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Model Compounds for Rigid-Rod Aromatic Heterocyclic Polymers. 1. X-ray Structures of 2,6-Diphenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole and 2,6-Diphenylbenzo[1,2-*d*:5,4-*d*′]bisthiazole

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ABSTRACT: The determination of the conformation of molecular chains and modes of packing of poly(*p*-phenylenebenzobisthiazole) (PBT) is assisted by the X-ray crystallographic analysis of two model compounds. Molecules of 2,6-diphenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole are packed in a monoclinic crystal system, space group $P2_1/c$, with a = 11.041 (3) Å, b = 6.633 (2) Å, c = 11.720 (3) Å, β = 112.36 (5)°, and Z = 2. The twist angle between the phenyl substituent and the benzobisthiazole segment is 23.2°. The length of the repeat unit, as measured by the C(8) to C(5′) separation, is 12.47 Å. Molecules of 2,6-diphenylbenzo[1,2-*d*:5,4-*d*′]bisthiazole exhibit slight distortions from planarity and are packed in an orthorhombic lattice, space group $Pca2_1$, with a = 24.223 (42) Å, b = 5.827 (6) Å, c = 22.903 (36) Å, and Z = 8. The length of the repeat unit, as measured by the C(14) to C(21) separation, is 12.35 Å. The calculated crystal densities are 1.44 g/cm^3 and 1.42 g/cm^3, respectively.

Introduction

Poly(*p*-phenylenebenzobisthiazole) (PBT) belongs to the class of rigid-rod aromatic heterocyclic polymers capable of being processed into fibers and films which exhibit high modulus and strength and high thermal stability. In corrosive acid solvents, such as methanesulfonic acid, PBT forms stable nematic solutions indicative of a high degree of molecular order.[1] Films can be prepared by casting or coagulation techniques, and spinning of the anisotropic dope followed by coagulation and neutralization can produce fibers.

Morphological and microstructural studies of PBT have recently been carried out by using laser Raman and FT IR spectroscopy, X-ray and electron diffraction, electron microscopy, and birefringence measurements.[2] X-ray structures of two crystalline model compounds, 2,6-diphenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole (hereafter referred to as t-bisthiazole) and 2,6-diphenylbenzo[1,2-*d*:5,4-*d*′]bisthiazole (referred to as c-bisthiazole), are now presented in an attempt to complement and corroborate the results of the microstructural studies. The crystallographic analyses also afford accurate molecular parameters for the PBT repeat unit for use in conformational and energy minimization calculations.[3]

Experimental Section

Materials. Crystals of t-bisthiazole and c-bisthiazole were grown by vacuum sublimation at 200 °C from material synthesized by Dr. J. F. Wolfe of SRI International, Menlo Park, California.[4] Crystals grew as colorless needles elongated along *b*, and the best crystals were obtained from material that had been previously sublimed.

Methods. Weissenberg and precession photographs showed t-bisthiazole to be monoclinic, $P2_1/c$, and c-bisthiazole to be orthorhombic, $Pbcm$ or $Pca2_1$. Acentric $Pca2_1$ was later selected as the correct space group for c-bisthiazole on the basis of the distribution of normalized structure factors.

Data collection was carried out on a Picker FACS-1 diffractometer employing Nb-filtered Mo Kα (0.71069 Å) radiation. Single crystals of volume 0.0553 mm^3 for t-bisthiazole and 0.0464 mm^3 for c-bisthiazole were mounted with their needle axes coincident with the goniostat axis. Unit cell dimensions were determined by least-squares refinement of the angular settings of 15 Friedel pairs ($34° < 2\theta < 49°$ for t-bisthiazole and $20° < 2\theta < 34°$ for c-bisthiazole). Intensities were measured at 21 °C, using the θ–2θ scan mode; the scan speeds were 1°/min for reflections with $2\theta < 50°$ and 0.5°/min for reflections in the range $50° < 2\theta < 65°$. Background count times were approximately one-half peak scan times. Three standard reflections were measured periodically and no significant change in their intensities was noted. For t-bisthiazole, a total of 7653 intensities were recorded, yielding 2868 independent reflections; the corresponding values for c-bisthiazole were 9445 and 5972. Corrections for Lorentz and polarization effects were applied and variances $\sigma(F)$ assigned on the basis of counting statistics, using the method of Miller, Lenhert, and Joesten.[5] Absorption corrections were calculated with the Oak Ridge absorption program ORABS.[6] The transmission factors ranged from 0.886 to 0.959, with an average of 0.937, for t-bisthiazole, and from 0.919 to 0.957, with an average of 0.944, for c-bisthiazole. The pertinent crystal data are summarized in Table I.

The structure was solved by the direct phasing method employing the XRAY 72 system.[7] For t-bisthiazole, the NORMSF, SINGEN and PHASE subprograms assigned the phases of 395 reflections with $|E| > 1.4$. For c-bisthiazole, three origin-fixing reflections [850, 0; 14,6,1, 0; 580, 0], an enantiomorphic-defining reflection [14,8,0, π], and one arbitrary phase reflection [8,1,10, $+\pi/2$] produced a starting set of 15 reflections with APHASE. These reflections then generated the phases of 656 reflections with $|E| > 1.5$ upon application of the tangent formula refinement procedure contained within TANGEN. The corresponding E maps revealed the location of all nonhydrogen atoms. Hydrogens were found in subsequent difference syntheses.

Atomic coordinates and anisotropic thermal parameters (isotropic for hydrogen) were refined by least-squares, using weights $w = 1/\sigma^2(F)$. The hydrogens in c-bisthiazole were assigned fixed isotropic U values of 0.06 Å^2. Atomic scattering factors for C, N, and S were taken from Cromer and Mann,[8] and those for hydrogen were from Stewart, Davidson, and Simpson.[9] The final R values were 0.053 for t-bisthiazole (based on 2468 reflections) and 0.071 for c-bisthiazole (based on 4492 reflections), all reflections having $F_o > 2\sigma(F_o)$. The average shift/error ratio in atom parameters on the last cycle was 0.002 for t-bisthiazole and 0.20 for c-bisthiazole. Final difference maps showed no peaks of structural significance. The final atom positions are presented in Table II.

Results and Discussion

Perspective views of the molecules, with their atom numbering schemes, are presented in Figures 1 and 2. The two molecules in the asymmetric unit of c-bisthiazole are

Table I
Crystal Data of t-Bisthiazole and c-Bisthiazole

	t-bisthiazole	c-bisthiazole
formula	$C_{20}H_{12}S_2N_2$	$C_{20}H_{12}S_2N_2$
formula weight	344.5	344.5
a, Å	11.041 (3)	24.223 (42)
b, Å	6.633 (2)	5.827 (6)
c, Å	11.720 (3)	22.903 (36)
β, deg	112.36 (5)	90.00
V, Å^3	793.8	3232.9
space group	$P2_1/c$	$Pca2_1$
Z, molecules per cell	2	8
μ(Mo Kα), cm^{-1}	3.32	3.26
D_{measd}, g·cm^{-3}	1.43 (aqueous CsCl)	1.42 (dichloromethane-chloroform mixture)
D_{calcd}, g·cm^{-3}	1.44	1.42

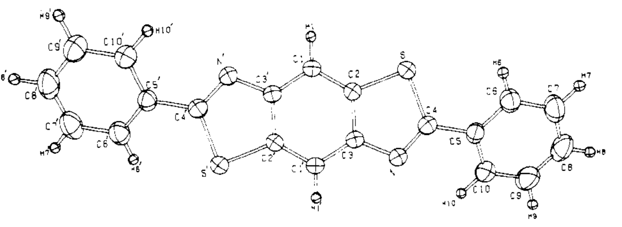

Figure 1. Perspective view of t-bisthiazole.

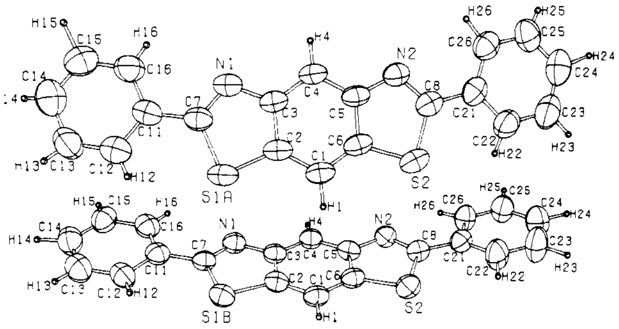

Figure 2. Perspective view of molecule A (top) and molecule B (bottom) of c-bisthiazole.

referred to as molecules A and B. The most significant bond distances and angles are summarized in Table III. Crystal packing diagrams are given in Figures 3–5.

t-Bisthiazole. The molecular structure is best described in terms of a centrosymmetric molecule consisting of two planar segments—the benzobisthiazole framework and the substituent phenyl rings—which are twisted from coplanarity by 23.2°. A completely planar molecule is sterically unfavorable on account of the expected close S···H(6) and N···H(10) intramolecular contacts. The values found for these contacts are 2.75 and 2.60 Å, respectively. The twist angles of ring systems bonded to the thiazole moiety show a wide variation but are usually less than 20°; e.g., 10° in thiabendazole,[10] 19° in 2-amino-4-phenylthiazole hydrobromide monohydrate,[11] and 1.5° in 5-benzyl-2-phenyl-4-tolylthiazole.[12] In cases where steric interference is an important factor, the angle can be as high as 36°, as in [2-phenyl-4-(*p*-chlorophenyl)-5-thiazolyl]acetic acid.[13]

A consideration of the bonds of the thiazole ring, as well as the C(4)–C(5) bond, attests to the delocalization of π-electron density throughout the benzobisthiazole moiety. According to the rather convincing arguments of Bart et. al.,[12] the two S–C distances of 1.736 (2) and 1.758 (2) Å are indicative of considerable S–C(sp^2) double-bond character. Matthews has reported a S–C(sp^2) single-bond distance of 1.813 Å, which is consistent with the value of 1.78 Å estimated from covalent radii for S and trigonal C.[14]. The endocyclic bond angles about S and N, 88.9 (1) and 110.8 (1)°, are in agreement with literature values, e.g., 89.3 and 111.8° in bis(benzothiazole-2-thiolato)bis(pyridine)cobalt(II),[15] 90.1 and 111.4° in the thiazole-substituted acetic acid,[13] and 89.3 and 109.9° in 2-amino-4,5-dihydro-7,8-dimethoxynaphtho[1,2-*d*]thiazole.[16]

Molecules of t-bisthiazole stack most efficiently along *b*. The repeat distance, which also corresponds to the distance between adjacent molecular centers, is the same as the *b*-axis length, 6.63 Å. The perpendicular separation of nearest bisthiazole segments is 3.74 Å. The *c*-glide plane generates two columns of molecules of different orientation but inclined to *b* by the same angle, 36.8°, as depicted in Figure 3. Although $\bar{1}$ symmetry requires bonds C(4)–C(5) and C(4′)–C(5′) to be parallel, they are displaced from collinearity by 0.6 Å.

c-Bisthiazole. The benzobisthiazole moieties in molecules A and B assume a slightly bowed conformation, in contrast to the planar arrangement found in t-bisthiazole. The bowing is a result of the planar thiazole rings being inclined in the same direction from the best plane through the atoms of the fused benzene ring by an average of 2.6°. The bowing is more pronounced if one considers the average inclination angle of 4.7° between the bonds connecting the end phenyls to the benzobisthiazoles, C(8)–

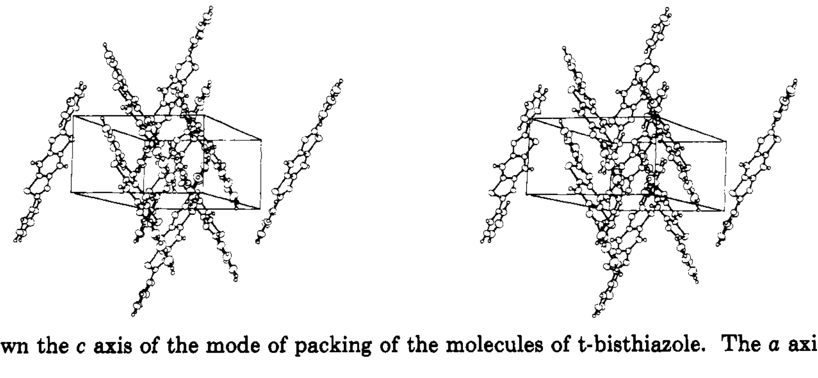

Figure 3. Stereoview down the *c* axis of the mode of packing of the molecules of t-bisthiazole. The *a* axis is horizontal and the *b* axis is vertical.

Table II
Final Fractional Coordinates with Esd's in Parentheses

t-BISTHIAZOLE

Atom	x	y	z	Atom	x	y	z
C(1)	0.49420(13)	0.02454(24)	0.11905(13)	S	0.34010(4)	0.36837(6)	0.02428(3)
C(2)	0.43260(13)	0.15676(22)	0.02413(12)	N	0.36994(11)	0.28036(19)	-.17986(10)
C(3)	0.43775(13)	0.13501(23)	-.09461(12)	H(1)	0.4888(11)	0.0400(19)	0.1969(11)
C(4)	0.31570(13)	0.40881(22)	-.13120(12)	H(6)	0.2541(13)	0.7521(23)	-.0533(13)
C(5)	0.23489(14)	0.57883(23)	-.19894(14)	H(7)	0.1244(14)	1.0178(27)	-.1605(14)
C(6)	0.21428(16)	0.74636(27)	-.13836(16)	H(8)	0.0187(16)	0.9927(28)	-.3732(15)
C(7)	0.13492(18)	0.90239(29)	-.20417(21)	H(9)	0.0533(15)	0.7156(27)	-.4821(16)
C(8)	0.07531(19)	0.89067(33)	-.33010(21)	H(10)	0.1902(15)	0.4468(24)	-.3707(14)
C(9)	0.09560(18)	0.72482(33)	-.39139(18)				
C(10)	0.17570(17)	0.57003(28)	-.32706(15)				

c-BISTHIAZOLE

MOLECULE A				MOLECULE B			
S(1)	0.2604(1)	-.0205(1)	.3033	S(1)	0.3217(1)	-.4911(2)	0.2198(1)
S(2)	0.4404(1)	0.0851(2)	0.4558(1)	S(2)	0.5038(1)	-.4252(1)	0.3709(1)
N(1)	0.2332(1)	0.3777(4)	0.3466(1)	N(1)	0.3577(1)	-.0939(4)	0.1855(1)
N(2)	0.3908(1)	0.4709(5)	0.4800(1)	N(2)	0.5163(1)	-.0334(4)	0.3173(1)
C(1)	0.3508(2)	0.0054(6)	0.3800(2)	C(1)	0.4131(1)	-.4846(6)	0.2952(2)
C(2)	0.3025(1)	0.0961(6)	0.3573(2)	C(2)	0.3816(1)	-.3870(6)	0.2521(2)
C(3)	0.2809(1)	0.3102(5)	0.3746(2)	C(3)	0.3945(1)	-.1709(6)	0.2272(1)
C(4)	0.3082(2)	0.4376(6)	0.4180(2)	C(4)	0.4402(2)	-.0480(6)	0.2475(2)
C(5)	0.3573(1)	0.3555(6)	0.4395(2)	C(5)	0.4714(1)	-.1427(5)	0.2912(2)
C(6)	0.3778(1)	0.1380(6)	0.4210(2)	C(6)	0.4576(1)	-.3579(6)	0.3150(2)
C(7)	0.2182(1)	0.2257(6)	0.3077(2)	C(7)	0.3179(1)	-.2400(6)	0.1770(2)
C(8)	0.4351(2)	0.3511(6)	0.4917(2)	C(8)	0.5365(1)	-.1581(6)	0.3593(1)
C(11)	0.1707(2)	0.2532(6)	0.2679(2)	C(11)	0.2713(1)	-.2034(6)	0.1377(2)
C(12)	0.1558(2)	0.0846(7)	0.2276(2)	C(12)	0.2310(2)	-.3642(6)	0.1288(2)
C(13)	0.1108(2)	0.1194(9)	0.1920(2)	C(13)	0.1882(2)	-.3283(8)	0.0911(2)
C(14)	0.0802(2)	0.3182(9)	0.1958(2)	C(14)	0.1849(2)	-.1274(8)	0.0607(2)
C(15)	0.0943(2)	0.4874(8)	0.2351(2)	C(15)	0.2241(2)	0.0434(7)	0.0695(2)
C(16)	0.1401(2)	0.4516(7)	0.2701(2)	C(16)	0.2670(2)	0.0043(7)	0.1074(2)
C(21)	0.4791(2)	0.4293(7)	0.5304(2)	C(21)	0.5835(1)	-.0884(7)	0.3958(2)
C(22)	0.5284(2)	0.3130(7)	0.5370(2)	C(22)	0.6015(2)	-.2179(7)	0.4426(2)
C(23)	0.5699(2)	0.3892(9)	0.5743(2)	C(23)	0.6461(2)	-.1427(9)	0.4753(2)
C(24)	0.5626(2)	0.5883(9)	0.6039(2)	C(24)	0.6722(2)	0.0566(8)	0.4616(2)
C(25)	0.5146(2)	0.7095(8)	0.5973(2)	C(25)	0.6545(2)	0.1866(7)	0.4164(2)
C(26)	0.4728(2)	0.6344(7)	0.5619(2)	C(26)	0.6101(2)	0.1135(7)	0.3839(2)
H(1)	0.3653(10)	-.1347(45)	0.3667(12)	H(1)	0.4067(11)	-.6217(46)	0.3132(13)
H(4)	0.2911(11)	0.5879(47)	0.4311(12)	H(4)	0.4465(11)	0.0903(47)	0.2292(12)
H(12)	0.1728(11)	-.0482(48)	0.2260(12)	H(12)	0.2326(11)	-.4940(43)	0.1514(12)
H(13)	0.0942(11)	0.0111(48)	0.1701(13)	H(13)	0.1632(11)	-.4138(47)	0.0833(13)
H(14)	0.0463(11)	0.3228(44)	0.1694(13)	H(14)	0.1517(11)	-.1271(46)	0.0325(13)
H(15)	0.0718(11)	0.5891(46)	0.2404(12)	H(15)	0.2266(10)	0.1790(45)	0.0481(13)
H(16)	0.1519(10)	0.5661(44)	0.2976(12)	H(16)	0.2941(11)	0.1379(46)	0.1107(13)
H(22)	0.5322(11)	0.1728(47)	0.5119(12)	H(22)	0.5849(11)	-.3656(48)	0.4542(13)
H(23)	0.6070(11)	0.3418(48)	0.5732(13)	H(23)	0.6593(11)	-.2485(45)	0.5098(12)
H(24)	0.5955(11)	0.6660(46)	0.6302(12)	H(24)	0.7058(11)	0.1188(46)	0.4871(13)
H(25)	0.5115(11)	0.8482(48)	0.6200(13)	H(25)	0.6733(11)	0.3184(45)	0.4064(13)
H(26)	0.4356(10)	0.7173(46)	0.5590(13)	H(26)	0.5972(11)	0.2068(45)	0.3463(12)

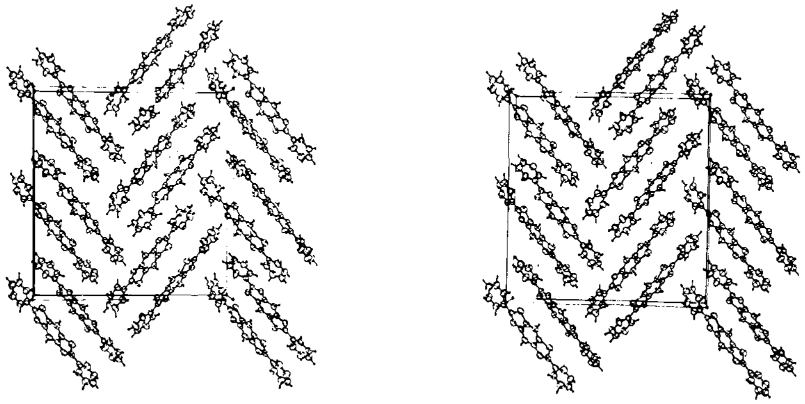

Figure 4. Stereoview of the mode of packing of the molecules of c-bisthiazole viewed down the *b* axis. The *c* axis is horizontal and the *a* axis is vertical.

C(21) and C(7)–C(11), and the best plane through each benzobisthiazole framework. The benzene rings of the benzobisthiazole moieties are only approximately planar; C(4) exhibits the largest deviation of 0.02 Å in molecule A, and C(1) has the largest deviation, 0.01 Å, in molecule B. Least-squares planes through the atoms of the benzobisthiazole moieties make a dihedral angle of 53.4°, as is seen in Figure 2.

The torsion angles about C(8)–C(21) and C(7)–C(11) range from 2.8 to 5.8° and are not expected to be greatly influenced by the S···H(ortho) (2.62–2.77 Å) and N···H-(ortho) (2.50–2.67 Å) intramolecular contacts. Thus, co-

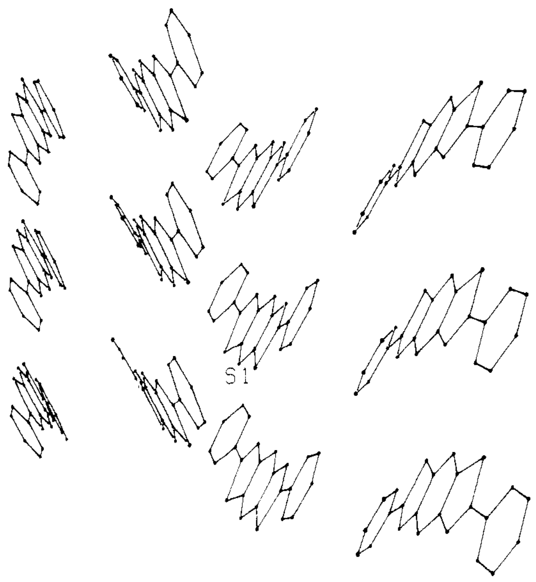

Figure 5. Edgewise view of the molecules of c-bisthiazole showing the bowing and curvature in the molecules.

Table III
Selected Bond Distances (Å) and Bond Angles (Deg) for t-Bisthiazole and c-Bisthiazole

t-Bisthiazole		c-Bisthiazole		
S-C2	1.736(2)		Molecule A	Molecule B
S-C4	1.758(2)	S1-C2	1.741(4)	1.737(4)
N-C3	1.385(2)	S1-C7	1.764(4)	1.764(4)
N-C4	1.292(2)	S2-C6	1.742(4)	1.745(4)
C1-C2	1.376(2)	S2-C8	1.759(4)	1.767(4)
C1-C3'	1.389(2)	N1-C3	1.380(5)	1.382(5)
C1-H1	0.94(1)	N1-C7	1.307(5)	1.302(5)
C2-C3	1.422(2)	N2-C5	1.406(5)	1.396(5)
C4-C5	1.469(2)	N2-C8	1.306(5)	1.301(4)
C5-C6	1.383(3)	C1-C2	1.384(6)	1.372(5)
C5-C10	1.392(2)	C1-C6	1.382(6)	1.382(5)
C6-C7	1.385(3)	C1-H1	0.94(3)	0.91(3)
C6-H6	0.92(1)	C2-C3	1.410(5)	1.418(5)
C7-C8	1.371(3)	C3-C4	1.406(5)	1.398(5)
C7-H7	0.95(2)	C4-C5	1.372(5)	1.370(5)
C8-C9	1.378(3)	C4-H4	1.01(3)	0.92(3)
C8-H8	0.93(2)	C5-C6	1.426(5)	1.407(5)
C9-C10	1.377(3)	C7-C11	1.476(6)	1.459(5)
C9-H9	0.99(2)	C8-C21	1.461(6)	1.469(5)
C10-H10	1.01(2)	C11-C12	1.396(6)	1.368(6)
		C11-C16	1.374(6)	1.398(5)
		C12-C13	1.377(7)	1.366(7)
		C12-H12	0.88(3)	0.92(3)
		C13-C14	1.378(8)	1.364(7)
		C13-H13	0.90(3)	0.81(3)
		C14-C15	1.378(7)	1.391(6)
		C14-H14	1.02(3)	1.03(3)
		C15-C16	1.385(6)	1.372(6)
		C15-H15	0.82(3)	0.93(3)
		C16-H16	0.96(3)	1.02(3)
		C21-C22	1.380(6)	1.382(6)
		C21-C26	1.404(6)	1.369(6)
		C22-C23	1.392(7)	1.387(7)
		C22-H22	1.00(3)	0.99(3)
		C23-C24	1.354(7)	1.359(7)
		C23-H23	0.94(3)	1.05(3)
		C24-C25	1.369(7)	1.354(7)
		C24-H24	1.10(3)	1.07(3)
		C25-C26	1.370(7)	1.376(6)
		C25-H25	0.96(3)	0.92(7)
		C26-H26	1.02(3)	1.06(3)

Bond Angles

C2-S-C4	88.9(1)		Molecule A	Molecule B
C3-N-C4	110.8(1)	C2-S1-C7	88.9(2)	89.5(2)
C2-C1-C3'	117.3(1)	C6-S2-C8	89.6(2)	88.8(2)
C2-C1-H1	121.3(8)	C3-N1-C7	110.9(3)	111.7(3)
C3'-C1-H1	121.4(8)	C5-N2-C8	110.7(3)	110.7(3)
S-C2-C1	128.6(1)	C2-C1-C6	116.1(3)	116.6(3)
S-C2-C3	109.0(1)	C2-C1-H1	122(2)	126(2)
C1-C2-C3	122.4(1)	C6-C1-H1	122(2)	117(2)
N-C3-C1'	124.6(1)	C1-C2-C3	123.2(3)	122.3(3)
N-C3-C2	115.1(1)	S1-C2-C1	127.7(3)	128.8(3)
C1'-C3-C2	120.4(1)	S1-C2-C3	109.1(3)	108.9(3)
S-C4-N	116.3(1)	C2-C3-C4	119.4(3)	119.8(3)
S-C4-C5	119.9(1)	N1-C3-C2	115.6(3)	115.1(3)
N-C4-C5	123.8(1)	N1-C3-C4	125.0(3)	125.1(3)
C4-C5-C6	121.6(1)	C3-C4-C5	118.5(3)	118.2(3)
C4-C5-C10	119.3(2)	C3-C4-H4	118(2)	115(2)
C6-C5-C10	119.1(2)	C5-C4-H4	123(2)	127(2)
C5-C6-C7	120.5(2)	C4-C5-C6	120.3(3)	120.7(3)
C5-C6-H6	118.9(10)	N2-C5-C4	124.8(3)	123.9(3)
C7-C6-H6	120.7(10)	N2-C5-C6	114.9(3)	115.3(3)
C6-C7-C8	120.0(2)	C1-C6-C5	122.4(3)	122.4(3)
C6-C7-H7	118.8(9)	S2-C6-C1	128.6(3)	128.3(3)
C8-C7-H7	121.2(9)	S2-C6-C5	109.0(3)	109.4(3)
C7-C8-C9	120.0(2)	S1-C7-N1	115.4(3)	114.8(3)
C7-C8-H8	119.5(11)	S1-C7-C11	120.4(3)	120.4(3)
C9-C8-H8	120.5(11)	N1-C7-C11	124.2(3)	124.8(3)
C8-C9-C10	120.5(2)	S2-C8-N2	115.9(3)	115.8(3)
C8-C9-H9	120.5(11)	S2-C8-C21	120.3(3)	120.4(3)
C10-C9-H9	119.0(11)	N2-C8-C21	123.8(4)	123.8(3)
C9-C10-C5	120.0(2)	C7-C11-C12	122.2(3)	122.8(3)
C9-C10-H10	121.3(8)	C7-C11-C16	119.3(3)	119.4(3)
C5-C10-H10	118.7(8)	C12-C11-C16	118.4(4)	117.8(3)
		C11-C12-C13	119.6(4)	122.0(4)
		C12-C13-C14	120.7(5)	119.9(4)
		C13-C14-C15	120.7(4)	120.0(4)
		C14-C15-C16	118.0(4)	119.3(4)
		C15-C16-C11	122.5(4)	120.9(4)
		C8-C21-C22	123.0(4)	122.4(4)
		C8-C21-C26	119.8(4)	119.2(3)
		C22-C21-C26	117.2(4)	118.4(4)
		C21-C22-C23	122.3(4)	119.5(4)
		C22-C23-C24	119.1(4)	120.6(4)
		C23-C24-C25	119.9(5)	120.4(4)
		C24-C25-C26	121.9(4)	119.3(4)
		C25-C26-C21	119.7(4)	121.7(4)
		Av C-C-H(phenyl)	119.5(1)	119.8(1)

planarity of phenyl substituents and the benzobisthiazole segment, in contrast to the observation made in t-bisthiazole, is not precluded by steric considerations.

Because of differences in the exocyclic bond angles about C(7) and C(8), a curvature—which is distinct from the bowing described above—is observed when viewed normal to the molecule (see Figure 5). Although slight, the curvature, as well as the bowing, serves to prevent the molecule from achieving a completely linear conformation.

Relationship to PBT Microstructure. The molecular structure and packing just described for the model compounds can be adapted, in part, to the fiber structure of PBT. In the absence of any fiber diffraction data, a plausible model for the packing in oriented fibers would involve chains of molecules extending in the direction of elongation, with ring systems comprising the fiber repeat unit in adjacent molecules being positioned in either a parallel or nonparallel arrangement. Within a particular chain, steric crowding might argue against a coplanar arrangement of the benzobisthiazole and *p*-phenylene segment, leading one to expect some torsional relief between these segments. Furthermore, intramolecular (conformational) energy calculations also predict nonplanarity of these segments.[3] But it is clear from Figures 3 and 4 that the packing in the polymer must differ from that observed in the model compounds. A different conformation could therefore be accommodated in the polymer in order to minimize the chain-packing effects.

Two groups, one at the University of Massachusetts and another at the University of Bristol, have recently reported structures for oriented PBT fibers. Adams, Azâroff, and Kulshreshtha have interpreted X-ray patterns of PBT fibers in terms of a nematic arrangement of molecules which are treated as periodic cylinders packed in an hexagonal array.[17] The cylinders are arrayed parallel to each other but have arbitrary relative displacements along the cylinder axis. Although the model explains the features of the X-ray pattern, it predicts a fiber density which is well below the experimental value. Roche, Takahashi, and Thomas have reported evidence for crystalline order in annealed fibers by electron diffraction.[18] Analysis of their most ordered patterns reveals a fiber repeat of 12.4 Å, which remains constant as the fiber processing conditions vary. This value compares favorably with the repeat unit length of 12.47 Å in t-bisthiazole, as measured by the C(8) to C(5′) separation. This implies that the PBT chain has the fully extended conformation, since the fiber repeat consists of only one repeat unit. The electron diffraction patterns have also been interpreted in terms of monoclinic and triclinic unit cells. A more definitive assignment may be possible with more highly ordered fibers.

Most recently, Atkins et al. have computed the molecular Fourier transform, cylindrically averaged, of a ten-unit repeat of the t-bisthiazole monomer unit.[19] The match between the simulated and experimental pattern is quite good. A very high number of equidistant meridional streaks are observed, together with broad equatorial and smeared out (*hkl*) reflections. The most prominent equatorial reflections have *d* spacings of 3.56 and 5.93 Å, which are interpreted in terms of the perpendicular and center-to-center separation of adjacent molecules.

The repeat unit length in c-bisthiazole is 12.35 Å, as measured by the C(14) to C(21) separation. Although polymer possessing this heteroatom disposition has not been prepared to date, the crystallographic analysis of the c-bisthiazole model compound implies that individual chains of such material, if synthesized, would adopt an all-planar conformation. Intramolecular steric effects appear to be minimal, and the relative orientation of ring moieties within a particular chain seems to be dominated by resonance and lattice energy terms.

Supplementary Material Available: Thermal parameters and structure factor tables for 2,6-diphenylbenzo[1,2-*d*:4,5-*d*′]-bisthiazole and 2,6-diphenylbenzo[1,2-*d*:5,4-*d*′]bisthiazole (51 pages). Ordering information is given on any current masthead page.

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Rheological Properties of Rodlike Polymers in Solution. 1. Linear and Nonlinear Steady-State Behavior

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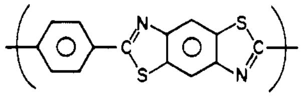
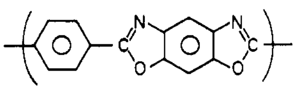
ABSTRACT: Steady-state rheological properties are reported for solutions of three mesogenic rodlike polymers. Concentrations c range from 0.02 to 0.15 g/mL, depending on the chain length L of the polymer studied, with all solutions being isotropic. The data include the viscosity η_κ and recoverable compliance R_κ determined as a function of shear rate κ, using a cone-and-plate rheometer, and their limiting values η_0 and R_0, respectively, at small κ. Rheooptical studies are also reported, giving the birefringence Δn_{13} as a function of κ. The dependence of η_0 and R_0 on concentration and chain length is compared with theoretical predictions. The rapid increase of $\eta_0/M[\eta]$ with increasing cL predicted theoretically is observed (with M the molecular weight and $[\eta]$ the intrinsic viscosity). Behavior attributed to intermolecular association is described for some of the solutions. The nonlinear rheological and rheooptical data show that η_κ/η_0, R_κ/R_0, and $\Delta n_{13}/c$ can be expressed as superposed functions of the reduced strain rate $\tau_c\kappa$ over the range of c, M, and temperature studied, where τ_c is equal to $\eta_0 R_0$. The dependence of η_κ/η_0 on $\tau_c\kappa$ found for the solutions of rodlike polymers is similar to that observed for flexible chains; a theoretical model for rodlike chains gives qualitatively similar behavior.

Rheological properties of three polymers with rodlike conformations will be described in a series of papers. The first two of this series will deal with certain steady-state rheological properties of isotropic solutions and optically anisotropic solutions. Later papers will concern transient rheological properties of these same materials. The polymers used in this study include poly(*p*-phenylene-2,6-benzobisthiazole) and poly(*p*-phenylene-2,6-benzobisoxazole) with the repeating units

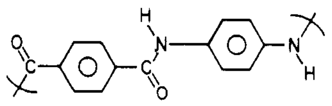


PBT



PBO

and poly(*p*-phenyleneterephthalamide) with repeating unit



PPTA

Both PBT and PBO have rodlike conformations, characterized by a persistence length ρ that is comparable with or larger than the contour length L, and for the PPTA molecules studied here the ratio ρ/L is of order unity. Thus, all three polymers can be expected to exhibit the properties of rodlike molecules. Indeed, all three will form