# A new topological index to elucidate apolar hydrocarbons

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## Summary

A new topological charge-transfer index is applied to elucidate the polar character of hydrocarbons. The dipole
moments calculated by algebraic and vector semisums of charge-transfer indices are defined in this work. The
combination of the charge-transfer indices allows the estimation of the molecular dipole moments. The ability of
the indices for the description of the molecular charge distribution is established by comparing them with the dipole
moment of a heterogeneous set of 57 polar and 53 apolar hydrocarbons. Linear and nonlinear correlation models
are obtained. The new charge-transfer index, $\mu_{vec}$, elucidates whether hydrocarbons are apolar, and improves the
multivariable nonlinear regression equation for the dipole moment. When comparing with previous results, smaller
superpositions of the corresponding pairs $G_k$, $J_k$ are observed in our fits. This diminishes the risk of colinearity.

## Introduction

A close relationship often exists between the mole-
cular structures of organic compounds and many of
their physical, chemical or biological properties [1–6].
A great deal of these relationships have been inves-
tigated using the topological descriptors of molecular
structures [7]. Particularly interesting are those indices
derived from the *distance matrix* in both topological
and topographic forms [8]. These forms were studied
comparatively by Mihalić et al. [9]. The constitutional
or structural formula of a chemical compound may
be viewed as an *structural graph*, where the *vertices*
represent atoms and the *edges* represent the covalent
bonds. Graph theory [10–12] is a well-established
branch of discrete mathematics and may be applied to
chemical problems [13–16].

Two of the matrices that characterize uniquely
molecular graphs are the *adjacency matrix* and the
*distance matrix*. It was shown [17–19] that when the
molecular graph represents the carbon skeleton of a
conjugated hydrocarbon, the eigenvalues of the ad-
jacency matrix are identical to those of the Hückel
matrix, so that there exists a complete equivalence

between the two treatments: graph-theoretical and
quantum-chemical in the Hückel molecular orbital
approximation.

Topological indices [20–21] need not be unique;
they should merely reflect the molecular topology and
should allow correlations with the structure. In the
past, topological indices, namely *charge-transfer in-
dices*, $C_{ij}$, have been used to evaluate the charge
transfers between pairs of atoms, and therefore the
global charge transfer in the molecule. However, the
reproduction of vanishing dipole moments for mole-
cules with appropriate symmetry elements is far from
trivial. In the next section, the charge-transfer indices
are revised. Following that, a new charge-transfer in-
dex, $\mu_{vec}$, is presented. Next, the results for the dipole
moment of a mixed set of 57 polar and 53 apolar hy-
drocarbons, as well as their edge component parts are
presented and discussed. Index $\mu_{vec}$ is proposed to
elucidate whether hydrocarbons are apolar. Linear and
nonlinear correlation models have been carried out for
the molecular dipoles. The last section summarizes my
conclusions.

*Table 1.* Values of the $G_k$ and $J_k$ charge-transfer indices up to the fifth order for a set of polar hydrocarbons

| Hydrocarbon | N | $G_1$ | $G_2$ | $G_3$ | $G_4$ | $G_5$ | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 3 | 0.5000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.2500 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Propene | 3 | 0.7500 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.3750 | 0.5000 | 0.0000 | 0.0000 | 0.0000 |
| Propyne | 3 | 1.0000 | 2.0000 | 0.0000 | 0.0000 | 0.0000 | 0.5000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| Cyclopropene | 3 | 2.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Butane (g$^+$) | 4 | 0.5000 | 0.2222 | 0.0000 | 0.0000 | 0.0000 | 0.1667 | 0.0741 | 0.0000 | 0.0000 | 0.0000 |
| *s-cis-* 1 ,3-butadiene | 4 | 0.5000 | 1.5556 | 0.0000 | 0.0000 | 0.0000 | 0.1667 | 0.5185 | 0.0000 | 0.0000 | 0.0000 |
| Cyclobutene | 4 | 0.5000 | 2.0000 | 0.0000 | 0.0000 | 0.0000 | 0.1667 | 0.6667 | 0.0000 | 0.0000 | 0.0000 |
| 1-butene | 4 | 0.7500 | 1.1111 | 0.2500 | 0.0000 | 0.0000 | 0.2500 | 0.3704 | 0.0833 | 0.0000 | 0.0000 |
| 1-butyne | 4 | 1.0000 | 2.2222 | 0.5000 | 0.0000 | 0.0000 | 0.3333 | 0.7407 | 0.1667 | 0.0000 | 0.0000 |
| 1,2-butadiene | 4 | 1.2500 | 1.3333 | 0.2500 | 0.0000 | 0.0000 | 0.4167 | 0.4444 | 0.0833 | 0.0000 | 0.0000 |
| 2-methylpropane | 4 | 1.5000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.5000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 2-methylpropene | 4 | 2.0000 | 2.0000 | 0.0000 | 0.0000 | 0.0000 | 0.6667 | 0.6667 | 0.0000 | 0.0000 | 0.0000 |
| Pentane | 5 | 0.5000 | 0.2222 | 0.1250 | 0.0000 | 0.0000 | 0.1250 | 0.0556 | 0.0313 | 0.0000 | 0.0000 |
| Cyclopentene | 5 | 0.5000 | 2.5000 | 0.0000 | 0.0000 | 0.0000 | 0.1250 | 0.6250 | 0.0000 | 0.0000 | 0.0000 |
| 1,3-cyclopentadiene | 5 | 0.5000 | 3.5000 | 0.0000 | 0.0000 | 0.0000 | 0.1250 | 0.8750 | 0.0000 | 0.0000 | 0.0000 |
| *Trans*-1,3-pentadiene | 5 | 0.7500 | 2.7778 | 0.1875 | 0.1111 | 0.0000 | 0.1875 | 0.6944 | 0.0469 | 0.0278 | 0.0000 |
| 1-pentyne | 5 | 1.0000 | 2.2222 | 0.6250 | 0.2222 | 0.0000 | 0.2500 | 0.5556 | 0.1563 | 0.0556 | 0.0000 |
| 1,3-pentadiyne | 5 | 1.0000 | 5.5556 | 0.2500 | 0.2222 | 0.0000 | 0.2500 | 1.3889 | 0.0625 | 0.0556 | 0.0000 |
| 2-methylbutane | 5 | 1.5000 | 0.4444 | 0.0000 | 0.0000 | 0.0000 | 0.3750 | 0.1111 | 0.0000 | 0.0000 | 0.0000 |
| 2-methyl-1,3-butadiene | 5 | 1.7500 | 2.6667 | 0.2500 | 0.0000 | 0.0000 | 0.4375 | 0.6667 | 0.0625 | 0.0000 | 0.0000 |
| Cyclohexene | 6 | 0.5000 | 2.2222 | 0.5000 | 0.0000 | 0.0000 | 0.1000 | 0.4444 | 0.1000 | 0.0000 | 0.0000 |
| *cis*-1,3,5-hexatriene | 6 | 0.5000 | 3.3333 | 0.1250 | 0.0622 | 0.0000 | 0.1000 | 0.6667 | 0.0250 | 0.0124 | 0.0000 |
| 1,3-cyclohexadiene | 6 | 0.5000 | 4.0000 | 0.5000 | 0.0000 | 0.0000 | 0.1000 | 0.8000 | 0.1000 | 0.0000 | 0.0000 |
| 1-hexyne | 6 | 1.0000 | 2.2222 | 0.6250 | 0.3022 | 0.1250 | 0.2000 | 0.4444 | 0.1250 | 0.0604 | 0.0250 |
| 3,3-dimethyl-1-butyne | 6 | 2.5000 | 2.6667 | 1.5000 | 0.0000 | 0.0000 | 0.5000 | 0.5333 | 0.3000 | 0.0000 | 0.0000 |
| Norbornadiene | 7 | 0.5000 | 4.5556 | 0.0000 | 0.0000 | 0.0000 | 0.0833 | 0.7593 | 0.0000 | 0.0000 | 0.0000 |
| 1,3,5-cycloheptatriene | 7 | 0.5000 | 5.5556 | 0.5000 | 0.0000 | 0.0000 | 0.0833 | 0.9259 | 0.0833 | 0.0000 | 0.0000 |
| 1,3,5-heptatriene | 7 | 0.7500 | 4.5556 | 0.1875 | 0.2533 | 0.0833 | 0.1250 | 0.7593 | 0.0313 | 0.0422 | 0.0139 |
| 1,3,5-heptatriyne | 7 | 1.0000 | 9.1111 | 0.2500 | 0.5067 | 0.1111 | 0.1667 | 1.5185 | 0.0417 | 0.0844 | 0.0185 |
| Toluene | 7 | 1.2500 | 6.6667 | 0.5000 | 0.2222 | 0.0000 | 0.2083 | 1.1111 | 0.0833 | 0.0370 | 0.0000 |
| Styrene | 8 | 1.0000 | 6.8889 | 0.4375 | 0.2133 | 0.0625 | 0.1429 | 0.9841 | 0.0625 | 0.0305 | 0.0089 |
| Ethylbenzene | 8 | 1.2500 | 6.7778 | 0.8125 | 0.4133 | 0.1250 | 0.1786 | 0.9683 | 0.1161 | 0.0590 | 0.0179 |
| *o*-xylene | 8 | 2.0000 | 8.2222 | 1.0000 | 0.4444 | 0.0000 | 0.2857 | 1.1746 | 0.1429 | 0.0635 | 0.0000 |
| *m*-xylene | 8 | 2.5000 | 8.0000 | 1.1250 | 0.4444 | 0.0000 | 0.3571 | 1.1429 | 0.1607 | 0.0635 | 0.0000 |
| 1,3,5,7-nonatetraene | 9 | 0.7500 | 6.3333 | 0.1875 | 0.3956 | 0.0833 | 0.0938 | 0.7917 | 0.0234 | 0.0494 | 0.0104 |
| 1,3,5,7-nonatetrayne | 9 | 1.0000 | 12.6667 | 0.2500 | 0.7911 | 0.1111 | 0.1250 | 1.5833 | 0.0313 | 0.0989 | 0.0139 |
| 1,3,5,7,9-undecapentaene | 11 | 0.7500 | 8.1111 | 0.1875 | 0.5378 | 0.0833 | 0.0750 | 0.8111 | 0.0187 | 0.0538 | 0.0083 |
| 1,3,5,7,9-undecapentayne | 11 | 1.0000 | 16.2222 | 0.2500 | 1.0756 | 0.1111 | 0.1000 | 1.6222 | 0.0250 | 0.1076 | 0.0111 |
| 1-methylnapthalene | 11 | 1.7500 | 12.2222 | 1.6875 | 0.9822 | 0.1250 | 0.1750 | 1.2222 | 0.1688 | 0.0982 | 0.0125 |
| 2-methylnapthalene | 11 | 2.2500 | 12.0000 | 1.5000 | 0.9911 | 0.1736 | 0.2250 | 1.2000 | 0.1500 | 0.0991 | 0.0174 |
| Biphenyl | 12 | 1.0000 | 12.4444 | 0.8750 | 0.4889 | 0.2778 | 0.0909 | 1.1313 | 0.0795 | 0.0444 | 0.0253 |
| Acenaphthylene | 12 | 1.5000 | 14.0556 | 1.4306 | 0.7356 | 0.0000 | 0.1364 | 1.2778 | 0.1301 | 0.0669 | 0.0000 |
| Acenaphthene | 12 | 2.0000 | 13.5556 | 2.0833 | 1.0133 | 0.0000 | 0.1818 | 1.2323 | 0.1894 | 0.0921 | 0.0000 |
| 1,3,5,7,9,11-tridecahexaene | 13 | 0.7500 | 9.8889 | 0.1875 | 0.6800 | 0.0833 | 0.0625 | 0.8241 | 0.0156 | 0.0567 | 0.0069 |
| 1,3,5,7,9,11-tridecahexayne | 13 | 1.0000 | 19.7778 | 0.2500 | 1.3600 | 0.1111 | 0.0833 | 1.6481 | 0.0208 | 0.1133 | 0.0093 |

*Table 1 continued.*

| Hydrocarbon | N | $G_1$ | $G_2$ | $G_3$ | $G_4$ | $G_5$ | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Fluorene | 13 | 2.0000 | 14.8333 | 2.2639 | 0.6733 | 0.3267 | 0.1667 | 1.2361 | 0.1887 | 0.0561 | 0.0272 |
| *Cis*-stilbene | 14 | 1.5000 | 14.0000 | 0.8750 | 0.5689 | 0.2083 | 0.1154 | 1.0769 | 0.0673 | 0.0438 | 0.0160 |
| 9,10-dihydroanthracene | 14 | 3.0000 | 15.5556 | 2.2500 | 1.4578 | 0.1389 | 0.2308 | 1.1966 | 0.1731 | 0.1121 | 0.0107 |
| 1,3,5,7,9,11,13-pentadecaheptaene | 15 | 0.7500 | 11.6667 | 0.1875 | 0.8222 | 0.0833 | 0.0536 | 0.8333 | 0.0134 | 0.0587 | 0.0060 |
| 1,3,5,7,9,11,13-pentadecaheptayne | 15 | 1.0000 | 23.3333 | 0.2500 | 1.6444 | 0.1111 | 0.0714 | 1.6667 | 0.0179 | 0.1175 | 0.0079 |
| Benzo[*a*]anthracene | 18 | 2.5000 | 21.5556 | 2.7500 | 2.0889 | 0.5694 | 0.1471 | 1.2680 | 0.1618 | 0.1229 | 0.0335 |
| Benzo[*a*]pyrene | 20 | 2.5000 | 25.1111 | 3.8750 | 2.4978 | 0.6111 | 0.1316 | 1.3216 | 0.2039 | 0.1315 | 0.0322 |
| Benzo[*b*]fluoranthene | 20 | 2.7500 | 23.6111 | 3.4722 | 2.3806 | 1.0456 | 0.1447 | 1.2427 | 0.1827 | 0.1253 | 0.0550 |
| Benzo[*k*]fluoranthene | 20 | 3.5000 | 24.1667 | 3.6181 | 2.2022 | 0.9975 | 0.1842 | 1.2719 | 0.1904 | 0.1159 | 0.0525 |
| Corannulene | 20 | 3.5000 | 25.7222 | 5.3056 | 2.7428 | 0.7217 | 0.1842 | 1.3538 | 0.2792 | 0.1444 | 0.0380 |
| Indeno[1,2,3-*cd*]pyrene | 22 | 3.2500 | 27.1667 | 4.2222 | 3.1317 | 1.2158 | 0.1548 | 1.2937 | 0.2011 | 0.1491 | 0.0579 |
| Benzo[*ghi*]perylene | 22 | 3.5000 | 28.0000 | 5.4375 | 3.8400 | 1.1458 | 0.1667 | 1.3333 | 0.2589 | 0.1829 | 0.0546 |

*Table 2.* Values of the $G_k$ and $J_k$ charge-transfer indices up to the fifth order for a set of apolar hydrocarbons

| Hydrocarbon | N | $G_1$ | $G_2$ | $G_3$ | $G_4$ | $G_5$ | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Methane | 1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Ethane | 2 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Ethene | 2 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Ethyne | 2 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Cyclopropane | 3 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Propane | 3 | 0.5000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.2500 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Alene | 3 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.5000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Butane (t) | 4 | 0.5000 | 0.2222 | 0.0000 | 0.0000 | 0.0000 | 0.1667 | 0.0741 | 0.0000 | 0.0000 | 0.0000 |
| *s-trans*-1,3-butadiene | 4 | 0.5000 | 1.5556 | 0.0000 | 0.0000 | 0.0000 | 0.1667 | 0.5185 | 0.0000 | 0.0000 | 0.0000 |
| 1,3-butadiyne | 4 | 0.5000 | 3.3333 | 0.0000 | 0.0000 | 0.0000 | 0.1667 | 1.1111 | 0.0000 | 0.0000 | 0.0000 |
| Pentane | 5 | 0.5000 | 0.2222 | 0.1250 | 0.0000 | 0.0000 | 0.1250 | 0.0556 | 0.0313 | 0.0000 | 0.0000 |
| 2,2-dimethylpropane | 5 | 3.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.7500 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Cyclohexane | 6 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Benzene | 6 | 0.0000 | 5.3333 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0667 | 0.0000 | 0.0000 | 0.0000 |
| Hexane | 6 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0000 | 0.1000 | 0.0444 | 0.0250 | 0.0160 | 0.0000 |
| *trans*-1,3,5-hexatriene | 6 | 0.5000 | 3.3333 | 0.1250 | 0.0622 | 0.0000 | 0.1000 | 0.6667 | 0.0250 | 0.0124 | 0.0000 |
| 1,3,5-hexatriyne | 6 | 0.5000 | 6.8889 | 0.1250 | 0.2044 | 0.0000 | 0.1000 | 1.3778 | 0.0250 | 0.0409 | 0.0000 |
| Heptane | 7 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0833 | 0.0370 | 0.0208 | 0.0133 | 0.0093 |
| Octane | 8 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0714 | 0.0317 | 0.0179 | 0.0114 | 0.0079 |
| 1,3,5,7-octatetraene | 8 | 0.5000 | 5.1111 | 0.1250 | 0.2044 | 0.0556 | 0.0714 | 0.7302 | 0.0179 | 0.0292 | 0.0079 |
| 1,3,5,7-octatetrayne | 8 | 0.5000 | 10.4444 | 0.1250 | 0.4889 | 0.0556 | 0.0714 | 1.4921 | 0.0179 | 0.0698 | 0.0079 |
| *p*-xylene | 8 | 2.5000 | 8.0000 | 0.8750 | 0.5244 | 0.0000 | 0.3571 | 1.1429 | 0.1250 | 0.0749 | 0.0000 |
| Nonane | 9 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0625 | 0.0278 | 0.0156 | 0.0100 | 0.0069 |
| Mesitylene | 9 | 3.7500 | 9.3333 | 1.8750 | 0.6667 | 0.0000 | 0.4688 | 1.1667 | 0.2344 | 0.0833 | 0.0000 |
| Decane | 10 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0556 | 0.0247 | 0.0139 | 0.0089 | 0.0062 |
| 1,3,5,7,9-decapentaene | 10 | 0.5000 | 6.8889 | 0.1250 | 0.3467 | 0.0556 | 0.0556 | 0.7654 | 0.0139 | 0.0385 | 0.0062 |
| 1,3,5,7,9-decapentayne | 10 | 0.5000 | 14.0000 | 0.1250 | 0.7733 | 0.0556 | 0.0556 | 1.5556 | 0.0139 | 0.0859 | 0.0062 |
| Naphtalene | 10 | 1.0000 | 10.6667 | 1.0000 | 0.5689 | 0.0000 | 0.1111 | 1.1852 | 0.1111 | 0.0632 | 0.0000 |
| Undecane | 11 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0500 | 0.0222 | 0.0125 | 0.0080 | 0.0056 |
| Dodecane | 12 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0455 | 0.0202 | 0.0114 | 0.0073 | 0.0051 |

*Table 2 continued.*

| Hydrocarbon | N | $G_1$ | $G_2$ | $G_3$ | $G_4$ | $G_5$ | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,3,5,7,9,11-dodecahexaene | 12 | 0.5000 | 8.6667 | 0.1250 | 0.4889 | 0.0556 | 0.0455 | 0.7879 | 0.0114 | 0.0444 | 0.0051 |
| 1,3,5,7,9,11-dodecahexayne | 12 | 0.5000 | 17.5556 | 0.1250 | 1.0578 | 0.0556 | 0.0455 | 1.5960 | 0.0114 | 0.0962 | 0.0051 |
| Biphenyl-coplanar | 12 | 1.0000 | 12.4444 | 0.8750 | 0.4889 | 0.2778 | 0.0909 | 1.1313 | 0.0795 | 0.0444 | 0.0253 |
| Tridecane | 13 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0417 | 0.0185 | 0.0104 | 0.0067 | 0.0046 |
| Tretradecane | 14 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0385 | 0.0171 | 0.0096 | 0.0062 | 0.0043 |
| 1,3,5,7,9,11,13-tetradecaheptaene | 14 | 0.5000 | 10.4444 | 0.1250 | 0.6311 | 0.0556 | 0.0385 | 0.8034 | 0.0096 | 0.0485 | 0.0043 |
| 1,3,5,7,9,11,13-tetradecaheptayne | 14 | 0.5000 | 21.1111 | 0.1250 | 1.3422 | 0.0556 | 0.0385 | 1.6239 | 0.0096 | 0.1032 | 0.0043 |
| *trans*-stilbene | 14 | 1.5000 | 14.0000 | 0.8750 | 0.5689 | 0.2083 | 0.1154 | 1.0769 | 0.0673 | 0.0438 | 0.0160 |
| Phenanthrene | 14 | 1.5000 | 16.2222 | 2.0000 | 1.3600 | 0.2639 | 0.1154 | 1.2479 | 0.1538 | 0.1046 | 0.0203 |
| Anthracene | 14 | 2.0000 | 16.0000 | 1.7500 | 1.2978 | 0.2500 | 0.1538 | 1.2308 | 0.1346 | 0.0998 | 0.0192 |
| Pentadecane | 15 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0357 | 0.0159 | 0.0089 | 0.0057 | 0.0040 |
| Hexadecane | 16 | 0.5000 | 0.2222 | 0.1250 | 0.0800 | 0.0556 | 0.0333 | 0.0148 | 0.0083 | 0.0053 | 0.0037 |
| 1,3,5,7,9,11,13,15-Hexadecaoctaene | 16 | 0.5000 | 12.2222 | 0.1250 | 0.7733 | 0.0556 | 0.0333 | 0.8148 | 0.0083 | 0.0516 | 0.0037 |
| 1,3,5,7,9,11,13,15-Hexadecaoctayne | 16 | 0.5000 | 24.6667 | 0.1250 | 1.6267 | 0.0556 | 0.0333 | 1.6444 | 0.0083 | 0.1084 | 0.0037 |
| Fluoranthene | 16 | 1.5000 | 19.6111 | 2.2500 | 1.2417 | 0.2600 | 0.1000 | 1.3074 | 0.1500 | 0.0828 | 0.0173 |
| Pyrene | 16 | 2.0000 | 19.5556 | 2.8750 | 1.9111 | 0.1389 | 0.1333 | 1.3037 | 0.1917 | 0.1274 | 0.0093 |
| Chrysene | 18 | 2.0000 | 21.5556 | 2.7500 | 2.0711 | 0.5278 | 0.1176 | 1.2680 | 0.1618 | 0.1218 | 0.0310 |
| Corannulene-planar | 20 | 3.5000 | 25.7222 | 5.3056 | 2.7428 | 0.7217 | 0.1842 | 1.3538 | 0.2792 | 0.1444 | 0.0380 |
| Bibenzo[*ah*]anthracene | 22 | 3.0000 | 26.6667 | 3.3750 | 2.5956 | 0.7222 | 0.1429 | 1.2698 | 0.1607 | 0.1236 | 0.0344 |
| Coronene | 24 | 3.2500 | 27.4444 | 6.1875 | 4.4489 | 1.1250 | 0.1413 | 1.1932 | 0.2690 | 0.1934 | 0.0489 |
| Fullerene-60 | 60 | 1.5000 | 106.1111 | 18.6528 | 16.9661 | 5.3217 | 0.0254 | 1.7985 | 0.3161 | 0.2876 | 0.0902 |
| Fullerene-70 | 70 | 3.0000 | 120.3333 | 25.0000 | 20.6922 | 7.6275 | 0.0435 | 1.7440 | 0.3623 | 0.2999 | 0.1105 |
| Fullerene-82 | 82 | 4.0000 | 137.1667 | 34.1250 | 23.7511 | 11.1136 | 0.0494 | 1.6934 | 0.4213 | 0.2932 | 0.1372 |

## Topological charge-transfer indices

The two most important matrices that delineate the labelled chemical graph are the *adjacency* ($\overline{\overline{A}}$) [22–24] and the *distance* ($\overline{\overline{D}}$) *matrices*, wherein $D_{ij} = l_{ij}$ if $i = j$, '0' otherwise; $l_{ij}$ is the shortest edge count between vertices $i$ and $j$ [25]. $\overline{\overline{A}}$ is the adjacency matrix where $A_{ij} = 1$ if vertices $i$ and $j$ are adjacent, '0' otherwise.

The role of charge transfer in pharmacology was reviewed by Shifrin [26]. However, none of the more widely used indicators describe in an explicit manner the *charge distribution* in the molecule, although Kier and Hall developed an atomic value of $\chi$ capable of representing the number of valence electrons on the carbon atom [6]. The $\overline{\overline{D}}{}^*$ matrix is the matrix whose elements are the squares of the reciprocal distances $D_{ij}^{-2}$. $\overline{\overline{D}}{}^*$ may be considered as the distance matrix of a class of specially weighted graphs in which weights between vertices mimic the Coulomb law between the sites in the corresponding structure. Now, the intermediate matrix $\overline{\overline{M}}$ is defined as the matrix product of $\overline{\overline{A}}$ by $\overline{\overline{D}}{}^*$ : $\overline{\overline{M}} = \overline{\overline{A}} \times \overline{\overline{D}}{}^*$

Notice that the product of two symmetric matrices, such as and $\overline{\overline{A}}$, $\overline{\overline{D}}{}^*$ does not necessarily result in a symmetric matrix, as occurs in $\overline{\overline{M}}$.

The *charge-transfer matrix* $\overline{\overline{C}}$ is defined as $\overline{\overline{C}} = \overline{\overline{M}} - \overline{\overline{M}}{}^T$, where $\overline{\overline{M}}{}^T$ is the transpose of $\overline{\overline{M}}$ [27]. By agreement, the main-diagonal entries of $\overline{\overline{M}}$ remain the same. Thus, $C_{ij} = M_{ij} - M_{ji}$ ($i \neq j$) and $C_{ii} = M_{ii}$. Notice that the $C_{ij}$ descriptors are *graph invariants*, i.e., they do not depend on the numerical order of the vertices in the molecular graph. For example, in butane ($C_1$-$C_2$-$C_3$-$C_4$), $C_{12} = -C_{34} = -0.25$ and $C_{23} = 0$. At this point, several facts should be emphasized. For $i \neq j$, the $C_{ij}$ terms represent a measure of the intramolecular *net charge* transferred from atom $j$ to $i$. Thus, if $C_{ij}$ is negative, atom $i$ will transfer net charge to $j$. The optimal topological picture of these descriptors would be a *digraph*. This implied charge distribution spectrum is surprisingly

similar to the real charge distribution in the molecule $C_1^{\delta-} - C_2^{\delta+} - C_3^{\delta+} - C_4^{\delta-}$.

It is evident, that the *algebraic* sum of the $C_{ij}$ terms, for $i > j$, will be null in the case of symmetric compounds, and it implies that this sum would be proportional to the dipole moment of the molecule. In fact, all the symmetric hydrocarbons, including those that are cyclic and aromatic, show virtually null dipole moments. For instance, in benzene [$C_1(C_6)$-$C_2$-$C_3$-$C_4$-$C_5$-$C_6(C_1)$], $C_{12} = C_{23} = C_{34} = C_{45} = C_{56} = 0$ and $C_{13} = -C_{24} = C_{35} = -C_{46} = -0.889$ characterize its aromaticity. However, asymmetric molecules show nonzero dipole moments. In this case, i.e., for asymmetric hydrocarbons, it is obvious that the algebraic sum of the $C_{ij}$ terms, for $i > j$, is not null. However, this sum would be dependent, in the case of branched molecules, on the numerical order of the different vertices.

Gálvez et al. defined the *topological charge-transfer indices* $G_k$ as the sum, in absolute value, of the $C_{ij}$ terms defined for the vertices $i$, $j$ placed at a topological distance $D_{ij}$ equal to $k$:

$$G_k = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} |C_{ij}| \delta(k, D_{ij}), \qquad (1)$$

where $N$ is the number of vertices in the graph, $D_{ij}$ are the entries of the $\overline{\overline{D}}$ matrix, and $\delta$ is the Kronecker $\delta$, being $\delta = 1$ for $i = j$ and $\delta = 0$ otherwise [27]. They defined $k$ as the *index order* of $G$, being this order $k$ a fixed value for the topological distance between vertices $i$ and $j$. Thus, $G_k$ represents the sum of all the $C_{ij}$ terms, for every pair of vertices $i$ and $j$ at topological distance $k$. These $G_k$ descriptors evaluate the total charge transfer between pairs of atoms placed at a topological distance $k$. Therefore, for a linear molecule there would exist $N - 1$ values of $G_k$. The $G_k$ topological charge-transfer indices describe the global charge distribution inside the molecule through the evaluation of the intramolecular charge transfer between pairs of atoms placed at 1–2 ($G_1$), 1–3 ($G_2$), etc. Notice that the $G_k$ descriptors are graph invariants.

Furthermore, Gálvez et al. also introduced other topological charge-transfer index, $J_k$, as

$$J_k = \frac{G_k}{N - 1}. \qquad (2)$$

This index represents the mean value of the charge transfer for each edge, since the number of edges for acyclic compounds is $N - 1$. Notice that the $J_k$ descriptors are graph invariants.

The $G_k$ and $J_k$ indices were applied to the calculation of the molecular dipole moment of hydrocarbons, the boiling temperature of hydrocarbons and alcohols, the vaporization enthalpy of alkanes [27], the activity of analgesic, antiviral, bronchodilator, antifungal, antihyperlipoproteinemic, hypoglycemic [28] and β-blocker [29] and antineoplastic drugs, quinolones, fluoroquinolones, flavonoids [30], the capacity and separation factors in chromatographic chiral separations of hydantoins, aromatic α-amino acids and arylamides [31], the resonance energy of hydrocarbons, the naphthalene bond lengths, the vibrational frequencies for C-C double bonds, the log $IC_{50}$ of the $D_2$ dopamine receptor and the σ receptor of piperidines, the sedative character of chiral barbiturates [32], and the aqueous solubility of organic compounds.

## Algebraic and vector semisum charge-transfer indices

Gálvez *et al.* suggested that the molecular dipole moment is related to the algebraic semisum of the $C_{ij}$ indices [27]. Therefore, the *algebraic semisum charge-transfer index* $\mu_{\mathrm{alg}}$ is defined as

$$\mu_{\mathrm{alg}} = \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} A_{ij} C_{ij} = \frac{1}{2} \sum_{e=1}^{M} C^e, \qquad (3)$$

where $C^e$ is the $C_{ij}$ index for vertices $i$ and $j$ connected by edge $e$. The sum extends for all pairs of adjacent vertices (i.e., for all the $M$ edges) in the molecular graph. Therefore, $\mu_{\mathrm{alg}}$ represents the dipole moment calculated by algebraic semisum of $C^e$.

An edge-to-edge partition analysis of $\mu$ suggests that each edge dipole moment $\mu^e$ connecting vertices $i$ and $j$, can be evaluated from the corresponding edge $C^e$ index as

$$\mu^e = \frac{1}{2} C^e.$$

Each edge dipole can be associated with a vector $\overline{\mu}^e$ in space. This vector has magnitude $\mu^e$, lies in the edge $e$ connecting vertices $i$ and $j$, and its direction is from $j$ to $i$. The molecular dipole moment vector $\overline{\mu}$ results the vector sum of the edge dipole moments as

$$\overline{\mu} = \sum_{e=1}^{M} \overline{\mu}^e = \frac{1}{2} \sum_{e=1}^{M} \overline{C}^e$$

summed for all the $M$ edges in the molecular graph.

The *vector semisum charge-transfer index* $\mu_{\mathrm{vec}}$ is defined as the norm of $\overline{\mu}$:

$$\mu_{\mathrm{vec}} = N(\overline{\mu}) = (\mu_1^2 + \mu_2^2 + \mu_3^2)^{1/2}. \qquad (4)$$

*Table 3.* Molecular dipole moment values, μ (D), of polar hydrocarbons with charge-transfer indices

| Hydrocarbon | Fit[a] | Algebraic semisum | Vector semisum | Experiment[b] |
|---|---|---|---|---|
| Propane | 0.071 | 0.000 | 0.204 | 0.083 |
| Propene | 0.401 | 0.125 | 0.301 | 0.360 |
| Propyne | 0.731 | 0.250 | 0.378 | 0.750 |
| Cyclopropene | 0.394 | 1.000 | 1.288 | 0.455 |
| Butane (g$^+$) | 0.036 | 0.000 | 0.282 | 0.091[c] |
| *s-cis*-1,3-butadiene | 0.222 | 0.000 | 0.259 | 0.031[d] |
| Cyclobutene | 0.284 | 0.250 | 0.358 | 0.130 |
| 1-butene | 0.383 | 0.125 | 0.166 | 0.340 |
| 1-butyne | 0.760 | 0.250 | 0.318 | 0.800 |
| 1,2-butadiene | 0.456 | 0.125 | 0.301 | 0.401 |
| 2-methylpropane | 0.089 | 0.250 | 0.342 | 0.132 |
| 2-methylpropene | 0.410 | 0.500 | 0.250 | 0.503 |
| Pentane (tt) | 0.064 | 0.000 | 0.205 | 0.087[c] |
| Pentane (g$^-$t) | 0.064 | 0.000 | 0.190 | 0.063[c] |
| Pentane (g$^-$g$^-$) | 0.064 | 0.000 | 0.205 | 0.060[c] |
| Pentane (g$^-$g$'^+$) | 0.064 | 0.000 | 0.342 | 0.123[c] |
| Cyclopentene | 0.150 | 0.250 | 0.330 | 0.955 |
| 1,3-cyclopentadiene | 0.221 | 0.250 | 0.233 | 0.416 |
| *Trans*-1,3-pentadiene | 0.439 | 0.125 | 0.300 | 0.680 |
| 1-pentyne | 0.821 | 0.250 | 0.386 | 0.810 |
| 1,3-pentadiyne | 0.830 | 0.250 | 0.377 | 0.022[e] |
| 2-methylbutane | 0.022 | 0.250 | 0.270 | 0.130 |
| 2-methyl-1,3-butadiene | 0.336 | 0.375 | 0.353 | 0.380 |
| Cyclohexene | 0.261 | 0.250 | 0.298 | 0.610 |
| *Cis*-1,3,5-hexatriene | 0.198 | 0.000 | 0.022 | 0.010[d] |
| 1,3-cyclohexadiene | 0.315 | 0.250 | 0.321 | 0.440 |
| 1-hexyne | 0.724 | 0.250 | 0.319 | 0.830 |
| 3,3-dimetyl-1-butyne | 0.716 | 0.500 | 0.385 | 0.660 |
| Norbornadiene | −0.049 | 0.000 | 0.251 | 0.117[f] |
| 1,3,5-cycloheptatriene | 0.156 | 0.250 | 0.171 | 0.250 |
| 1,3,5-heptatriene | 0.361 | 0.125 | 0.299 | 0.355[g] |
| 1,3,5-heptatriyne | 0.732 | 0.250 | 0.377 | 0.024[e] |
| Toluene | 0.426 | 0.125 | 0.366 | 0.370 |
| Styrene | 0.223 | 0.000 | 0.164 | 0.095[h] |
| Ethylbenzene | 0.611 | 0.125 | 0.310 | 0.590 |
| *o*-xylene | 0.644 | 1.000 | 0.628 | 0.620 |
| *m*-xylene | 0.658 | 1.000 | 0.355 | 0.370 |
| 1,3,5,7-nonatetraene | 0.300 | 0.125 | 0.301 | 0.423[g] |
| 1,3,5,7-nonatetrayne | 0.639 | 0.250 | 0.377 | 0.023[e] |
| 1,3,5,7,9-undecapentaene | 0.246 | 0.125 | 0.293 | 0.422[g] |
| 1,3,5,7,9-undecapentayne | 0.548 | 0.250 | 0.377 | 0.023[e] |
| 1-methylnaphtalene | 0.902 | 0.375 | 0.362 | 0.280 |
| 2-methylnaphtalene | 0.830 | 0.375 | 0.367 | 0.440 |
| Biphenyl-perpendicular | −0.024 | 0.500 | 0.001 | 0.002[g] |
| Biphenyl-twisted | −0.024 | 0.500 | 0.001 | 0.002[g] |
| Acenaphthylene | 0.285 | 0.500 | 0.038 | 0.342[g] |
| Acenaphthene | 0.784 | 0.750 | 0.400 | 0.810 |
| 1,3,5,7,9,11-tridecahexaene | 0.195 | 0.125 | 0.299 | 0.470[g] |
| 1,3,5,7,9,11-tridecahexayne | 0.458 | 0.250 | 0.377 | 0.023[e] |

*Table 3 continued.*

| Hydrocarbon | Fit[a] | Algebraic semisum | Vector semisum | Experiment[b] |
|---|---|---|---|---|
| Fluorene | 0.138 | 0.500 | 0.287 | 0.280 |
| *cis*-stilbene | −0.268 | 0.250 | 0.026 | 0.080[i] |
| 9,10-dihydroanthracene | 0.914 | 0.500 | 0.133 | 0.400 |
| 1,3,5,7,9,11,13-pentadecaheptaene | 0.146 | 0.125 | 0.269 | 0.452[g] |
| 1,3,5,7,9,11,13-pentadecaheptayne | 0.368 | 0.250 | 0.377 | 0.023[e] |
| Benzo[*a*]anthracene | 1.026 | 0.750 | 0.026 | 0.045[g] |
| Benzo[*a*]pyrene | 1.241 | 1.000 | 0.020 | 0.037[g] |
| Benzo[*b*]fluoranthene | 1.132 | 0.625 | 0.162 | 0.300[g] |
| Benzo[*k*]fluoranthene | 0.754 | 0.750 | 0.092 | 0.120[g] |
| Corannulene-bowl | 1.565 | 1.250 | 0.567 | 2.799[g] |
| Corannulene-*fullerene* | 1.565 | 1.250 | 0.896 | 5.352[g] |
| Indeno[1,2,3-*cd*]pyrene | 1.685 | 0.875 | 0.142 | 0.466[g] |
| Benzo[*ghi*]perylene | 2.678 | 1.250 | 0.268 | 0.064[g] |

[a]Calculations carried out with the method of *Gálvez* et al. (Equation 5).
[b]References 36 and 37.
[c]Calculations carried out with the Gaussian-2 composite *ab initio* method taken from Reference 38.
[d]Calculations carried out with the CAS-SCF method taken from Ref. 39.
[e]Calculations carried out with the POLAR method.
[f]Calculations carried out with the CAS-SCF method taken from Reference 40.
[g]Calculations carried out with the MOPAC-AM1 program.
[h]Calculations carried out with the CASPT2 method [41].
[i]Calculations carried out with the CASPT2 method [42].

Therefore, $\mu_{vec}$ represents the molecular dipole moment calculated by vector semisum of edge $\overline{C}^e$.

For example, in symmetric butane (*t*) $C_1$-$C_2$-$C_3$-$C_4$, $\overline{\mu}_{12}^1 = (-0.139, -0.116, -0.011)$, $\overline{\mu}_{23}^2 = (0, 0, 0)$ and $\overline{\mu}_{34}^3 = (0.139, 0.116, 0.011)$. Therefore, $\overline{\mu} = (0, 0, 0)$ and $\mu_{vec} = 0$. However, in asymmetric 2-methylbutane [$C_1$-$C_2$($C_3$)-$C_4$-$C_5$], $\overline{\mu}_{12}^1 = (-0.029, -0.335, -0.139)$, $\overline{\mu}_{23}^2 = (-0.133, 0.005, 0.338)$, $\overline{\mu}_{24}^3 = (0.173, 0.056, -0.007)$ and $\overline{\mu}_{45}^4 = (0.024, 0.171, 0.055)$. Therefore, $\overline{\mu} = (0.035, -0.103, 0.247)$ and $\mu_{vec} = 0.270$.

## Calculation results and discussion

### Polar hydrocarbons

The $G_k$ and $J_k$ values, up to the fifth order for a set of 57 polar hydrocarbons, are listed in Table 1, together with the number of carbon atoms, $N$. The $G_1$ term is clearly related to the degree of branching, although many repeated values may be observed (0.5 for linear alkanes, 1.5 for alkanes containing tertiary carbons, higher values for more branched alkanes, etc.). The $G_2$ term is related to the number of unsaturations in the hydrocarbon. For big hydrocarbons, the dominant $G_k$ index is $G_2$.

Gálvez *et al.* [27] selected a group of 30 heterogeneous hydrocarbons (24 polar hydrocarbons included in Table 1, and 6 apolar ones included in Table 2) to correlate the molecular dipole moment with the topological charge-transfer indices $G_k$ and $J_k$. They fitted the following linear regression equation:

$$\mu = -0.037 - 0.179G_1 - 0.134G_2 + 1.365G_4 + 0.789J_1 + 0.820J_2 + 2.421J_3,$$
$$n = 30, r = 0.941, SD = 0.107,$$
$$F = 28.0, p < 0.001. \tag{5}$$

The dipole moment for all the polar hydrocarbons in Table 1 have been calculated with this fit (Equation 5). The results are shown in the second column of Table 3. Despite the good results obtained with the method of Gálvez *et al.* for polar hydrocarbons, a negative dipole moment is predicted for 3 molecules: norbornadiene, biphenyl (both perpendicular and twisted conformers) and *cis*-stilbene.

The $\mu_{alg}$ results for the polar and apolar hydrocarbons obtained by Equation 3 are shown in the third column of Tables 3 and 4, respectively. Although the negative dipole moment is corrected for the 3 molecules with negative fit in Table 3, the value is strongly overestimated now for 2 of them: biphenyl and *cis*-stilbene.

*Table 4.* Molecular dipole moment values, $\mu$ (D), of apolar hydrocarbons with charge-transfer indices[a]

| Hydrocarbon | Fit[b] | Algebraic semisum | Experiment[c] |
|---|---|---|---|
| Methane | −0.037 | 0.000 | 0.000 |
| Ethane | −0.037 | 0.000 | 0.000 |
| Ethene | −0.037 | 0.000 | 0.000 |
| Ethyne | −0.037 | 0.000 | 0.000 |
| Cyclopropane | −0.037 | 0.000 | 0.000 |
| Propane | 0.071 | 0.000 | 0.000 |
| Alene | 0.179 | 0.000 | 0.000 |
| Butane (t) | 0.036 | 0.000 | 0.000[d] |
| *s-trans*-1,3-butadiene | 0.222 | 0.000 | 0.000 |
| 1,3-butadiyne | 0.469 | 0.000 | 0.000 |
| Pentane | 0.064 | 0.000 | 0.000 |
| 2,2-dimethylpropane | 0.018 | 0.750 | 0.000 |
| Cyclohexane | −0.037 | 0.000 | 0.000 |
| Benzene | 0.123 | 0.000 | 0.000 |
| Hexane | 0.129 | 0.000 | 0.000 |
| *Trans*-1,3,5-hexatriene | 0.198 | 0.000 | 0.000[e] |
| 1,3,5-hexatriyne | 0.499 | 0.000 | 0.000 |
| Heptane | 0.099 | 0.000 | 0.000 |
| Octane | 0.079 | 0.000 | 0.000 |
| 1,3,5,7-octatetraene | 0.166 | 0.000 | 0.000 |
| 1,3,5,7-octatetrayne | 0.464 | 0.000 | 0.000 |
| *p*-xylene | 0.681 | 1.000 | 0.000 |
| Nonane | 0.063 | 0.000 | 0.000 |
| Mesitylene | 0.845 | 0.875 | 0.000 |
| Decane | 0.051 | 0.000 | 0.000 |
| 1,3,5,7,9-decapentaene | 0.129 | 0.000 | 0.000 |
| 1,3,5,7,9-decapentayne | 0.406 | 0.000 | 0.000 |
| Naphthalene | 0.460 | 0.000 | 0.000 |
| Undecane | 0.041 | 0.000 | 0.000 |
| Dodecane | 0.033 | 0.000 | 0.000 |
| 1,3,5,7,9,11-dodecahexaene | 0.089 | 0.000 | 0.000 |
| 1,3,5,7,9,11-dodecahexayne | 0.337 | 0.000 | 0.000 |
| Biphenyl-coplanar | −0.024 | 0.500 | 0.000[f] |
| Tridecane | 0.026 | 0.000 | 0.000 |
| Tetradecane | 0.021 | 0.000 | 0.000 |
| 1,3,5,7,9,11,13-tetradecaheptaene | 0.048 | 0.000 | 0.000 |
| 1,3,5,7,9,11,13-tetradecaheptayne | 0.262 | 0.000 | 0.000 |
| *trans*-stilbene | −0.268 | 0.250 | 0.000[g] |
| Phenanthrene | 0.864 | 0.500 | 0.000 |
| Anthracene | 0.689 | 0.250 | 0.000 |
| Pentadecane | 0.016 | 0.000 | 0.000 |
| Hexadecane | 0.012 | 0.000 | 0.000 |
| 1,3,5,7,9,11,13,15-hexadecaoctaene | 0.006 | 0.000 | 0.000 |
| 1,3,5,7,9,11,13,15-hexadecaoctayne | 0.183 | 0.000 | 0.000 |
| Fluoranthene | 0.276 | 0.250 | 0.000 |

*Table 4 continued.*

| Hydrocarbon | Fit[b] | Algebraic semisum | Experiment[c] |
|---|---|---|---|
| Pyrene | 1.231 | 0.000 | 0.000 |
| Chrysene | 1.068 | 0.500 | 0.000[f] |
| Corannulene-planar | 1.565 | 1.250 | 0.000[f] |
| Dibenzo[*ah*]anthracene | 0.939 | 0.750 | 0.000[f] |
| Coronene | 3.518 | 0.125 | 0.000 |
| Fullerene-60 | 10.895 | 0.000 | 0.000 |
| Fullerene-70 | 13.888 | 0.250 | 0.000 |
| Fullerene-82 | 15.734 | 0.250 | 0.000[h] |

[a]The vector semisum is 0.000 for all entries.
[b]Calculations carried out with the method of *Gálvez* et al. (Equation 5).
[c]Ref. 36 and 37.
[d]Calculations carried out with the Gaussian-2 composite *ab initio* method taken from Ref. 38.
[e]Calculations carried out with the CAS-SCF method taken from Ref. 39.
[f]Calculations carried out with the MOPAC-AM1 program.
[g]Calculations carried out with the CASPT2 method [42].
[h]Calculatons carried out with the POLAR program.

The $\mu_{vec}$ dipole moments obtained by Equation 4 are shown in the fourth column of Table 3 for polar hydrocarbons. The overestimations for biphenyl and *cis*-stilbene are corrected now.

*Apolar hydrocarbons*

The $G_k$ and $J_k$ values for a set of 53 apolar hydrocarbons, are listed in Table 2. The dipole moment for all the apolar hydrocarbons in Table 2 have been calculated (Equation 5) and reported in Table 4. Notice that a small negative or positive dipole moment is predicted for all the molecules. Therefore, the reproduction of vanishing dipole moments for molecules with appropriate symmetry elements is far from trivial for pure topological (nongeometric) methods.

As may be observed, the algebraic semisum method (Equation 3) corrects the dipole moment for all the apolar molecules in Table 4 except 2,2-dimethylpropane, *p*-xylene, mesitylene, biphenyl-coplanar, *trans*-stilbene, phenanthrene, anthracene, fluoranthene, crysene, corannulene-planar, dibenzo[*a, h*]anthracene, coronene, fullerene-70 and fullerene-82. However, the vector semisum method (Equation 4) correctly predicts a dipole of 0.000D for all the apolar molecules.

Some reference calculations of the dipole moments of molecules presenting several conformations are either carried out with the MOPAC-AM1 [33] and POLAR programs [34] or taken from the literature. Both Equation (5) and the algebraic semisum method (Equation 3) cannot elucidate torsional isomers, viz., butane ($g^+$ and $t$), pentane (*tt*, $g^-t$, $g^-g^-$ and $g^-g'^+$), biphenyl (perpendicular, twisted and coplanar) and corannulene (bowl, *fullerene* and planar), as seen in Tables 3 and 4. However, this differentiation is achieved with the vector semisum method (Equation 4).

*Linear and nonlinear correlation models*

The molecular dipole moment and the charge-transfer indices $G_k$ and $J_k$ for all the hydrocarbons in Tables 3 and 4 have been correlated. The best linear regression results:

$$\begin{aligned} \mu = & -0.0000330 - 0.112G_5 + 0.295J_1 \\ & +3.41J_3 - 0.755J_4, \\ & n = 115, r = 0.419, SD = 0.548, \\ & F = 5.9. \end{aligned} \tag{6}$$

The correlation of Equation 6 is worse than that of Equation 5. The correponding interpretation is that the set of hydrocarbons selected in Equation 5 are apolar or have low dipole moment as far as 0.8D, whereas the hydrocarbon set in Equation 6 can have higher dipoles up to 5.4D. For Equation 6, the mean absolute percentage error (MAPE) is 101.74% and the approximation error variance (AEV) is 0.8250. All other models with greater MAPE and AEV have been discarded. The presence of charge-transfer indices such as $G_5$, $J_1$, $J_3$ and $J_4$ is representative of charge-transfer processes and clearly conditions the polar character of the correlated compounds. The best nonlinear model for the

dipole moment results:

$$\mu = 0.233 + 1.16z_{12} - 0.484z_{11}z_{12},$$
$$z_{11} = -1.04 + 6.32J_1,$$
$$z_{12} = -0.203 + 15.0J_1J_3, \tag{7}$$
$$\text{MAPE} = 102.55\%, \text{AEV} = 0.8028$$

and AEV decreases 3%.

Notice that the variance can be decreased if the fit is limited to a subset of similar hydrocarbons. For instance, for the polar hydrocarbons the best linear model for the dipole moment results:

$$\mu = 0.263 + 0.672G_3 - 2.16G_5 - 0.166J_2, \tag{8}$$
$$\text{MAPE} = 81.93\%, \text{AEV} = 0.6098$$

and AEV decreases 26%. No tested nonlinear model outperforms these results. If $\mu_{\text{vec}}$ is included in the model of polar and apolar hydrocarbons, the best linear regression for $\mu$ results:

$$\mu = -0.146 - 0.0475G_5 + 1.67J_3$$
$$+1.67\mu_{\text{vec}}, \text{MAPE} = 97.02\%, \tag{9}$$
$$\text{AEV} = 0.5718$$

and AEV decreases 31% . The best nonlinear model for the dipole moment results:

$$\mu = 0.233 - 0.0529z_{51} + 0.632z_{52},$$
$$z_{51} = -0.420 + 1.17\mu_{\text{vec}} + 2.33G_4\mu_{\text{vec}},$$
$$z_{52} = -0.152z_{41} + 1.13z_{42},$$
$$z_{41} = -0.365 + 25.9J_3\mu_{\text{vec}},$$
$$z_{42} = 0.101z_{31} + 0.942z_{32},$$
$$z_{31} = -0.775 + 4.85\mu_{\text{vec}},$$
$$z_{32} = 0.226z_{21} + 0.782z_{22},$$
$$z_{21} = 0.229z_{12} + 0.121z_{11}z_{12} - 0.163z_{11}^2$$
$$+0.178z_{12}^2,$$
$$z_{11} = -1.42 + 1.79J_2,$$
$$z_{12} = -0.365 + 25.9J_3\mu_{\text{vec}},$$
$$z_{22} = 0.666z_{13} - 1.38z_{13}z_{14} + 1.24z_{13}^2,$$
$$z_{13} = -0.390 + 0.998\mu_{\text{vec}} + 1.46G_3\mu_{\text{vec}},$$
$$z_{14} = -0.420 + 1.17\mu_{\text{vec}} + 2.33G_4\mu_{\text{vec}},$$
$$\text{MAPE} = 47.32\%, \text{AEV} = 0.0768 \tag{10}$$

and AEV decreases 91% . Due to the complexity of Equation (10), a Fortran program has been written to calculate $\mu$. The program is available from the author at Internet (Francisco.Torrens@uv.es).

When comparing Equations (6–10) with (5), smaller superpositions of the corresponding $G_k$ and $J_k$ pairs are observed in Equations (6–10). This diminishes the risk of colinearity [35] in the fit given the close relationship between each pair $G_k$, $J_k$ through Equation (2).

## Conclusions

From the preceding discussion the following conclusions can be drawn.

(1) The dipole moments calculated by algebraic and vector semisums of the charge-transfer indices are defined in this work. A new topological charge-transfer index, $\mu_{\text{vec}}$, is applied to the calculation of dipole moments. The combination of the charge-transfer indices allows the estimation of the molecular dipole moments. $\mu_{\text{vec}}$ elucidates clearly whether a molecule is either polar or apolar.

(2) The reproduction of vanishing dipole moments for molecules with appropriate symmetry elements is far from trivial for pure topological (nongeometric) methods (Equation 5).

(3) Linear and nonlinear correlation models have been obtained for the molecular dipole moments of hydrocarbons. The new charge-transfer index, $\mu_{\text{vec}}$, has improved the multivariable nonlinear regression equation for $\mu$. The variance of the fit has decreased 31%. It has also diminished the risk of colinearity in the fit.

(4) Even with the large number of fitted parameters, the predictions of this model are not of good quality. However, the objective of this work was to elucidate whether a molecule is apolar. Better fits for polar molecules are proposed in the literature.

An extension of the present study to heteroatoms would give an insight into a possible generality of these conclusions. Work is in progress to take into account the presence of heteroatoms in terms of valence charge-transfer indices. The electronegativity value of each heteroatom is introduced in the corresponding entry of the main diagonal of the adjacency matrix $\overline{\overline{A}}$. The new method will be applied to the calculation of the dipole moment of isoelectronic series of aromatic molecules, and of homologous series of phenyl alcohols and 4-alkylanilines (percutaneous enhancers).

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