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NOVEL APPLICATION OF RANVIC MOLECULAR CONNECTIVITY
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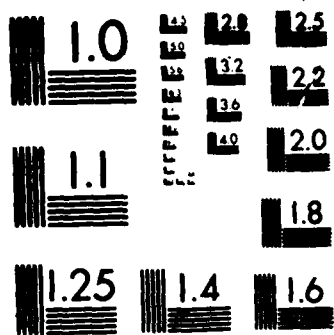
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Novel Application of Randić Molecular Connectivity Index
On Data Reduction of Chemical Graphs

by

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Novel Applications of Randić Molecular Connectivity Index

On data reduction of chemical graphs

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Benzenoid hydrocarbons are studied in terms of the much simpler caterpillar trees. Using molecular connectivity indices of the latter almost exact linear relations are obtained with natural logarithms of five properties of benzenoid hydrocarbons including all self-avoiding paths, conjugated circuits, number of Kekulé structures, electronic absorption spectra, and heats of atomizations.

Key words:

- Graph Theory
- Randić Molecular Connectivity Index
- Data Reduction
- Caterpillar trees
- Benzenoid Hydrocarbons

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1. Introduction and definitions

One of the main goals of every science is the endeavoring to arrange and collate the numerous individual observations and details which present themselves, in order that they become part of one comprehensive picture.¹ Such an objective may be achieved through the use of data reduction which is an essential part of chemical and physical data analysis. In the past the task of data reduction involved mainly curve fitting procedures which have recently become more efficient due to increased availability of computers. Topological approaches which consider additivities of molecular properties have been almost ignored in the past. However some recognition of the role of graph theory became apparent soon after the (important) work of Smolenskii² and (to a lesser degree) the work of Gordon and Kennedy³ who formalized their schemes of general approaches to molecular additivities. Revival of interest in chemical graph theory is probably due to Balaban via his (editing) of a book⁴ which provided a source of problems and numerous other papers. Several counting polynomials were defined which act as descriptors of the connectivity pattern of various types of molecular graphs. The latter are well-defined mathematical objects which describe the bonding relation between atoms in the original molecules. Such counting polynomials are then a combinatorial form of data reduction. Equation 1 describes the general form of a graph-theoretical counting polynomial⁵, $F(G;x)$, for an arbitrary graph G, containing n vertices:

$$F(G;x) = \sum_{k=0}^M \rho \theta(G;k) x^{f(k,n)} \tag{1}$$

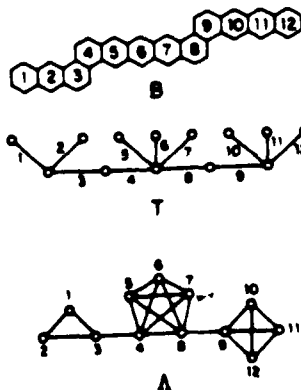
where ρ is either 1 or $(-1)^k$, $\theta(G;k)$ enumerates certain selected graph-invariants in G taken in k independent tuples (i.e. no two of them are adjacent) and M is

the maximal value of k . For the purpose of this paper we consider three polynomials for all of which $\rho = 1$ and $f(k,n) = n$. These are:

- i) The counting polynomial (of Hosoya)⁶, $H(G;x)$ for which $\theta(G;k) = p(G;k) =$ the number of k -matchings in G .
- ii) The sextet polynomial (of Hosoya and Yamaguchi)⁷, $\sigma(B;x)$ of which $\theta(G;k) = r(B;k) =$ the number of selections of k mutually resonant but nonadjacent aromatic sextet in a benzenoid system (\equiv polyhex graph⁸), B .
- iii) The independence polynomial (of Gutman)⁹, $\omega(G;x)$, for which $\theta(G;k) = 0(G;k) =$ the number of selections of k independent vertices of G .

2. The Caterpillar Tree¹⁰, the Polyhex Graph¹¹ and the Clar Graph^{9,12}

In a given Kekulé structure an (aromatic) sextet is defined as a set of three double bonds circularly conjugated so that no two sextets can have a common bond. When two rings (hexagons) can have aromatic sextets so that all other carbon atoms are spanned by a sextet or by double bond, such two rings are called resonant.^{9,12} The individual hexagons of a given benzenoid system may or may not be resonant⁷. Information on such resonance relations (among the individual hexagons) are best "reduced" (i.e. described) using either a caterpillar tree¹⁰ or a Clar graph.⁹ To illustrate this fundamental relation¹³ we consider the three graphs shown below:



The hexagons of B may be grouped into three subsets, viz., {1,2,3}; {4,5,6,7,8}; {9,10,11,12}. One observes that no two hexagons are resonant if they belong to one subset. Similarly the edges of T may be subdivided into analogous three subsets observing that no two edges of the same subset can be adjacent. A similar description obtains for the vertices of graph Λ . In fact bijective (i.e. one-to-one, onto)¹⁴ mapping might be defined between the hexagons of B, the edges of T and the vertices of Λ : the latter is called the Clar graph^{9,12} of B. It is easy to verify the following identity:

$$\sigma(B;x) = H(T;x) = \omega(\Lambda;x) = 1 + 12X + 45X^2 + 53X^3 \quad (2)$$

A caterpillar tree such as T whose counting polynomial is identical to the sextet polynomial of a benzenoid hydrocarbon B will be called an equivalent caterpillar to the benzenoid hydrocarbon. the set of graphs {B,T, Λ } shown above will be called a set of equivalent graphs. Gutman¹⁵ demonstrated that for every nonbranched¹⁶ benzenoid hydrocarbon there is an "equivalent" caterpillar tree.

3. Conjecture

The physical properties of a benzenoid hydrocarbon which depend on its topological structure may be predicted from graph-theoretical properties of its equivalent graphs.

4. Results and tests of Conjectures

Fig. 1 shows benzenoid hydrocarbons and their equivalent caterpillar trees studied in this work.

4.a Graph theoretical (combinatorial) properties

Three graph-theoretical properties of benzenoid hydrocarbons, viz., self-avoiding paths¹⁹, conjugated circuits²⁰ and the number of Kekulé structures (i.e. number of perfect matchings) are correlated with the molecular connectivity indices,²¹ χ 's of the equivalent caterpillar (or pseudocaterpillar) trees. Fig. 2 shows the types of linear correlations obtained. In all cases correlation coefficients ≥ 0.999 were obtained.

4b. Physical properties

Two physical properties viz., electronic absorption spectra²², and heats of atomizations²³ of several homologous series of benzenoid hydrocarbons are linearly correlated with χ (T)s; the molecular connectivity indices²¹ of the corresponding equivalent trees. Details of data are available on request¹⁷ but as an illustration Table 1 is included which contains β and ρ bands of the electronic spectra of two families of hydrocarbons of Fig. 3. A separate manuscript is submitted elsewhere²⁴ dealing with electronic absorption spectra of 27 arene systems all linearly correlated with χ (T) values. The same type of data reduction is obtainable¹⁷ when molecular properties (topological or physical) of benzenoid hydrocarbons are studied in terms of connectivity functions of their equivalent Clar graphs.²⁵ Fig. 4 is a plot of heats of atomizations of some benzenoid hydrocarbons versus connectivity indices of the corresponding caterpillar trees.

6. Discussion

Caterpillar trees and Clar graphs seem to be quite promising "storage devices" which preserve many properties of (the much larger) equivalent polyhex graphs. In contrast to the Balaban-Harary dualist graphs²⁶ they do not have a geometric element and as such, connectivity alone best describes them. It is amazing that some of the studied properties such as the total number of paths¹⁹ in a polyhex graph (Fig. 2) take nearly 30 minutes on a Corona computer,²⁷ yet can be retrieved by very simple hand calculation of the connectivity index of a much simpler graph! Table 2 lists percent retrievals of the total number of self-avoiding paths for a series of nonbranched benzenoid hydrocarbons shown in Fig. 1. All the above mentioned correlations imply classification of molecules into families (i.e. homologous series). The concept of classification is well-known in science: the periodic table of the elements and recently table of alkanes introduced by Randić and Wilkins²⁸ and more recently table of benzenoid hydrocarbons of Dias²⁹ are all non-mathematical forms of set theory. However in contrast to the latter two tables, which result from graph theoretical considerations, the "old" periodic table is a result of group theory as it follows from symmetry properties of atoms.

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Table 1

Electron absorption spectra of the β bands, λ_{β} , of the homologous series of benzenoid hydrocarbons shown in Fig. 3. $\chi(T)$ s are molecular connectivity indices of the equivalent pseudocaterpillar trees.

<u>Hydrocarbon*</u>	<u>$\chi(T)$</u>	<u>λ_{β} (Å)</u>	<u>λ_{ρ} (Å)</u>
A	3.914	2570	
B	4.684	2870	
C	5.293	3130	
D	5.812	3430	
1	1.000		2068
2	1.414		2850
3	1.732		3745
4	2.000		4710
5	2.236		5755
6	2.449		6930

*c.f. Fig. 3

Table 2

Percent retrieval of the total number of self-avoiding paths for the series of nonbranched benzenoid hydrocarbons shown in Fig. 2. The regression line is $Y = 4.374 + 0.484X$ with a correlation coefficient = 1.0000.

<u>Hydrocarbon*</u>	<u>Calcd. $\Sigma p_i(B)^*$</u>	<u>Actual $\Sigma p_i(B)^*$</u>	<u>Difference</u>	<u>% Retrieval^{a)}</u>
E	3254	3277	23	99.298
F	7391	7413	22	99.704
G	16055	16055	0	100.000
H	33827	33879	52	99.846
I	69675	69857	182	99.740
J	141060	142645	1585	98.889

*c.f. Fig. 2

$$a) = 100 - 100 | \text{Calcd} - \text{Actual} | / \text{Actual}$$

Fig. Legends

Fig. 1

Polyhex graphs of benzenoid hydrocarbons studied in this work together with the molecular graphs of their corresponding caterpillar trees.

Fig. 2

Combinatorial properties of benzenoid hydrocarbons studied: $K(B)$, $\Sigma p(B)$ and $\Sigma R_{\text{tot}}(B)$ respectively indicate number of Kekulé structures, total number of self-avoiding paths and total number of conjugated circuits of a benzenoid system, B , plotted versus the connectivity index of the corresponding caterpillar tree, $\chi(T)$ raised to various powers. (The hydrocarbons and their caterpillars are shown in Fig. 1).

Fig. 3

Electronic absorption spectra of benzenoid hydrocarbons: Points 1-6 indicate benzene, naphthalene, anthracene, tetracene, pentacene and hexacene; the line passing through these points is a plot of their absorption para bánd (in \ln units) vs. the connectivity index of the corresponding caterpillar trees, $\chi(T)$. The line passing through points A-D is a plot of the beta band vs. $\chi(T)$ where the hydrocarbons and their trees are shown in Fig. 1.

Fig. 4

A plot of the natural logarithms of the heats of atomizations of some benzenoid hydrocarbons, $\ln H_t A_t(B)$, against the connectivity indices, $\chi(T)$'s, of the corresponding caterpillar trees shown in Fig. 1.

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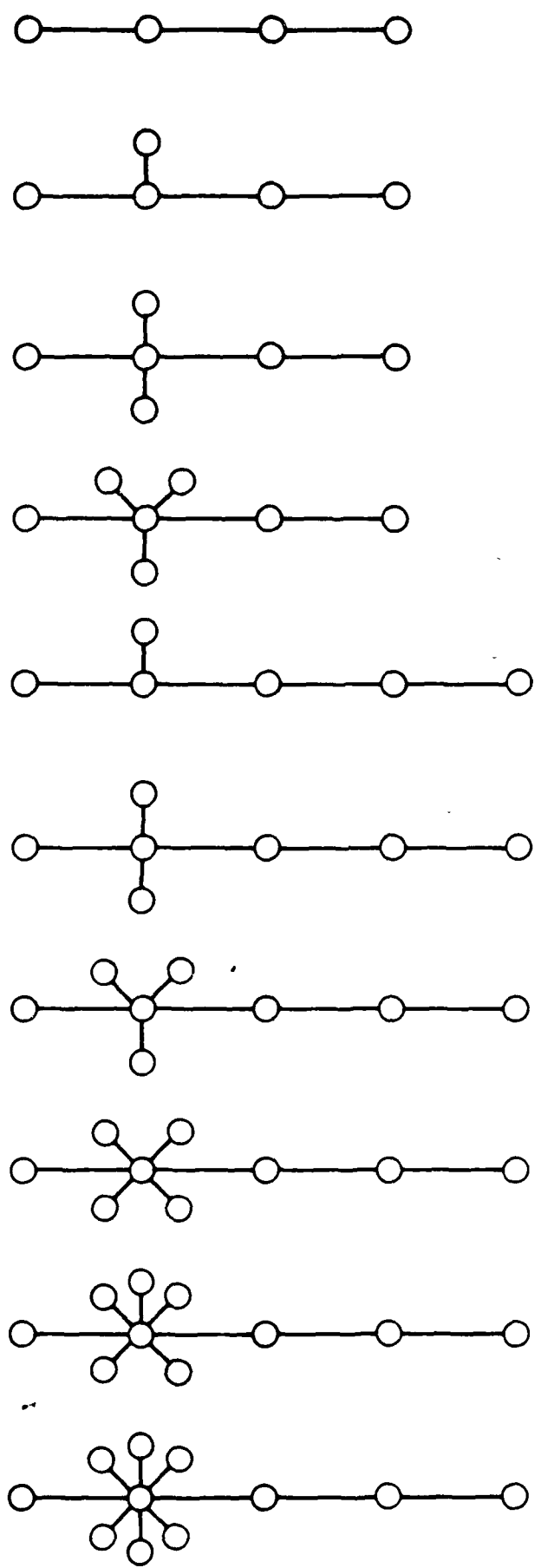
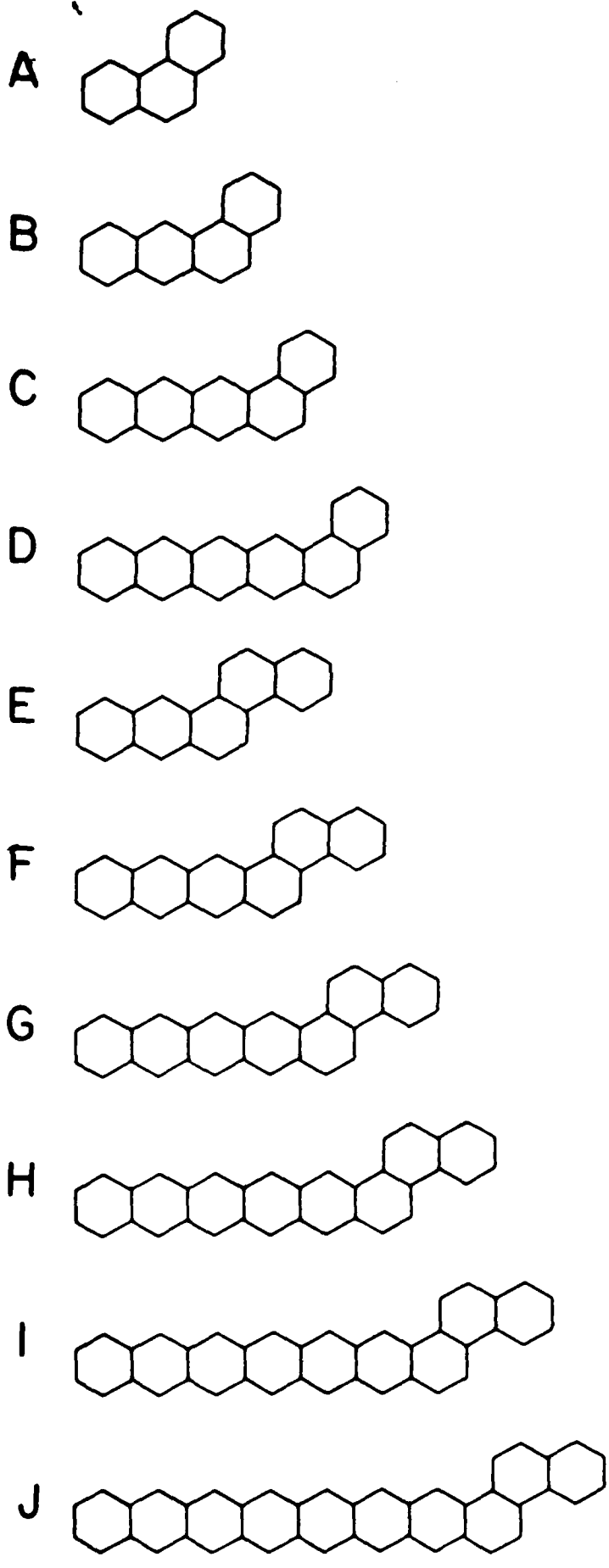
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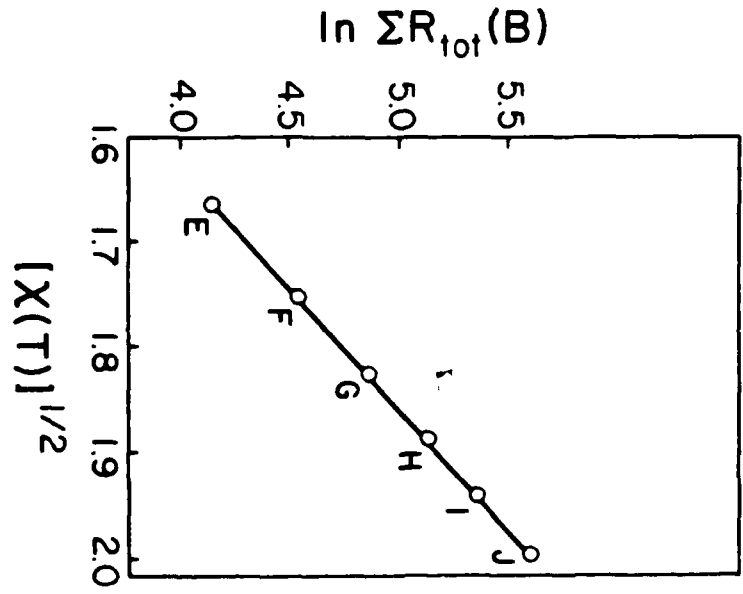
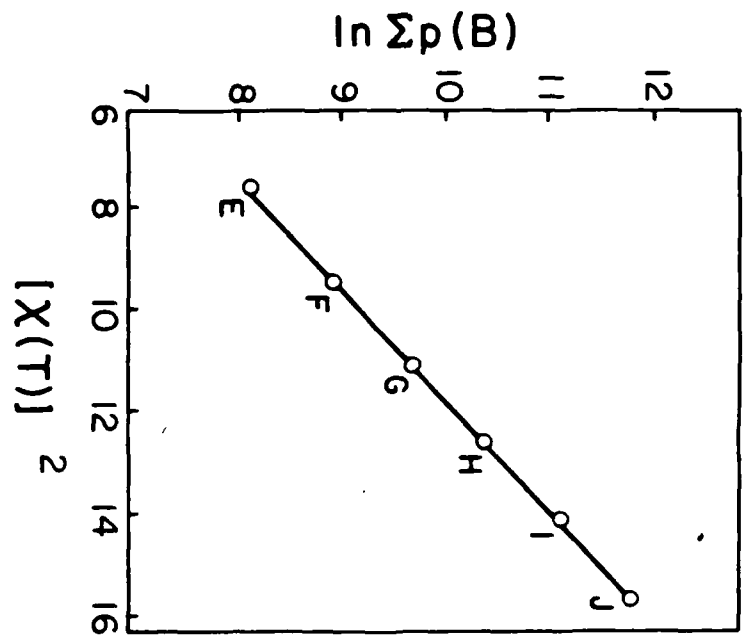
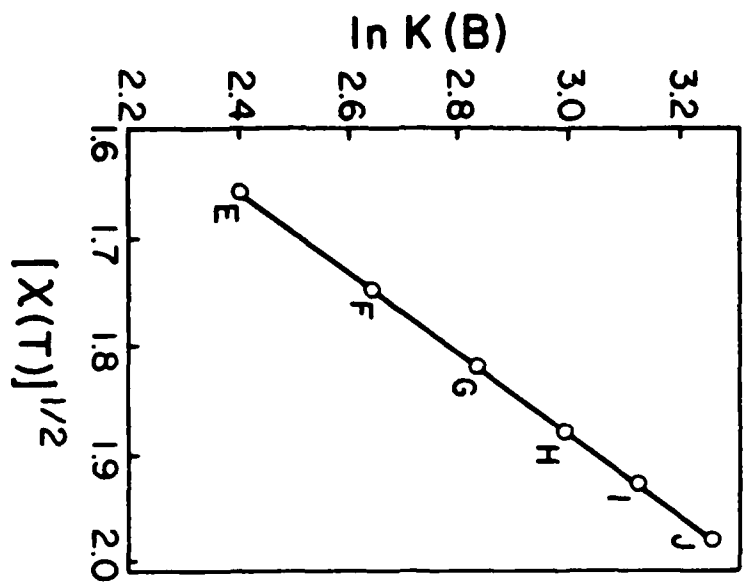
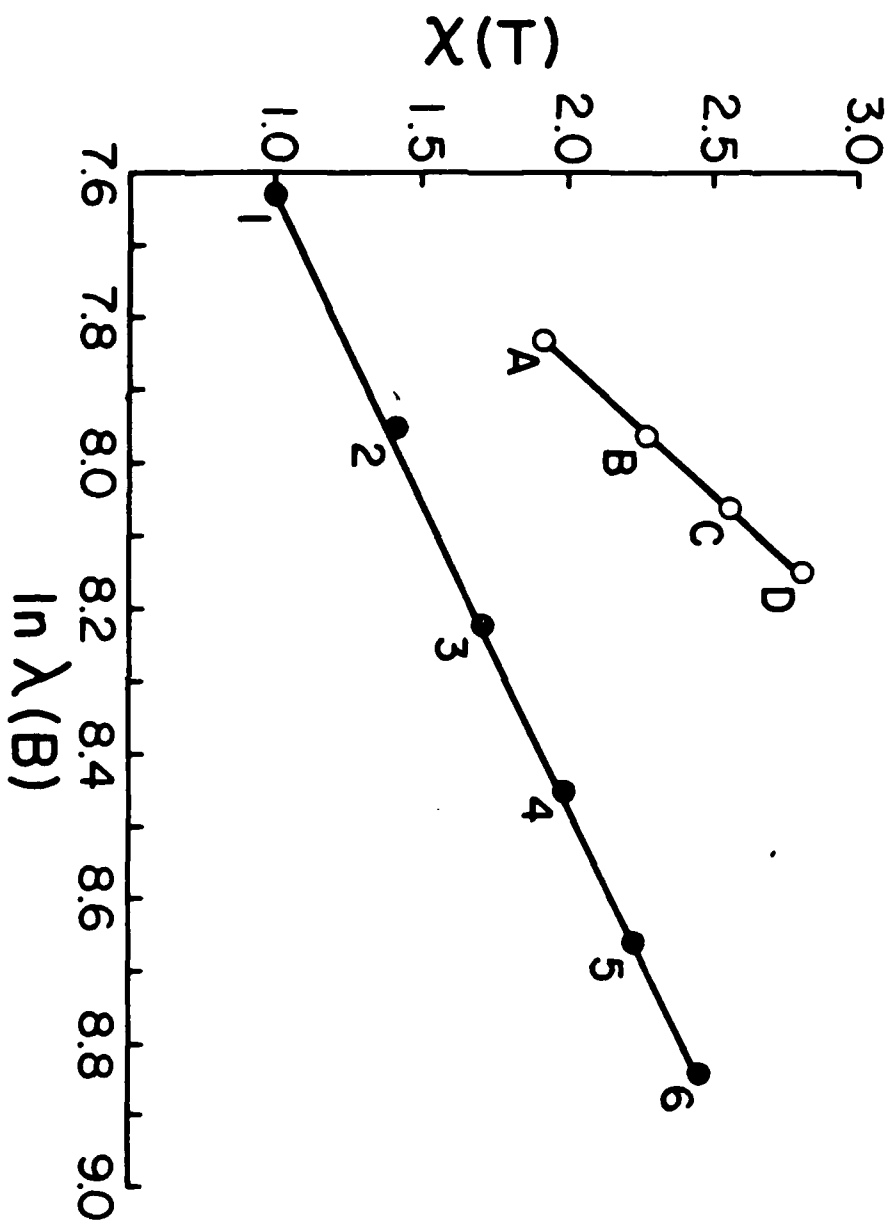


Fig. 2



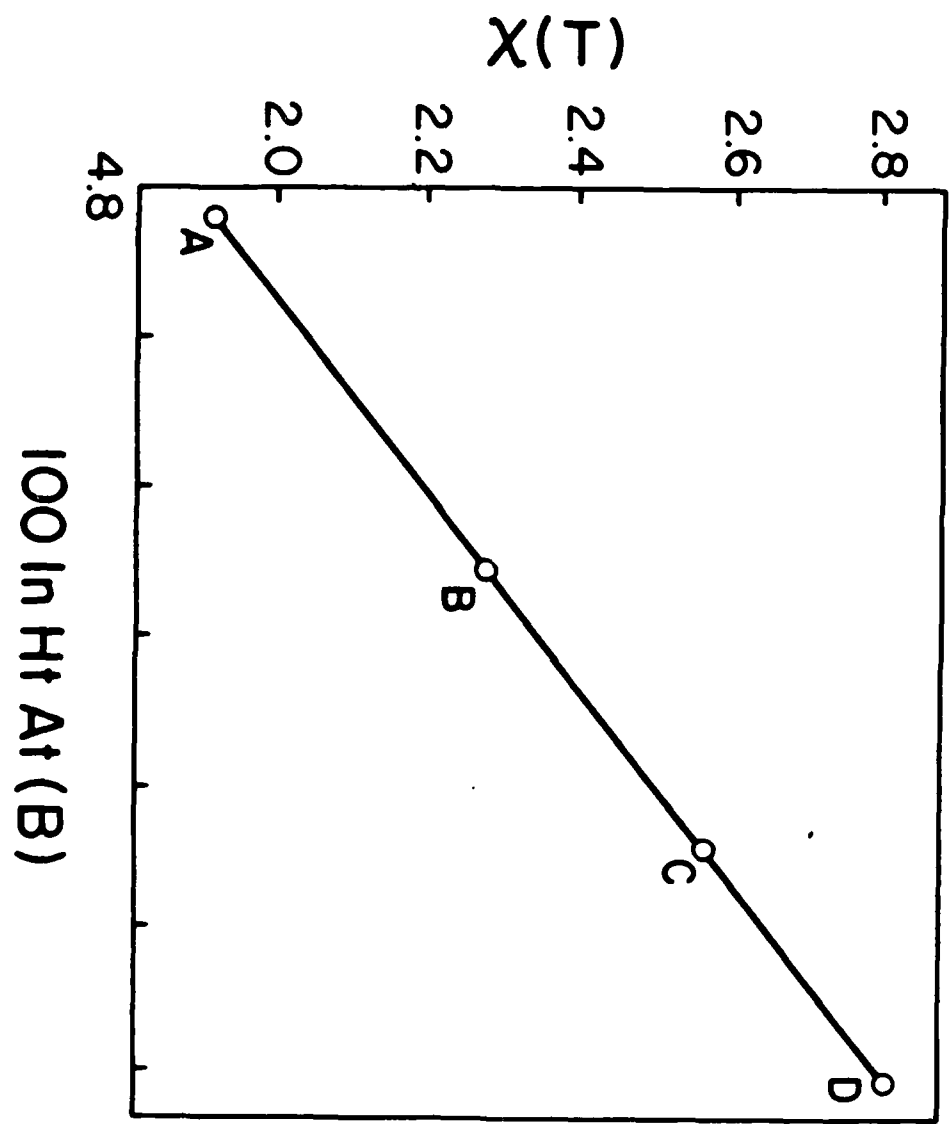


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