The Crystal and Molecular Structure of Bis(*o*-ethoxyphenyl)butadiyne

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The crystal structure of bis(*o*-ethoxyphenyl)butadiyne has been determined by the statistical method of X-ray analysis. The space group is $P2_1/a$ with two molecules in the unit cell of dimensions $a=14.64$, $b=11.27$, $c=5.19$ Å, and $\beta=105.6°$. The crystal structure is built up from columns of the molecules packed along the *c*-axis. The molecule has a center of symmetry and is almost planar. The diacetylene group is slightly twisted and the three conjugated bond distances of the diacetylene group are 1.434, 1.201, and 1.371 Å.

This is the first paper of a series on the crystal structure of ω,ω'-diphenylpolyynes and their derivatives. A short note on the crystal structure of ω,ω'-diphenyltetrayne and ω,ω'-diphenylpentayne has been repotred by Watanabé, Taguchi, and Masaki.1)

In a number of papers dealing with the molecular structure of compounds containing the diacetylene group,2–11) it was reported that the carbon atoms of the diacetylene group are almost linear, and the three conjugated diacetylene bonds lie between 1.44—1.47 Å for the side C–C, 1.18—1.21 Å for the triple C–C and 1.33—1.39 Å for the central C–C bonds, respectively.

The aim of this investigation is to provide accurate values for bond distances and angles in the molecule of bis(*o*-ethoxyphenyl)butadiyne using three-dimensional data. The influence of the ethoxy group substituted in the phenyl ring on the molecular structure as well as on the molecular packing was also investigated.

Experimental

Crystals for the experiment were obtained from ethanol solution. They are monoclinic, colorless needles elongated along the direction of the *c*-axis. The crystallographic data and some physical properties are listed in Table 1. The cell dimensions were determined from Weissenberg and oscillation photographs about the *c*-axis and the space group was determined unambiguously from the systematic absence of reflections. The crystal density was measured by the flotation method in ammonium chloride solutions, and was in good agreement with the calculated density value assuming two molecules per unit cell.

TABLE 1. CRYSTALLOGRAPHIC DATA

Bis(*o*-ethoxyphenyl)butadiyne $C_{20}H_{18}O_2$
Molecular Weight=290.4
Monoclinic, Melting Point=72°C
Space Group $P2_1/a$ (No.14), $Z=2$
Cell Dimensions $a=14.64\pm0.01$ Å
$b=11.27\pm0.06$ Å
$c=5.194\pm0.003$ Å
$\beta=105.6\pm0.3°$
$V=825.9$ Å^3
$D_m=1.17\ \mathrm{g\cdot cm^{-3}}$, $D_x=1.168\ \mathrm{g\cdot cm^{-3}}$
$\mu=6.16\ \mathrm{cm^{-1}}$ (for *Cu Kα*), $F_{000}=308$
Systematic absences of the reflections;
$h0l$ for $h=2n+1$, $0k0$ for $k=2n+1$

Intensities of the reflections $hk0$ to $hk4$ were visually estimated from the Weissenberg photographs, recorded with nickel-filtered *Cu Kα* radiation. They were reduced to 1033 independent structure factors after corrections for the layer scale, the Lorentz, polarization and spot shape factors being applied. No absorption corrections were applied, since the size of the crystal was small (0.12×0.15×1.3 mm). The scale factors for each layer, used in the above correction, were estimated from a preliminary examination in which the reflections of the different layers were recorded on the same film, using the anti-equi-inclination Weissenberg technique. The normalized structure factors were calculated from the observed structure factors, using the scale and overall temperature factors obtained by the Wilson method. The average values of $|E|$ and $|E^2-1|$ are 0.852 and 0.981, respectively. The maximum value of $|E|$ is 3.99 and the number of the reflections with $|E|$ value above 1.7 is 124.

Structure Determination

The structure was determined by the statistical method.12) The origin was specified by assinging positive signs to three reflections, 121, 211, and $86\bar{3}$.13) For the sign-determining procedure, the sign relation formula $S(E_{\mathrm{h}})=S(\sum_{\mathrm{k}}E_{\mathrm{k}}E_{\mathrm{h-k}})$ was applied to the reflections with $|E|$ value above 1.7. In this procedure the value of the triple product $E_{\mathrm{h}}E_{\mathrm{k}}E_{\mathrm{h-k}}$ was required to exceed 8.1 if a single sign indication was accepted, and the new signs were added to the list of known signs and subsequently used to determine other signs. At the end of the procedure, signs of 124 reflections were

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determined and an E-map was synthesized from them. The highest eleven peaks in this map correspond to all the nonhydrogen atoms in the structure.

The structure was refined first by the isotropic diagonal least squares method. After three cycles of refinement the R index was 0.179. The positions of the hydrogen atoms were found from the difference Fourier map calculated at this stage. Further refinements were carried out by the block diagonal least squares method, including the positional parameters of the hydrogen atoms and the anisotropic thermal parameters of the nonhydrogen atoms. Five cycles of this refinement with the Cruickshank weighting scheme reduced the R index to 0.084 for all the observed reflections.[14] The parameter shifts of all the nonhydrogen atoms in the last cycle were less than 2σ.

TABLE 2. POSITIONAL PARAMETERS IN FRACTIONAL COORDINATES

The estimated standard deviations are given in parentheses

Atom	x/a	y/b	z/c
C(1)	0.0401(3)	0.4659(3)	0.0367(8)
C(2)	0.1105(3)	0.4062(3)	0.1004(8)
C(3)	0.1956(3)	0.3367(3)	0.1656(8)
C(4)	0.2676(3)	0.3601(4)	0.0389(9)
C(5)	0.3491(3)	0.2914(5)	0.0979(9)
C(6)	0.3599(3)	0.2009(4)	0.2834(9)
C(7)	0.2895(3)	0.1745(4)	0.4088(8)
C(8)	0.2067(3)	0.2420(3)	0.3492(7)
C(9)	0.1390(3)	0.1223(4)	0.6348(8)
C(10)	0.0498(3)	0.1222(4)	0.7315(8)
O	0.1327(2)	0.2228(2)	0.4575(5)
H(1)	0.2549(28)	0.4269(39)	−0.0887(82)
H(2)	0.4004(30)	0.3148(40)	0.0307(87)
H(3)	0.4188(29)	0.1498(41)	0.3298(87)
H(4)	0.3012(30)	0.1108(40)	0.5458(86)
H(5)	0.1957(30)	0.1296(40)	0.7979(87)
H(6)	0.1433(29)	0.0451(39)	0.5234(85)
H(7)	0.0599(29)	0.0589(40)	0.8746(86)
H(8)	0.0417(30)	0.1980(40)	0.8109(86)
H(9)	−0.0098(30)	0.1072(40)	0.5655(87)

TABLE 3. THERMAL PARAMETERS OF NONHYDROGEN ATOMS

β as given here is defined by

$$T=\exp(-10^{-4}\times(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23}))$$

Their estimated standard deviations referred to the last decimal positions of the respective values are given in parentheses.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	59(2)	66(3)	454(2)	−3(2)	51(5)	14(5)
C(2)	55(2)	67(3)	475(2)	−10(2)	42(4)	−2(6)
C(3)	47(2)	71(3)	438(2)	−7(2)	39(4)	−31(5)
C(4)	64(2)	94(4)	540(2)	−18(2)	69(5)	−51(7)
C(5)	53(2)	138(5)	662(3)	−19(2)	77(6)	−102(8)
C(6)	51(2)	123(4)	592(2)	10(2)	36(5)	−94(8)
C(7)	48(2)	99(4)	472(2)	12(2)	22(5)	−36(6)
C(8)	44(2)	76(3)	337(2)	5(2)	28(4)	−24(5)
C(9)	60(2)	78(3)	358(2)	−1(2)	32(4)	14(5)
C(10)	64(2)	101(4)	469(2)	−7(2)	53(5)	5(6)
O	50(1)	83(2)	434(1)	12(1)	49(3)	40(4)

TABLE 4. OBSERVED AND CALCULATED STRUCTURE FACTORS

(The values are tabulated on ten times absolute scale)

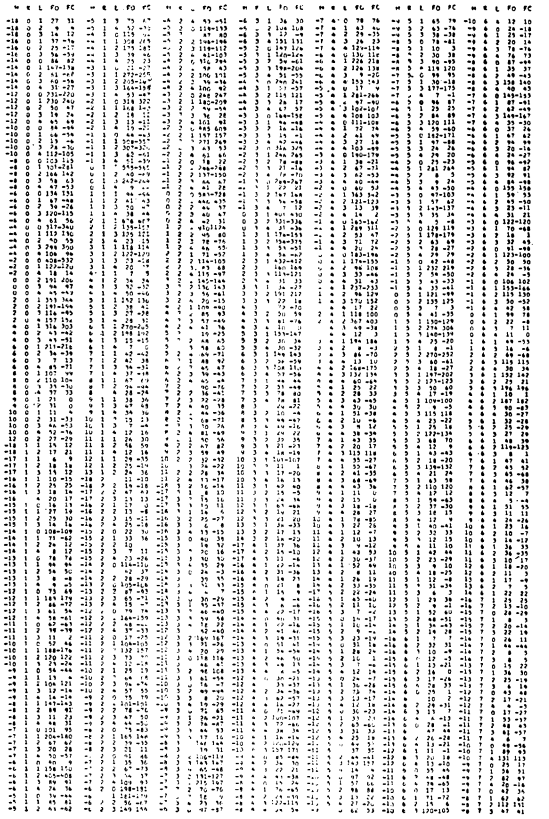
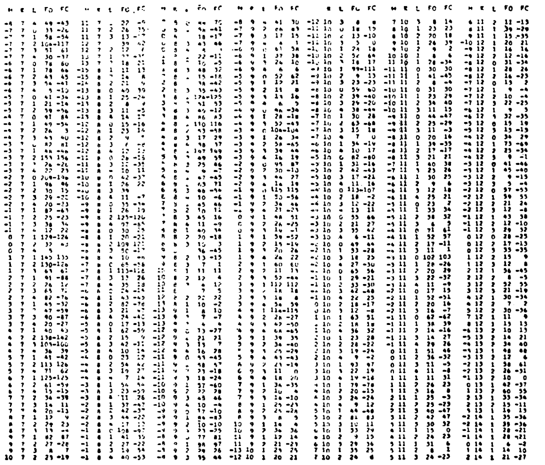


Table 4. (Continued)



The final positional and thermal parameters are given in Tables 2 and 3, respectively. The observed and calculated structure factors are listed in Table 4.

Results and Discussion

The resulting crystal structure is shown in Figs. 2 and 3, as viewed in the projections along the c- and b-axes, respectively. The center of the molecule lies

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[14] D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-ray Analysis," ed. by Pepinsky *et al.*, Pergamon Press, New York (1961), p, 45.

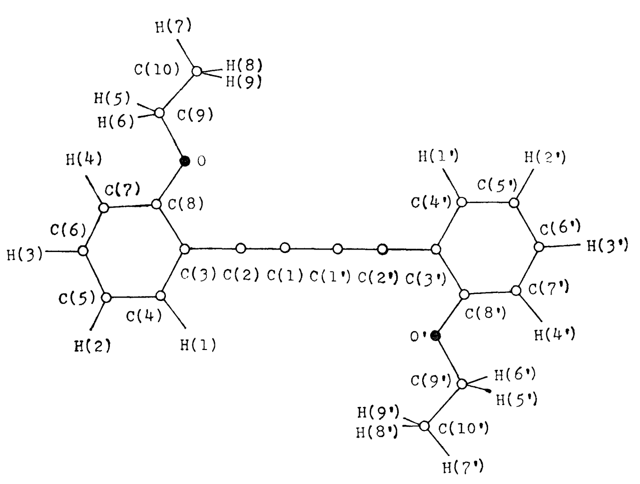

Fig. 1. Conventional numbering and identification of the atoms in bis(*o*-ethoxyphenyl)butadiyne molecule.

at the special position of crystal symmetry ($\bar{1}c$), so that the molecule has a center of symmetry and is almost planar (Fig. 1). The diacetylene chain lies approximately on a plane perpendicular to the *c*-axis and the plane of the phenyl ring is inclined about 49.5° to this plane. The crystal structure is built up from columns of the molecules packed along the *c*-axis, since a large number of short contacts occur between atoms of the molecules related by translation along the *c*-axis, *viz*; 3.49 Å between C(4) and O, 3.59 Å between C(3) and C(9) and 3.59 Å between C(3) and C(10). Only one very short intermolecular distance is found between the columns, namely 3.50 Å between C(4) and C(9). However all other intermolecular distances between the columns are larger than 3.7 Å. These intermolecular distances are considered to be the normal van der Waals distances.

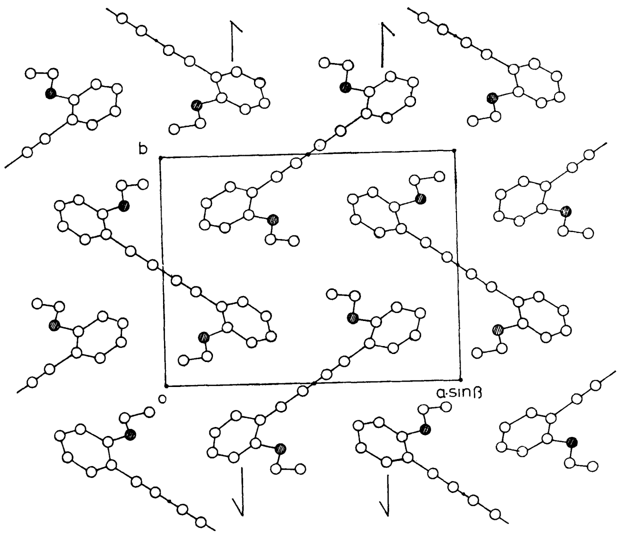

Fig. 2. Projection of the crystal structure along the *c*-axis.

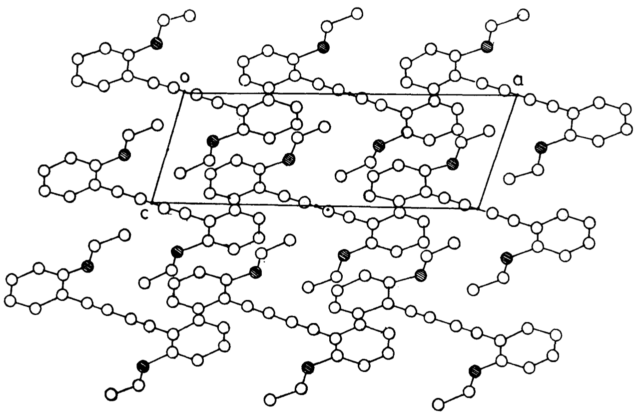

Fig. 3. Projection of the crystal structure along the *b*-axis.

The covalent bond distances and angles in the molecule are listed in Table 5. The carbon-carbon distances of the diacetylene group were corrected for the effect of the thermal motion. The mean square displacement of each atom from its equillibrium position was calculated from the anisotropic thermal parameters given in Table 3. The results indicate that the thermal motion of the molecule cannot be treated as a rigid body motion, and the dominant motion of the atoms of the diacetylene group are considered to be caused by the torsional oscillation about the axis perpendicular to the bond vector, plus the translational motion of the molecule as a whole. Since atoms C(1) and C(1′) are related by the center of symmetry, the C(1)–C(1′) distance was corrected on the basis of the assumption of the upper limit model of Johnson, which corresponds

Table 5. Covalent bond lengths (Å) and angles (°)
Estimated standard deviations are given in parentheses.

Bond	Length	Bond	Angle
C(1)-C(1′)	1.371(6)	C(1′)-C(1)-C(2)	179.6(0.6)
C(1)-C(2)	1.201(6)	C(1)-C(2)-C(3)	177.4(0.5)
C(2)-C(3)	1.434(6)	C(2)-C(3)-C(4)	120.0(0.4)
C(3)-C(4)	1.411(7)	C(2)-C(3)-C(8)	120.5(0.5)
C(4)-C(5)	1.388(7)	C(4)-C(3)-C(8)	119.5(0.4)
C(5)-C(6)	1.379(7)	C(3)-C(4)-C(5)	120.0(0.4)
C(6)-C(7)	1.396(8)	C(4)-C(5)-C(6)	119.8(0.5)
C(7)-C(8)	1.394(6)	C(5)-C(6)-C(7)	121.6(0.4)
C(8)-C(3)	1.411(5)	C(6)-C(7)-C(8)	119.2(0.4)
C(9)-C(10)	1.520(7)	C(3)-C(8)-C(7)	119.9(0.5)
C(8)-O	1.367(6)	C(3)-C(8)-O	116.0(0.4)
C(9)-O	1.447(5)	C(7)-C(8)-O	124.1(0.4)
C(4)-H(1)	0.987(43)	C(8)-O-C(9)	117.7(0.3)
C(5)-H(2)	0.946(49)	C(10)-C(9)-O	107.3(0.4)
C(6)-H(3)	1.011(42)	C(3)-C(4)-H(1)	115.3(2.7)
C(7)-H(4)	0.992(45)	C(5)-C(4)-H(1)	124.7(2.7)
C(9)-H(5)	1.018(40)	C(4)-C(5)-H(2)	118.9(2.6)
C(9)-H(6)	1.057(45)	C(6)-C(5)-H(2)	120.6(2.5)
C(10)-H(7)	1.012(45)	C(5)-C(6)-H(3)	121.1(2.8)
C(10)-H(8)	0.969(46)	C(7)-C(6)-H(3)	117.3(2.8)
C(10)-H(9)	1.063(38)	C(6)-C(7)-H(4)	118.9(2.7)
		C(8)-C(7)-H(4)	121.8(2.7)
		C(10)-C(9)-H(5)	107.9(2.8)
		O-C(9)-H(5)	111.4(2.6)
		C(0)-C(9)-H(6)	111.3(2.5)
		O-C(9)-H(6)	107.4(2.5)
		H(5)-C(9)-H(6)	111.5(3.3)
		C(9)-C(10)-H(7)	105.9(2.7)
		C(9)-C(10)-H(8)	110.8(2.8)
		C(9)-C(10)-H(9)	108.9(2.8)
		H(7)-C(10)-H(8)	108.6(3.7)
		H(7)-C(10)-H(9)	114.2(3.4)
		H(8)-C(10)-H(9)	108.5(3.7)

to the out-of-phase displacement of these-atoms perpendicular to the bond.[15] The corrections to distances C(1)–C(2) and C(2)–C(3), although small, were also calculated by the lower limit model.

The central C(1′)–C(1) bond distance 1.371 Å and the triple C(1)–C(2) bond distance 1.201 Å found in this investigation, agree with the corresponding values 1.376 and 1.205 Å, for diacetylene reported by Callomon and Stoicheff and the values 1.375 and 1.199 Å, for dimethyldiacetylene reported by Himes within experimental errors,[6,9] while the side C(2)–C(3) bond distance 1.434 Å, is close to that of diphenyldiacetylene, 1.44 Å, given by Wiebenga.[11] From these values, the bond order of the C(1′)–C(1) and C(2)–C(3) bonds are estimated to be about 1.63 and 1.27, respectively, indicating that the C(1′)–C(1) bond has considerable double bond character.[16] Concerning the bonds in the ethoxy group, the C(8)–O bond of 1.367 Å has a partial double bond character through the influence of the aromatic ring, while the C(9)–O bond of 1.447 Å and the C(9)–C(10) bond of 1.520 Å are normal paraffinic single bonds. The mean value of the carbon-carbon distances in the phenyl ring is 1.396 Å, which is in good agreement with the normal value 1.395 Å. The mean value of the C–H distances is 1.006 Å.

TABLE 6. DEVIATIONS OF EACH ATOM FROM THE BEST PLANE (see text) AND THEIR ESTIMATED STANDARD DEVIATIONS IN THE DIRECTION OF THE PLANE NORMAL

Atom	Deviation(Å)	E.S.D.(Å)
C(1)	0.011	0.006
C(2)	0.028	0.006
C(3)	0.030	0.006
C(4)	0.007	0.007
C(5)	−0.020	0.007
C(6)	−0.008	0.007
C(7)	−0.005	0.006
C(8)	0.006	0.006
C(9)	−0.111	0.006
C(10)	−0.078	0.007
O	−0.010	0.004

The best plane equation of the molecule except for the four atoms of the ethyl groups is expressed by

$$0.2224x + 0.6368y + 0.7376z = 3.589,$$

where x, y, and z are the orthogonal coordinates in Ångstrom unit. Deviations of each atom from this plane are given in Table 6. Atoms C(9) and C(10) of the ethyl group deviate from this plane about 0.111 Å and 0.078 Å, respectively, and the plane through these atoms and the nearest oxygen atom is inclined about 4.7° to the above best plane. The deviations of atoms C(2) and C(3) from the best plane are about 0.028 Å and 0.030 Å, respectively, which are significantly large in comparison with their estimated standard deviations of positions. Four atoms of the diacetylene group lie approximately on the straight line, while atoms C(2), C(3), and C(6) also are almost linear. However, atoms C(3) and C(6) do not lie on the line connecting atom C(2) to the center of the molecule, so that the diacetylene chain is slightly bent at atoms C(2) and C(2′), and the ethoxy groups are kept away from the center of the molecule. The diacetylene group has no short intermolecular contacts in the crystal, while the ethoxy and phenyl groups have a large number of short contacts with the nearest molecules. Thus the diacetylene chain can be bent by the intramolecular interactions based upon asymmetry of the molecule about the diacetylene group. It may be also affected by steric effects induced from the side groups which are closely packed in the crystal.

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16) L. Pauling, "The Nature of the Chemical Bond," 3rd edition, Cornell University Press, New York (1962), p. 240.