

STRUCTURAL CHARACTERIZATION OF HEXACHLOROCYCLOPENTADIENYL-DIBROMOCYCLOOCTANE (HCDBCO)

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1 INTRODUCTION

Hexachlorocyclopentadienyl-dibromocyclooctane (**1**, HCDBCO, see Fig. 1) is a commercial brominated flame retardant (BFR) used in styrenic polymers.¹ BFRs have been used in a variety of products to protect human life and property against fires. However, there is a growing concern that certain BFR compounds are becoming significant environmental contaminants because of their widespread presence in the environment and in human and wildlife samples.² Very little is known about HCDBCO, but recent work has identified it as a component in house dust.³ We have now completed NMR and 3D modeling studies as well as an x-ray structure determination which proves that HCDBCO has the structure **1**. This information should be useful to researchers wishing to model and predict the behaviour of HCDBCO. Also reported are thermal stability issues for HCDBCO which have important consequences for its analysis by GC/MS.

2 MATERIALS & METHODS

2.1 Synthesis of Hexachlorocyclopentadienyl-dibromocyclooctane (**1**)

Synthesis of hexachlorocyclopentadienyl-dibromocyclooctane was carried out following the literature procedure.³ The IUPAC name is *rac*-(5*R*,6*R*)-5,6-dibromo-1,10,11,12,13,13-hexachlorotricyclo[8,2,1,0^{2,9}]-[1*R*,2*R*,9*S*,10*S*]-tridec-11-ene.

2.2 ¹H NMR Spectroscopy

¹H-NMR analyses were performed on a 600 MHz Bruker instrument using deuteriochloroform (CDN Isotopes) as the solvent and TMS as an internal standard.

2.3 Computer Modelling

Computer modelling for HCDBCO was done using the semi-empirical method available in Spartan'02 Windows version.⁴

2.4 GC/MS

Analyses were performed on a Shimadzu GC/MS-QP2010 using a J&W 30m DB-5 column (0.25 mm ID, 0.25 μm film). All injections were done in splitless mode. Unless otherwise stated, the experiments were done with the following GC conditions: helium carrier gas flow at 1.0 ml/minute, injector temperature at 250°C, temperature program set to the following parameters: initial oven temperature at 100°C, hold for 5 minute, ramp at 50°C/minute to 200°C, hold for 5.5 minutes, ramp at 10°C/minute to 325°C, hold for 20 minutes. Spectra (50 to 1000 u) were obtained in positive ion, electron impact mode (EI+).

3 RESULTS & DISCUSSIONS

3.1 NMR Characterization of HCDBCO

HCDBCO was synthesized following the procedure outlined in previous work.³ The product was previously characterized by ¹H NMR spectroscopy.³ In this work, we report the ¹H NMR spectrum (Fig. 2a) taken on a 600 MHz instrument. At this field strength the signals clearly separate and the individual protons signals in the spectrum were assigned to the HCDBCO structure (Fig. 3) with the aid of a ¹H-¹H COSY (Fig. 2b) and a ¹H-¹³C HSQC NMR experiment (Fig. 2c). The ¹H-¹³C HSQC NMR experiment allowed us to assign the pair of protons on each of the CH₂ moieties and we have arbitrarily designated them as H_{c/d}, H_{e/f}, H_{i/j} and H_{k/l}. The ¹H-¹H COSY experiment allowed identification of the proton sequence around the structure as: a-b-(c/d)-(e/f)-g-h-(i/j)-(k/l). Protons H_a and H_b are clearly those of the CHBr moieties as they would be expected to appear at a lower field relative to the other protons. However, at the outset, one has to decide, with respect to the CHBr moieties,

which group contains H_a and which H_b. This was first attempted by comparing the magnitudes of the relevant coupling constants observed in the ¹H NMR spectrum (see Table 1) with those expected on the basis of the dihedral angles between vicinal protons as calculated from a 3D model structure which would be expected to provide a good first approximation of the lowest energy conformer for HCDBCO. However, in general, we found only a very poor correlation between the observed proton-proton couplings constants from the ¹H NMR spectrum and the measured dihedral angles between vicinal protons from the 3D model structure. This result led us to examine whether an X-ray structure (see below) might provide a suitable starting point for calculating the conformation in solution. Indeed, the measured dihedral angles (see Table 1) from this structure correlated very well with those calculated from the proton-proton coupling constants indicating that the conformations in solution and in the solid state are probably very similar. As a result, all twelve individual protons observed in the ¹H NMR spectrum could be specifically assigned to the structure shown in figure 3.

3.2 X-ray structure determination

Crystals of HCDBCO (**1**) were grown from dichloromethane and hexane and submitted for x-ray structure determination. There are two molecules in the asymmetric unit “molecule A” (see Fig. 3) and “molecule B”. Molecule B is disordered with respect to C5 and C6 resulting in slightly different torsional angles for this moiety in the two contributing structures. The space group is centrosymmetric which causes an inversion of the asymmetric cell giving overall a 1:1 ratio of enantiomers. This work confirms that HCDBCO has the structure *rac*-(5*R*,6*R*)-5,6-dibromo-1,10,11,12,13,13-hexachlorotricyclo[8,2,1,0^{2,9}]-(*1R,2R,9S,10S*)-tridec-11-ene. Importantly, the measured dihedral angles between vicinal protons for molecule A correlate very well with the coupling constants obtained from the ¹H NMR spectrum (Table 1).

3.3 GC/MS

The GC/MS analysis of HCDBCO has been well documented in previous work.³ However, it was observed during our work that HCDBCO debrominates in the injector port at 250°C. Reducing the temperature to 200°C eliminated the problem. HCDBCO only exists as one pair of enantiomers, therefore, thermal rearrangement as seen for other cycloaliphatic polybrominated compound such as hexabromocyclododecane (HBCD)⁵, tetrabromocyclooctane (TBCO)⁶ and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECHE)⁷ is not a problem. Nevertheless, thermal rearrangement between enantiomers may still exist which would create problems when analyzing enantiomeric composition using a chiral column.

4 SUMMARY

A detailed analysis of HCDBCO was completed by various NMR experiments, 3D modeling and an X-ray structure determination. Our results allowed us to assign a conformation for HCDBCO in solution. Indeed, it appears that the conformations of HCDBCO in solution and in the solid state are very similar. This information should be useful to researchers wishing to model and predict the physicochemical behaviour of HCDBCO.

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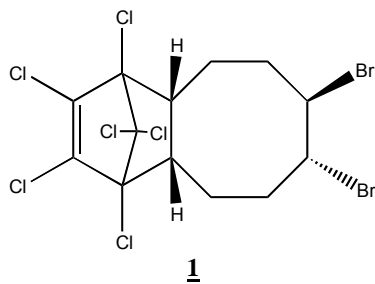


Figure 1. Structure of Hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO)

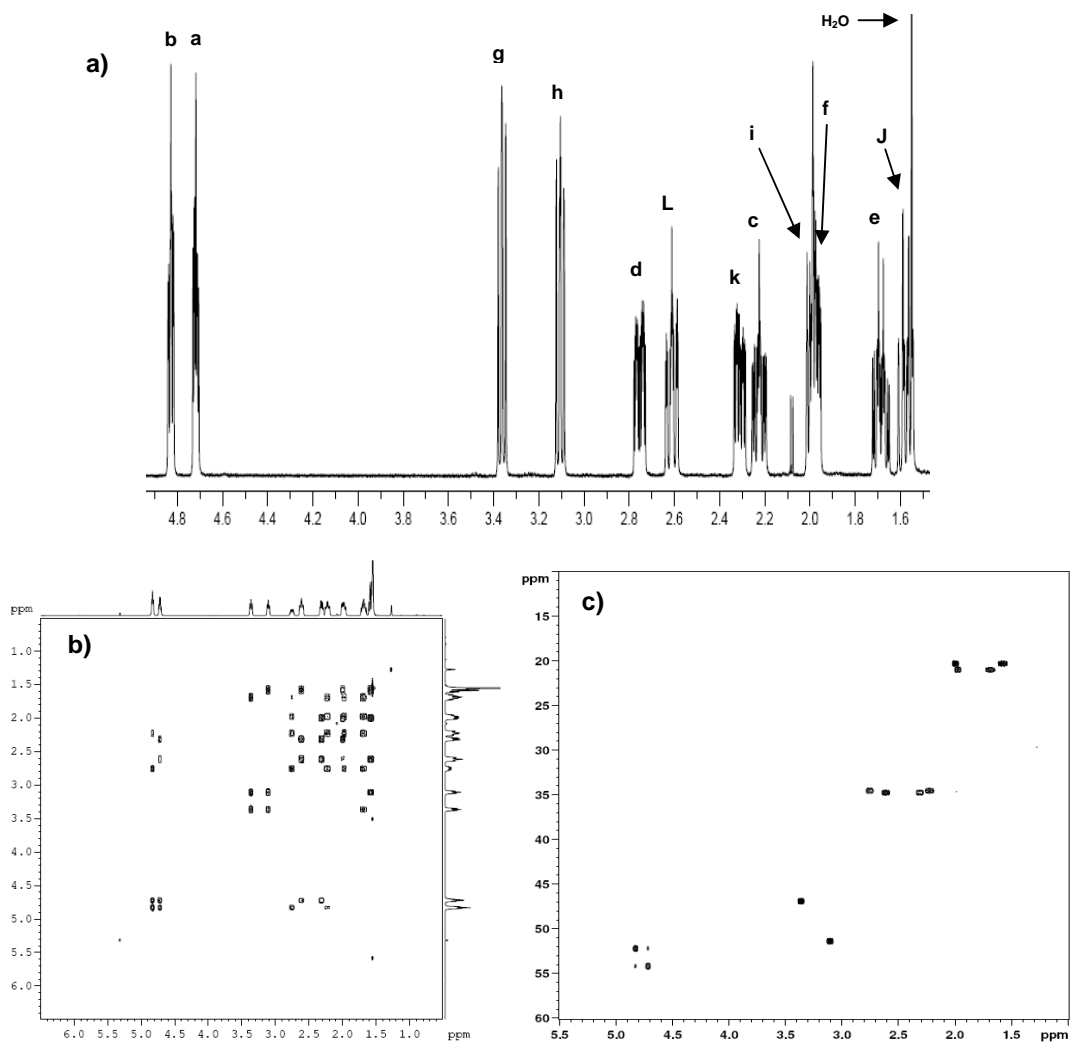


Figure 2. The a) ^1H NMR spectrum, b) ^1H - ^1H NMR experiment and c) ^1H - ^{13}C NMR experiment for HCDBCO

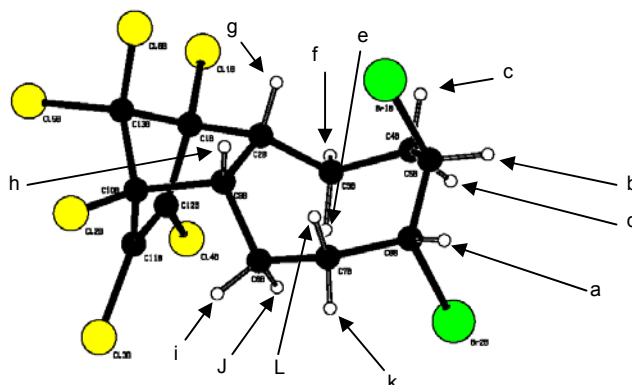


Figure 3. The molecular structure of (5*R*,6*R*)-5,6-dibromo-1,10,11,12,13,13-hexachlorotricyclo[8,2,1,0^{2,9}]- (1*R*,2*R*,9*S*,10*S*)-tridec-11-ene (**1**, HCDBCO). Displacement ellipsoids are at the 30% probability level.

Table 1. Dihedral angles between vicinal protons from the calculated structure of HCDBCO and the observed $3J(^1\text{H}-^1\text{H})$ interactions from the $^1\text{H}-^1\text{H}$ COSY experiment.

Protons	Observed $3J(^1\text{H}-^1\text{H})$ interaction from the $^1\text{H}-^1\text{H}$ COSY experiment (Fig. 2b)	Observed $3J(^1\text{H}-^1\text{H})$ coupling constants (Hz) ^a (Fig 2a)	Dihedral angle (°) measured from the x-ray structure ^b (Fig. 3)	Calculated $3J(^1\text{H}-^1\text{H})$ coupling constants ^c
H _a -H _b	Yes	7.7	40.3	7.1
H _b -H _c	Weak	1.9	73.9	2.5
H _b -H _d	Yes	5.5	40.3	7.1
H _c -H _e	Yes	13.5	171.5	12.8
H _c -H _f	Yes	5.0	55.1	4.7
H _d -H _e	Yes	4.4	57.3	4.4
H _d -H _f	Yes	3.2	59.1	4.1
H _e -H _g	Yes	11	155.7	11.2
H _f -H _g	No	0.7	87.9	2.0
H _g -H _h	Yes	9.5	0.02	11.0
H _h -H _j	Yes	11.7	158.5	11.6
H _h -H _i	No	1.1	85.1	2.0
H _j -H _k	No	1.3	82.3	2.0
H _j -H _l	Yes	11.7	162.8	12.0
H _i -H _k	Yes	7.5	34.2	8.0
H _i -H _l	No	1.5	80.8	2.1
H _k -H _a	Yes	4.5	55.5	4.6
H _l -H _a	Yes	3.1	59.4	4.1
H _c -H _d	Yes	16.5	Geminal protons	
H _e -H _f	Yes	15.0		
H _i -H _j	Yes	15.45		
H _k -H _l	Yes	16.5		

a Some of the coupling constants were determined with the help of a simulation program (SpinWorks version 2.5.5) to disentangle the complex second order spectra.

b Dihedral angles measured from x-ray structure shown in Fig. 3.

c Coupling constants calculated using the Karplus equation⁸ and the dihedral angles measured from the x-ray structure (Fig. 3).