

Two Forms of 1,6-Diphenoxy-2,4-hexadiyne and the Hydrogenated Analog, 1,6-Diphenoxyhexane*

BY B. MOROSIN AND L. HARRAH

Sandia Laboratories, Albuquerque, New Mexico 87115, USA

(Received 2 August 1976; accepted 10 November 1976)

1,6-Diphenoxy-2,4-hexadiyne ($C_{18}H_{14}O_2$; FW 262.3) crystallizes in two forms: I in *Pcab* with $a = 11.179$ (4), $b = 14.979$ (6) and $c = 8.527$ (9) Å, $D_x = 1.220$, $D_m = 1.24$ g cm⁻³, $Z = 4$; and II in *P2₁/c* with $a = 7.469$ (3), $b = 11.368$ (12), $c = 8.591$ (9) Å and $\beta = 109.42$ (2)°, $D_x = 1.266$ g cm⁻³, $Z = 2$. Molecules lie on inversion centers (*trans* configuration) in both cases, with packing consistent with the lack of radiation-induced polymerization typical of diacetylenes. An expected, significant shortening of the C–C bond (1.392 Å) between the two C≡C bonds (1.176 Å) is observed. 1,6-Diphenoxyhexane ($C_{18}H_{22}O_2$; FW 270.4) crystallizes in *P2₁/c* with $a = 16.041$ (8), $b = 7.349$ (4), $c = 6.523$ (5) Å and $\beta = 92.60$ (2)°, $D_x = 1.171$ g cm⁻³, $Z = 2$. These molecules also lie on inversion centers. The configurations of the phenoxy portions of the molecules are very similar; in particular, the O–C–C angles of 115 and 124° significantly deviate from 120° in all three structure determinations.

Introduction and experimental results

Many substituted 2,4-hexadiynediols undergo radiation-induced polymerization in the solid state (Baughman, Witt & Yee, 1974; Wegner, 1971) provided the proper structural arrangement exists (Hadicke, Penzien & Schnell, 1971; Baughman, 1972). Studies in our laboratory on many such materials have shown their usefulness as radiation dosimeters (Trujillo, 1975). Neither of two crystalline forms of 1,6-dibenzoyloxy-2,4-hexadiyne undergoes such solid state polymerization at 1 bar pressure and, hence, detailed structures have been reported (Hanson, 1975). Similarly, two forms of 1,6-diphenoxy-2,4-hexadiyne, $C_6H_5OCH_2C\equiv C-C\equiv CCH_2OC_6H_5$, (referred to as the diyne) also do not undergo the polymerization reaction and their structures are reported here. The diyne is, however, useful as a room-temperature hydrogen fixer when combined with a palladium–alumina catalyst (Anderson, Courtney & Harrah, 1975). The structure of the hydrogenated compound, 1,6-diphenoxyhexane (hereafter referred to as HEXAN), which results from this reaction, is also reported.

Large, thin plates of the diyne were grown from acetone and found usually to belong to orthorhombic symmetry; however, occasionally during photographic examination, specimens of a different form were found and established to be twinned monoclinic (hereafter referred to as ORTHO and MONO). Plates of the HEXAN compound were grown from ether. Lattice parameters given in the abstract were determined on a Picker diffractometer with Mo $K\alpha$ radiation. Crystal

specimens for data collection were cleaved from large plates and no single dimension exceeded 0.35 mm (μ for Mo $K\alpha < 1$ cm⁻¹ for these materials). Although no systematic variations were found on standard reflections monitored through the data collection, the diyne specimen darkened very slightly after constant irradiation in excess of two weeks. The θ – 2θ scan technique and a scintillation detector employing pulse-height discrimination were used to measure the Mo $K\alpha$ intensity data to 50° 2θ . A twinned MONO specimen was used to collect intensity measurements; $hk0$ values were adjusted based on the well-resolved, stronger $h0l$ pairs. Upper-level photographs aided selection of close, but resolved hkl intensities in order to narrow receiver aperture; nine large-valued intensity values were adjusted after the heavy atoms were introduced in the refinement. Of 1214 intensities employed for MONO, 843 intensities were greater than 3σ where $\sigma = (N_{sc} + K^2 N_b)^{1/2}$ and N_{sc} , N_b and K are the total scan counts, background counts and the time ratio of the scan to background respectively; from ORTHO, two quadrants of measured intensities yielded 814 observed and 442 ‘less than’ intensities. Similarly, two quadrants of measured intensities from HEXAN yielded 868 observed and 482 ‘less than’ intensities. Scattering factors computed from Hartree–Fock wave functions for O and C (Cromer & Mann, 1968) and from Stewart, Davidson & Simpson (1965) for H were used. The positions of the heavy atoms were obtained by direct methods. In these structures, the molecules are located about special positions. Initially, for each of the structures, a model using these heavy-atom positional parameters together with isotropic thermal parameters was subjected to full-matrix least-squares refinement. The function $W(F_o - F_c)^2$ was minimized with $W =$

* Prepared for the US Energy Research and Development Administration under Contract AT(29-1)-789.

Table 1. *Positional and thermal parameters* ($\times 10^4$) for 1,6-diphenoxy-2,4-hexadiyne U_{ij} are of the form: $\exp(-2\pi^2 \sum U_{ij} h_i h_j a_i^* a_j^*)$; both positional and thermal (\AA^2) parameters are $\times 10^4$.

(a) Orthorhombic form

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	3331 (2)	1022 (2)	-332 (4)	32 (2)	67 (2)	49 (2)	-5 (1)	-1 (1)	17 (2)
C(1)	586 (4)	109 (4)	179 (6)	42 (3)	67 (3)	49 (3)	-7 (2)	-5 (2)	7 (3)
C(2)	1581 (4)	300 (3)	475 (6)	43 (3)	65 (3)	49 (3)	-5 (2)	4 (2)	3 (2)
C(3)	2811 (4)	517 (4)	929 (6)	37 (3)	69 (3)	46 (3)	12 (2)	2 (2)	3 (3)
C(5)	4491 (4)	1296 (3)	-124 (5)	34 (2)	38 (2)	49 (3)	2 (2)	5 (2)	4 (2)
C(6)	5187 (4)	1062 (3)	1151 (6)	43 (3)	53 (3)	46 (3)	-9 (2)	0 (2)	2 (2)
C(7)	6362 (4)	1381 (4)	1238 (7)	45 (3)	66 (3)	64 (3)	-8 (3)	-5 (3)	-1 (3)
C(8)	6818 (5)	1925 (3)	88 (7)	46 (3)	56 (3)	79 (4)	-9 (3)	9 (3)	-4 (3)
C(9)	6108 (5)	2148 (4)	-1184 (7)	54 (3)	65 (3)	84 (4)	-7 (3)	14 (3)	18 (3)
C(10)	4937 (5)	1820 (4)	-1302 (7)	46 (3)	70 (3)	65 (3)	0 (3)	-1 (3)	24 (3)

	<i>x</i>	<i>y</i>	<i>z</i>	U		<i>x</i>	<i>y</i>	<i>z</i>	U
H(31)	3275 (50)	-229 (39)	1035 (67)	109 (20)	H(8)	7774 (60)	2364 (41)	291 (74)	150 (23)
H(32)	2784 (44)	903 (32)	1965 (61)	68 (16)	H(9)	6266 (61)	2848 (48)	-2304 (89)	187 (28)
H(6)	4920 (53)	633 (38)	2157 (73)	113 (21)	H(10)	4415 (55)	2033 (42)	-2155 (78)	113 (24)
H(7)	6850 (56)	1137 (43)	2514 (86)	156 (25)					

(b) Monoclinic form

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	2125 (6)	3303 (3)	975 (4)	55 (2)	21 (2)	27 (2)	-8 (2)	4 (2)	1 (2)
C(1)	229 (8)	585 (5)	-103 (7)	41 (3)	26 (3)	31 (3)	-5 (2)	7 (2)	-5 (2)
C(2)	628 (8)	1566 (5)	-275 (7)	42 (3)	31 (3)	34 (3)	-4 (2)	10 (2)	-5 (2)
C(3)	1104 (8)	2776 (4)	-594 (6)	39 (3)	24 (3)	32 (3)	-7 (2)	8 (2)	-4 (2)
C(5)	2665 (7)	4461 (4)	941 (6)	28 (3)	20 (2)	28 (2)	-3 (2)	9 (2)	0 (2)
C(6)	2320 (8)	5115 (5)	-495 (6)	37 (3)	31 (3)	28 (3)	-7 (2)	10 (2)	3 (2)
C(7)	2931 (8)	6274 (5)	-373 (7)	47 (3)	30 (3)	47 (3)	-8 (3)	18 (3)	4 (3)
C(8)	3893 (9)	6769 (5)	1148 (8)	46 (3)	28 (3)	53 (4)	-12 (3)	17 (3)	-7 (3)
C(9)	4214 (8)	6105 (5)	2555 (7)	40 (3)	32 (3)	40 (3)	-3 (2)	7 (3)	-12 (3)
C(10)	3582 (8)	4961 (5)	2456 (7)	44 (3)	32 (3)	30 (3)	4 (2)	5 (2)	3 (2)

	<i>x</i>	<i>y</i>	<i>z</i>	U		<i>x</i>	<i>y</i>	<i>z</i>	U
H(31)	2088 (79)	2660 (51)	-1330 (68)	42 (16)	H(8)	4474 (103)	7500 (72)	1379 (88)	81 (24)
H(32)	-414 (94)	3268 (59)	-1263 (79)	70 (20)	H(9)	5116 (93)	6364 (60)	3582 (83)	59 (20)
H(6)	1749 (145)	4785 (93)	-1641 (128)	128 (39)	H(10)	3651 (79)	4493 (53)	3278 (71)	47 (17)
H(7)	1702 (149)	6917 (95)	-1873 (131)	209 (43)					

Table 2. *Positional and thermal parameters* ($\times 10^4$) for 1,6-diphenoxyhexane

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	1789 (1)	-217 (4)	5083 (4)	45 (2)	68 (2)	40 (1)	-7 (1)	-3 (1)	9 (1)
C(1)	438 (2)	358 (6)	307 (6)	45 (2)	46 (2)	46 (2)	O(2)	1 (2)	4 (2)
C(2)	743 (3)	-301 (7)	2407 (6)	45 (2)	53 (3)	49 (2)	-2 (2)	-4 (2)	5 (2)
C(3)	1597 (2)	416 (6)	3037 (6)	44 (2)	49 (3)	42 (2)	1 (2)	-1 (2)	4 (2)
C(5)	2599 (2)	-39 (5)	5838 (5)	49 (2)	39 (2)	39 (2)	1 (2)	-2 (2)	-3 (2)
C(6)	3214 (2)	919 (6)	4906 (6)	48 (2)	47 (2)	40 (2)	0 (2)	1 (2)	8 (2)
C(7)	4022 (2)	942 (6)	5792 (6)	48 (2)	55 (2)	53 (2)	-2 (2)	-1 (2)	1 (2)
C(8)	4206 (3)	20 (6)	7587 (6)	49 (2)	59 (3)	49 (2)	4 (2)	-7 (2)	-2 (2)
C(9)	3589 (3)	-891 (6)	8541 (6)	72 (3)	52 (3)	42 (2)	5 (2)	-11 (2)	4 (2)
C(10)	2780 (3)	-933 (6)	7703 (6)	63 (3)	44 (2)	37 (2)	-3 (2)	1 (2)	2 (2)

	<i>x</i>	<i>y</i>	<i>z</i>	U		<i>x</i>	<i>y</i>	<i>z</i>	U
H(11)	785 (2)	-115 (50)	-774 (53)	44 (10)	H(6)	3109 (24)	1580 (56)	3887 (60)	54 (12)
H(12)	466 (22)	1737 (59)	216 (57)	56 (11)	H(7)	4562 (28)	1792 (71)	4917 (72)	105 (17)
H(21)	344 (21)	213 (49)	3470 (52)	47 (10)	H(8)	4739 (25)	-13 (60)	8243 (61)	72 (13)
H(22)	733 (26)	-1608 (66)	2446 (64)	67 (14)	H(9)	3696 (29)	-1524 (68)	9727 (72)	86 (16)
H(31)	1618 (24)	1713 (60)	2902 (58)	57 (12)	H(10)	2317 (25)	-1602 (59)	8342 (61)	68 (13)
H(32)	1982 (14)	-247 (33)	2080 (35)	44 (5)					

Table 3. Bond angles and lengths for ORTHO and MONO

	ORTHO	MONO		ORTHO	MONO
C(1)—C(1')	1.385 (7) Å	1.398 (8) Å	C(1)—C(1)—C(2)	179.5 (6)°	179.5 (7)°
C(1)—C(2)	1.175 (7)	1.177 (8)	C(1)—C(2)—C(3)	176.9 (5)	176.6 (6)
C(2)—C(3)	1.466 (7)	1.469 (8)	C(2)—C(3)—O	107.4 (4)	107.5 (4)
C(3)—O	1.437 (6)	1.440 (6)			
O—C(5)	1.372 (5)	1.379 (6)	C(3)—O—C(5)	116.3 (3)	116.4 (4)
C(5)—C(6)	1.382 (6)	1.390 (7)	C(6)—C(5)—O	123.9 (4)	124.1 (4)
C(6)—C(7)	1.400 (7)	1.386 (8)	C(10)—C(5)—O	114.9 (4)	115.5 (4)
C(7)—C(8)	1.373 (8)	1.384 (8)	C(6)—C(5)—C(10)	121.2 (4)	120.4 (5)
C(8)—C(9)	1.385 (8)	1.377 (9)	C(5)—C(6)—C(7)	118.9 (4)	118.8 (5)
C(9)—C(10)	1.403 (8)	1.377 (8)	C(6)—C(7)—C(8)	120.9 (5)	120.8 (6)
C(10)—C(5)	1.370 (7)	1.376 (7)	C(7)—C(8)—C(9)	119.4 (5)	119.4 (5)
C(3)—H(31)	1.23 (6)	1.13 (7)	C(8)—C(9)—C(10)	120.4 (5)	120.5 (5)
C(3)—H(32)	1.06 (5)	1.22 (6)	C(9)—C(10)—C(5)	119.3 (5)	120.1 (5)
C(6)—H(6)	1.11 (6)	1.01 (10)			
C(7)—H(7)	1.27 (7)	1.50 (10)			
C(8)—H(8)	1.27 (7)	0.92 (8)			
C(9)—H(9)	1.43 (7)	0.96 (6)			
C(10)—H(10)	0.99 (6)	0.87 (6)			

Table 4. Bond angles (°) and lengths (Å) for 1,6-diphenoxyhexane

C(1)—C(1')	1.534 (5)	C(7)—H(7)	1.23 (5)
C(1)—C(2)	1.512 (6)	C(8)—H(8)	0.94 (4)
C(2)—C(3)	1.503 (6)	C(9)—H(9)	0.91 (5)
C(3)—O	1.433 (4)	C(10)—H(10)	1.00 (4)
O—C(5)	1.373 (4)		
C(5)—C(6)	1.375 (5)	C(1')—C(1)—C(2)	112.3 (3)
C(6)—C(7)	1.391 (5)	C(1)—C(2)—C(3)	112.7 (4)
C(7)—C(8)	1.373 (6)	C(2)—C(3)—O	107.1 (3)
C(8)—C(9)	1.367 (6)	C(3)—O—C(5)	117.5 (3)
C(1)—C(10)	1.382 (6)	O—C(5)—C(6)	125.1 (3)
C(10)—C(5)	1.401 (5)	O—C(5)—C(10)	114.8 (3)
C(1)—H(11)	0.98 (4)	C(6)—C(5)—C(10)	120.0 (3)
C(1)—H(12)	1.02 (4)	C(5)—C(6)—C(7)	119.6 (4)
C(2)—H(21)	1.04 (4)	C(6)—C(7)—C(8)	120.4 (4)
C(2)—H(22)	0.96 (5)	C(7)—C(8)—C(9)	120.0 (4)
C(3)—H(31)	0.96 (4)	C(8)—C(9)—C(10)	121.0 (4)
C(3)—H(32)	1.02 (2)	C(9)—C(10)—C(5)	119.0 (4)
C(6)—H(6)	0.83 (4)		

n/σ^2 ; 'less than' intensities were included only when exceeded by the calculated values. Subsequent ($F_o - F_c$) difference Fourier syntheses clearly showed the positions of H atoms. The positional, anisotropic thermal parameters for the heavy atoms, and isotropic thermal parameters for H were included as variables in subsequent refinement cycles. Refinement was concluded when shift-to-error ratios were below 0.2. Final residual values, $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$, were 0.070, 0.082, and 0.055 for ORTHO, MONO, and HEXAN respectively.* These positional and thermal parameters are given in Tables 1 and 2 and the corresponding interatomic separations in Tables 3 and 4. The labeling of

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32304 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the atoms is shown in Fig. 1. H atoms are numbered in a manner consistent with the C atoms to which they are attached. For HEXAN the same labeling sequence is used. As evident from bond-length values, several H atom positions are of questionable reliability. As expected, the smaller values for the anisotropic thermal parameters are those essentially along the chain while values perpendicular to the chains are slightly larger. The computations were performed with the X-RAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

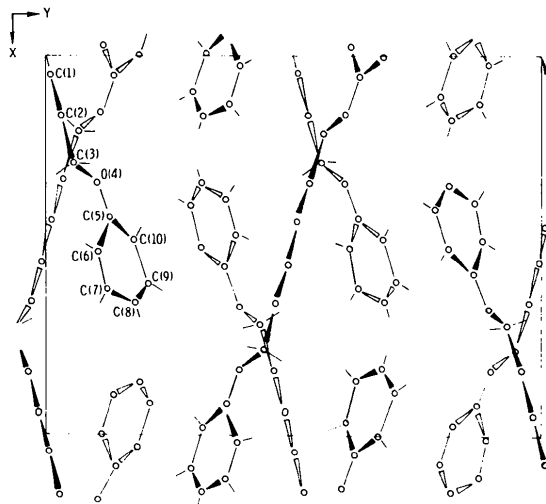


Fig. 1. View along z for the crystal structures of 1,6-diphenoxy-2,4-hexadiyne. The labeling sequence for both forms is identical and shown upper left. For the ORTHO form (as shown) the molecules located at about $z = 0$ are dark, those at about $z = \frac{1}{2}$ light, with x and y as labeled. For the MONO form, x is along the top with two unit cells shown, y down: hence, the molecules down the center of the sketch need to have their tilt and darkness reversed to appear identical with those molecules along the edges.

Discussion

(a) 1,6-Diphenoxy-2,4-hexadiyne (ORTHO, MONO)

In projection along z , the structures have a marked similarity (Fig. 1). In both forms, molecules are centered on the origin and on the symmetry-equivalent points. The relative elevations differ, however, as is indicated in Fig. 1. The differences in molecular packing appear to result from the manner in which the phenyl groups stack upon each other. In MONO, the phenyl groups are nearly correctly positioned for an infinite stack (along x) whereas this is not the case in ORTHO (Fig. 2). Since the phenyl groups in such a stack are attached to the remainder of the molecule, pointing in opposite directions, the sequence resembles a zipper in MONO. In such a stack, the separations of C atoms are somewhat closer for MONO than they are for the pair of phenyl groups in ORTHO (see Table 5). An

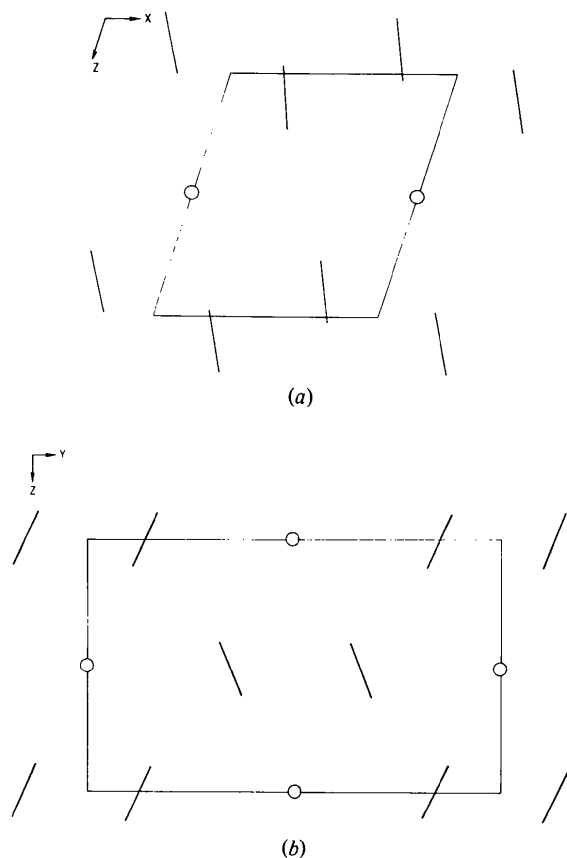


Fig. 2. Sketches showing the stacking of the phenyl groups. (a) Slice near $y = \frac{1}{2}$ for MONO with open circle indicating center of molecules and lines essentially the C(6)-C(10) separation (phenyl ring contacts closest to $y = \frac{1}{2}$). Note that this form has a stack along x of phenyl groups overlapping as in a zipper. (b) Slice near $x = \frac{1}{2}$ for ORTHO. Packing sequence does not contain stacks, only pairs of phenyl groups. Note that the top layer along y is similar to that in MONO along the long diagonal [101].

alternative viewpoint for comparing the molecular packing might be to consider the arrangement of a layer along the long diagonal, [101], of MONO with that along y in ORTHO (Fig. 2). In MONO such layers stack upon each other while in ORTHO, such a layer stacks upon its mirror image, with phenyl groups slanted in the opposite direction. Interestingly, this difference in molecular packing has only a small effect on the molecules; the possible twisting of the molecule involves the rotation about C(2)-C(3)-O-C(5), *i.e.* the dihedral angle about the C(3)-O bond as well as rotation of the phenyl group about O-C(5) relative to C(3)-O. Plane A defined by C(2), C(3) and O and plane B defined by C(3), O and C(5) give the dihedral angle while plane C defined by the phenyl C atoms allows a measure of the rotation angle relative to the other planes. The angles between A and B , A and C , and B and C are 0.42 , 4.39 and 4.53° , respectively, for ORTHO and 1.45 , 1.20 and 1.51° , respectively, for MONO.

The configurations of the molecules found in the two structures are very similar (Table 3). The shortening of the single C-C bond distance located between the two triple bonds in this conjugated system is not as large as that found in other compounds. However, care should be exercised in such comparisons. For example, the values quoted for C-C (1.379 \AA) and for C \equiv C (1.205 \AA) in butadiyne (Dewar & Schmeising, 1959; Sutton,

Table 5. Nearest-neighbor contact separations (\AA)

ORTHO		MONO	
$1-x, -y, -z$		$-x, 1-y, -z$	
C(3)-C(7)	3.514 (8)	C(3)-C(7)	3.550 (9)
O-C(6)	3.602 (6)	O-C(6)	3.676 (7)
C(5)-C(6)	3.657 (6)*	C(5)-C(6)	3.646 (8)*
C(7)-O	3.697 (6)	C(7)-O	3.669 (8)
C(3)-C(6)	3.708 (7)	C(8)-C(2)	3.724 (9)
C(2)-C(7)	3.710 (7)	C(2)-C(7)	3.793 (9)
C(6)-C(6)	3.762 (7)*	C(6)-C(6)	3.843 (9)*
C(8)-C(3)	3.782 (8)	C(8)-C(3)	3.639 (9)
$\frac{1}{2}-x, y, \frac{1}{2}+z$		$x, \frac{1}{2}-y, \frac{1}{2}+z$	
C(3)-O	3.516 (6)	O-C(3)	3.503 (7)
C(2)-O	3.736 (6)	O-C(2)	3.748 (8)
$\frac{1}{2}+x, \frac{1}{2}-y, z$		$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	
C(8)-O	3.528 (6)	C(8)-O	3.621 (6)
C(9)-O	3.770 (6)	C(9)-O	3.609 (7)
$1\frac{1}{2}-x, y, \frac{1}{2}+z$		$x, 1\frac{1}{2}-y, \frac{1}{2}+z$	
C(7)-C(9)	3.761 (8)	C(9)-C(7)	3.755 (9)
$\frac{1}{2}-x, -y, \frac{1}{2}-z$		$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	
C(6)-C(1)	3.615 (7)	C(6)-C(1)	3.664 (7)
C(7)-C(2)	3.776 (8)		
$1-x, \frac{1}{2}-y, z$		$1-x, 1-y, -z$	
C(7)-C(10)	3.710 (8)	C(7)-C(5)	3.581 (9)*
C(6)-C(9)	3.800 (8)	C(6)-C(7)	3.724 (8)*
		C(8)-C(6)	3.736 (9)*

* Values between stacked phenyl groups.

1958) depend on assumed values from other similar molecules which are used in the calculations of spectroscopic data (Craine & Thompson, 1953). The average values of 1.392 (8) Å for C—C and of 1.176 (8) Å for C≡C are found in the present study; the corresponding values for the dibenzoxy compound are 1.372 (5) and 1.193 (4) Å respectively (Hanson, 1975).

Unlike most substituted 2,4-hexadiynediols which undergo a radiation-induced polymerization reaction in the solid state, these crystals showed only a very slight darkening after approximately two weeks of continuous exposure to X-radiation. For compounds which undergo polymerization, the proper packing arrangement with the unsaturated bonds adjacent to each other [presumably less than 4.02 Å; Hanson (1975)] is usually found. In the present material, the closest contacts (Table 5; listed for comparison of similar separations) to the triple bond between C(1)—C(2) involve phenyl C or the ether O atoms. This packing arrangement appears to be unfavorable for polymerization.

(b) 1,6-Diphenoxyhexane (HEXAN)

The molecular packing of this material resembles that of the unsaturated compounds. The chains, centered on the origin and symmetry-equivalent points, are near a plane $y = 0$ and extend along [102]; however, the extension does not exceed one half of a cell translation along x so there is no overlap of molecules related by this translation operation (Fig. 3). The same numbering sequence is used for this compound. The

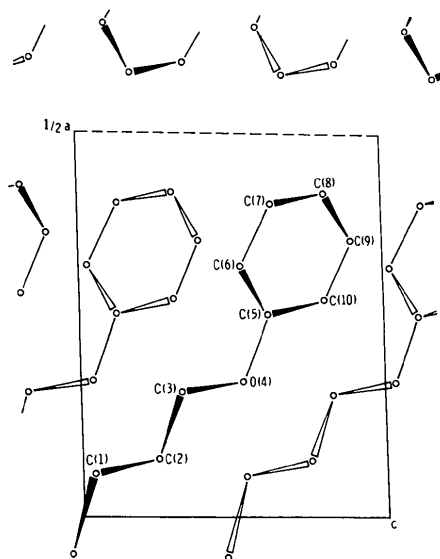


Fig. 3. View along y for HEXAN. Molecules located at about $y = 0$ are dark, those at about $y = \frac{1}{2}$ are light.

phenyl groups are not oriented in any manner to resemble stacks (or pairs) as was the case for the diyne structures above. There are only seven non-hydrogen separations between molecules shorter than 3.8 Å; these are a 3.620 (3) Å C(7)—C(7) and a 3.742 (6) Å C(8)—C(7) distance with the second atoms related by $1-x, -y, 1-z$, a 3.734 (6) Å C(8)—C(6) and a 3.650 (6) Å C(8)—C(7) distance related by $x, \frac{1}{2}-y, \frac{1}{2}+z$ and a 3.628 (5) Å C(10)—O, a 3.617 (5) Å C(10)—C(5), and a 3.732 (6) Å C(9)—C(5) distance related by $x, -\frac{1}{2}-y, \frac{1}{2}+z$.

The bond lengths and angles about O and C(5) are similar to those for the diyne molecules. In particular, the O—C—C angles deviate from 120° in a similar manner suggesting that the C—O vector is bent back; this distortion results from steric hindrance since the C(3)—C(6) distances, 2.78–2.83 Å in these compounds, are shorter than many of the above mentioned intermolecular distances.

Conclusions

The molecular packing found for the two forms of diyne appear to account for the observed stability of the material to radiation. The intermolecular arrangement is unfavorable for the type of topochemical polymerization generally encountered with other substituted hexadiynes. Intramolecular bond lengths and angles are similar to those found for other organic materials.

References

- ANDERSON, R., COURTNEY, R. L. & HARRAH, L. (1975). US Patent No. 3,896,042.
- BAUGHMAN, R. H. (1972). *J. Appl. Phys.* **43**, 4362–4370.
- BAUGHMAN, R. H., WITT, J. D. & YEE, K. C. (1974). *J. Chem. Phys.* **60**, 4755–4759.
- CRAINE, G. D. & THOMPSON, H. W. (1953). *Trans. Faraday Soc.* **49**, 1273–1280.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DEWAR, M. J. S. & SCHMEISING, H. N. (1959). *Tetrahedron*, **5**, 166–178.
- HADICKE, E., PENZIEN, K. & SCHNELL, W. (1971). *Angew. Chem. Int. Ed.* **10**, 940–941.
- HANSON, A. W. (1975). *Acta Cryst.* **B31**, 831–834.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Spec. Publ. No. 11. London: The Chemical Society.
- TRUJILLO, R. (1975). Unpublished.
- WEGNER, G. (1971). *Makromol. Chem.* **145**, 85–94.