of the 2651 reflections which were collected, 2583 were unique(R_{int}=0.015). The intensities of three representative reflections which were measured after every 150 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Mo Kα is 0.70cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structures were solved by a direct method (SIR88)[9] and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by Fourier difference synthesis. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2331 observed reflection, and 173 variable parameters. Reliability factors are defined as $R1=\Sigma||F_o|-|F_c||/\Sigma|F_c|$ and $wR2=[\Sigma(F_o^2-F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$. The final *R1* and *wR2* values were 0.060 and 0.207, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and -0.34e$Å^{-3}$, respectively. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV.[10] All calculations were performed using the program teXsan crystallographic software package.[11]

Table 1 Details of crystal data for **1**

Formula	$C_{15}H_9$
Formula weight	189.24
Crystal system	Monoclinic
Space group	*C*2/c
a (Å)	22.855(5)
b (Å)	5.359(5)
c (Å)	16.939(3)
β (°)	99.98(2)
U ($Å^3$)	2043(1)
Z	8
D_{calc} (gcm^{-3})	1.230
μ_{eff} (cm^{-1})	0.070
Radiation	Mo Kα (0.7107Å)
Measurement method	ω-2θ
No. of reflections measured	2651 (total)
No. Observations	2331 (all data)
R1	0.060
wR2	0.207

Table 2 Atomic coordinates for **1**

Atom	*X*	*Y*	*Z*	*Beq*
C(1)	0.1635(1)	-0.0641(5)	0.8349(1)	5.99(6)
C(2)	0.2071(1)	-0.0625(5)	0.9014(1)	6.85(6)
C(3)	0.2505(1)	0.1152(6)	0.9102(1)	6.30(6)
C(4)	0.2490(1)	0.2975(6)	0.8536(1)	6.54(6)
C(5)	0.2051(1)	0.2984(5)	0.7861(1)	5.76(5)
C(6)	0.16188(8)	0.1146(4)	0.7754(1)	4.46(4)
C(7)	0.11830(8)	0.1007(4)	0.7045(1)	4.81(4)
C(8)	0.08316(8)	0.0758(4)	0.6430(1)	4.71(4)
C(9)	0.04147(8)	0.0385(4)	0.5713(1)	4.37(4)
C(10)	0.04343(8)	0.1909(4)	0.5037(1)	4.32(4)
C(11)	0.08588(9)	0.3884(4)	0.5054(1)	5.09(5)
C(12)	0.08661(10)	0.5352(4)	0.4404(1)	5.45(5)
C(13)	0.04504(10)	0.4977(5)	0.3695(1)	5.49(5)
C(14)	0.00406(9)	0.3120(4)	0.3650(1)	5.04(5)
C(15)	0.00183(8)	0.1530(4)	0.4319(1)	4.31(4)

3. Results and discussion

Molecular structure[12] of **1** is shown in Fig. 1, together with the atomic labeling scheme. The compound **1** possesses an inversion center of symmetry at the center of anthracene ring. The dihedral angle between the phenylethynyl group and anthracene ring and is 9.7°. The central anthracene ring and two substituted phenylethynyl groups are nearly coplanar. The bond distance and bond angles of **1** are listed in Table 3. These distances and angles are close to those found in analogous compounds.[1d,13] The crystal packing view of **1** is presented in Fig. 2. The half portion of the central anthracene rings is overlapping each other. The close separation of 3.43Å is indicative of the occurrence of the π-π stacking.

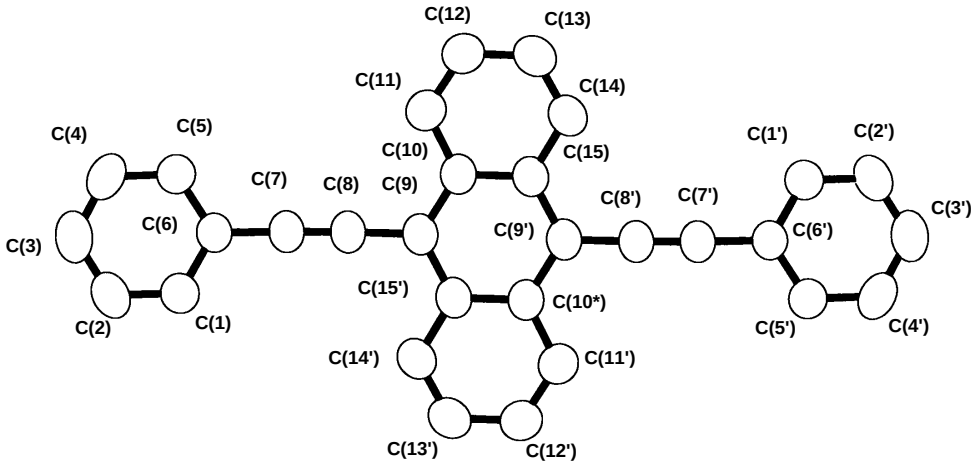
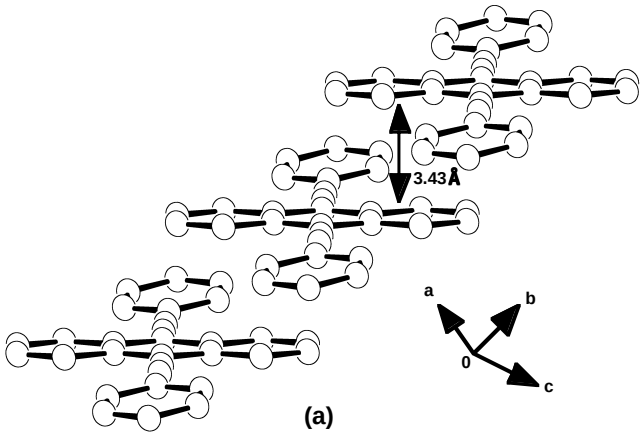


Fig. 1 Molecular structure of **1** with the atomic labeling scheme



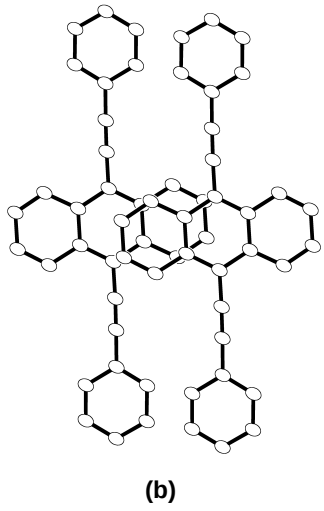


Table 3 Selected bond distances and bond angles for **1**

C(1)-C(2)	1.369(3)	C(1)-C(6)	1.386(3)
C(2)-C(3)	1.365(4)	C(3)-C(4)	1.365(4)
C(4)-C(5)	1.385(3)	C(5)-C(6)	1.384(3)
C(6)-C(7)	1.423(2)	C(7)-C(8)	1.207(2)
C(8)-C(9)	1.422(2)	C(9)-C(10)	1.414(3)
C(9)-C(15)	1.420(3)	C(10)-C(11)	1.432(3)
C(10)-C(15)	1.423(2)	C(11)-C(12)	1.356(3)
C(12)-C(13)	1.410(3)	C(13)-C(14)	1.360(3)
C(14)-C(15)	1.425(3)		
C(2)-C(1)-C(6)	121.2(2)	C(1)-C(2)-C(3)	120.4(2)
C(2)-C(3)-C(4)	119.6(2)	C(3)-C(4)-C(5)	120.6(2)
C(4)-C(5)-C(6)	120.3(2)	C(1)-C(6)-C(5)	117.9(2)
C(1)-C(6)-C(7)	120.3(2)	C(5)-C(6)-C(7)	121.8(2)
C(6)-C(7)-C(8)	175.9(2)	C(7)-C(8)-C(9)	178.2(2)
C(8)-C(9)-C(10)	120.0(2)	C(8)-C(9)-C(15)	119.6(2)
C(10)-C(9)-C(15)	120.4(2)	C(9)-C(10)-C(11)	121.8(2)
C(9)-C(10)-C(15)	120.0(2)	C(11)-C(10)-C(15)	118.2(2)
C(10)-C(11)-C(12)	121.1(2)	C(11)-C(12)-C(13)	120.5(2)
C(12)-C(13)-C(14)	120.5(2)	C(13)-C(14)-C(15)	120.8(2)
C(9)-C(15)-C(10)	119.6(2)	C(9)-C(15)-C(14)	121.5(2)
C(10)-C(15)-C(14)	118.9(2)		

Fig. 2 Crystal packing views of **1**. Side view (a) and top view (b).

References and Notes

[1] (a)L. Cassar, *J. Organomet. Chem.*, 1975, **93**, 253; (b)H. A. Dieck and R. F. Heck, *J. Organomet. Chem.*, 1975, **93**, 259; (c)K. Sonogashira, T. Toda and N. Habihara, *Tetrahedron Lett.*, **1975**, 4467; (d)P. Nguyen, S. Todd, D. V. den Biggelaar, N. J. Taylor, T. B. Marder, F. Wittmann and R. H. Friend, *SYNLETT*, **1994**, 299.

[2] (a)L. D. Ciana and A. Haim, *J. Heterocyclic Chem.*, 1984, 21, 607; (b)T. X. Neenan and G. M. Whiteside, *J. Org. Chem.*, 1988, **53**, 2489; (c)A. E. Stiegman, E. Graham, K. J. Perry, L. K. Khundkar, L. -T. Cheg and J. W. Perry, *J. Am. Chem. Soc.*, 1991, **113**, 7658.

[3] (a)M. d'Alarcoa and N. J. Lemonard, *J. Org. Chem.*, 1985, **50**, 2462; (b)A. N. Tischler and T. J. Lanza, *Tetrahedron Lett.*, 1986, **27**, 1653; (c)B. M. Trost, C. Chan, G. Ruhter, *J. Am. Chem. Soc.*, 1987, **109**, 3486; (d)Y. Zhang and J. Wen, *J. Am. Chem. Soc.*, 1990, **112**, 727.

[4] (a)T. Tahara, K. Seto and S. Takahashi, *Polym. J.*, 1987, **19**, 301; (b)E. M. Graham, V. M. Miskowski, J. W. Perry, D. R. Coulter, A. E. Stiegman, W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, 1989, **111**, 8771; (c)C. Viney, R. J. Twieg, C. M. Dannels and M. Y. Chang, *Mol. Cryst. Lig. Cryst. Lett*, 1990, **75**, 147; (d)S. J. Davies, B. F. G. Johnson, M. S. Khan and J. Lewis, *J. Chem. Soc., Chem. Comm.*, **1991**, 187.

[5] W. Ried, W. Donner, W. Schlegemilch, *Chem. Ber.*, 1961, **94**, 105.

[6] (a)P. J. Hanhela and D. B. Paul, *Aust, J. Chem.*, 1981, **34**, 1669; (b)P. J. Hanhela and D. B. Paul, *Aust, J. Chem.*, 1981, **34**, 1701.

[7] C. A. Heller and R. A. Henry, B. A. Mclaughlin and D. E. Bliss, *J. Chem. Eng. Data*, 1974, **19**, 214.

[8] S. K. Gill, *Aldrichimica Acta*, 1983, **16**, 59.

[9] "SIR88", M, C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, J. Appl. Cryst., 1989, **22**, 389

[10] "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, 1974.

[11] "teXsan", TEXRAY structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, USA (1985 and 1992).

[12] Complex **1** has a polymorphous structure, which has been reported in ref 1(d): Fw=$C_{30}H_{18}$; Mw= 378.4; crystal system, orthormbic, P_{bcn}; a=24.305(4); b=11.512(1); c=7.099(1)Å; U=1986.1(5)Å^3; Z=4; D_{calc}=1.226g/cm^3; μ=0.67cm^{-1}; R=0.042 and R_w=0.042.

[13] (a)P. P. Korkas, E. Weber, M. Czugler and G. Náray-Szabó, *J. Chem. Chem. Comm.*, **1995**, 2229; (b)H. -D. Becker, V. A. Patrick and A. H. White, *Aust. J. Chem.*, 1984, **37**, 2215; (c)F. Vögtle, H. Koch and K. Rissanen, *Chem. Ber.*, 1992, **125**, 2129.