

NOVEL APPLICATION OF TOPOLOGICAL INDICES 2 PREDICTION
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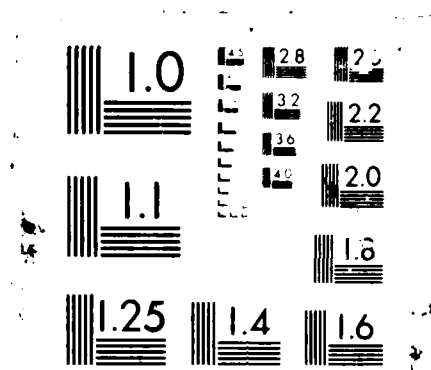
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NOVEL APPLICATIONS OF TOPOLOGICAL INDICES. 2. PREDICTION
OF THE THRESHOLD SOOT INDEX FOR HYDROCARBON FUELS.

by

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Novel Applications of Topological Indices. 2. Prediction of the Threshold Soot Index for Hydrocarbon Fuels.

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ABSTRACT

The propensity of hydrocarbons to form soot in a diffusion flame is correlated here for the first time against various topological indices. Two of the indices, the hydrogen deficiency index and the Balaban distance sum connectivity index, were found to be especially valuable for correlational purposes. For a total of 98 hydrocarbon fuel molecules of differing types, regression analyses yielded good correlations between the threshold soot indices (TSIs) for diffusion flames and these two indices. An equation which can be used to estimate TSI values in fuel molecules is presented.

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Introduction

In the search for ways to relate molecular structure to the physicochemical properties and reactivity of chemical compounds, a set of molecular descriptors known as topological indices (TIs) has found widespread use [1]. These indices are usually graph invariants, i.e. they are constants for a given chemical graph and so do not depend on the orientation of the graph or the labeling of vertices of the graph. TIs have proved themselves extremely valuable in relating the structure of molecules to their properties. In fact, TIs have been used to date to correlate and predict an extensive range of properties [2]. Examples include the correlation and prediction of physicochemical properties (e.g. boiling point [3], solubility [4], and refractive index [5]); thermodynamic properties (e.g. heats of formation [6], and vaporization [7]); biophysical properties (e.g. bioconcentration factor [8], biodegradability [9], and soil sorption [10]); and physiological properties of molecules (e.g. carcinogenicity [11] and toxicity [12]). Over 100 different TIs have been put forward in the literature so far, though a much smaller number has actually been demonstrated to be of significance in correlative or predictive studies. Applications of some of the more well-known TIs are to be found in recent review articles on the subject [13-16]. TIs have also formed the exclusive topic of four books [17-20].

The present series of papers is devoted to an examination of the applicability of TIs to the prediction of a broad range of molecular properties. In general, our emphasis will be on establishing correlations for properties that have not previously been investigated using TIs. In the first paper in the series [21], it was shown how TIs can be applied to the prediction of the velocity of sound in various alkane and alcohol species. In this paper, we attempt to correlate for the first time a property used widely in the characterization of hydrocarbon fuels. The property we have selected is the threshold soot index (TSI) [22]; our data set is based on experimental

measurements for 98 hydrocarbon fuel molecules of differing types. The threshold soot index provides a measure of the tendency of a fuel to form soot when burned; further details of this index are given in the next section.

The formation of soot during the combustion or thermal decomposition of hydrocarbon molecules is of major technological and ecological importance. Soot production takes place principally in internal combustion engines, in gas turbines and in furnaces. The propensity to form soot is a matter of considerable concern in the syn-fuel industry and for manufacturers of fuel used in cars, trucks and aircraft engines. Soot formation is a complex, multistep process and investigations of the molecular factors which lead to the production of soot in a flame have gone on for over thirty years [see Ref. 22 for citations]. Although Calcote and Manos [22] organized the data from the several investigations to date in a manner which allows for direct comparison, they discovered no simple relationship between molecular structure and sooting tendency [22, figs. 1 and 3]. TSIs have been shown to be additive for diffusion flames; accordingly, soot forming tendencies may be estimated for fuel mixtures [23]. A means of estimating the TSIs for new compounds would make TSIs even more useful. It appeared to us a worthwhile project to examine possible correlations of various topological indices with TSIs and to determine whether any were significant enough to be employed in a predictive capacity for unknown molecules. It is shown here that the diffusion flame TSIs for a group of 98 compounds do indeed correlate with several topological indices, and that in one case a useful predictive equation is obtained.

In this study of the threshold soot index, the TIs chosen for our correlations were the number of carbon atoms in the molecule, n_C ; the Wiener Index, $W(G)$ [3]; the average distance sum connectivity index of Balaban, $J(G)$ [24]; the molecular identification number of Randić, MID [25]; the molecular connectivity index, $^1\chi$, [15]; the graph covering index of Hosoya, $Z(G)$ [26]; and the hydrogen deficiency

index, HD [27]. Appropriate computer programs were written to calculate the indices for the molecules included in our study. In calculating the indices related to the distance matrix for compounds containing multiple bonds, the inverse of the bond order was used, as suggested by Balaban [24]. The hydrogen deficiency index, HD, is not usually included in lists of topological indices, even though it is topological in origin, as shown by Rouvray [28]. Moreover, it is a useful descriptor of the degree of unsaturation and/or cyclicity of a molecule. In organic chemistry, this index is often defined as the sum of the number of rings and multiple bonds present in a molecule. Any hydrocarbon molecule can be characterized by the general formula, $C_nH_{2n+2-2x}$, where n is the number of atoms and x is the hydrogen deficiency index. The index has integer values which include the value 0 for alkanes, 4 for benzene, and 7 for naphthalene.

Threshold Soot Index

Study of the soot forming characteristics of fuels has been carried out by several investigators [22]. In spite of the fact that the results of each of these studies was internally self-consistent, because each group used somewhat different experimental apparatus, the manner of reporting the results also differed significantly. Thus, it was not possible to compare the results in any simple manner. In view of this problem, Calcote and Manos [22] proposed the setting up of threshold soot index (TSI) which would reflect the tendency of a fuel to form soot on a scale ranging from 0-100, with 0 representing the least tendency to soot. The results of the various different investigators were adjusted to fit on this common scale. The objective was to obtain a quantitative value for each molecule which would be independent of the particular experimental apparatus and which could be used to consider the effect of molecular structure on soot formation.

The data on incipient soot formation are commonly subdivided into two categories: those for diffusion flames and those for premixed flames. The difference between the categories is the time at which the oxidant is mixed with the fuel before combustion takes place. TSIs have been tabulated for both categories; but the data need to be considered separately, however, as they are not comparable.

In premixed flames the fuel and oxidant are brought into a mixing chamber and thoroughly stirred to form a homogeneous mixture which is then ignited in a burner. The fuel/air ratio is increased until a yellow tip is observed on the flame. This critical composition, ϕ_c , is recorded and used to determine the TSI according to the formula:

$$\text{TSI} = a + b \phi_c, \quad (1)$$

where a and b are scalar constants for a given set of data. Some systematic studies on the sooting correlations for premixed flames have been reported by Takahashi and Glassman [29].

In diffusion flames, the fuel is vaporized and the oxidant diffuses into the fuel stream as it goes into the flame. A typical example of a diffusion flame is a candle flame. The maximum smoke-free laminar diffusion flame height, called the smoke point, is a relative measurement of the tendency of fuels to produce soot and is the subject of an ASTM [30] test. The TSI for diffusion flames is based on the smoke point but it is corrected for the amount of air required to burn a given quantity of fuel. This correction parameter correlates with the molecular weight of the fuel; the TSI thus defined as follows:

$$\text{TSI} = a(\text{MW}/h) + b, \quad (2)$$

where MW is the fuel molecular weight, h is the flame height at which soot is first observed, and the constants a and b scale the data from 0 to 100 and adjust for systematic variations among different experimental set ups. Each data set has a unique a and b. These constants were evaluated by comparing compounds common to various pairs of data sets, minimizing the differences in predicted TSI values and appropriately adjusting the scale. Calcote and Manos [22] did this for a total of six data sets for diffusion flames. Olson et al. [31] added 42 additional measurements and recalculated the TSIs using the formula:

$$TSI = a(MW/m) + b, \quad (3)$$

where m is the fuel mass consumption rate at the smoke point. They found that m could be measured with greater precision than the flame height and that it is linearly related to it. They report values for 98 pure compounds and three isomeric mixtures. The values of diffusion flame TSIs obtained by them are the subject of the present study.

The precision of the data is in most cases very low. When multiple values were available for the same compound they were averaged. The mean scatter among values calculated by Calcote and Manos [22] was $\pm 13\%$; the scatter for one point, however, was $\pm 117\%$. For many compounds only a single measurement has been made. In view of the imprecision of the values forming the data set, a fairly large standard deviation is to be expected for any correlation that is found.

Calcote and Manos [22] summarized the effects of molecular structure on TSI for diffusion flames as being roughly in the following order of decreasing importance:

- (i) TSI increases 6-12 units per carbon atom except for alkane and alkene molecules.
- (ii) Aromatic character greatly increases the tendency to form soot. The TSI

increases 25-60 units when a saturated ring becomes aromatic.

(iii) Both alkanes and alkenes have low sooting tendencies with their TSI values normally being less than 7, but alkenes have TSIs which are 2-6 units greater than those for alkanes with the same number of carbons.

(iv) Increasing the degree of branching or the compactness of a molecule increases its soot forming character.

(v) Multi-ring structures have an increased tendency to produce soot.

(vi) The effect of side chains on aromatic rings is complex. The addition of long chains tends to decrease the TSI but the addition of short chains generally increases it.

They presented plots of TSI versus the number of carbon atoms and versus the carbon/hydrogen ratio in the fuel. Although distinct trends manifested themselves among the various members of different homologous series, and molecular structure appeared to play an important role, no coherent relationship could be found which would embrace all the various fuel molecules and place them on a single curve.

Results

Here we present the results of our attempts to correlate the TSI with topological indices. The TSI data for diffusion flames were correlated with the selected TIs both linearly, semilogarithmically and logarithmically. The linear correlation values are shown in Table 1 for those correlations with simple correlation coefficients greater than 0.9. There is a high correlation ($r = 0.945$) with the hydrogen deficiency index. The correlations with all of the other indices were poor using the entire data set, although certain subsets correlated quite well. Figure 1 shows a plot of the Balaban index versus TSI and illustrates the almost random scatter in the plot.

The correlation of TSI with HD is not a very satisfying one, for HD is a non-discriminating index. For example, all of the predicted values of TSI for benzene and its alkyl derivatives would be the same because they all have the same HD index (Fig. 2). Since several of the other indices have a much greater discriminating power, i.e. they are much more likely to possess differing values for different compounds, we decided to investigate the use of a combined index. The index we took was the product of HD and each of the other indices in turn. Table 1 reveals that the Balaban index product, $J \times HD$ and the carbon number product $n_C \times HD$, have improved correlation coefficients ($r = 0.950$ and 0.954 , respectively) and reduced standard deviations for the data set of 98 values. Since both n_C and HD are not discriminating indices, we focussed our attention on the product index $J \times HD$. A compilation of the observed and calculated TSIs together with the $J(G)$, HD and $HD \times J$ indices is presented in Table 2. The plot of TSI vs $HD \times J$ is shown in Figure 3. The best linear regression equation to describe the relationship was found to be:

$$TSI = 4.6 (\pm 0.2) HD \times J + 5 (\pm 2) J - 14 (\pm 5) \quad (4)$$

where n (number of TSI values) = 98; r (correlation coefficient) = 0.958; s (standard deviation) = 7.30, $F_{1,95}$ (Fisher constant) = 520. This equation, along with several other correlations involving HD and J , is presented in Table 3. In Table 3 the various correlation coefficients are very similar; the best of them (equation (4) above) has the product variable $HD \times J$ and J as its independent variables. When these analyses are refined by removing the five outlying data points which are more than two standard deviations from the predicted value, an improved result is obtained; the relationship then becomes:

$$\text{TSI} = 4.7 (\pm 0.1) \text{ HD} \times \text{J} + 6 (\pm 2) \text{J} - 15 (\pm 4) \quad (5)$$

where $n = 93$, $r = 0.974$, $s = 5.7$, $F_{1,90} = 817$. The outlying points are shown as solid bullet points in Figure 3.

The TSIs were also measured for three mixtures of isomers, namely for xylenes, trimethylbenzenes and dimethylnaphthalenes. The corresponding data points have not been included in the analysis but are plotted in Figure 3 as crosses using an average value for $\text{HD} \times \text{J}$. The TSI values for these mixtures all fall within 2 standard deviations of the expected value. It thus appears that mixtures, as well as pure compounds, can be satisfactorily incorporated into our plots.

Discussion of Results

It has been demonstrated that diffusion flame threshold soot indices may be correlated with hydrogen deficiency and the Balaban index to afford a correlation coefficient of just over 0.97 and a standard deviation of 5.70 TSI units. This excellent correlation was obtained in spite of the unreliability of the data which clearly have large associated error limits. Our results are interesting because correlation of the TSIs with structural parameters over a broad range of molecular types has not been achieved previously. An equation which can be used to estimate the TSI for any new compound is also reported for the first time. At present, because of the magnitude of the standard deviation, the error of prediction is still fairly large. If the measurements are repeated in a systematic manner, however, it seems highly likely that the scatter will be reduced and that the standard deviation will be correspondingly smaller.

As indicated, the standard deviation of 5.70 TSI units leads to a rather large predictive error. The uncertainty in the data for many of the points, however,

is at about the same level, and in one case it was $\pm 117\%$. Plots are presented in Figures 4 and 5 of the experimental TSI values versus the best predicted TSI values, based on the third and fourth equations in Table 3, with coefficients given for $n = 93$ data points. With this new ability to estimate TSI values, and, in particular, the indications we have given of data points which are suspect, it is to be hoped that experimentalists will be prompted to remeasure the data base values employed here to increase their accuracy and thereby decrease the prediction error. Bearing in mind the very wide range of data points we have used, our ability to predict TSI values based on the simple techniques of topological analysis is most gratifying. It demonstrates once again that relatively simple molecular descriptors can be used to yield reliable correlations with many different molecular properties.

Concerning the outlying values, plotted as solid points in Figure 3, one (t-butylbenzene) is obtained from a single TSI determination, while for three of them (acetylene, n-butylbenzene, and cyclohexylbenzene) two measurements have been reported which are widely divergent. The fifth outlying point (benzene) is the average of three determinations (26, 30, and 31; TSI = 29), all of which show reasonable agreement. Assuming that the experimental TSI determinations are reliable, rejection of the points corresponding to acetylene and benzene could be justified on the grounds that both represent the first member of a homologous series and might therefore be expected to be associated with anomalous behavior. This seems to be confirmed in that both have abnormally high flame temperatures, a fact which might well tend to mask the influence of molecular structure and emphasize other factors [22]. Rejection of the remaining three points is more difficult to justify on theoretical grounds. We have already noted that short alkyl chains attached to aromatic rings tend to decrease the TSI whereas longer chains have the reverse effect [22]. A possible clue is provided by the work of Herndon [32], who studied the thermal reactivities of the alkyl derivatives of aromatic

hydrocarbons. Since derivatives with short chains are more likely to approach planarity than those having long chains, the former should display enhanced π -character. The resulting increase in aromaticity and stability could be reflected in a greater propensity to form soot, and thus lead to larger TSI values than might otherwise have been expected.

The Balaban index has been demonstrated to be appropriate for combination with the hydrogen deficiency index to form a product index which can characterize this data set. Within a given compound class, this index increases with increasing chain length, and among isomers it is known to increase with increasing branching and molecular compactness. These tendencies serve to make the requisite adjustments to the significant yet somewhat insensitive hydrogen deficiency index. The product index which correlates next most strongly is that involving the number of carbon atoms. The latter correlates very highly with the subset of linear alkanes ($r = 0.99$), though it fails to discriminate among branched isomers at all. It cannot therefore be employed to improve on HD x J as a molecular descriptor whenever branched species are included.

The mechanism of soot formation in flames has been discussed at length in several reviews and books [33-40]. To reiterate the arguments and theories here would be out of place, though a brief mention of certain hypotheses illustrates how the results we report serve to reinforce current thinking on the subject. It has been proposed [41] that the soot formation process may be divided into four steps: inception (nucleation), growth, agglomeration (coagulation), and oxidation [42]. Inception, the process in which nascent soot particles are formed from gas-phase hydrocarbons, is of primary interest since we are concerned in the present context with the first incipient appearance of soot particles and not with the nature or amount of the soot which is formed. The fuel hydrocarbon structure is of critical importance for the inception process, for the products formed from the initial

decomposition of this structure provide the surface area for the subsequent growth processes. Growth itself is believed to be independent of the fuel structure. Moreover, it seems likely that the amount of soot produced is determined exclusively by the inception process. Aromatic species are believed to produce more soot than nonaromatics because aromatic rings, which can survive even at high temperatures, can function as inception sites. Similarly, aliphatic and other molecules which can readily form such rings, will also yield considerable soot. The ability to form rings during the inception can markedly increase the number of nascent soot particles. A greater number of nascent particles will clearly speed the first appearance of soot. It is interesting that the new correlations we report involve the hydrogen deficiency index, HD. This index provides a measure of the extent of unsaturation or aromaticity existing in hydrocarbon fuel molecules. Our results support the contention that the topological structure of fuel molecules plays a major role in soot formation, and that aromaticity in particular is of key importance.

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Table 1. Correlations between diffusion flame TSIs for hydrocarbon fuel molecules and various indices.

<u>Index</u>	<u>n</u>	<u>r</u>	<u>r²</u>	<u>s</u>	<u>F_{1,n-2}</u>
HD	98	0.945	0.892	8.50	797
HD x n_C	98	0.954	0.908	7.80	963
HD x J	98	0.950	0.902	8.10	888
HD x I_X	98	0.927	0.857	9.80	582

Table 2. Threshold soot index and topological indices for hydrocarbon fuel molecules

Compound	TSI			HD	J(G)	HDxJ
	(obs) ^a	(calc) ^b	(calc) ^c			
cyclopropane	5.4	8.3	7.9	1	2.250	2.250
propane	0.8	-10.7	-6.2	0	1.633	0.000
n-butane	1.4	-7.3	-4.2	0	1.975	0.000
isobutane	2.8	-3.8	-2.1	0	2.324	0.000
cyclopentane	3.5	6.6	6.1	1	2.083	2.083
pentane	1.5	-5.1	-2.9	0	2.191	0.000
isopentane	1.6	-1.6	-0.8	0	2.540	0.000
neopentane	3.5	3.2	2.1	0	3.024	0.000
methylcyclopentane	5.0	7.6	7.2	1	2.184	2.184
cyclohexane	3.5	5.8	5.2	1	2.000	2.000
n-hexane	2.6	-3.6	-2.0	0	2.339	0.000
2-methylpentane	2.9	-0.7	-0.2	0	2.627	0.000
3-methylpentane	3.0	0.5	0.5	0	2.754	0.000
2,2-dimethylbutane	3.7	4.7	3.0	0	3.168	0.000
2,3-dimethylbutane	3.2	2.9	2.0	0	2.993	0.000
methylcyclohexane	4.9	7.0	6.5	1	2.123	2.123
n-heptane	2.6	-2.5	-1.3	0	2.447	0.000
2-methylhexane	3.2	-0.2	0.1	0	2.678	0.000
3-methylhexane	3.2	1.3	1.0	0	2.832	0.000
2,3-dimethylpentane	3.5	4.4	2.9	0	3.144	0.000
2,4-dimethylpentane	3.6	2.5	1.7	0	2.953	0.000
cyclooctane	5.9	5.8	5.2	1	2.000	2.000
1,3-dimethylcyclohexane	5.9	8.1	7.6	1	2.231	2.231
ethylcyclohexane	5.4	7.1	6.5	1	2.125	2.125
n-octane	3.2	-1.7	-0.8	0	2.530	0.000
2-methylheptane	3.5	0.2	0.3	0	2.716	0.000
3-methylheptane	3.7	1.6	1.2	0	2.862	0.000
4-methylheptane	4.0	2.2	1.5	0	2.920	0.000
3-ethylhexane	4.0	3.7	2.4	0	3.074	0.000
2,2-dimethylhexane	4.5	4.1	2.7	0	3.112	0.000
2,3-dimethylhexane	3.8	4.7	3.0	0	3.171	0.000
2-methyl-3-ethylpentane	4.4	6.5	4.1	0	3.355	0.000

Table 2 (cont'd)

2,2,4-trimethylpentane	6.4	6.9	4.3	0	3.389	0.000
2,3,3-trimethylpentane	5.7	10.1	6.2	0	3.708	0.000
2,3,4-trimethylpentane	5.7	7.6	4.8	0	3.464	0.000
n-nonane	3.1	-1.1	-0.4	0	2.592	0.000
2-methyloctane	3.8	0.4	0.5	0	2.742	0.000
decalin	15.0	13.7	6.9	2	1.925	3.851
n-decane	4.2	-0.5	-0.1	0	2.648	0.000
n-undecane	4.5	-0.1	0.1	0	2.691	0.000
bicyclohexyl	12.0	16.6	11.4	2	1.800	3.599
n-dodecane	5.1	0.3	0.4	0	2.727	0.000
n-tridecane	5.2	0.6	0.5	0	2.758	0.000
n-tetradecane	5.4	0.8	0.7	0	2.785	0.000
ethylene	0.7	5.8	5.2	1	2.000	2.000
propylene	8.2	7.7	7.2	1	2.187	2.187
1,3-butadiene	35.0	25.9	25.5	2	2.732	5.464
1-butene	6.0	8.8	8.3	1	2.297	2.297
2-butene	5.9	11.3	11.0	1	2.549	2.549
isobutene	6.6	13.8	13.7	1	2.803	2.803
cyclopentene	16.0	21.8	19.3	2	2.324	4.648
1-pentene	4.6	9.8	9.5	1	2.402	2.402
cyclohexene	5.9	21.2	18.3	2	2.255	4.510
1-hexene	4.5	10.7	10.4	1	2.488	2.488
4-methylcyclohexene	11.0	21.8	19.2	2	2.319	4.638
1-heptene	4.5	11.4	11.1	1	2.559	2.559
2-heptene	4.7	12.7	12.5	1	2.689	2.689
1,5-cyclooctadiene	17.0	34.3	29.3	3	2.286	6.857
2,5-dimethyl-1,5-hexadiene	25.0	30.4	32.4	2	3.182	6.364
1-octene	5.8	12.0	11.7	1	2.616	2.616
2-octene	4.4	13.0	12.8	1	2.719	2.719
1-nonene	7.4	12.4	12.2	1	2.664	2.664
α -pinene	24.0	33.7	28.2	3	2.231	6.693
1-decene	6.4	12.8	12.7	1	2.704	2.704
1-dodecene	8.4	13.5	13.3	1	2.767	2.767
1-tridecene	11.0	13.7	13.6	1	2.792	2.792
1-tetradecene	9.6	13.9	13.8	1	2.814	2.814

Table 2 (cont'd)

1-hexadecene	11.0	14.3	14.2	1	2.851	2.851
1-octadecene	9.2	14.6	14.5	1	2.880	2.880
acetylene	11.0	28.6	29.6	2	3.000	6.000
propyne	11.0	23.4	21.6	2	2.476	4.951
1-pentyne	17.0	23.4	21.8	2	2.484	4.967
1-hexyne	20.0	24.0	22.7	2	2.544	5.088
1-heptyne	16.0	24.6	23.5	2	2.599	5.198
1-octyne	18.0	25.1	24.2	2	2.647	5.294
1-decyne	19.0	25.8	25.4	2	2.723	5.447
benzene	29.0	54.2	57.2	4	3.000	12.000
toluene	44.0	54.4	57.7	4	3.021	12.086
styrene	67.0	66.9	70.7	5	2.991	14.955
ethylbenzene	54.0	52.5	53.1	4	2.832	11.328
indene	62.0	76.1	72.2	6	2.625	15.752
1-phenyl-1-propyne	87.0	79.2	82.7	6	2.937	17.622
n-propylbenzene	47.0	50.3	47.8	4	2.615	10.460
cumene	61.0	52.7	53.5	4	2.848	11.393
tetralin	61.0	61.1	54.0	5	2.414	12.071
p-cymene	61.0	53.1	54.6	4	2.894	11.575
n-butylbenzene	62.0	48.5	43.2	4	2.427	9.706
s-butylbenzene	60.0	51.7	51.0	4	2.747	10.988
t-butylbenzene	84.0	53.9	56.4	4	2.966	11.864
m-diethylbenzene	60.0	52.9	54.1	4	2.871	11.485
n-pentylbenzene	50.0	47.0	39.5	4	2.276	9.103
s-pentylbenzene	58.0	50.3	47.7	4	2.611	10.443
t-pentylbenzene	58.0	53.5	55.5	4	2.928	11.714
cyclohexylbenzene	78.0	57.8	44.4	5	2.083	10.413
m-diisopropylbenzene	51.0	55.1	59.3	4	3.086	12.346
naphthalene	100.0	90.0	88.5	7	2.735	19.146
1-methylnaphthalene	91.0	90.3	89.7	7	2.767	19.366
2-methylnaphthalene	89.0	89.6	87.1	7	2.699	18.890
xylene	49.0	55.0	59.2	4	3.082	12.327
trimethylbenzenes	52.0	55.9	61.3	4	3.169	12.675
dimethylnaphthalenes	98.0	90.6	91.0	7	2.801	19.610

^aTaken from reference 31. ^bCalculated using the equation $TSI = aHD + bJ + c$ for 93 data points. ^cCalculated using equation (5).

Table 3. Equations incorporating HD and J used to predict TSI in hydrocarbon fuel molecules

Equation	Coefficients (standard error)			Statistical Data			
TSI =	a	b	c	N	r	s	F
aHD + c	13.0(0.5)		-1.6(1)	98	0.945	8.5	797
aHD x J + c	4.7(0.2)		-0.7(1)	98	0.950	8.1	888
	4.7(0.1)		-0.6(0.8)	93	0.967	6.0	1435
aHD + bJ + c	13.0(0.4)	9(2)	-26(6)	98	0.955	7.8	488
	12.8(0.3)	10(2)	-27(4)	93	0.971	6.0	754
aHD x J + bJ + c	4.6(0.2)	5(2)	-14(5)	98	0.958	7.3	520
	4.7(0.1)	6(2)	-15(4)	93	0.974	5.7	817
a[HD x J] ² + bHD x J + c	0.08(0.03)	3.5(0.5)	1(1)	98	0.954	7.8	482

Captions to Figures

Figure 1. Plot of the diffusion flame threshold soot index against the Balaban index J for 98 different hydrocarbon fuel molecules.

Figure 2. Plot of the diffusion flame threshold soot index against the hydrogen deficiency index HD for 98 different pure hydrocarbons.

Figure 3. The linear regression line for the plot of the diffusion flame threshold soot index against $HD \times J$ for 98 different hydrocarbon molecules and three isomeric mixtures. Isomeric mixtures are represented by crosses. Outlying points are represented by bullet points (1 = acetylene, 2 = benzene, 3 = n-butylbenzene, 4 = cyclohexylbenzene, 5 = t-butylbenzene).

Figure 4. Plot of the predicted threshold soot index using the third equation in Table 3 ($TSI = 12.8 HD + 10J - 27$) against the experimental threshold soot index for 93 hydrocarbon fuel molecules.

Figure 5. Plot of the predicted threshold soot index using the fourth equation in Table 3 ($TSI = 4.7 (HD \times J) + 6J - 15$) against the experimental threshold soot index for 93 hydrocarbon fuel molecules.

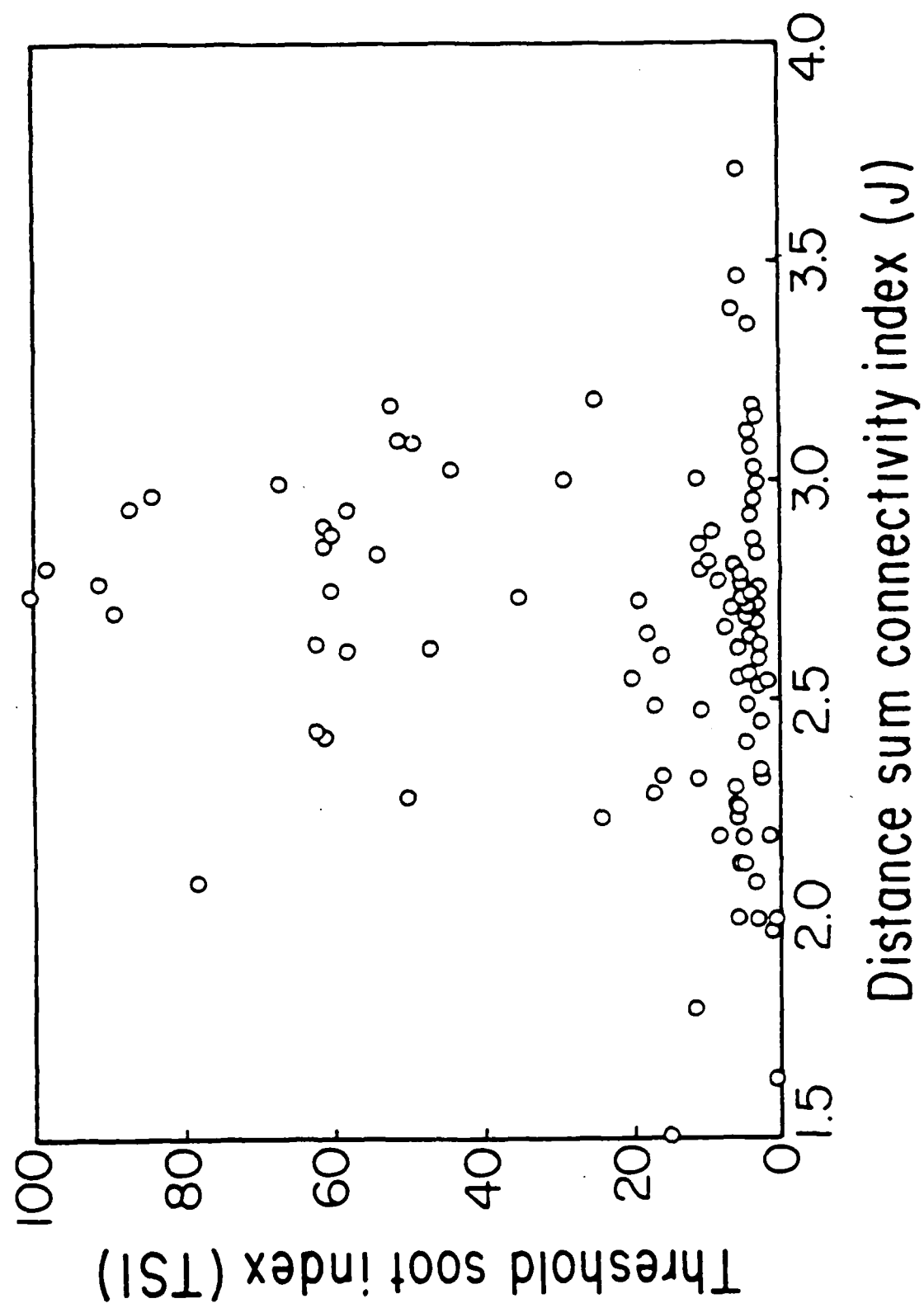


Figure 1

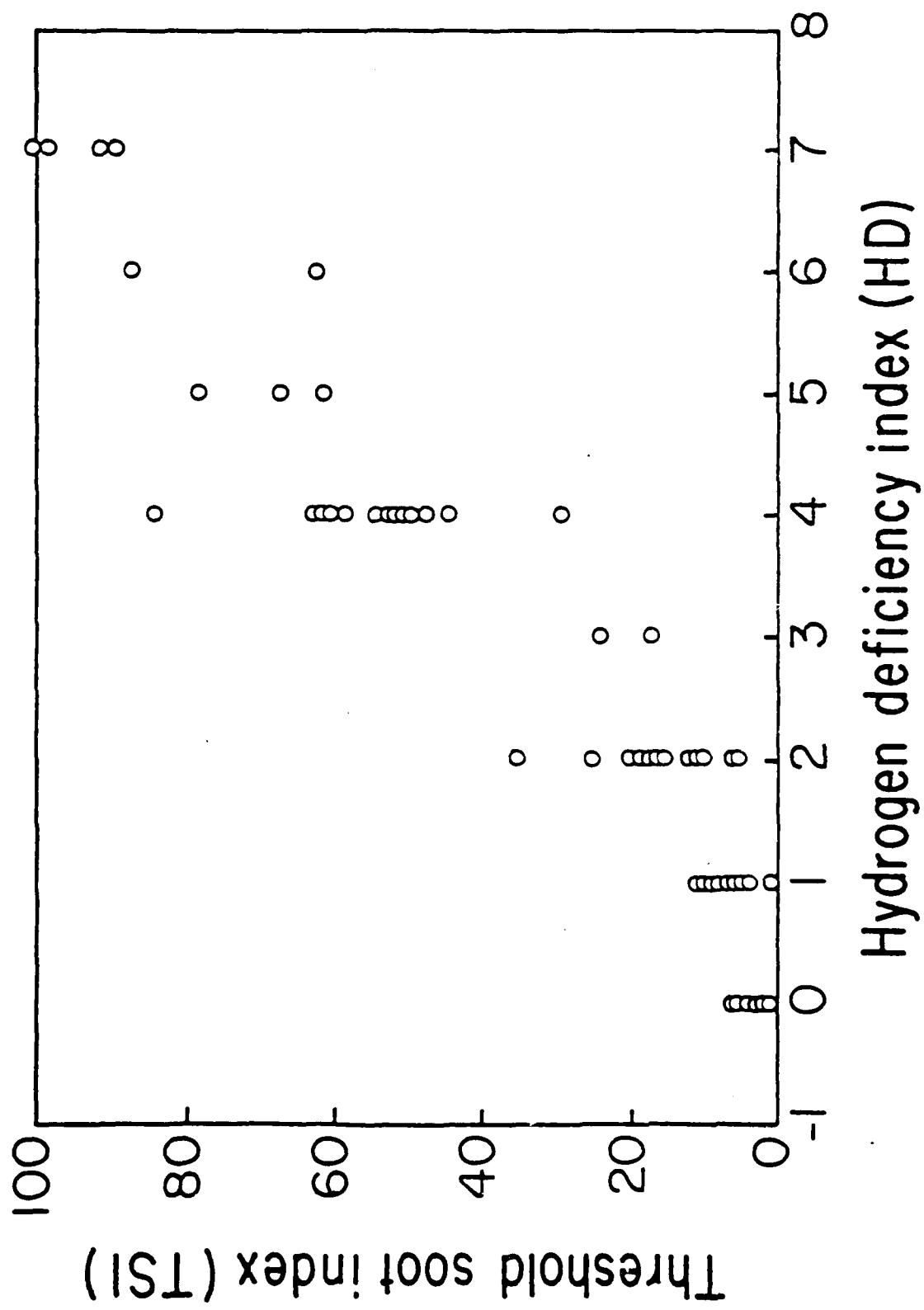


Figure 2

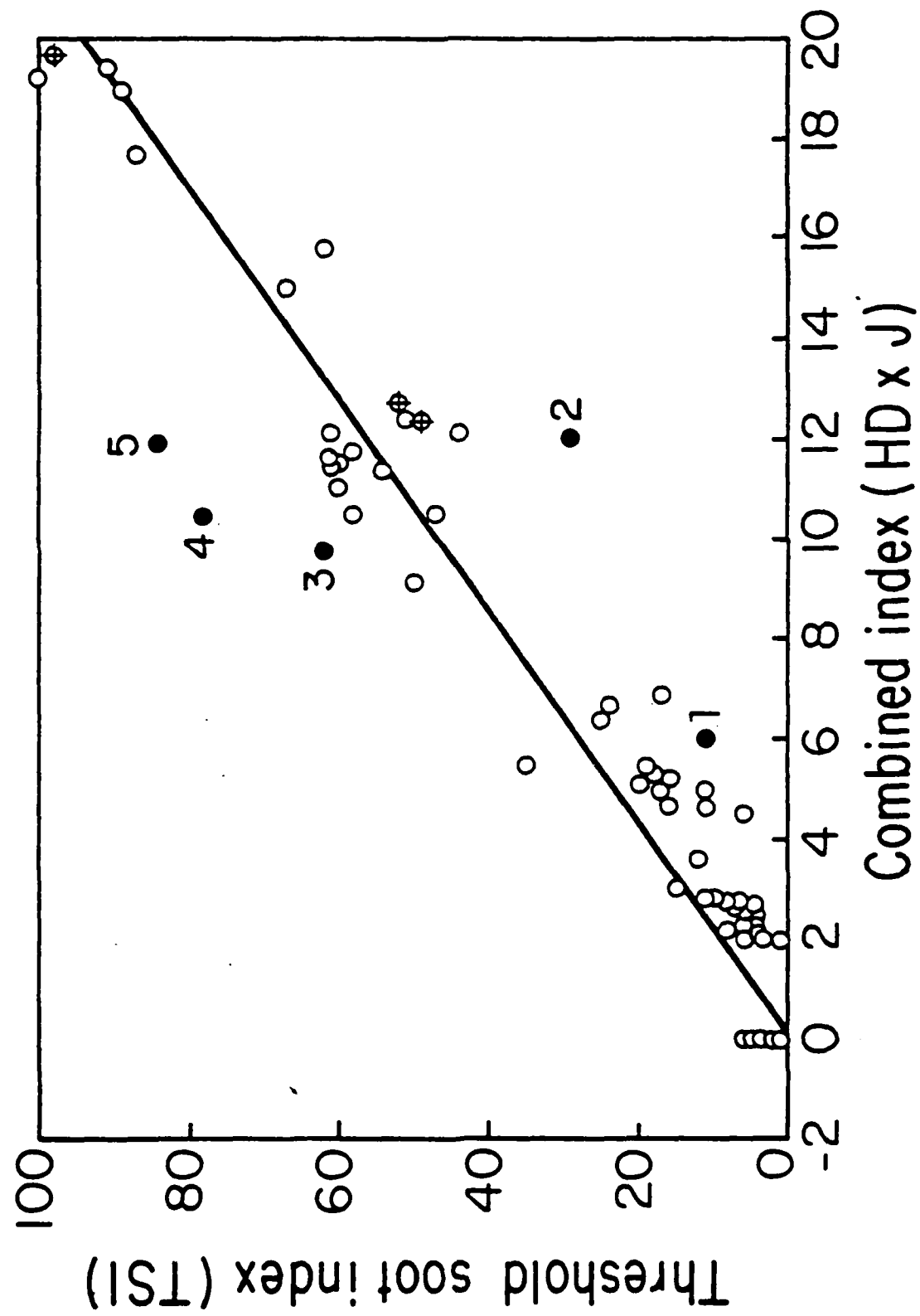


Figure 3

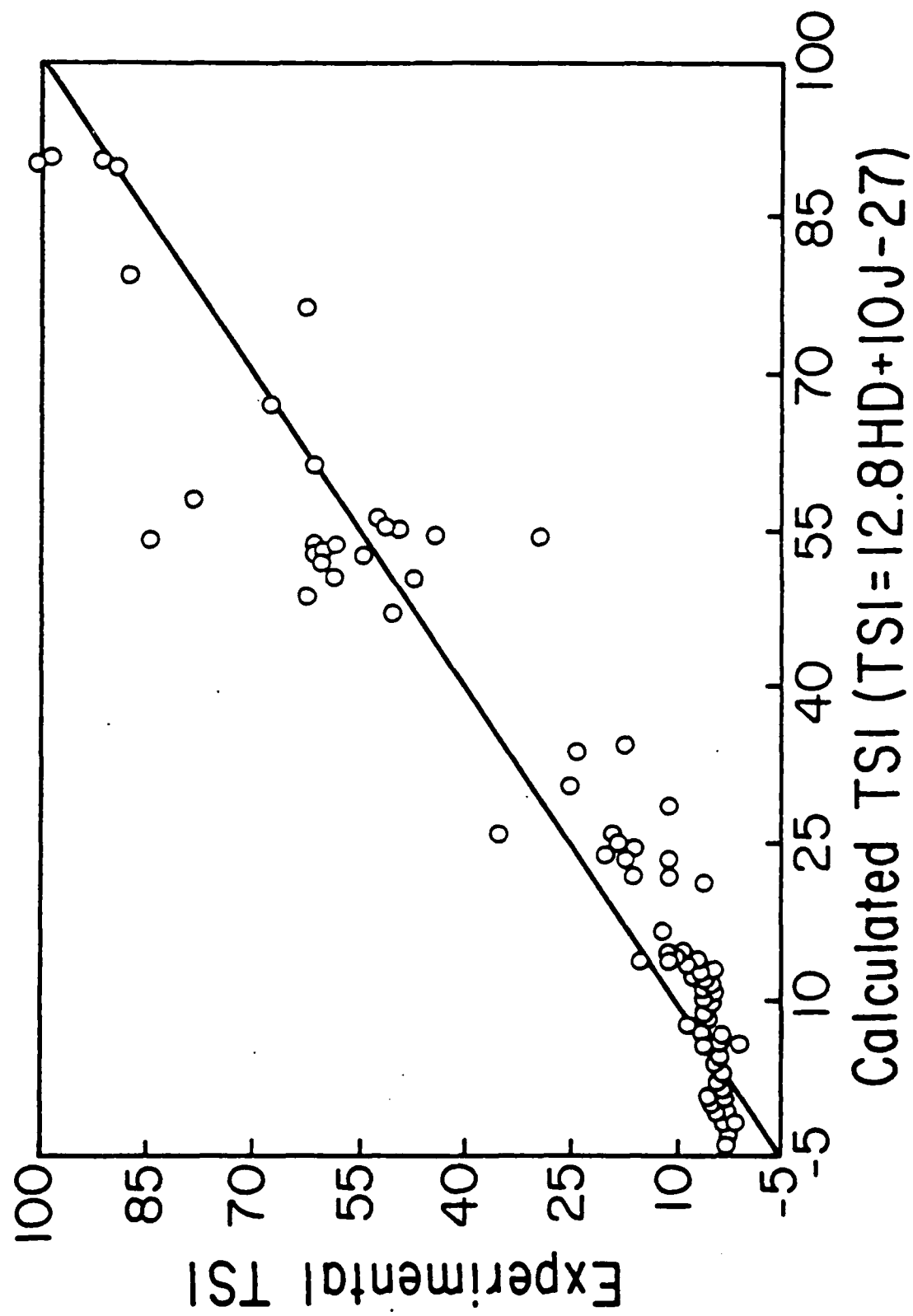


Figure 4

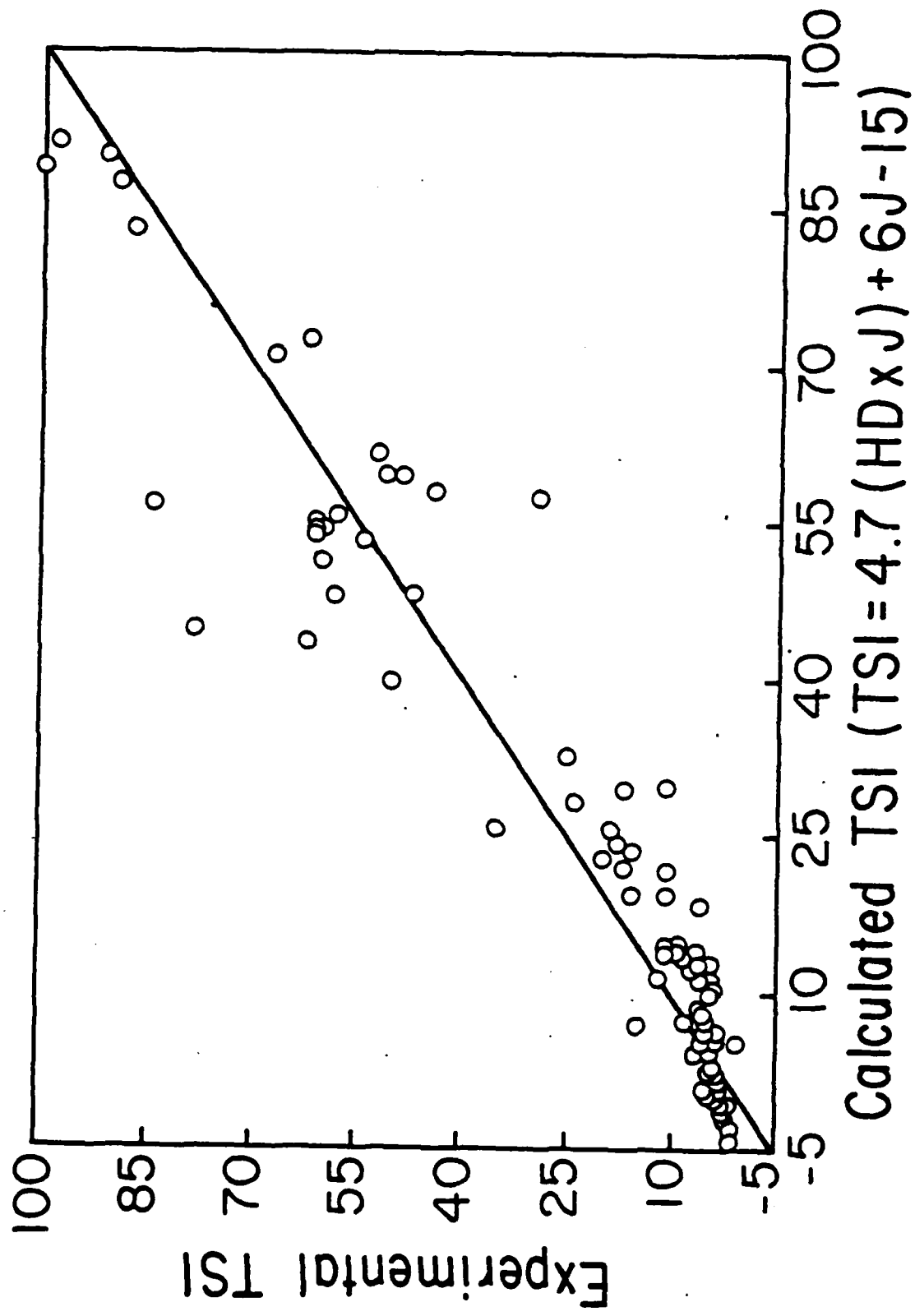


Figure 5

END

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