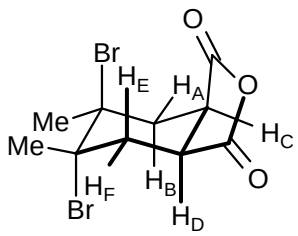
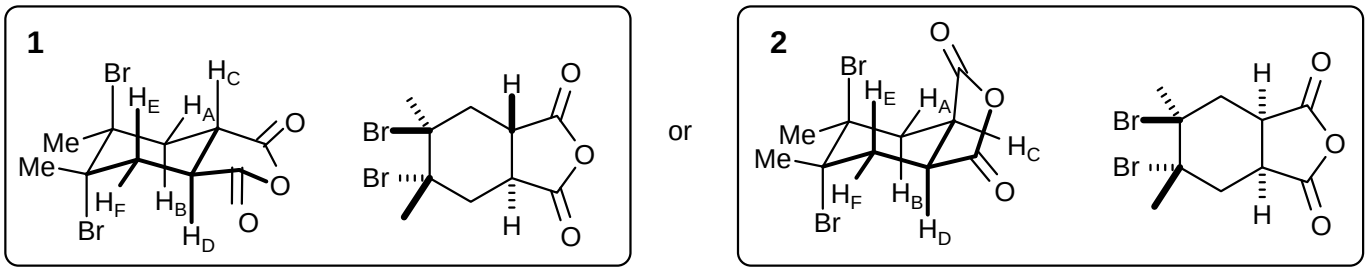
Problem R-09J ($C_{10}H_{12}Br_2O_3$)
300 MHz ^{1}H NMR spectrum in $CDCl_3$
(Source: Allen Clauss 11/32) g

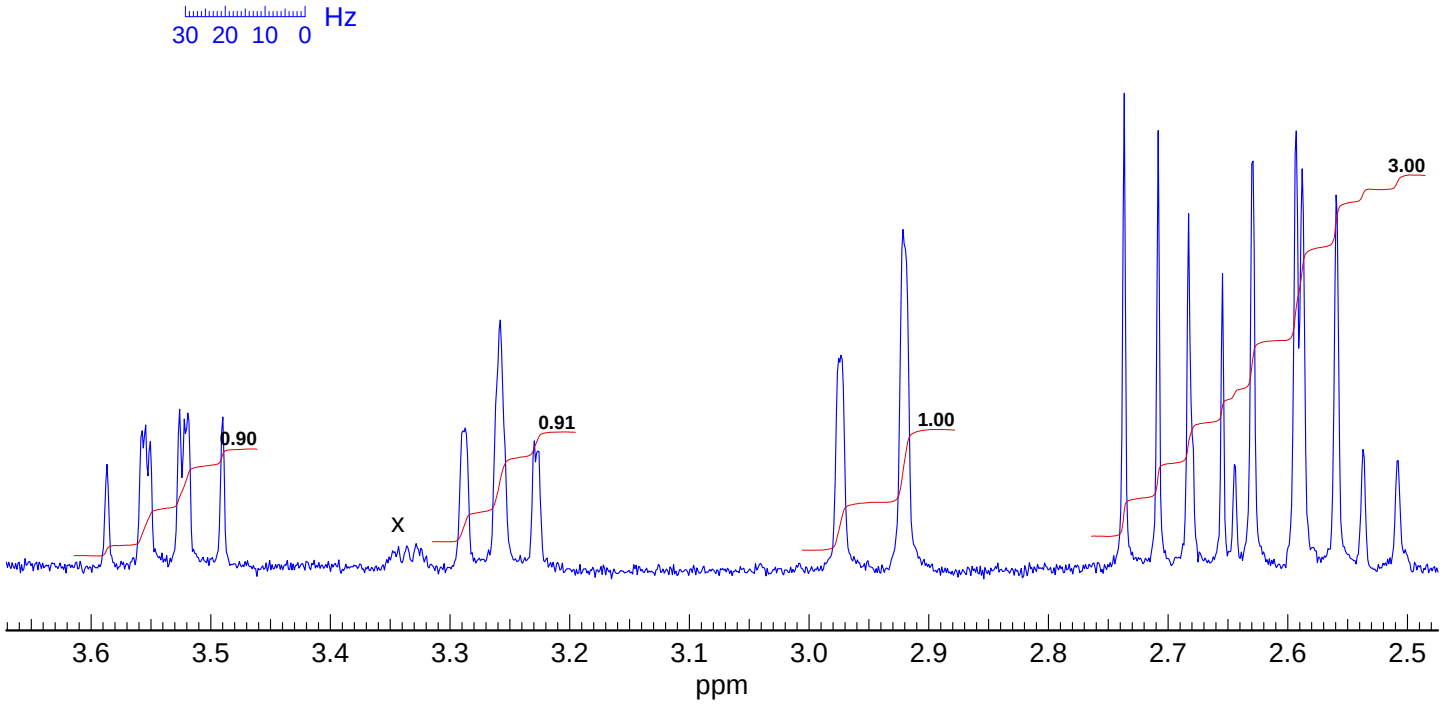


PLT ex-2-2009-10-gq.plt

Problem R-09J. You are asked to determine which of two possible isomers of a dibromo anhydride is the correct one, and assign the protons . The complete spectrum is shown on the next page.

(a) Assign the protons, draw appropriate coupling trees on the spectrum below, and label each one with a proton assignmment (H_A, H_B, etc). It is not necessary to report couplings, although you might wish to measure them to aid in your analysis.





(b) Which isomer ____ (**1** or **2**) is correct? Explain briefly how you decided which was correct.

(c) Explain why the proton at δ 2.95 shows such a simple multiplet.

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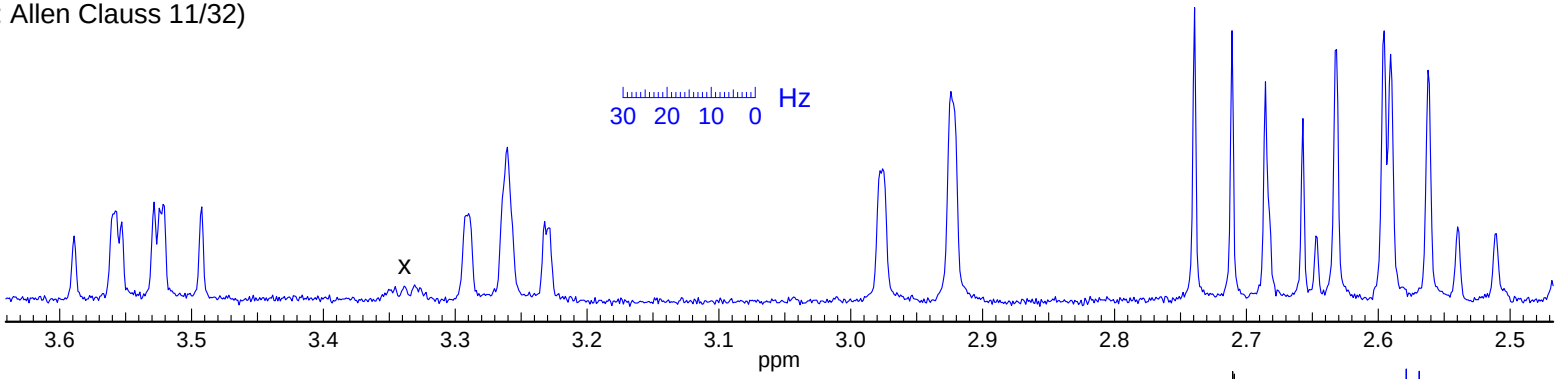

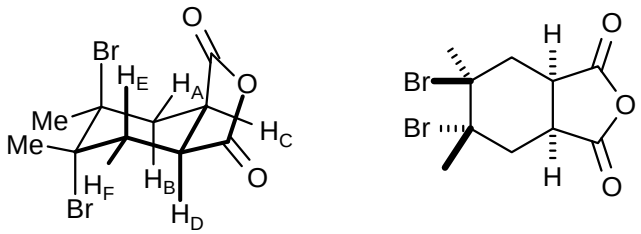

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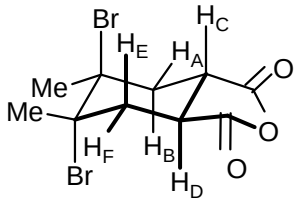
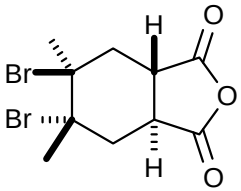


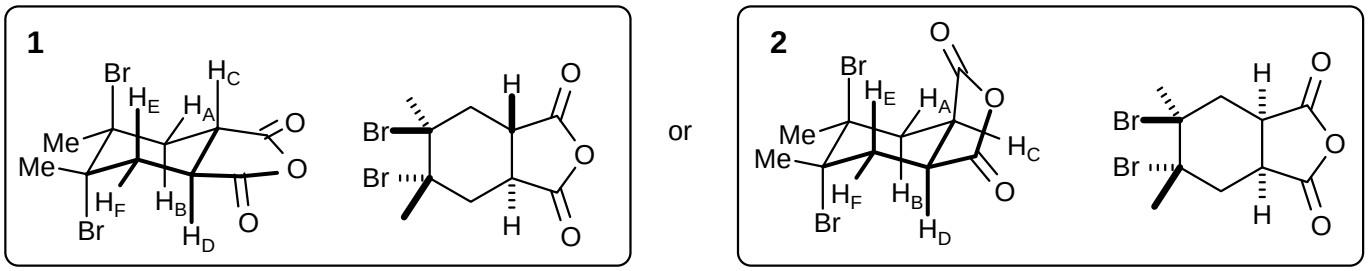


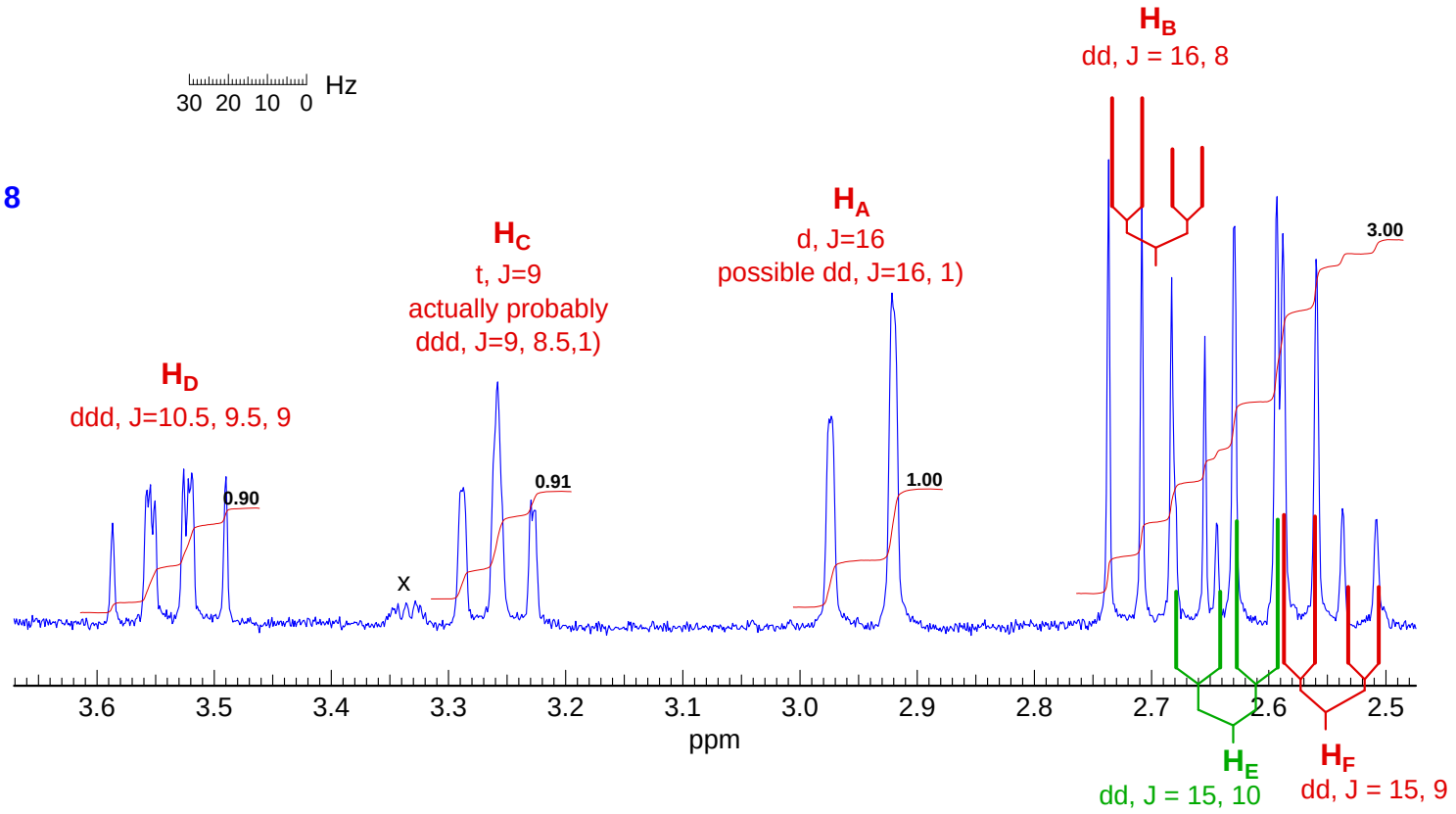
PLT ex-2-2009-10-gq.plt

15

Problem R-09J. You are asked to determine which of two possible isomers of a dibromo anhydride is the correct one, and assign the protons . The complete spectrum is shown on the next page.

(a) Assign the protons, draw appropriate coupling trees on the spectrum below, and label each one with a proton assignmment (H_A, H_B, etc). It is not necessary to report couplings, although you might wish to measure them to aid in your analysis.



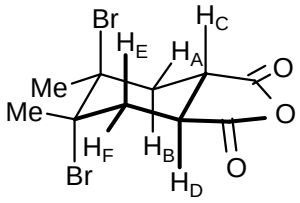


(b) Which isomer __2__ (**1** or **2**) is correct? Explain briefly how you decided which was correct.

5

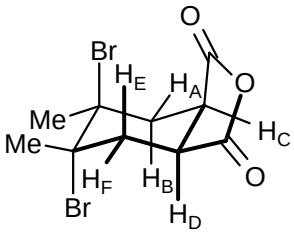
Isomer 1 has an axis of symmetry, $H_C = H_D$, $H_A = H_F$ and $H_B = H_E$, so spectrum would be much simpler (only 3 chemical shifts, rather than 6)

Can also make arguments based on the individual coupling constants: in isomer 1, H_C should be coupled to H_A and H_D with large couplings (aa), and H_A with a small one (ae), we see only two medium sized couplings. On the other hand, for isomer 2, H_C might be coupled to H_A by only a very small J, since the ee coupling should be near 0 for a flattened ring like this.



1

or

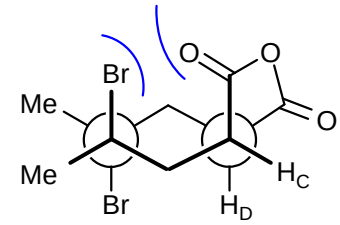


2

The ring-flip isomer of **2** would place two methyl groups axial; methyls are much larger than bromines in a cyclohexane (1.7 vs 0.4 kcal/mole)

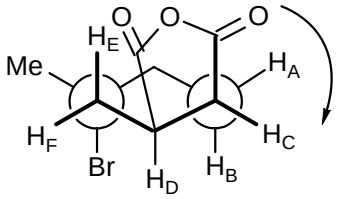
(c) Explain why the proton at δ 2.95 shows such a simple multiplet.

2

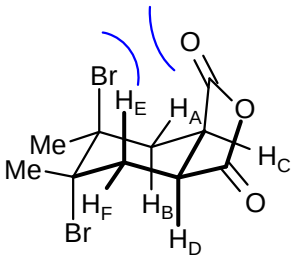


Proton at δ 2.95 is H_A

The diaxial group steric interaction will significantly flatten the ring. This makes J_{ee} get smaller, and J_{ae} get larger (J_{CD})

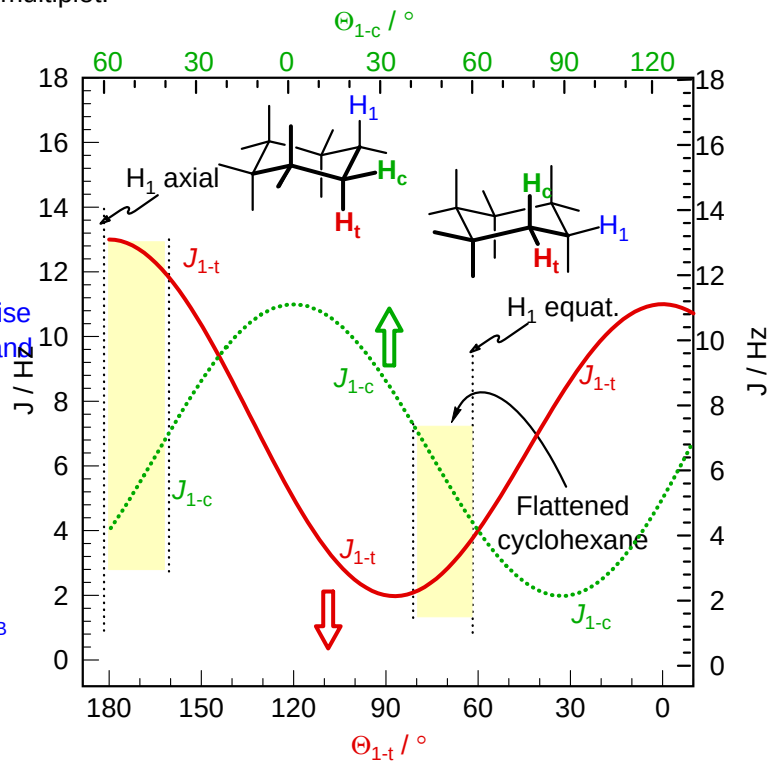


Front carbon rotates clockwise - $\Theta_{AC} \rightarrow 90$, J_{AC} goes to 0, and $\Theta_{BC} \rightarrow 0$ J_{BC} gets larger



2

H_C is basically a triplet because $J_{CA} \rightarrow 0$, leaving only the eq-ax couplings, J_{CB} and J_{CD}, which are unusually large



PLT ex-2-2009-10-gq.plt

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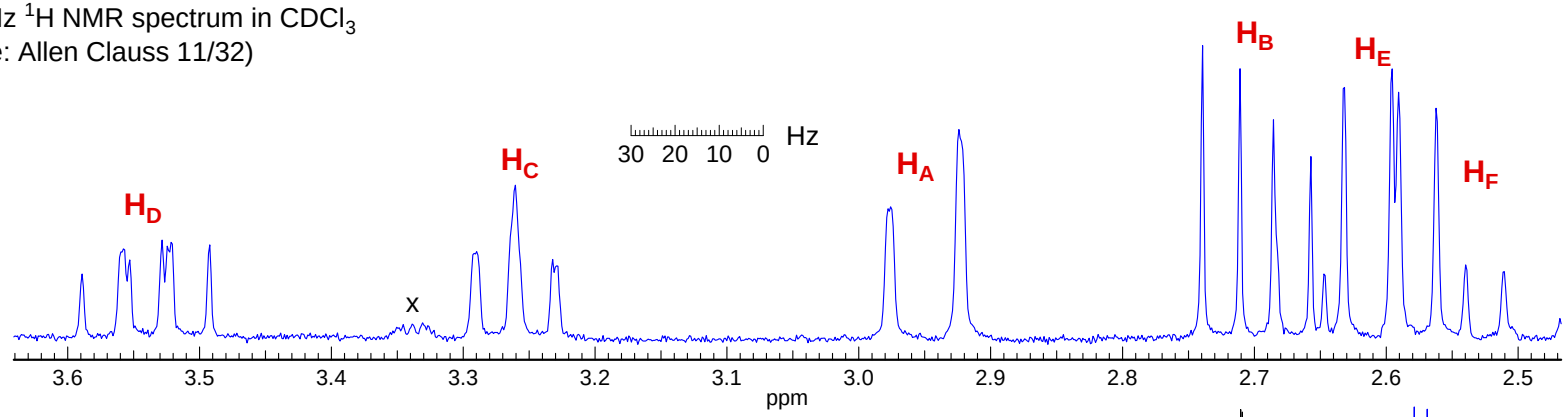

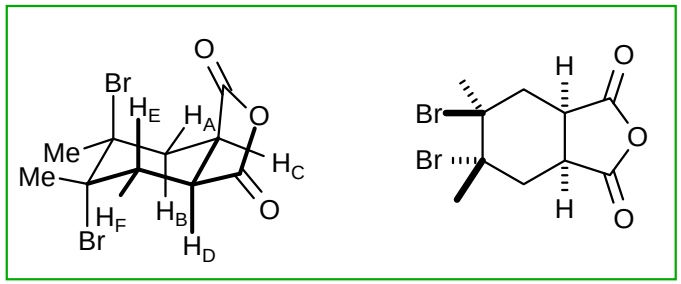

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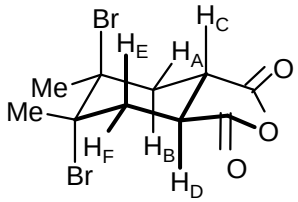

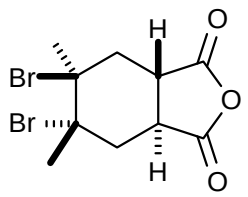

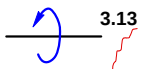

Rotate 180° - gives identical structure

PLT ex-2-2009-10-gq.plt