of soybean proteins in water but also agglomerates 7 S proteins. These observations suggest that sonication may cause significant changes in physical properties of soybean proteins and their food products.

The major storage proteins in soybeans (7 S and 11 S) are globular in nature and water soluble. Mechanical stirring produces water extracts with ~80% of the total proteins from fresh defatted soybean meal. The yield is lower if the meal is toasted, alcohol-washed, or stored for several months. Ultrasonic extraction, however, improves protein solubility from many of these treated meals (Wang, 1978). Present findings indicate that sonication promotes aggregate formation and that one of the major storage proteins, the 7 S fraction, is involved in the aggregation process. Thus, 7 S proteins may have unique properties that, unlike other soybean proteins (2 S and 11 S), are sensitive to ultrasonic treatment. Perhaps under sonication 7 S transforms into an aggregate of bilayer, micelle structures and aggregates. At high protein concentration such as 0.8 mg/mL the aggregates are more stable (Figure 3 and Table I). The aggregation formation may have no relationship to increased protein solubility as observed previously (Wang, 1975, 1978).

Ultrasonic action promotes agglomeration rather than dissociation of soybean proteins. Agglomeration of the 7 S proteins may affect physical properties in such a way, as observed by Saio et al. (1971) in making tofu. Tofu coagulated from 7 S and 11 S protein fractions has distinct differences in hardness. Ultrasonic action may serve as an alternative means to achieve desired properties in soybean food products.

Further studies on the mechanism of aggregate formation by sonication may reveal several possibilities; ultrasonic action may promote hydrophobic interaction of globular proteins in water (Tanford, 1977, 1978), may induce formation of complex mixture as in apolipoproteins (Forte et al., 1974), or may alter the equilibrium condition of protein–protein or protein–lipid interactions to favor the formation of a cluster type of structure. More results along these lines of investigation should be helpful to broadening this basic understanding of soybean proteins.

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COMMUNICATIONS

Synthesis of Some Highly Brominated Naphthalenes

The chemical synthesis and characterization of 2,3,6,7-tetra-, 1,2,4,6,7-penta-, and 1,2,3,5,6,7- and 1,2,3,4,6,7-hexabromonaphthalene are reported. These compounds are representative of the brominated naphthalene contaminants of the fire-retardant chemicals polybrominated biphenyls.

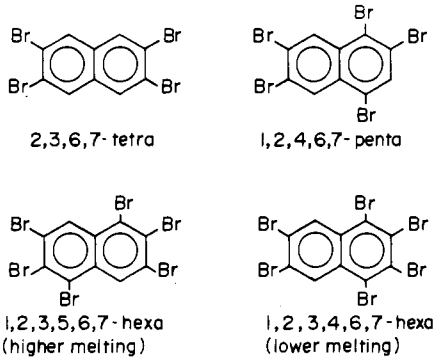
Highly brominated naphthalenes (primarily penta and hexa) have been identified (Hass et al., 1978) as associated contaminants of the fire-retardant chemicals polybrominated biphenyls (PBB's). The PBB's were introduced to the Michigan environment through accidental contamination of animal feeds, thereby exposing a large part of the population of the state to these substances. While the PBB's themselves have not been found (Allen et al., 1978) to be particularly toxic to animals, there is a great deal of concern about the highly toxic potential of associated contaminants such as the brominated naphthalenes. Interest in carrying out toxicity studies on these potentially toxic environmental contaminants engendered a need for synthesis of selected isomers and homologues. In view of the demonstrated (McConnell et al., 1978; McKinney et al., 1980) dependence of toxicity on the number and position of halogens in related planar compounds, it was important to have regiospecific synthetic methodology. A search of the chemical literature revealed a scarcity of information on synthetic methodology for the highly brominated naphthalenes. Our specific interest was in synthesizing symmetrical tetra-, penta-, and hexa-substituted isomers. Especially important was the need to have methodology that would permit substitution in at least three of the lateral positions (2, 3, 6, 7) which is always a requirement for high toxicity in these compounds (McKinney et al., 1980). It was clear that the easiest route into these systems would be selective functionalization of

Table I. Partial Mass Spectra of Selected Polybromonaphthalenes

compd	relative abundance, %,[a] of observed ions									
	M^+	$M-Br^+$	$M-2Br^+$	$M-3Br^+$	$M-4Br^+$	$M-5Br^+$	$M-6Br^+$	M^{2+}	$M-2Br^{2+}$	$M-4Br^{2+}$
2,3,6,7-tetrabromonaphthalene	100	10.3	37.5	6.3	25.9			8.3	16.0	
1,2,4,6,7-pentabromonaphthalene	100	11.5	31.1	11.6	21.2	25.7		6.3	14.4	7.2
1,2,3,5,6,7-hexabromonaphthalene	100	11.1	49.1	16.2	25.9	25.7	40.0	9.6	21.8	14.6
1,2,3,4,6,7-hexabromonaphthalene	100	8.3	22.8	2.7	17.3	13.6	51.8	2.0	10.6	7.6

[a] The relative abundance of each ion has been determined by taking into account the abundance of all ions included in the bromine pattern.

Chart I. Structures of Highly Brominated Naphthalenes Characterized



the naphthalene nucleus with subsequent modification to afford the desired halogenated naphthalene.

In earlier work (Levy, 1978), the 2,3,6,7-tetrabromo isomer (Chart I) was conveniently prepared from the known tetrakis(trimethylsilyl)naphthalene (Funk and Vollhardt, 1976). Later work was aimed at synthesizing the symmetrical 1,2,3,5,6,7- and 2,3,4,5,6,7-hexabromo isomers. Several attempts to prepare these isomers via direct bromination of 1,5- and 1,8-diamino (or dinitro)-naphthalene or the 1,8-dicarboxylic acid anhydride were unsuccessful. The 1,2,3,5,6,7-hexa isomer was successfully prepared following the published procedure of Hamill et al. (1971) for bromination of *endo*-2,3-trimethylenenorbornane. The structure assignment was established by a complete X-ray crystallographic analysis (Ferguson and Subramanian, 1977). This product was presumed to occur via the intermediacy of *cis*-decalin which was shown by previous workers (Zelinsky and Turowa-Pollak, 1929) to be an apparent synthone for this isomer (mp 317 °C) under $AlBr_3$-catalyzed oxidative brominating conditions. This early work with decalin had also afforded a second unidentified hexabromo isomer, mp 269 °C. There was at least one other report (Gessner, 1876) of the formation of a hexabromo isomer from direct bromination of naphthalene under $AlCl_3$-catalyzed conditions. This isomer had a melting point (252 °C) similar to that of the lower melting isomer derived from the early work with decalin. This was an interesting result in view of the early work (Zelinsky and Turowa-Pollak, 1929) where $AlBr_3$-catalyzed direct bromination of naphthalene afforded the higher melting hexa isomer which was later identified (Ferguson and Subramanian, 1977) as 1,2,3,5,6,7-hexabromonaphthalene.

In our hands the direct bromination of naphthalene with bromine catalyzed by iron powder in refluxing methylene bromide for 16 h afforded the lower melting hexa isomer exclusively. The ^1H NMR spectrum of this isomer shows a singlet at 8.74 ppm. The 1,2,3,5,6,7 isomer also shows a singlet in its ^1H NMR spectrum but at 9.05 ppm. Subsequent to this work we had received as a gift a sample of a pentabromonaphthalene which had been prepared similarly through direct bromination of naphthalene with bromine catalyzed by $FeBr_3$ in carbon tetrachloride (40 °C). Further bromination of this isomer with bromine catalyzed by iron powder in refluxing methylene bromide afforded the same lower melting hexa isomer as obtained from direct bromination of naphthalene under identical conditions. Simultaneously with the chemical work a complete X-ray analysis revealed that the lower melting isomer was 1,2,3,4,6,7-hexabromonaphthalene as shown in the crystal packing diagram in Figure 1. All the Br atoms range from 3.272 Å between Br(1) and Br(2) to 3.334 Å between Br(5) and Br(6) (see Figure 1).

Table II. Exact Mass Measurements and Elemental Composition of the Molecular Ion from Polybrominated Naphthalenes

compd	calcd mass	measd mass	elemental compd
2,3,6,7-tetrabromonaphthalene	439.7049	439.7072	$C_{10}H_4Br_4$
1,2,4,6,7-pentabromonaphthalene	517.6154	517.6150	$C_{10}H_3Br_5$
1,2,3,5,6,7-hexabromonaphthalene	595.5260	595.5190	$C_{10}H_2Br_6$
1,2,3,4,6,7-hexabromonaphthalene	595.5260	595.5247	$C_{10}H_2Br_6$

The structure of the pentabromonaphthalene was assigned on the basis of its ^1H NMR spectrum and the fact that it undergoes further bromination to 1,2,3,4,6,7-hexabromonaphthalene. The ^1H NMR spectrum of the penta isomer exhibits three singlets of equal intensity at 7.38, 8.17, and 8.28 ppm. Of the possible isomeric pentabromonaphthalenes, only 1,2,4,6,7-pentabromonaphthalene is consistent with the NMR data (the other isomers can be ruled out on the basis of no coupling between the protons being observed and the chemical shift values) and is a direct precursor to the 1,2,3,4,6,7-hexa isomer.

Mass spectral measurements were also consistent with the assigned structures. The electron impact mass spectra of these four polybromonaphthalenes are characterized by the presence of intense molecular ions (base peak) and fragment ions which are explained by the loss of bromine radical(s) and/or neutral molecule(s) (see Table I). Each compound shows an ion specific for the degree of substitution of the naphthalene ring, whose mass to charge ratio is respectively m/z 124 for 2,3,6,7-tetrabromonaphthalene, m/z 123 for 1,2,4,6,7-pentabromonaphthalene, and m/z 122 for 1,2,3,4,6,7- and 1,2,3,5,6,7-hexabromonaphthalene. Some doubly charged ions were also observed in all the mass spectra (see Table I).

Elemental compositions were assigned on the basis of exact mass measurements (see Table II).

In contrast, the chlorination of naphthalene appears to proceed in a nonregiospecific manner to yield a mixture of chlorinated naphthalenes (halowaxes, chlorinated naphthalene oils, and waxlike solids, Koppers Co., Inc.) which can be exhaustively chlorinated to octachloronaphthalene (Hutzinger et al., 1973). Bromination of naphthalene using our method proceeds in a relatively

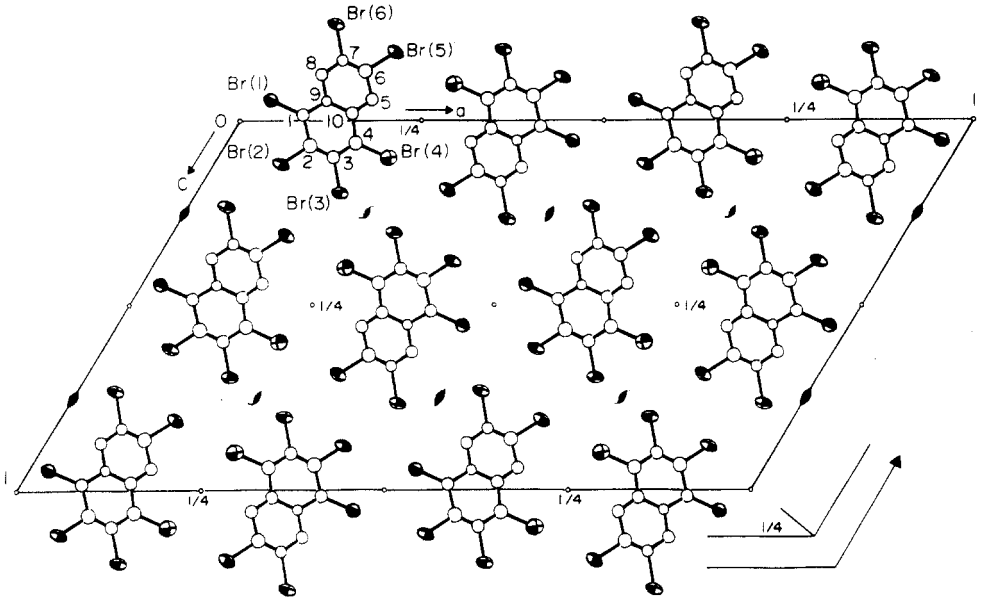


Figure 1. Crystal packing diagram for 1,2,3,4,6,7-hexabromonaphthalene.

regiospecific manner presumably via the 1,2,4,6,7-penta isomer to 1,2,3,4,6,7-hexabromonaphthalene. We were unable to find reported syntheses of hepta- and octabromonaphthalenes.

Although it is possible to prepare the 1,2,3,5,6,7-hexabromo isomer from direct bromination of naphthalene, the reaction conditions appear to require bromine as solvent and $AlBr_3$ as catalyst (Zelinsky and Turowa-Pollak, 1929) [e.g., $AlCl_3$ apparently directs another reaction pathway (Gessner, 1876)]. It is also possible to prepare hexabromonaphthalenes from precursors other than naphthalene itself; however, the role of naphthalene or partially brominated naphthalenes as intermediates is not completely clear.

Stereoelectronic differences in physical and chemical properties and modified biological activity of compounds as a result of the larger size and greater ionic character of bromine (vs. chlorine) are well documented (Sexton, 1963). Another example of this was seen in our early work toward the preparation of 2,3,6,7-tetrasubstituted naphthalenes. It was not possible to conveniently prepare the 2,3,6,7-tetrachloro isomer (Levy, 1978) via the known tetrakis(trimethylsilyl)naphthalene intermediate (Hamill, et al., 1971) used for the 2,3,6,7-tetrabromo isomer. The 2,3,6,7-tetrachloro isomer is at least 18 times less toxic in the guinea pig (McKinney et al., 1980).

EXPERIMENTAL SECTION

NMR Spectroscopy. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates XL-100-12 spectrometer operating in the Fourier-transform mode. Samples were run in 5-mm sample tubes and peaks were calibrated with respect to the residual solvent peaks and later converted to the Me_4Si scale. The pentabromonaphthalene was run as a saturated solution in benzene-d_6 and the hexabromonaphthalenes were run as saturated solutions in tetrahydrofuran-d_8 (H_4furan).

Mass Spectrometry. Low-resolution electron impact (70 eV) mass spectra were obtained on a Hewlett-Packard 5700A gas chromatograph/VG-Micromass ZAB/2F mass spectrometer system interfaced to a Finnigan/INCOS 2300 data system. Sample was introduced by means of a 0.25 mm i.d. × 20 m glass capillary column coated with OV-1, programmed from 120 to 250 °C at 8 °C/min or from 180 to 250 °C/min for the hexabromonaphthalenes. The injection port and transfer lines were maintained between 250 and 280 °C.

Table III. Positional Parameters and Their ESD's for 1,2,3,4,6,7-Hexabromonaphthalene[a]

atom	x	y	z
Br(1)	0.0265 (2)	−0.0082 (20)	−0.0556 (3)
Br(2)	0.0924 (2)	0.2116 (17)	0.1183 (3)
Br(3)	0.1964 (2)	0.0876 (18)	0.1964 (3)
Br(4)	0.2352 (2)	−0.2709 (26)	0.1006 (4)
Br(5)	0.1580 (2)	−0.7315 (19)	−0.1880 (3)
Br(6)	0.0522 (2)	−0.6015 (18)	−0.2669 (3)
C(1)	0.081 (2)	−0.064 (16)	−0.017 (3)
C(2)	0.115 (2)	0.017 (18)	0.064 (3)
C(3)	0.157 (2)	−0.034 (16)	0.097 (3)
C(4)	0.177 (2)	−0.187 (17)	0.058 (3)
C(5)	0.165 (2)	−0.432 (15)	−0.057 (3)
C(6)	0.131 (2)	−0.549 (16)	−0.136 (3)
C(7)	0.092 (1)	−0.476 (13)	−0.166 (2)
C(8)	0.074 (1)	−0.321 (14)	−0.129 (3)
C(9)	0.102 (1)	−0.223 (14)	−0.053 (2)
C(10)	0.148 (2)	−0.277 (14)	−0.020 (3)

[a] Lists of structure factors and anisotropic thermal parameters will be supplied upon request.

Exact mass measurements were made with the mass spectrometer operated at 10 000 static resolving power, scanned at 10 s/dec. Source temperature was 200 °C when the sample was introduced by the direct probe with 200-μA trap current. Data acquisition and processing were again accomplished with the Finnigan/INCOS data system using perfluorokerosene as the reference compound.

Crystallographic Data. $C_{10}H_2Br_6$: M_r 601.6, colorless, long thin needles from dibromoethane, mp 260–263 °C. Cu Kα (λ = 1.5418 Å), monoclinic, a = 36.22 (4) Å, b = 3.995 (2) Å, c = 20.94 (2) Å, β = 121.26 (6)°, $C2/c$, f_c = 3.09 for Z = 8, ν = 2590.1 Å^3, μ = 225.0 for Cu Kα.

Intensity data were measured on a Syntex P1 diffractometer with a crystal of dimensions 0.60 × 0.06 × 0.005 mm by the θ/2θ scan technique at a scan rate of 1° min^{-1} up to 100° in 2θ. A total of 1322 reflections were measured, of which 819 had intensities ≥ 3σ(I), and were used in the analysis. The intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by using the computer program MULTAN (Main et al., 1978) and refined by full-matrix least squares to R and R_w of 0.108 and 0.123, respectively, al-

lowing bromine atoms anisotropic and carbon atoms isotropic vibration. Hydrogen atoms were not located. Atomic fractional coordinates are given in Table III.

Synthesis of 2,3,6,7-Tetrabromonaphthalene. To an ice-cooled solution of 624 mg (1.5 mmol) of 2,3,6,7-tetrakis(trimethylsilyl)naphthalene (Funk and Vollhardt, 1976) in 5 mL of CCl_4 and 250 μL of pyridine was added 14 mL of 1.9 M Br_2 in CCl_4 solution. The reaction mixture was stirred for 10 h. The course of the reaction was followed by GLC (OV-101; 250 °C). The first-formed product was the dibromobis(trimethylsilyl) derivative, the structure of which was assigned by mass spectral analysis. The next product to appear was the desired tetrabromonaphthalene. Aqueous $Na_2S_2O_3$ was added to remove excess bromine and the reaction mixture extracted twice with ether. The organic phase was dried and evaporated to yield 320 mg of product. One recrystallization from benzene yield 235 mg of 2,3,6,7-tetrabromonaphthalene, mp 259–261 °C, with the expected NMR and MS spectral properties [for X-ray structural work, see Singh et al. (1980)].

Synthesis of 1,2,3,4,6,7-Hexabromonaphthalene. To a solution of 624 mg (5.0 mmol) of naphthalene in 25 mL of dibromoethane and 2.0 mL of liquid bromine was added 40 mg of iron powder. The reaction mixture was refluxed for 4 h with stirring. After the mixture was cooled at room temperature, the crude product was isolated by suction filtration and dried in vacuo. One crystallation from hot dibromoethane afforded chromatographically (GLC; 3% OV-101) pure 1,2,3,4,6,7-hexabromonaphthalene, mp 260–263 °C, with the expected NMR and MS spectral properties.

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Odor Threshold of Thiamin Odor Compound 1-Methylbicyclo[3.3.0]-2,4-dithia-8-oxaoctane

An odor threshold of 4 parts of compound per 10^{13} parts of water was found for the thiamin odor compound (1-methylbicyclo[3.3.0]-2,4-dithia-8-oxaoctane or 2,3-methylenedithio-2-methyltetrahydrofuran, I) believed to be responsible for the characteristic odor of thiamin hydrochloride (vitamin B_1) preparations. This threshold is among the lowest ever reported for any odor compound in water solution. A possible mechanism pathway for the formation of the thiamin odor compound from thiamin is proposed.

Some of the authors (Seifert et al., 1978) had already reported on the determination of the structure of the thiamin odor compound as 1-methylbicyclo[3.3.0]-2,4-dithia-8-oxaoctane (I, Figure 1) which they had found from the photolysis of thiamin hydrochloride (vitamin B_1). This compound appeared to be responsible for the characteristic aroma of commercial thiamin and multivitamin preparations. The structure was recently confirmed by its synthesis from simple starting materials (Gygax, 1979).

The present study was undertaken because of the need