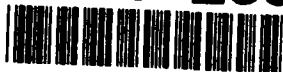


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average 1 hour per reference, including the time for reviewing instructions, searching existing data sources, gathering the collection of information, and completing the review of the collection of information, 1215 Jefferson
Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson
Management and Budget, Paperwork Reduction Project (0704-0180), Washington, DC 20503.

ATF

3. REPORT TYPE AND DATES COVERED

reprint

4. TITLE AND SUBTITLE

Crystal structures of poly-paraphenylene Oligomers
containing pendant phenyl groups

5. FUNDING NUMBERS

61102F 2303/A3

6. AUTHOR(S)

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8. PERFORMING ORGANIZATION
REPORT NUMBER

AFOSR-TR- 91 0471

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NC
Building 410, Bolling AFB DC
20332-6448

10. SPONSORING/MONITORING
AGENCY REPORT NUMBER

AFOSR-88-0044

DTIC

11. SUPPLEMENTARY NOTES

POLYMER, 1990, Vol. 31, September, pg 1623-1631

MAY 07 1991

12. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The room temperature crystal structures of 1,2,4-triphenylbenzene (TPB), $C_{24}H_{18}$; 2,2',4,4'-diphenyl-p-quinquephenyl (DPQ), $C_{42}H_{30}$; and 2,2',6,6'-diphenyl-p-septiphenyl (DPS), $C_{54}H_{38}$, have been investigated as part of a research programme in rigid-rod polymers, materials which are of great interest for aerospace and electro-optical applications. The molecules are non-planar, in contrast to the planar structures found at room temperature for the unsubstituted polyphenyls. The oligomer axis does not align with any of the crystallographic axes. The pendant-oligomer bond, however, does align with the longest crystallographic axis. The pendant torsion angle is greater than 45° and increases with increasing chain length. Knowledge of molecular structure and crystal packing of oligomeric model compounds will be useful in further calculations of mechanical, optical, and electro-optical properties for the corresponding rigid-rod polymer structures.

Availability Code

DTIC GRA&I
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Justification

By
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Availability Codes

Dist Avail and/or
Special

A-1

20



14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION

UNCLASSIFIED

18. SECURITY CLASSIFICATION

UNCLASSIFIED

19. SECURITY CLASSIFICATION

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

Crystal structures of poly-paraphenylene oligomers containing pendant phenyl groups

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(Received 11 July 1989; revised 25 September 1989; accepted 30 September 1989)

The room temperature crystal structures of 1,2,4-triphenylbenzene (TPB), $C_{24}H_{18}$; 2,2',4,5'-diphenyl-*p*-quinquephenyl (DPQ), $C_{42}H_{30}$; and 2,2',6,6'-diphenyl-*p*-septiphenyl (DPS), $C_{54}H_{38}$, have been investigated as part of a research programme in rigid-rod polymers, materials which are of great interest for aerospace and electro-optical applications. The molecules are non-planar, in contrast to the planar structures found at room temperature for the unsubstituted polyphenyls. The oligomer axis does not align with any of the crystallographic axes. The pendant-oligomer bond, however, does align with the longest crystallographic axis. The pendant torsion angle is greater than 45° and increases with increasing chain length. Knowledge of molecular structure and crystal packing of oligomeric model compounds will be useful in further calculations of mechanical, optical, and electro-optical properties for the corresponding rigid-rod polymer structures.

(Keywords: polyphenyls; poly-*p*-phenylenes; crystal structure; rigid-rod polymers; conducting polymers)

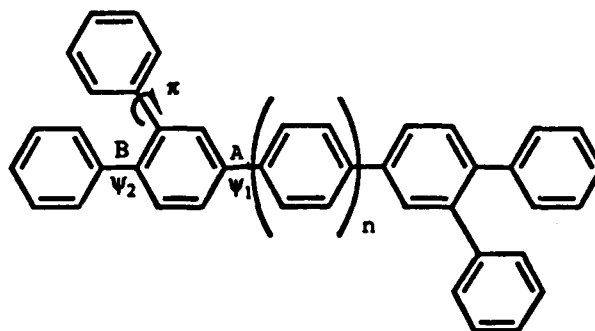
INTRODUCTION

The past few years have seen the activity in the area of conducting polymers grow at a very rapid rate. The widespread interest in conducting polymers clearly reflects their perceived technological potential¹. Attention has focused on the pi-bonded polymers such as poly-paraphenylene (PPP) for several reasons. It can be oxidized to a polymeric cation rather than undergo other chemistry and thereby be made electrically conducting; it is thermally stable: pi-orbital overlap may create interesting non-linear optical (NLO) properties; and improved methods have been reported for the synthesis of oligomeric soluble prepolymer².

The generation of charge carriers in the polyphenyls occurs by doping and the subsequent formation of ionic species, e.g., a polymeric cation and a counter ion. Electrical conductivity as high as $500 \text{ ohm}^{-1} \text{ cm}^{-1}$ has been achieved with dopants such as Li, K, and AsF_5 (ref. 3). The polymer chains, as for organic molecules in general, adopt a different conformation in the ionized state compared to the neutral state. Conformation differences would lead to changes in the amount of pi-orbital overlap along the polymer axis as well as affect the electro-optical properties of the polymer.

In an ongoing study of PPP as new electrically conducting rigid-rod polymers, the room temperature structures of 2,2',4,4'-diphenyl-*p*-quinquephenyl (DPQ), 2,2',6,6'-diphenyl-*p*-septiphenyl (DPS), and 1,2,4-triphenylbenzene (TPB) have been determined. TPB was included in the present study because its room temperature crystal structure had not been reported. The first two compounds

have the general structure,



where $n=1$ for DPQ and $n=3$ for DPS. Letters (A, B, etc.) refer to the connecting bond along the main chain and the Greek letters (ψ and π) refer to the torsion angles between adjacent phenyl groups. These compounds were synthesized in order to obtain a better understanding of how rigid-rod molecules pack in solids and how chain length affects packing. In addition, recent calculations⁴ have indicated that PPP is a very stiff molecule which, if processed into fibres using high molecular weight polymer, would have very high tensile modulus.

EXPERIMENTAL

Oligomers were synthesized by Bruce Reinhardt, Materials Laboratory, Wright Patterson Air Force Base, according to a new method which involves intermolecular cyclization². The highly crystalline samples required no additional purification and/or crystal growth. Density

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measurements were made by flotation in mixed solvents containing methyl alcohol and methylene chloride.

Reflection data were collected on an Enraf Nonius CAD4 diffractometer coupled with a DEC micro PDP-11 computer and processed on a VAX 11/730 using software in the *Structure Determination Package* (SDP)⁵. Structure solutions were determined by MULTAN 11/82⁶ and SHELXS-86⁷. The method of refinement followed the general scheme: (1) isotropic refinement of carbon atoms using unit-weighted reflections; (2) isotropic refinement of carbon atoms using unit-weighted reflections; hydrogen atoms, with fixed thermal factors, positioned in idealized geometries and constrained to its attached carbon atom with a bond length of 0.95 Å; (3) anisotropic refinement of carbon atoms using unit weights with hydrogen atoms still constrained to attached carbon atoms; (4) anisotropic refinement of carbon atoms to convergence using $1/\sigma^2(F)$ weights with hydrogen atoms riding on attached carbon atoms. Subsequent isotropic refinement of hydrogen atoms, as expected, did not yield appreciably better results due to the reduced data-to-parameter ratio.

RESULTS

Table 1 lists crystallographic and data collection parameters, and final refinement results. Figure 1 shows the TPB molecule with the carbon atoms labelled. Tables 2 and 3 contain the atomic positions, bond distances, and bond angles, respectively. Figure 2 shows a stereo view of the molecular packing in the unit cell.

DPQ is shown in Figure 3 with the carbon atoms of the asymmetric unit labelled. Tables 4 and 5 present the atomic positions, bond distances, and bond angles, respectively. The stereo view of the molecular packing in the unit cell is shown in Figure 4. The molecule possesses a centre of symmetry.

The DPS molecule with the carbon atoms of the asymmetric unit labelled is shown in Figure 5. Atomic positions, bond distances, and bond angles are presented

Table 2 Atomic positions of 1,2,4-triphenylbenzene. Numbers in parentheses are estimated standard deviations in the least significant digits

Atom	x	y	z	B (Å ²)
C1	0.6605(2)	0.1066(1)	-0.02818(9)	3.51(3)
C2	0.6238(2)	0.0967(1)	-0.0998(1)	3.95(4)
C3	0.5698(2)	0.1542(1)	-0.1390(1)	4.38(4)
C4	0.5516(2)	0.2233(1)	-0.1076(1)	4.76(5)
C5	0.5875(3)	0.2341(1)	-0.0369(1)	5.76(5)
C6	0.6419(2)	0.1764(1)	0.0022(1)	5.17(5)
C7	0.7186(2)	0.0445(1)	0.01392(9)	3.46(3)
C8	0.6704(2)	-0.0279(1)	0.0092(1)	3.87(4)
C9	0.7261(2)	-0.0854(1)	0.04820(9)	3.81(4)
C10	0.8327(2)	-0.0736(1)	0.09264(9)	3.38(3)
C11	0.8815(2)	-0.0007(1)	0.09859(9)	3.34(3)
C12	0.8232(2)	0.0567(1)	0.05922(9)	3.65(4)
C13	0.8905(2)	-0.1397(1)	0.12927(9)	3.57(4)
C14	0.8133(2)	-0.1891(1)	0.1676(1)	4.24(4)
C15	0.8641(2)	-0.2526(1)	0.1991(1)	5.05(5)
C16	0.9928(3)	-0.2682(1)	0.1922(1)	5.53(5)
C17	1.0707(2)	-0.2197(1)	0.1547(1)	5.53(5)
C18	1.0206(2)	-0.1558(1)	0.1236(1)	4.49(4)
C19	0.9919(2)	0.01889(9)	0.14651(9)	3.41(4)
C20	0.9958(2)	-0.0032(1)	0.2188(1)	4.26(4)
C21	1.0960(2)	0.0181(1)	0.2634(1)	5.17(5)
C22	1.1940(2)	0.0621(1)	0.2362(1)	5.21(5)
C23	1.1915(2)	0.0842(1)	0.1647(1)	5.02(5)
C24	1.0910(2)	0.0629(1)	0.1201(1)	4.15(4)
H2	0.637	0.050	-0.122	5.0
H3	0.543	0.146	-0.188	5.6
H4	0.516	0.263	-0.135	6.0
H5	0.575	0.282	-0.015	6.9
H6	0.666	0.184	0.051	6.5
H8	0.599	-0.038	-0.022	5.0
H9	0.691	-0.134	0.045	4.8
H12	0.857	0.106	0.063	4.6
H14	0.724	-0.179	0.172	5.3
H15	0.810	-0.286	0.226	6.4
H16	1.028	-0.312	0.213	7.0
H17	1.160	-0.230	0.150	6.9
H18	1.076	-0.122	0.098	5.7
H20	0.929	-0.034	0.237	5.4
H21	1.097	0.003	0.313	6.6
H22	1.263	0.077	0.267	6.5
H23	1.260	0.114	0.146	6.6
H24	1.089	0.079	0.071	5.4

Table 1 Crystal data

Name	1,2,4-Triphenyl benzene	2',4'-Diphenyl-p-quinquephenyl	2',6'-Diphenyl-p-septiphenyl
Formula	C ₂₄ H ₁₈	C ₄₂ H ₃₀	C ₅₄ H ₃₈
FW	306.4	534.7	686.9
T _m (°C)	123	288	375
Space group	Pbca	P2 ₁ c	P1
Z	8	2	1
a (Å)	10.368(6)	6.304(3)	11.713(2)
b (Å)	17.898(4)	31.437(9)	13.596(2)
c (Å)	18.474(5)	7.651(3)	6.138(2)
α (degrees)	90.0	90.0	102.33(2)
β (degrees)	90.0	106.18(4)	96.51(2)
γ (degrees)	90.0	90.0	102.71(1)
Vol (Å ³)	3428.3(4)	1456.4(2)	918.3(8)
Density _{cal} (g cm ⁻³)	1.187	1.219	1.242
Density _{xrp} (g cm ⁻³)	1.186	1.188	1.236
Number of total reflections	19 698	5204	3558
Number of unique reflections > 3σ	1839	1061	1537
Number of parameters varied	217	190	244
R ^a	0.036	0.049	0.046
RW ^b	0.050	0.061	0.062

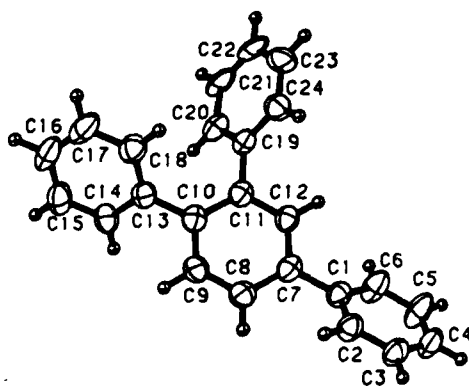
$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b RW = \sqrt{\frac{\sum W(|F_o| - |F_c|)^2}{\sum W(F_o)^2}}$$

Table 3 Bond distances and angles for 1,2,4-triphenylbenzene. Numbers in parentheses are estimated standard deviations in the least significant digit

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
C1	C2	1.388(2)	C11	C12	1.396(3)
C1	C6	1.382(3)	C11	C19	1.489(2)
C1	C7	1.486(2)	C13	C14	1.387(3)
C2	C3	1.377(3)	C13	C18	1.383(3)
C3	C4	1.379(3)	C14	C15	1.382(3)
C4	C5	1.373(3)	C15	C16	1.369(3)
C5	C6	1.381(3)	C16	C17	1.373(3)
C7	C8	1.392(3)	C17	C18	1.382(4)
C7	C12	1.387(2)	C19	C20	1.394(3)
C8	C9	1.383(3)	C19	C24	1.384(3)
C9	C10	1.393(3)	C20	C21	1.380(4)
C10	C11	1.405(2)	C21	C22	1.381(3)
C10	C13	1.489(2)	C22	C23	1.380(3)
			C23	C24	1.382(2)

Atom 1	Atom 2	Atom 3	Angle (deg)	Atom 1	Atom 2	Atom 3	Angle (deg)
C2	C1	C6	117.8(2)	C12	C11	C19	118.0(2)
C2	C1	C7	121.0(2)	C7	C12	C11	122.5(2)
C6	C1	C7	121.3(2)	C10	C13	C14	120.4(2)
C1	C2	C3	121.2(2)	C10	C13	C18	121.5(2)
C2	C3	C4	120.4(2)	C14	C13	C18	118.0(2)
C3	C4	C5	119.4(2)	C13	C14	C15	121.2(2)
C4	C5	C6	120.2(3)	C14	C15	C16	120.0(2)
C1	C6	C5	121.3(2)	C15	C16	C17	119.4(3)
C1	C7	C8	121.2(2)	C16	C17	C18	120.9(2)
C1	C7	C12	121.1(2)	C13	C18	C17	120.4(4)
C8	C7	C12	117.7(2)	C11	C19	C20	121.7(2)
C7	C8	C9	120.6(2)	C11	C19	C24	119.7(2)
C8	C9	C10	121.8(2)	C20	C19	C24	118.6(2)
C9	C10	C11	118.2(2)	C19	C20	C21	121.0(2)
C9	C10	C13	117.9(2)	C20	C21	C22	119.7(2)
C11	C10	C13	123.9(2)	C21	C22	C23	120.0(2)
C10	C11	C12	119.2(2)	C22	C23	C24	120.4(2)
C10	C11	C19	122.9(2)	C19	C24	C23	120.4(2)

**Figure 1** 1,2,4-Triphenylbenzene with carbon atom ellipsoids drawn at the 50% probability level

in Tables 6 and 7, respectively. Figure 6 depicts a stereo view of the molecular packing of the structure in the unit cell. This molecule also possesses a centre of symmetry. (Observed and calculated structure factor amplitudes and other details of the structure analysis have been deposited at the British Library Copyright Receipt Office* as supplementary material to this paper.)

DISCUSSION

Table 8 summarizes the bond lengths between neighbouring phenyl units for structures determined at room

temperature. The values are not significantly different than the corresponding distances in the unsubstituted PPP⁸⁻¹¹. A significant shortening of these bond distances in the substituted oligomers would have indicated more double bond character and increased electron delocalization. It should be noted that the contribution of the quinoid resonance structure is believed to increase upon doping of PPP³ with alkali metals. This is accompanied by a decrease in aromaticity and an increase in electron delocalization. Thus, it is not certain whether pendant-containing PPP could therefore be doped with alkali metal ions to produce better electronic conductors and/or NLO materials.

The bond angles are very close to the expected 120° value with the largest deviations in angles associated with connecting phenyl units. The oligomer axis of each molecule is essentially coaxial and small deviations are probably due to steric hindrance of the phenyl pendant groups. Deviations of the oligomer axis carbon atoms from the best least squares line fit, plotted in Figure 7, show that DPS is distorted the most of the three oligomers. When viewed down the chain axis, DPQ has a small sinusoidal-shaped wave perpendicular to the plane of the central ring, whereas TPB and DPS are bowed. The terminal phenyl ring of TPB (C13–C18) is 7° from being collinear with the oligomer axis. These contortions of the oligomer axis are shown in Figure 8.

In all three oligomers, the oligomer axis does not align with any of the crystallographic axes; however, the bond connecting the pendant to the oligomer aligns preferentially along (or nearly so) one of the crystallographic axes. In TPB the pendant-oligomer bond aligns close to

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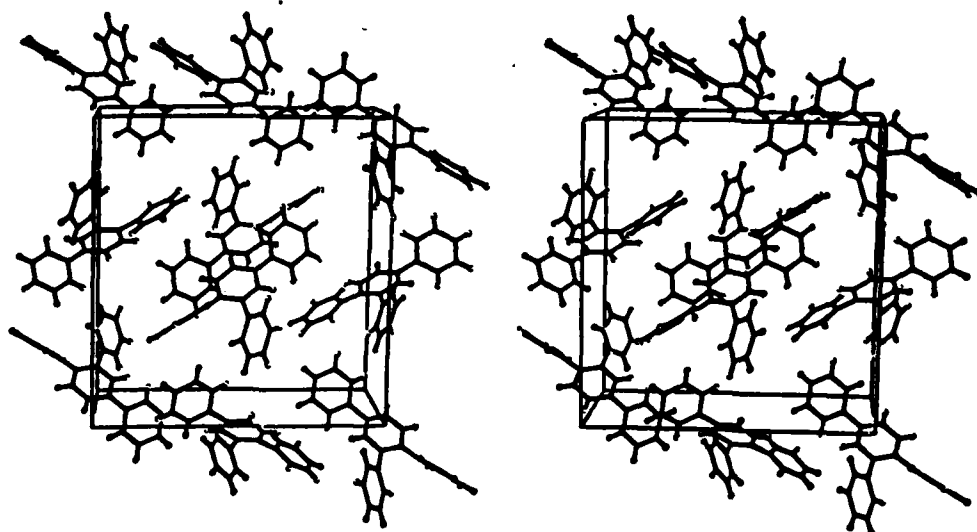


Figure 2 Stereo view of the partial contents of the unit cell of TPB. Selected molecules are omitted for clarity. The *b* axis is horizontal and the *c* axis is vertical

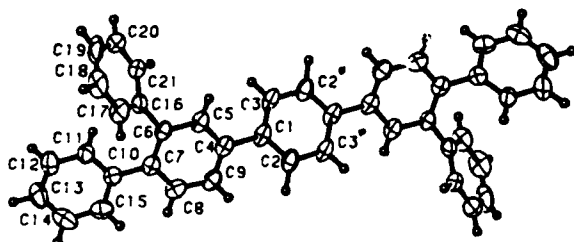


Figure 3 2,2',4,4'-Diphenyl-*p*-quinquephenyl with carbon atom ellipsoids drawn at the 50% probability level

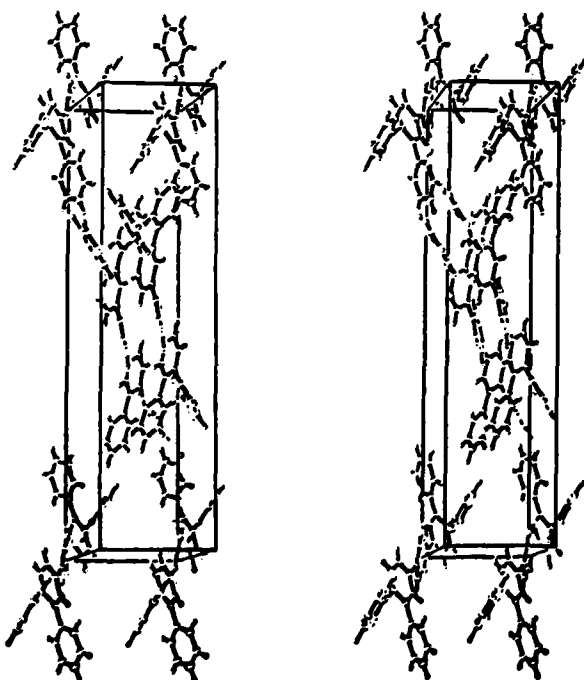


Figure 4 Stereo view of DPQ showing molecular packing in unit cell. Molecules positioned on front corners are omitted for clarity. The *c* axis is horizontal and the *b* axis is vertical

Table 4 Atomic positions of 2,2',4,4'-diphenyl-*p*-quinquephenyl. Numbers in parentheses are estimated standard deviations in the least significant digit

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
C1	0.8032(5)	0.0213(1)	0.9088(4)	3.68(7)
C2	1.1965(5)	0.0219(1)	1.0586(5)	4.48(8)
C3	1.0016(5)	0.0428(1)	0.9683(5)	4.40(8)
C4	0.5973(5)	0.0439(1)	0.8084(4)	3.67(7)
C5	0.5685(5)	0.0868(1)	0.8359(4)	3.79(7)
C6	0.3824(5)	0.1093(1)	0.7367(4)	3.42(7)
C7	0.2203(5)	0.0877(1)	0.6023(4)	3.67(7)
C8	0.2476(5)	0.0446(1)	0.5776(4)	4.25(8)
C9	0.4317(5)	0.0227(1)	0.6810(5)	4.22(8)
C10	0.0256(5)	0.1101(1)	0.4820(4)	3.66(7)
C11	0.0476(5)	0.1467(1)	0.3885(5)	4.51(8)
C12	-0.1353(6)	0.1669(1)	0.2777(5)	5.3(1)
C13	-0.3438(6)	0.1512(1)	0.2611(5)	5.4(1)
C14	-0.3688(6)	0.1145(1)	0.3490(5)	5.37(9)
C15	-0.1869(5)	0.0937(1)	0.4609(5)	4.48(8)
C16	0.3637(5)	0.1548(1)	0.7810(4)	3.83(8)
C17	0.1831(6)	0.1700(1)	0.8328(5)	4.92(9)
C18	0.1711(7)	0.2117(1)	0.8807(6)	6.2(1)
C19	0.3376(7)	0.2395(1)	0.8793(6)	6.6(1)
C20	0.5186(7)	0.2252(1)	0.8288(6)	6.0(1)
C21	0.5316(6)	0.1832(1)	0.7798(5)	4.70(9)
H2	0.665	-0.044	0.874	4.0
H3	1.004	0.073	0.947	5.2
H5	0.678	0.101	0.926	4.5
H8	0.138	0.030	0.488	5.5
H9	0.445	-0.007	0.663	5.5
H11	0.191	0.158	0.402	5.3
H12	-0.117	0.192	0.212	6.4
H13	-0.471	0.166	0.190	6.9
H14	-0.512	0.103	0.333	6.5
H15	-0.206	0.069	0.524	5.8
H17	0.066	0.151	0.835	6.0
H18	0.048	0.222	0.917	7.9
H19	0.330	0.268	0.914	8.2
H20	0.633	0.245	0.825	7.1
H21	0.657	0.173	0.746	5.6

a. while the pendant-oligomer bond in DPQ and DPS aligns approximately parallel to the *b* axis. In results to be published, *para*-quinquephenyl and *para*-sexiphenyl have their oligomer axes preferentially aligning with *b* (ref. 12). Thus, with the exception of TPB, the pendant-oligomer bond aligns with the longest crystallographic

Table 5 Bond distances and angles for 2²,4³-diphenyl-*p*-quinquephenyl. Numbers in parentheses are estimated standard deviations in the least significant digit

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
C1	C3	1.381(4)	C8	C9	1.388(4)
C1	C2	1.380(4)	C10	C11	1.382(5)
C2	C3*	1.392(4)	C10	C15	1.401(4)
C3	C2*	1.392(4)	C11	C12	1.379(4)
C1	C4	1.490(4)	C12	C13	1.379(4)
C4	C5	1.385(4)	C13	C14	1.367(6)
C4	C9	1.386(4)	C14	C15	1.387(5)
C5	C6	1.389(5)	C16	C17	1.390(5)
C6	C7	1.405(4)	C16	C21	1.385(5)
C6	C16	1.483(4)	C17	C18	1.367(5)
C7	C8	1.385(5)	C18	C19	1.367(6)
C7	C10	1.489(4)	C19	C20	1.377(6)
			C20	C21	1.382(5)

Atom 1	Atom 2	Atom 3	Angle (deg)	Atom 1	Atom 2	Atom 3	Angle (deg)
C2	C1	C3	117.1(4)	C4	C9	C8	120.5(3)
C1	C2	C3*	120.5(4)	C7	C10	C11	122.0(3)
C1	C3	C2*	121.7(4)	C7	C10	C15	119.5(4)
C2	C3*	C1*	121.7(4)	C11	C10	C15	118.5(3)
C3	C2*	C1*	120.5(4)	C10	C11	C12	120.9(3)
C3	C1	C4	121.0(4)	C11	C12	C13	120.3(4)
C1	C4	C5	121.2(3)	C12	C13	C14	119.7(4)
C1	C4	C9	120.9(3)	C13	C14	C15	120.9(4)
C5	C4	C9	118.1(3)	C10	C15	C14	119.8(4)
C4	C5	C6	122.4(4)	C6	C16	C17	121.5(4)
C5	C6	C7	118.8(4)	C6	C16	C21	120.7(3)
C5	C6	C16	118.1(3)	C17	C16	C21	117.9(3)
C7	C6	C16	123.0(3)	C16	C17	C18	121.1(5)
C6	C7	C8	118.7(4)	C17	C18	C19	120.7(4)
C6	C7	C10	122.1(3)	C18	C19	C20	119.4(4)
C8	C7	C10	119.4(4)	C19	C20	C21	120.3(4)
C7	C8	C9	121.6(3)	C16	C21	C20	120.7(4)

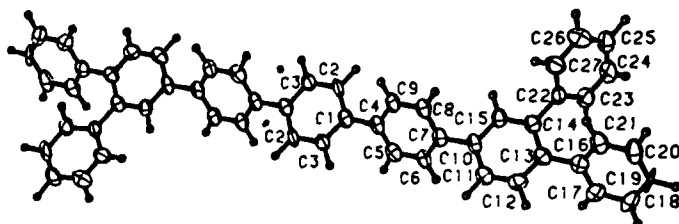
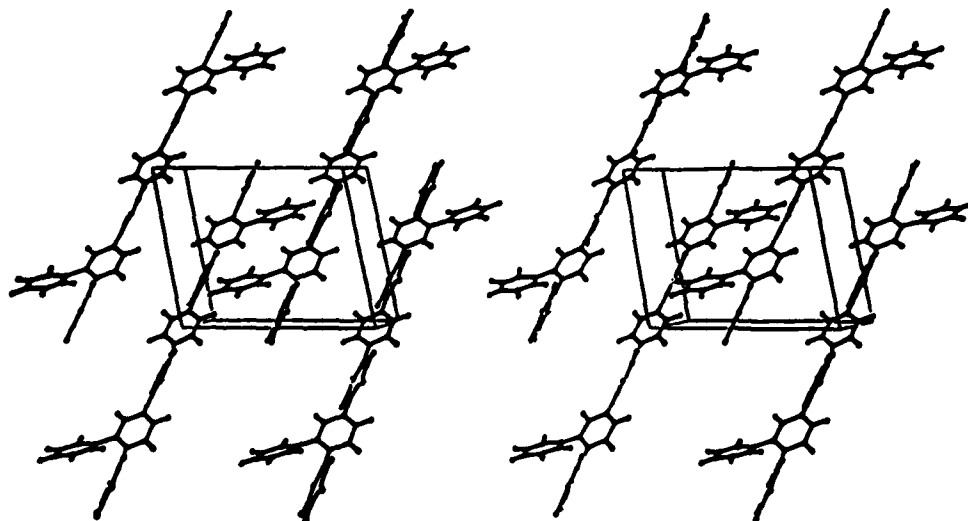
**Figure 5** 2²,6⁶-Diphenyl-*p*-septiphenyl with carbon atom ellipsoids drawn at the 50% probability level**Figure 6** The *c* axis stereo view of DPS showing molecular packing in unit cell. Molecules on rear corners are omitted for clarity. The *a* axis is horizontal

Table 6 Atomic positions of 2²,6⁵-diphenyl-*p*-septiphenyl. Numbers in parentheses are estimated standard deviations in the least significant digit

Atom	x	y	z	B (Å ²)	Atom	x	y	z	B (Å ²)
C1	0.5955(2)	0.5334(2)	0.3887(5)	3.77(6)	C24	1.1891(3)	1.0774(2)	-0.2842(6)	5.77(9)
C2	0.5515(3)	0.6040(2)	0.5322(5)	4.39(7)	C25	1.2395(3)	1.1418(2)	-0.0761(6)	5.46(8)
C3	0.5417(3)	0.4279(2)	0.3591(5)	4.35(7)	C26	1.2498(3)	1.1055(2)	0.1086(6)	5.63(9)
C4	0.6961(2)	0.5681(2)	0.2739(4)	3.68(6)	C27	1.2106(3)	0.9936(2)	0.0831(5)	4.86(8)
C5	0.6946(2)	0.5225(2)	0.0484(5)	4.14(7)	H2	0.584	0.686	0.542	4.0
C6	0.7882(2)	0.5537(2)	-0.0607(5)	4.02(7)	H3	0.581	0.376	0.252	4.0
C7	0.8867(2)	0.6335(2)	0.0543(4)	3.64(6)	H5	0.616	0.461	-0.056	5.3
C8	0.8885(2)	0.6795(2)	0.2815(5)	4.00(7)	H6	0.780	0.520	-0.236	5.1
C9	0.7949(2)	0.6472(2)	0.3898(5)	3.96(7)	H8	0.965	0.737	0.377	5.1
C10	0.9859(2)	0.6701(2)	-0.0632(4)	3.72(6)	H9	0.801	0.681	0.560	5.0
C11	1.0330(2)	0.6003(2)	-0.2050(5)	4.10(7)	H11	0.999	0.519	-0.223	5.3
C12	1.1240(2)	0.6361(2)	-0.3156(5)	4.02(7)	H12	1.164	0.586	-0.415	5.3
C13	1.1701(2)	0.7422(2)	-0.2927(5)	3.71(6)	H15	1.001	0.828	0.064	4.8
C14	1.1220(2)	0.8133(2)	-0.1541(4)	3.64(6)	H17	1.188	0.679	-0.719	5.7
C15	1.0324(2)	0.7763(2)	-0.0412(5)	3.79(6)	H18	1.337	0.717	-0.932	7.4
C16	1.2689(2)	0.7753(2)	-0.4146(5)	3.87(6)	H19	1.520	0.852	-0.735	7.6
C17	1.2621(3)	0.7288(2)	-0.6430(5)	4.42(7)	H20	1.536	0.938	-0.309	7.2
C18	1.3543(3)	0.7581(2)	-0.7584(5)	5.70(8)	H21	1.378	0.882	-0.126	6.0
C19	1.4544(3)	0.8336(2)	-0.6477(6)	6.00(9)	H23	1.105	0.920	-0.476	6.0
C20	1.4637(3)	0.8798(2)	-0.4215(6)	5.67(9)	H24	1.172	1.102	-0.430	7.4
C21	1.3727(2)	0.8515(2)	-0.3039(5)	4.57(7)	H25	1.274	1.230	-0.048	6.8
C22	1.1624(2)	0.9279(2)	-0.1274(5)	3.77(6)	H26	1.291	1.148	0.283	7.1
C23	1.1510(3)	0.9711(2)	-0.3105(5)	4.89(8)	H27	1.221	0.967	0.224	6.1

Table 7 Bond distances and angles for 2²,6⁵-diphenyl-*p*-septiphenyl. Numbers in parentheses are estimated standard deviations in the least significant digit

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
C1	C2	1.387(4)	C13	C14	1.404(4)
C1	C3	1.397(3)	C13	C16	1.487(5)
C2	C3*	1.380(4)	C14	C15	1.384(4)
C3	C2*	1.380(4)	C14	C22	1.493(3)
C1	C4	1.481(4)	C16	C17	1.395(4)
C4	C5	1.387(4)	C16	C21	1.404(3)
C4	C9	1.393(4)	C17	C18	1.390(5)
C5	C6	1.383(4)	C18	C19	1.372(4)
C6	C7	1.394(4)	C19	C20	1.378(5)
C7	C8	1.397(4)	C20	C21	1.384(5)
C7	C10	1.486(4)	C22	C23	1.382(4)
C8	C9	1.384(4)	C22	C27	1.380(4)
C10	C11	1.395(4)	C23	C24	1.384(4)
C10	C15	1.399(3)	C24	C25	1.386(4)
C11	C12	1.382(5)	C25	C26	1.374(5)
C12	C13	1.395(4)	C26	C27	1.393(4)

Atom 1	Atom 2	Atom 3	Angle (deg)	Atom 1	Atom 2	Atom 3	Angle (deg)
C2	C1	C3	117.1(3)	C12	C13	C14	118.7(3)
C2	C1	C4	121.5(2)	C12	C13	C16	118.6(2)
C3	C1	C4	121.4(2)	C14	C13	C16	122.8(2)
C1	C4	C5	120.9(2)	C13	C14	C15	119.3(2)
C1	C2	C3*	121.8(2)	C13	C14	C22	122.2(2)
C1	C3	C2*	121.1(2)	C15	C14	C22	118.5(2)
C2	C3*	C1*	121.1(2)	C10	C15	C14	122.4(3)
C3	C2*	C1*	121.8(2)	C13	C16	C17	120.5(3)
C1	C4	C9	120.9(2)	C13	C16	C21	121.6(2)
C5	C4	C9	118.2(3)	C17	C16	C21	117.8(3)
C4	C5	C6	121.5(2)	C16	C17	C18	121.1(2)
C5	C6	C7	120.3(2)	C17	C18	C19	120.1(3)
C6	C7	C8	118.2(3)	C18	C19	C20	119.9(3)
C6	C7	C10	120.8(2)	C19	C20	C21	120.8(2)
C8	C7	C10	121.0(2)	C16	C21	C20	120.3(3)
C7	C8	C9	121.1(3)	C14	C22	C23	121.2(2)
C4	C9	C8	120.6(2)	C14	C22	C27	120.4(3)
C7	C10	C11	121.6(2)	C23	C22	C27	118.4(2)
C7	C10	C15	120.7(2)	C22	C23	C24	120.9(2)
C11	C10	C15	117.7(3)	C23	C24	C25	120.5(3)
C10	C11	C12	120.6(2)	C24	C25	C26	119.5(3)
C11	C12	C13	121.4(3)	C25	C26	C27	120.1(3)
				C22	C27	C26	120.6(4)

Table 8 Summary of bond lengths between phenyl units measured at room temperature. Nomenclature of the phenyl links is relative to the centre of symmetry in the molecule such that the phenyl link is that bond which lies on the symmetry centre or the nearest phenyl link if the symmetry centre exists at a phenyl unit (see general structure). Numbers in parentheses are estimated standard deviations in the least significant digit. P means planar conformation and N means non-planar conformation

Compound name	A (Å)	B (Å)	C (Å)	π (Å)	Conformation
Biphenyl ⁹	1.495(5)	—	—	—	P
<i>p</i> -Terphenyl ¹⁰	1.505(5)	—	—	—	P
<i>p</i> -Quaterphenyl ¹¹	1.502(4)	1.486(5)	—	—	P
<i>p</i> -Quinquephenyl ¹²	1.481(5)	1.482(5)	—	—	P
<i>p</i> -Sexiphenyl ¹²	1.506(6)	1.501(8)	1.461(8)	—	P
1,2,4-Triphenyl-benzene	1.486(2)	1.489(2)	—	1.489(2)	N
2 ² ,4 ⁵ -Diphenyl- <i>p</i> -quinquephenyl	1.490(4)	1.489(4)	—	1.483(4)	N
2 ² ,6 ⁵ -Diphenyl- <i>p</i> -septiphenyl	1.481(4)	1.486(4)	1.487(5)	1.493(3)	N

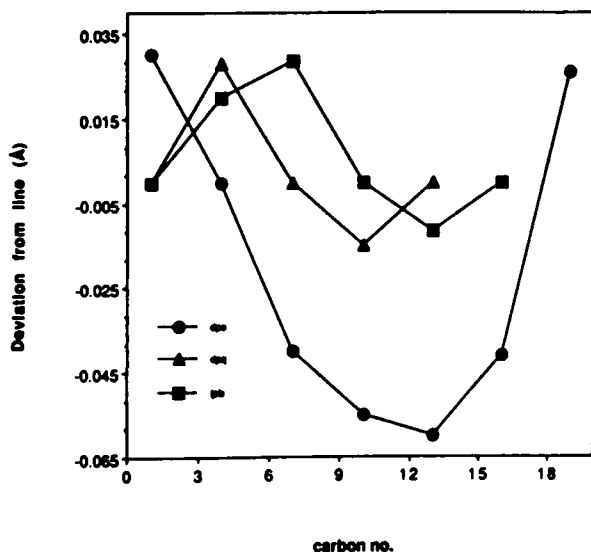


Figure 7 Deviation of the carbon atoms composing the oligomer axis from least squares line

axis. The short chain axis of TPB and lack of molecular symmetry appear to play an important role in this alignment.

The addition of the phenyl pendant groups disrupts the planarity of the polyphenyls observed in the room temperature structures of biphenyl¹³, *para*-terphenyl¹⁴, *para*-quaterphenyl¹¹, *para*-quinquephenyl and *para*-sexiphenyl¹², as seen in Tables 9 and 10. This is most probably due to steric hindrance of the pendant groups with the oligomer chain and crystal packing forces. Hydrogen-to-hydrogen distances between phenyl rings (H2-H9 in DPS, for example) are approximately equal to 2.5 Å. Hydrogen atoms on the terminal phenyl ring closest to the pendant group are approximately equidistant from one of the *ortho* hydrogen atoms on the pendant group. In DPQ, for example, H11 and H15 on the terminal phenyl ring are both approximately 3.6 Å from H17 on the pendant ring (see Figure 9). The corresponding values in DPS are 3.7 Å. For the three pendant-substituted oligomers, the pendant hydrogen atom-to-terminal phenyl hydrogen atom contact increases with oligomer length (from approximately 3.5 Å in TPB to 3.7 Å in DPS).

The average torsion angle within the oligomer chain

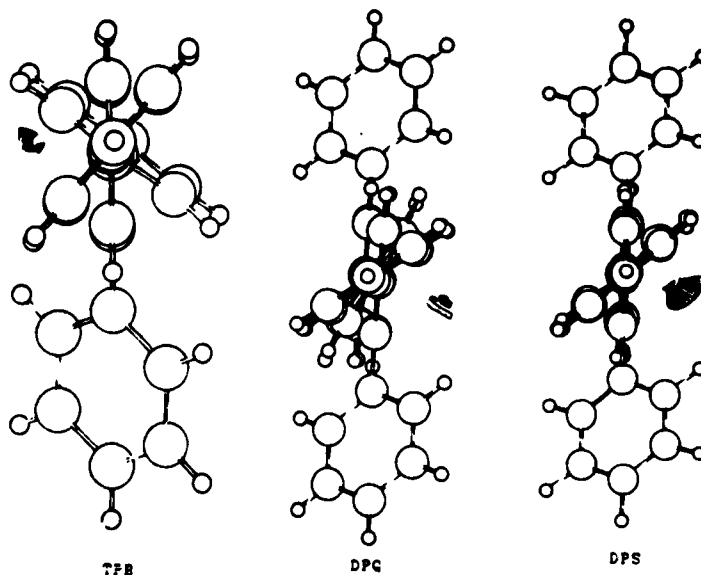


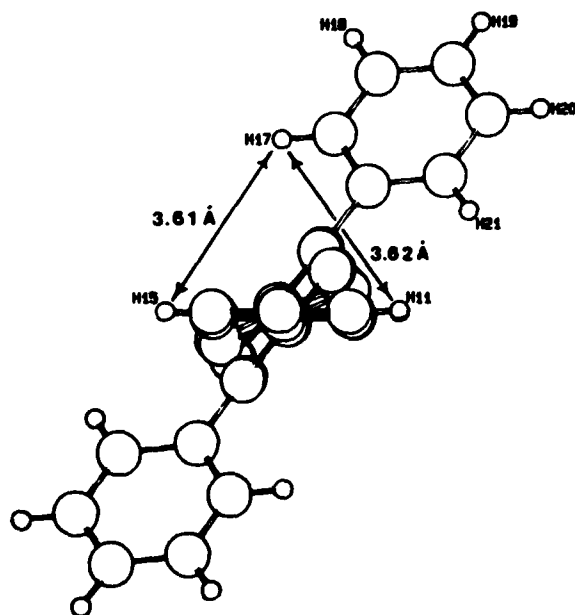
Figure 8 View down oligomer axes of TPB, DPQ, and DPS showing tortuosity of axis

Table 9 Torsion angles of straight chain polyphenyls. The torsion angles are labelled relative to the symmetry centre of the molecule such that if a symmetry centre exists on the bond connecting two phenyl units the torsion angle refers to the two adjacent rings. If a centre of symmetry exists in a phenyl unit the torsion angle refers to the nearest chain link (see general structure)

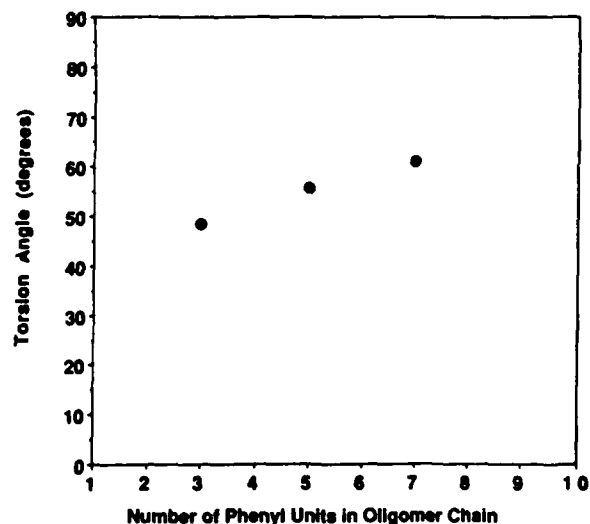
Name	Formula	Temperature (K)	ψ_1 (deg)	ψ_2 (deg)	ψ_3 (deg)
Biphenyl	$C_{12}H_{10}$	298 ¹³	0	-	-
		40 ⁹	10	-	-
<i>p</i> -Terphenyl	$C_{18}H_{14}$	298 ¹⁴	0	-	-
		110 ¹⁵	16	-	-
<i>p</i> -Quaterphenyl	$C_{24}H_{18}$	298 ¹¹	0	0	-
		110 ¹⁶	17.1	22.7	-
<i>p</i> -Quinquephenyl	$C_{30}H_{22}$	298 ¹²	0	0	-
		110	Work in progress	0	-
<i>p</i> -Sexiphenyl	$C_{36}H_{26}$	298 ¹²	0	0	0
		110	Work in progress		
<i>p</i> -Septiphenyl	$C_{42}H_{30}$	298	Work in progress		
		110	Work in progress		

Table 10 Torsion angles of pendant polyphenyls. The torsion angles are labelled relative to the symmetry centre of the molecule such that if a symmetry centre exists on the bond connecting two phenyl units the torsion angle refers to the two adjacent rings. If a centre of symmetry exists in a phenyl unit the torsion angle refers to the nearest chain link. Pendant refers to the torsion angle between the pendant group and the phenyl group to which it is attached (see general structure)

Name	Formula	Temperature (K)	ψ_1 (deg)	ψ_2 (deg)	ψ_3 (deg)	π (deg)
1,2,4-Triphenyl-benzene	$C_{24}H_{18}$	298	42.8	49.8	-	48.4
		110	Work in progress			
2 ² ,3 ⁵ -Diphenyl- <i>p</i> -quaterphenyl	$C_{36}H_{26}$	298	Work in progress			
		110	Work in progress			
2 ² ,4 ⁵ -Diphenyl- <i>p</i> -quinquephenyl	$C_{42}H_{30}$	298	-28.0	51.2	-	55.7
		110	Work in progress			
2 ² ,5 ⁵ -Diphenyl- <i>p</i> -sexiphenyl	$C_{48}H_{34}$	298	Work in progress			
		110	Work in progress			
2 ² ,6 ⁵ -Diphenyl- <i>p</i> -septiphenyl	$C_{54}H_{38}$	298	43.2	-45.6	48.6	61.0
		110	Work in progress			

**Figure 9** Hydrogen atom repulsion distances between pendant and oligomer axis for 2²,4⁵-diphenyl-*p*-quinquephenyl

is 45°, which is approximately twice the value of 23° predicted for PPP from structural data and further supported by *ab initio* quality quantum mechanical calculations³. The exception is DPQ which has torsion angles of approximately -28° at the centre ring, but angles of 51° for the terminal ring. The reason for this

**Figure 10** Graph of pendant torsion angle vs. total number of phenyl units in oligomer chain

large difference unique to this oligomer is not clear at this time.

The torsion angle between the pendant group and the oligomer chain is greater than 45°, increasing with chain length. As the hydrogen atoms of the main chain approach the hydrogen atoms of the pendant group, the pendant torsion angle decreases. This trend is not yet understood and more measurements on different model systems are under consideration. Fully-optimized

AMPAC AM1 conformational calculations for the low energy structure of *ortho*-phenyl-substituted biphenyl reveal torsion angles of approximately 40° (ref. 17). A line with a positive slope is obtained when the pendant torsion angle is plotted against the number of phenyl units in the oligomer chain (see Figure 10).

CONCLUSIONS

The non-planar structures of the phenyl-substituted oligomers contrast with average planar structures observed for the unsubstituted polyphenyls. The average torsion angle along the oligomer chain is 45° . The oligomer axis does not align with a crystallographic axis; however, the pendant connect bond prefers to align parallel to one of the crystallographic axes. The pendant torsion angle increases with chain length. More research is needed on oligomers with even numbers of phenyl units along the main chain to compare and contrast with those which have an odd number. Also the pendant groups of the title compounds occupy positions closest to the terminal phenyl unit. Similar measurements of compounds where the pendant group is attached closest to the central phenyl unit are needed to identify the major reasons for variations in the torsion angles along the oligomer axis.

ACKNOWLEDGEMENTS

Research was sponsored in part by the Air Force Office of Scientific Research, Air Force Systems Command, AFSC, under Grant Number AFOSR-88-0044. Further acknowledgements go to Timothy Resch for X-ray photography and density measurements and to Edward Soloski for d.s.c. analysis.

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