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PROOF THAT HYDROGENS OF BENZENE ARE HOMOTOPIC

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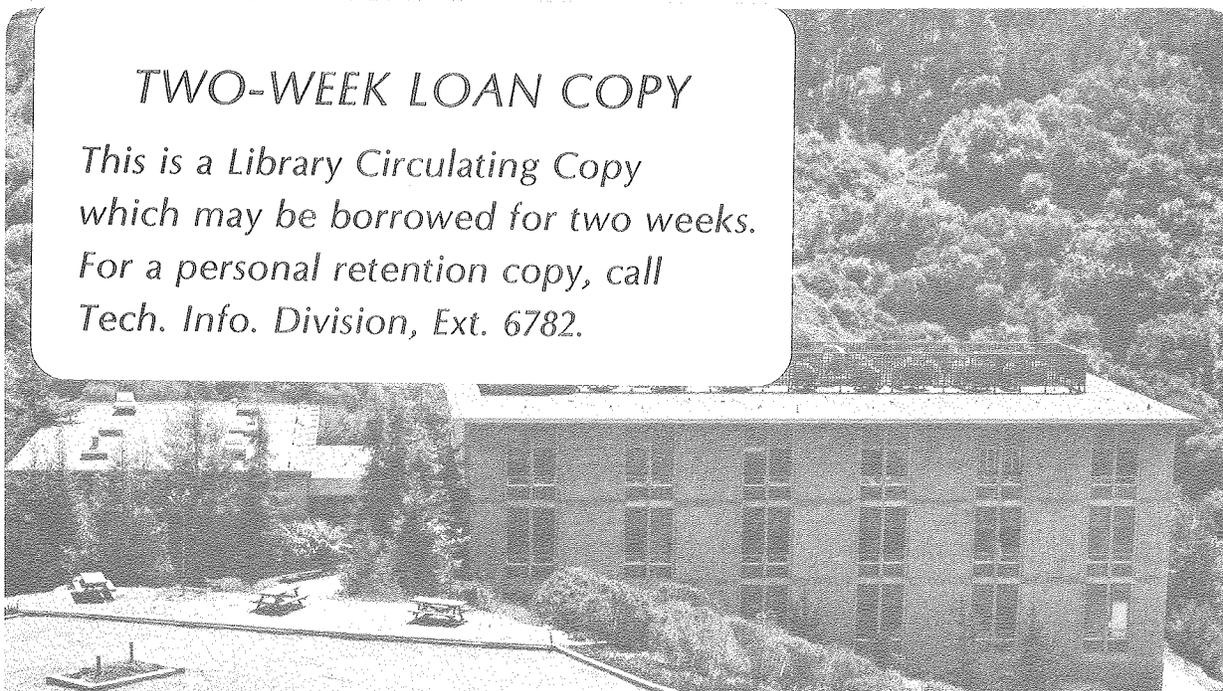
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Comments on McBride's Completion of Kroner's Proof  
That Hydrogens of Benzene are Homotopic

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Abstract

This paper shows that McBride's completion of Kroner's proof (J. M. McBride, J. Am. Chem. Soc. 102, 4134 (1980)) can be immediately obtained using methods developed by the author in the context of isomer enumeration and NMR-signal enumeration using a theorem of Pólya. The method is illustrated with both rigid and non-rigid molecules.

I noted with interest the recent paper of McBride on the homotopy of the hydrogens of benzene.<sup>[1]</sup> I have been interested in developing combinatorial and group theoretical methods,<sup>[2-8]</sup> in general, for several problems in chemistry. One of the problems that I have been interested in is to partition a set of nuclei present in a molecule (both rigid and non-rigid) into equivalence classes of nuclei, wherein all the nuclei in a class are equivalent under the action of the rotational subgroup of the molecule. I feel that this proof which McBride has outlined follows immediately from this technique which I present below.

Let  $G$  be the rotational subgroup of the point group of the molecule and define the cycle index of  $G$ ,  $P_G$  to be

$$P_G = \frac{1}{|G|} \sum_{g \in G} x_1^{b_1} x_2^{b_2} \dots \quad (1)$$

where  $x_1^{b_1} x_2^{b_2} \dots$  is a representation of a typical permutation  $g \in G$  having  $b_1$  cycles of length 1,  $b_2$  cycles of length 2, etc. Consider  $D$  as the set of atoms whose equivalence is under consideration. For the benzene problem  $D$  is the set of hydrogen atoms. Let  $R$  be a set consisting of 2 elements. Let  $N = |D|$ , be the number of elements in  $D$ . Let  $l$  and  $f$  be the weights of the 2 elements in the set  $R$ . Then the present author<sup>[2]</sup> showed in the context of isomer enumeration and enumeration of NMR signals that the coefficient of  $f^{N-1}$  or  $f$  in the expression (2) obtained using a theorem of Polya<sup>[9,10]</sup> gives the number of equivalence classes of the nuclei in the set  $D$ .

$$G.F. = P_G (x_k \rightarrow (1+f)^k). \quad (2)$$

For the benzene problem  $P_G$  and G.F. are given by Eqs. (3) and (4).

$$P_G = 1/12 (x_1^6 + 2x_6 + 2x_3^2 + 4x_2^3 + 3x_1^2 x_2^2) \quad (3)$$

$$G.F. = f^6 + f^5 + 3f^4 + 3f^3 + 3f^2 + f + 1. \quad (4)$$

Since the coefficient of  $f^5$  in (4) is 1 there is just one equivalence class of hydrogen atoms establishing McBride's proof in a straightforward manner. The method can be applied very easily to many polyatomic molecules. For example, expressions thus obtained for naphthalene and anthracene are shown below (Eqs. 5 and 6).

$$G.F. = f^8 + 2f^7 + 10f^6 + 14f^5 + 22f^4 + 14f^3 + 10f^2 + 2f + 1 \quad (5)$$

$$G.F. = f^{10} + 3f^9 + 15f^8 + 32f^7 + 60f^6 + 66f^5 + 60f^4 + 32f^3 + 15f^2 + 3f + 1. \quad (6)$$

For non-rigid molecules using the author's generalized wreath product methods<sup>[2,6]</sup> this can be done. For example, I give below the expressions (7) and (8) that I obtained for rigid and non-rigid propane molecules.<sup>[4]</sup>

$$1/4((1+f)^8 + 2(1+f)^2(1+f^2)^3 + (1+f^2)^4) \quad (7)$$

$$1/36[(1+f)^8 + 4(1+f)^5(1+f^3) + 4(1+f)^2(1+f^3)^2 + 3(1+f^2)^4 + 6(1+f^2)(1+f^6) + 12(1+f)^2(1+f^2)^3 + 6(1+f)^2(1+f^6)]. \quad (8)$$

The coefficients of  $f^7$  in (7) and (8) are given by (9) and (10), respectively, establishing the fact that there are 3 and 2 classes of protons for rigid and non-rigid molecules, respectively.

$$\frac{1}{4} \left[ \binom{8}{7} + 2 \binom{2}{1} \right] = 3 \quad (9)$$

$$\frac{1}{36} \left[ \binom{8}{7} + 4 \binom{5}{1} + 4 \binom{2}{1} + 12 \binom{2}{1} + 6 \binom{2}{1} \right] = 2. \quad (10)$$

However, when one considers the rotational subgroups instead of the point groups, we obtain the number of classes of protons for rigid and non-rigid propanes to be 4 and 2, indicating that there is a pair of enantiotopic protons for the rigid molecule.

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