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

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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 the methods developed by the author in the context of isomer enumeration and NMR-signal enumeration with a theorem of Pólya. The method is illustrated with both rigid and non-rigid molecules.

Key words: Kroner's proof – completion of ~ – Pólya's theorem.

I noted with interest the recent paper of McBride on the homotopy of the hydrogens of benzene [1]. I have been interested in developing combinatorial and group theoretical methods [2–9], 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

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

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

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number of elements in D. Let 1 and f be the weights of the 2 elements in the set R. Then the present author [2] 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 Pólya [10, 11] gives the number of equivalence classes of the nuclei in the set D.

$$G.F. = P_G(x_k \to 1+f^k). \tag{2}$$

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

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

$$G.F. = f^6+f^5+3f^4+3f^3+3f^2+f+1. \tag{4}$$

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 straight forward 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).

$$G.F. = f^8+2f^7+10f^6+14f^5+22f^4+14f^3+10f^2+2f+1 \tag{5}$$

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

It can be inferred from Eqs. (5) and (6) that naphthalene and anthrocene have 2 and 3 classes of protons, respectively.

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

$$1/4((1+f)^8+2(1+f)^2(1+f^2)^3+(1+f^2)^4) \tag{7}$$

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

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

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

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

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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