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Identification of a Major Component of Polybrominated Biphenyls as 2, 2′, 3, 4, 4′, 5, 5′-Heptabromobiphenyl

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Polybrominated biphenyls (PBBs), which were synthesized for use as flame retardants, have been found as environmental contaminants in New York, New Jersey (ANONYMOUS, 1977), and Michigan (CARTER, 1976). PBBs are complex mixtures of thirty or more components, and different biological consequences may be expected to result from exposure to the different components. Toxicological analysis of these mixtures has been hampered both by their complexity and by a lack of information as to their composition. The only published structure is that of the major component of Firemaster, a mixture averaging six bromines per molecule (Michigan Chemical Corp.), which has been identified as 2,2',4,4',5,5'-hexabromobiphenyl (HBB_6) (SUNDSTRÖM et al., 1976; JACOBS et al., 1976). We report here the structural identification and spectral analysis of a major component of both Firemaster and a more extensively brominated mixture of PBBs, which we have identified as 2,2',3,4,4',5,5'-heptabromobiphenyl (HBB_7).

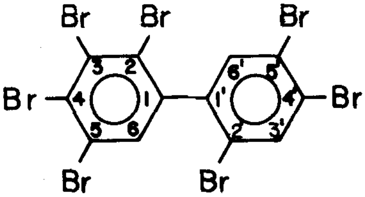

Figure 1. 2,2',3,4,4',5,5'-heptabromobiphenyl.

EXPERIMENTAL

HBB_7 was isolated from a mixture of PBBs sold by the Aldrich Chemical Company as 2,2'3,3',5,5',6,6'-octabromobiphenyl. While the origin of this sample is uncertain, its gas chromatographic profile closely resembles that of octabromobiphenyl (OBB) (The Dow Chemical Company). The compound we have isolated corresponds to the Br_7 peak in OBB, as published by ZITKO (1977), and has identical column and gas chromatographic properties to the second largest component of Firemaster (peak 6, JACOBS et al., 1976; com-

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ponent II, SUNDSTRÖM et al., 1976).

One gram of OBB was dissolved in 400 ml of pesticide grade, glass distilled hexane (Burdick and Jackson Laboratories, Inc.) and applied to a 2.2 x 30 cm column containing 113 g of neutral alumina, activity grade I (Sigma Chemical Co.). Fractions eluting with between 3.0 and 4.3 l of hexane were pooled, evaporated to dryness, and recrystallized from hexane. Purity was 98%, as determined by gas chromatography on 3% OV-1 at 270° with a ^{63}Ni electron capture detector (MOORE et al., 1977). The only contaminant was HBB_6. The percentage composition of HBB_7 in both Firemaster and OBB was determined by gas chromatographic analysis of standard (w/v) solutions.

The melting point determination was performed using a Hoover Uni-melt capillary melting point apparatus.

The proton magnetic resonance (PMR) spectrum was obtained on a Bruker WP 180 spectrometer at ambient temperature, with 0.02 M HBB_7 in $CDCl_3$. Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (TMS).

The ^{13}C-nuclear magnetic resonance (CMR) spectrum was determined at ambient temperature on a Bruker WP 60 spectrometer, equipped with quadrature detection, on 0.1 M HBB_7 in $CDCl_3$. Chemical shifts are reported in ppm relative to internal TMS.

The infrared (IR) spectrum was taken as a KBr pellet on a Perkin-Elmer 167 grating infrared spectrophotometer.

RESULTS AND DISCUSSION

HBB_7 was found to melt at 165-166°, which is 6° higher than HBB_6 melts at (NORSTRÖM et al., 1976; MOORE et al., 1977). The chlorinated analogues of these compounds also melt 6° apart (HUTZINGER et al., 1974). HBB_7 was found to constitute 27% by weight of Firemaster, and 25% of OBB.

HBB_7 was previously known to be a heptabromobiphenyl from GC-MS analysis of PBBs, but mass spectrometry provides no structural information for brominated or chlorinated biphenyls beyond molecular composition (SUNDSTRÖM et al., 1976). There are twenty-four possible heptabromobiphenyls, of which six have all three protons on one ring, and eighteen have one proton on one ring and two on the other.

It can be seen from Figure 2 that the PMR spectrum shows the presence of three distinct protons of equal intensity which do not observably split each other ($J < 0.5$ Hz). This limits the possible struc-

Figure 2. 180 MHz PMR spectrum of HBB$_7$.

tures to the three, each having two protons para to each other on one ring, at the 3' and 6' positions. Two of the proton signals are significantly upfield of the third, which requires that two protons be ortho to bridge carbons. The proton on the second ring must therefore be at the 6 position, and so the PMR spectrum alone identifies the compound as 2,2',3, 4,4',5,5'-heptabromobiphenyl. The 3' proton is ortho to two bromines and gives rise to the downfield signal at δ = 7.93 ppm. The signals at δ = 7.47 and 7.45 ppm are assigned to the 6 and 6' protons, respectively, based on peak widths. SUNDSTRÖM et al. (1976) have shown HBB$_6$ to give PMR peaks at δ = 7.93 and 7.47 ppm, and the addition of one bromine at the 3 position of HBB$_6$ to give HBB$_7$ apparently has little effect on the shieldings of the other protons; only an upfield shift of 0.02 ppm in the signal from the 6' proton is observed. The PMR spectrum for the chlorinated analogue is similar to that of HBB$_7$; three signals are observed at δ = 7.64, 7.35, and 7.30 ppm, which can be attributed to the 3', 6', and 6 protons, respectively (TAS and VOS, 1971).

The most useful information derived from the CMR spectrum is that there are ten distinct carbons in addition to the two which appear as a broadened peak

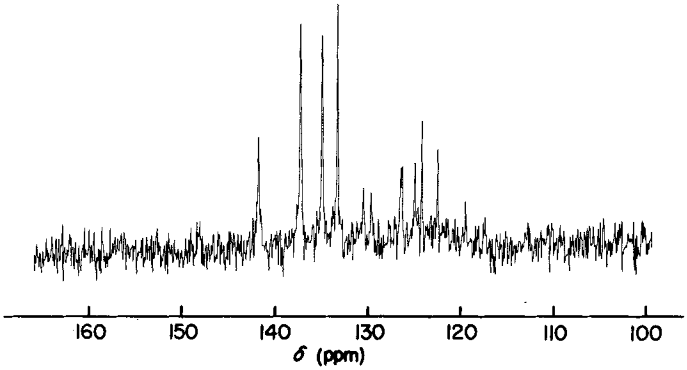

Figure 3. CMR spectrum of HBB_7.

at δ = 141.8 ppm (Figure 3). It has been shown, with chlorinated biphenyls, that chemically equivalent carbons on one ring do not give rise to different CMR peaks even when there is an asymmetric substitution pattern on the other ring (HUTZINGER et al., 1974). Four of the possible structures have an axis of symmetry and would show a maximum of eight signals, while twelve are symmetrical on one ring and would show a maximum of ten peaks. Since eleven or twelve peaks are observed, these structures cannot be HBB_7. Given the present scarcity of information about the CMR properties of brominated biphenyls, it is not possible to definitively rule out any of the final eight potential structures for HBB_7 on the sole basis of its CMR spectrum. However, since the structure of HBB_7 is now known, and since the CMR assignments have been made for the closely related molecule HBB_6 (JACOBS et al., 1976), it is possible to assign most of the peaks to single carbons. The broadened peak at δ = 141.8 ppm is assigned to the bridge carbons, while the large peaks at 137.2, 134.9, and 133.3 are assigned to the protonated carbons at the 3', 6', and 6 positions, respectively. Other assignments are: C3 at 130.5; C4 at 129.7; and C2' at 122.5 ppm. The peaks at 126.5 and 126.3 ppm are extremely close; one is assigned to C4' while the other is from either C2 or C5. The peak at 125.0 ppm is from C2 or C5, or possibly C5', while the peak at 124.2 ppm is probably from C5', though possibly from C2 or C5. WILSON (1975) has shown that the substitution of chlorines onto biphenyl causes CMR signals to shift in an approximately additive manner, and these assignments have been made based on this observation, the CMR spectrum of HBB_6 (JACOBS et al., 1976), and the shifts observed upon the bromination of benzene (SADTLER, 1976) and of biphenyl at the 3 position (LEVY et al., 1973).

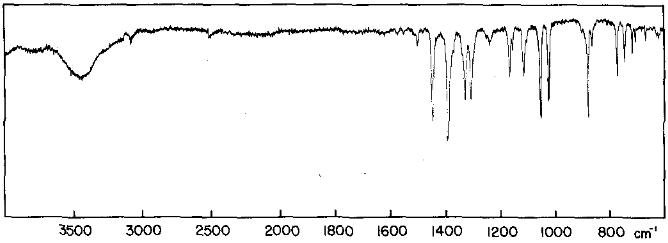

Figure 4. IR spectrum of HBB_7.

The IR spectrum of HBB_7 is shown in Figure 4. As is the case with CMR spectra, IR spectra should become increasingly useful in structural analysis as more brominated biphenyls are characterized.

PBBs are complex mixtures whose components are expected to differ in their biological effects. We have determined, for example, that the effects of HBB_6 on liver microsomal drug metabolizing enzymes are distinct from the effects of PBBs (MOORE et al., 1977). A similar study on the effects of HBB_7 is in progress.

ACKNOWLEDGMENTS

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