Using theoretical descriptors in quantitative structure–property relationships: gas phase acidity of some hydrocarbons and nitrohydrocarbons

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Calculation of the gas phase acidity of some hydrocarbons and nitrohydrocarbons is studied using direct (quantum mechanical) methods as well as a model equation, derived with the aid of correlation analysis, relating empirical values to computational molecular parameters. Agreement between directly calculated and empirical values is improved by correlation equations. The correlation analysis model is statistically significant and physically reasonable; gas phase acidity increases with acidity modelling parameters and decreases with basicity modelling parameters.

Introduction

This study is based on an interest in 'energetic' (small, strained, easily oxidizable) molecules and the need to predict their properties. In principle, properties may be predicted using direct (quantum mechanical) methods as well as equations derived with the aid of correlation analysis. This study explores the use of direct and correlation analysis methods to calculate a property, gas phase acidity, directly amenable to these methods. The gas phase acidity, defined as Δ_aH or Δ_aG for the process in eqn. (1), can be directly found from first principles (semiempirical

$$\mathrm{RH(g)} = \mathrm{R^-(g)} + \mathrm{H^+(g)};\ \Delta_aH(\mathrm{RH}) \qquad (1)$$

and *ab initio* quantum mechanical methods) through calculation of the heats of formation of the species; $\Delta_aH(\mathrm{RH}) = \Delta_fH(\mathrm{R^-}) + \Delta_fH(\mathrm{H^+}) - \Delta_fH(\mathrm{RH})$. (Note that increasing Δ_aH implies decreasing conventional acidity.) In addition, theoretical calculations have been done for a number of compounds using *ab initio* and semiempirical quantum mechanical methods. Often, such calculated results are more useful for examining trends rather than providing exact values. *Ab initio* results depend on the basis set and the level of theory. Diffuse functions are required for the anion calculations, and sometimes result in linear dependence which makes convergence of Hartree–Fock equations difficult.[1] Δ_aH has been measured for a large number of compounds; as a result there is a large NIST Standard Reference Database.[2]

The existence of empirical values for a set of compounds permits the use of correlation analysis (statistics) to find coefficients in an equation relating empirical property values to a set of molecular parameters. This approach has been used in quantitative structure–activity (property) relationships (QSAR, QSPR) in which measured bulk properties have been correlated with predominantly empirical molecular structural parameters. Using experiment, statistics and theory may seem to lack rigour in describing nature but Otto Exner's statement, 'any regularity found in nature raises some kind of satisfaction'[3] is appropriate. Hansch,[4] Kamlet, Taft and Abraham (KTA)[5] have extended linear free energy relationship (LFER) type work,[6] a subset of QSAR, to involve solute–solvent interactions.[7] The resulting model, a linear solvation energy relationship (LSER), has used an empirical solvatochromatic (KTA) descriptor set and a more recently developed solvation parameter set to give successful correlations for well over 200 properties.[8]

Based on, and complementary to, the LSER philosophy, a set of molecular theoretical linear solvation energy relationship (TLSER) descriptors (computational) has been developed. These have shown good correlations and physical interpretations for many properties.[9–15] By their very nature, theoretical descriptors can give near *a priori* predictions; their calculations (and interpretations) are straightforward. Eqn. (2) gives one

$$\log P = aV_{\mathrm{mc}} + b\pi_{\mathrm{I}} + c\varepsilon_{\mathrm{B}} + dq_{-} + \mathrm{e}\varepsilon_{\mathrm{A}} + fq_{+} + \log P_{0} \qquad (2)$$

form of an LSER equation in terms of the TLSER parameters for some property, *P*; log P_0 represents an intercept. In this paper, Δ_aG and Δ_aH are used in place of log *P* since these are direct energy quantities. Often, *P* is related to an equilibrium or rate constant, *K*; hence, ln *K* is linearly related to a free energy.

Table 1 TLSER descriptors

Symbol	Name	Definition	Units[a]	Range
V_{mc}	Molecular volume	Molecular volume	100 Å^3	0.3–3
π_{I}	Polarizability index	Polarizability/V_{mc}	none	0.07–0.16
ε_{B}	'Covalent' HB basicity	0.30–0.01($E_{\mathrm{lw}} - E_{\mathrm{h}}$)	heV	0.1–0.17
q_{-}	'Electrostatic' HB basicity	Maximum |(−) charge| on an atom	acu	0–0.8
ε_{A}	'Covalent' HB acidity	0.30–0.01($E_{\mathrm{l}} - E_{\mathrm{hw}}$)	hev	0.14–0.2
q_{+}	'Electrostatic' HB acidity	Maximum (+) charge on an H atom	acu	0–0.8

[a] Å = Ångstrom; heV = hecto-electronvolt (1 heV = 10^2 eV = 9.6485×10^3 kJ mol^{-1}); acu = atomic charge unit; HB = hydrogen bond; E_{l} = LUMO energy; E_{h} = HOMO energy; E_{lw} and E_{hw} refer to the E_{l} = 5.4428 eV and E_{h} = −12.1911 eV for water, respectively; \| \| indicate absolute magnitudes.

Table 2 Compounds with TLSER descriptors and empirical $\Delta_a G$ and $\Delta_a H$ values (kJ mol^{-1}) at 298 K; compounds used in the direct semiempirical calculations for $\Delta_a H$ (Table 5) are marked with an asterisk (*)

Acidic H[a]	Molecule	V_{mc}	π_I	ε_B	q_-	ε_A	q_+	$\Delta_a G$/kJ mol^{-1}	$\Delta_a H$/kJ mol^{-1}
	Nitric acid*	0.3250	0.1190	0.1223	0.3483	0.1861	0.2380	1329.7	1357.7
C12	Fluoradene	2.1263	0.1584	0.1601	0.0980	0.1832	0.0629	1359.4	1391.6
C1	1,3-Diphenylindene*	2.5669	0.1437	0.1581	0.0905	0.1794	0.0748	1375.7	1402.9
C1	1,2,3-Triphenylindene	3.1988	0.1482	0.1586	0.0901	0.1801	0.0642	1373.2	1404.2
C3	2-Phenyl-5-*p*-tolylcyclopentadiene	2.2264	0.1461	0.1557	0.1015	0.1772	0.0743	1381.1	1412.5
C3	2,5-Diphenylcyclopentadiene	2.0717	0.1458	0.1558	0.1006	0.1771	0.0742	1382.8	1412.9
	Nitrous acid	0.2767	0.1001	0.1239	0.2496	0.1800	0.2032	1391.6	1423.8
C9	9-Phenylfluorene	2.3265	0.1438	0.1596	0.0826	0.1818	0.0629	1403.7	1436.4
C9	9-Neopentylfluorene	23701	0.1356	0.1595	0.1026	0.1818	0.0617	1419.2	1451.8
C9	9-Isobutylfluorene	2.2496	1.1347	0.1595	0.0808	0.1818	0.0616	1435.1	1467.7
C9	9-Methylfluorene	1.6875	0.1475	0.1596	0.0810	0.1818	0.0616	1437.2	1468.2
C9	9-*tert*-Butylfluorene	2.2719	0.1341	0.1597	0.0864	0.1819	0.0618	1437.6	1468.6
C9	9-Ethylfluorene	1.9069	0.1405	0.1596	0.0818	0.1818	0.0616	1436.8	1469.4
C9	9-Isopropylfluorene	2.0524	0.1394	0.1596	0.0386	0.1818	0.0616	1437.2	1469.8
C9	Fluorene*	1.5606	0.1475	0.1595	0.0940	0.1818	0.0616	1439.3	1471.9
C1	Indene	1.1307	0.1370	0.1580	0.1100	0.1793	0.0730	1441.8	1472.8
CH_3	4-Nitrotoluene*	1.1348	0.1362	0.1427	0.3298	0.1872	0.0858	1444.7	1474.9
C9	2-Methylfluorene	1.7758	0.1431	0.1598	0.0996	0.1824	0.0618	1442.6	1475.3
CH_3	6,6-Dimethylfulvene	1.2171	0.1247	0.1565	0.0798	0.1841	0.0723	1453.9	1481.6
C4	Nitrobenzene*	0.9644	0.1375	0.1425	0.3288	0.1860	0.0851	1449.8	1482.0
C1	Nitro-2,2-dimethylpropane	1.1326	0.1118	0.1314	0.3368	0.1804	0.0519	1457.7	1486.2
C1	Nitroethane*	0.6204	0.1145	0.1308	0.3353	0.1808	0.0557	1462.3	1489.5
	Nitroethyne	0.4735	0.1233	0.1283	0.3142	0.1887	0.1829	1456.9	1489.5
C2	2-Nitropropane	0.7967	0.1130	0.1314	0.3372	0.1799	0.0615	1464.4	1489.9
CH_3	2-Nitrotoluene*	1.1241	0.1362	0.1440	0.3297	0.1861	0.0848	1458.5	1489.9
	Nitromethane*	0.4495	0.1151	0.1302	0.3348	0.1818	0.0498	1463.1	1491.2
	Triphenylmethane*	2.3784	0.1383	0.1540	0.0794	0.1760	0.0603	1467.3	1500.8
C5	Pentamethylcyclopentadiene	1.5310	0.1212	0.1574	0.1266	0.1776	0.0350	1485.3	1509.6
C1	Nitroethene	0.5616	0.1206	0.1312	0.3465	0.1882	0.1147	1482.8	1514.6
CH_3	9-Methylanthracene	1.8081	0.1604	0.1654	0.0617	0.1872	0.0613	1485.7	1515.4
CH_3	3-Nitrotoluene*	1.1128	0.1383	0.1439	0.3290	0.1860	0.0854	1488.2	1518.4
	Diphenylmethane	1.7133	0.1301	0.1533	0.0879	0.1763	0.0600	1498.7	1521.3
C1	Nitrocyclopropane	0.6836	0.1230	0.1310	0.3322	0.1807	0.0996	1509.2	1534.3
C1	1-Phenylprop-2-ene*	1.2433	0.1279	0.1528	0.1155	0.1756	0.0599	1512.6	1540.1
C1,2	Penta-1,4-diene*	0.8050	0.1163	0.1464	0.1147	0.1679	0.0496	1524.2	1544.7
	Phenylethyne	0.9919	0.1396	0.1551	0.1251	0.1786	0.1581	1518.4	1551.0
C1,2	Cyclohexa-1,3-diene	0.9149	0.1169	0.1561	0.0938	0.1758	0.0579	1530.5	1561.9
CH_3	1-Methylnaphthalene	1.3470	0.1475	0.1601	0.0831	0.1820	0.0608	1530.5	1565.2
C7	Cycloheptatriene	0.9877	0.1267	0.1578	0.1046	0.1799	0.0678	1544.7	1569.8
C5	Cyclooctadiene	1.2243	0.1206	0.1539	0.0877	0.1747	0.0487	1548.5	1576.1
C1	3,3-Dimethylbutyne	0.9959	0.1067	0.1389	0.1653	0.1588	0.1570	1548.9	1581.6
	Ethyne*	0.3248	0.0841	0.1355	0.1546	0.1568	0.1546	1547.2	1581.6
C3	Benzyne	0.7252	0.1299	0.1499	0.1137	0.1822	0.0832	1552.3	1584.5
C2	2-Phenylpropane	1.2978	0.1241	0.1527	0.0759	0.1755	0.0602	1560.2	1585.7
C4	Bicyclo[3.2.1]octa-2,6-diene	1.0960	0.1202	0.1498	0.1027	0.1695	0.0752	1559.0	1588.2
C1	Phenylethane*	1.1783	0.1206	0.1528	0.0880	0.1755	0.0599	1561.9	1589.1
C1	Pentyne	0.8625	0.1020	0.1387	0.1787	0.1595	0.1564	1556.4	1589.1
	Propadiene	0.5090	0.1112	0.1454	0.2047	0.1668	0.0474	1556.4	1592.4
CH_3	Toluene*	0.9721	0.1266	0.1528	0.1007	0.1756	0.0598	1563.6	1593.3
C1	Propyne	0.4767	0.1035	0.1384	0.1874	0.1597	0.1562	1561.9	1594.5
CH_3	3-Methyltoluene	1.1531	0.1250	0.1532	0.1057	0.1761	0.0600	1564.4	1594.5
CH_3	4-Methyltoluene	1.1391	0.1271	0.1538	0.0947	0.1768	0.0576	1568.2	1597.9
CH_3	2-Phenylpropene*	1.2241	0.1312	0.1526	0.1115	0.1753	0.0597	1585.7	1613.4
CH_3	2-Methylbutadiene*	0.7960	0.1194	0.1478	0.1220	0.1687	0.0523	1585.7	1613.8
C3	Cyclohexene	0.9593	0.1142	0.1481	0.0960	0.1685	0.0537	1617.1	1617.1
C3	Cyclooctene	1.2958	0.1131	0.1476	0.0915	0.1686	0.0479	1585.7	1617.1
C2	Methylenecyclobutane	0.8212	0.1103	0.1467	0.1806	0.1675	0.0402	1585.7	1620.0
C3	2-Methylenenorbornene	1.1833	0.1190	0.1476	0.1518	0.1675	0.0400	1599.5	1628.8
C3	5-Methylenenorbornene	1.1257	0.1204	0.1495	0.1505	0.1688	0.0777	1602.9	1632.2
CH_3	2-Methylpropene*	0.7252	0.1086	0.1473	0.1727	0.1686	0.0380	1602.1	1633.0
C4	Bicyclo[3.2.1]octa-2-ene	1.1951	0.1153	0.1486	0.1037	0.1683	0.0590	1603.7	1634.7
C1	1-Phenylethene	1.0857	0.1303	0.1526	0.0683	0.1754	0.0598	1604.1	1635.9
C1	Phenylcyclopropane	1.2277	0.1278	0.1530	0.0661	0.1754	0.0597	1606.7	1639.3
C1	Vinylcyclopropane	0.7866	0.1168	0.1465	0.0787	0.1667	0.0500	1617.1	1647.2
C1	Naphthalene	1.2165	0.1460	0.1598	0.0576	0.1814	0.0599	1605.8	1649.3
C1	Cyclobutene	0.6245	0.1118	0.1479	0.1168	0.1683	0.0859	1627.6	1661.9
C1	Bicyclobutane*	0.6287	0.1124	0.1456	0.1741	0.1601	0.0991	1635.9	1670.3
C2	Norbornadiene	0.9380	0.1173	0.1509	0.1035	0.1699	0.0786	1637.2	1671.5
	Benzene*	0.8003	0.1273	0.1517	0.0593	0.1744	0.0593	1635.5	1676.5
C2	Norbornene	1.0219	0.1149	0.1492	0.1030	0.1680	0.0771	1648.1	1682.4
	Cyclohexane	1.0065	0.1115	0.1282	0.0101	0.1461	0.0051	1665.2	1690.3
C2	Propene*	0.5618	0.1056	0.1459	0.1291	0.1669	0.0487	1665.2	1697.9
CH_3	2,2-Dimethylpropane*	0.9351	0.1062	0.1244	0.1257	0.1429	−0.0068	1673.6	1710.8
CH_3	3,3-Dimethylbutene*	1.0592	0.1082	0.1459	0.0956	0.1666	0.0467		1711.3
Cl	Methylcyclopropane*	0.7079	0.1072	0.1349	0.1273	0.1521	0.0436	1679.5	1712.1
	Ethene*	0.3811	0.1017	0.1438	0.0799	0.1649	0.0399	1677.8	1712.9

Table 2 (*continued*)

Acidic H[a]	Molecule	V_{mc}	π_I	ε_B	q_-	ε_A	q_+	Δ_aG/kJ mol^{-1}	Δ_aH/kJ mol^{-1}
C1	Bicyclopentane*	0.7866	0.1111	0.1289	0.0936	0.1467	0.0677	1719.6	1719.6
CH_3	But-1-ene*	0.7275	0.1075	0.1459	0.1165	0.1667	0.0490	1690.3	1723.8
C2	2-Methylpropane*	0.7787	0.1040	0.1244	0.0823	0.1442	0.0130	1691.2	1727.6
C2	Propane*	0.6412	0.0974	0.1222	0.0346	0.1430	0.0046	1703.3	1738.9
C2	Butane*	0.8215	0.0989	0.1235	0.0203	0.1440	0.0043	1703.3	1739.3
	Cyclopentane*	0.8609	0.1062	0.1250	0.0165	0.1462	0.0082	1704.1	1741.0
	Methane*	0.2715	0.0904	0.1069	−0.0704	0.1342	−0.0176	1709.6	1743.5
	Cyclopropane*	0.5203	0.1084	0.1313	0.0736	0.1502	0.0368	1707.9	1744.7
	Cyclobutane*	0.7089	0.1033	0.1275	0.0336	0.1452	0.0168	1708.7	1746.4
	Ethane*	0.4391	0.0994	0.1186	−0.0166	0.1405	−0.0055	1720.9	1757.7
The following compounds have no empirical values or are outliers. Outliers have empirical values listed									
CH_3	But-2-ene	0.7232	0.1113	0.1479	0.1028	0.1686	0.0486		
	Cubane	0.9431	0.1252	0.1361	0.0661	0.1460	0.0661		
C3	Cycloocta-1,4-diene	1.1933	0.1198	0.1524	0.1073	0.1721	0.0550		
C3	Cyclopentadiene*	0.7321	0.1147	0.1552	0.1182	0.1750	0.0726	1454.8	1480.7
	Dinitramide	0.5490	0.1450	0.1178	0.4055	0.1994	0.2688	1242.6	
CH_3	2-Methyltoluene	1.1800	0.1217	0.1533	0.0809	0.1762	0.0603		
	NH_3*	0.2199	0.0847	0.1337	0.2268	0.1347	0.0756	1657.3	1688.7
C1	Nitrocubane	1.1531	0.1272	0.1321	0.3358	0.1804	0.0912		
	Nitramine	0.3699	0.1267	0.1261	0.3249	0.1839	0.1625		
C1	1-Nitropropane	0.7867	0.1145	0.1310	0.3357	0.1807	0.0551		
CH_3	2-Nitropropane	0.6998	0.1246	0.1368	0.3414	0.1810	0.0746		
	Trinitromethane	0.7720	0.1494	0.1154	0.2695	0.2018	0.1593		
	Triphenylcyclopropene	2.5265	0.1601	0.1616	0.0791	0.1851	0.0643	1577.4	1612.9

[a] Acidic H, the number of the carbon or type of group (CH_3) to which the acidic hydrogen is attached; numbering is based on IUPAC protocol. See Fig. 1 for some complex structures. Assignments are from the Negion database, original references, calculations on isomers and/or consultation with organic chemistry colleagues. Experimental results do not necessarily provide knowledge of the acidic site. Nothing is written when there is no acid site ambiguity.

In turn, the free energy is linearly related to an energy term such as enthalpy.

The TLSER descriptors are summarized in Table 1; they apply to a neutral molecular model. V_{mo}, the molecular volume, can model the size of a cavity for placing the solute in a solvent and/or can be related to dispersive interactions. The polarizability index, π_I, models the polarizability and may be related to dispersive interactions. The ε_B and ε_A terms model the covalent hydrogen bond acceptor basicity (HBAB) and hydrogen bond donor activity (HBDA), respectively; while the q_- and q_+ terms model electrostatic HBB and HBA, also respectively. The ε_B and ε_A use linear functions of the highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy, respectively. The electrostatic HBB descriptor is the largest negative atomic formal charge, q_-; the corresponding HBA descriptor is the formal charge, q_+, on the most positive H atom.

In this application the LUMO (and electron affinity) and HOMO (and ionization potential) are assumed to be vertical quantities in the sense of the Franck–Condon principle; however, this is not always the case for the LUMO. An added electron does not necessarily attach to the molecule to form a bound anion; the added electron may remain free. The LUMO and HOMO are used here as models; by their very nature models do not completely represent the real system.

Eqn. (2) can be used in two ways; it can predict values and serve as a molecular probe. For prediction, the molecular parameters are calculated for a compound and substituted into the equation. As a probe, the physical meaning of a statistically significant parameter can suggest something about the process associated with the property. For example, if the hydrogen bonding activity, ε_A or q_+, is significant for some biological property then a receptor site might have a hydrogen bond basicity function. Their coefficients, *e* or *f*, could be interpreted as a measure of the hydrogen bond basicity of the receptor site.

This paper calculates Δ_aH(RH) values with direct methods, which have a good theoretical basis, and with the TLSER correlation equation in order to explore, further, the applicability of the TLSER descriptors for calculating properties for energetic materials. A previous study of energetic compounds (including trinitrotoluene) examined the correlation of HPLC (high performance liquid chromatography) capacity factors with TLSER parameters.[16] A statistically significant and physically reasonable equation can suggest using TLSER descriptors in relationships for other properties.

An earlier, related paper[12] examined correlations for gas phase acidities of some carboxylic acids, alcohols, silanols, anilines and a small number of hydrocarbons. For the hydrocarbons the measured quantity was the activation energy for the process in eqn. (1). This paper uses a much larger set of hydrocarbons (and related nitro derivatives). Because of the need for an adequate statistical sample size, this study focuses on hydrocarbons and nitrohydrocarbons. Azides, for example, are not included.

Procedure

The MNDO, AM1 and PM3 protocols in MOPAC6 were used to get the semiempirical theoretical ΔH_a values for 37 molecules (marked with * in Table 2).The heats of formation of the anion and molecule were taken from the MOPAC output while the heat formation of the hydrogen ion was taken as the empirical value, 1530 kJ mol^{-1}.[15] The model for the radical anions was kept simple; Jahn–Teller distortions due to degeneracy (such as with methane) were ignored and their (often) unbound nature was not considered as relevant. GAUSSIAN92 was used to calculate the 6-31+G values for those compounds not found in the literature.

Data for the compounds listed in Table 2 were taken from the 19A and 19B NIST Positive and Negative Ion Energetics Database.[1] The compound set was selected to provide a reasonable number of small hydrocarbons and nitro group containing derivatives. In addition, some compounds for which there were no empirical data were included so that their values could be calculated. Δ_aH (rather than Δ_aG) values were used in the correlations since the semiempirical calculations yield Δ_fH values directly. In fact, the semiempirical methods are parameterized based on heats of formation. In converting to kJ from kcal one

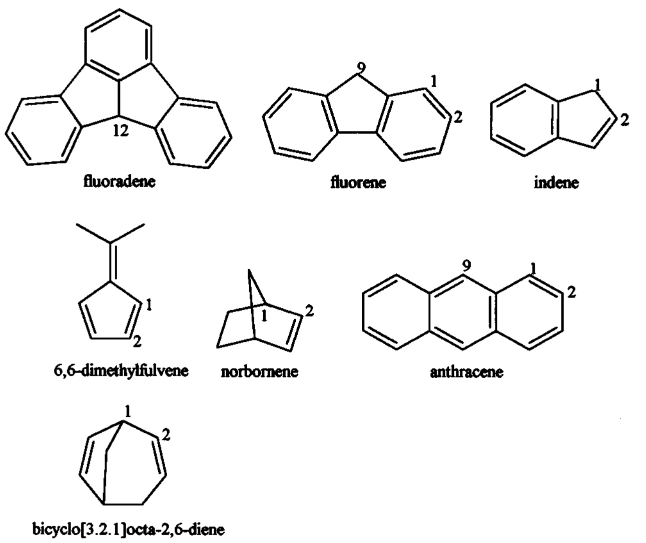

Fig. 1 Representative compound structures with position indicators

more digit was retained than was significant so as to minimize error. Not all data were of the same uncertainty; many uncertainties are around ±8 kJ mol^{-1} while some were ±20 kJ mol^{-1} or higher.

When data for more than one H atom on a molecule were available, often the site with the lowest Δ_aH value was chosen. In the case of phenylethane, for example, the database indicates that the $PhCH_2CH_2^-$ ion involves *ca.* 110 kJ mol^{-1} more energy than the $PhCH^-CH_3$ ion. Fig. 1 contains some structures to help identify compounds; position numbers, based on IUPAC protocol, are provided to help locate acidic sites. Experiment, particularly ion cyclotron resonance (ICR), does not necessarily identify the acidic site;[17] however, the apparent acidic sites (as gathered from the Negion Database, original references, some isomer calculations and consultation with organic chemistry colleagues) are indicated before the name in Table 2. When there is only one site possible nothing is written. From the standpoint of these calculations it was only necessary to identify the acidic sites for the compounds in Table 4.

The molecular geometry description (Z-matrix) was modelled and viewed using PCMODEL (Serena Software, Bloomington, IN 47402-3076) and MMADS (in house program).[18] The Hamiltonian was modelled with the MNDO, AM1 and PM3 algorithms in MOPAC6 (QCPE); the output gave the optimized geometry, energies, polarizabilities and Coulson formal charges and heats of formation. The MOPAC calculations were done with keywords, EF and PRECISE. The TLSER molecular parameters were taken from the MNDO results; they were extracted from the MOPAC files with MADCAP (in house program).[19]

The equation parameters were obtained by multilinear correlation (regression) analysis. The quality of the correlation equations was judged by the statistical parameters. Guidelines for acceptance were: correlation coefficient, *R*, near 0.90 or higher (variance, $R^2 > 0.80$); terms significant at the 0.95 level or higher [P(2-tail) < 0.05], and low variable collinearity [variance inflation factor (VIF) < 5]. While it is stated that VIF values less than 10 are statistically satisfactory, we chose the more stringent criterion. When there was too much cross-correlation the parameter with the least (lowest t-stat) significance was eliminated. Outliers were compounds with Student deleted residuals greater than three.

Results

Table 4 contains some selected values calculated directly by TLSER [eqn. (7) in Table 6], MNDO, AM1, PM3 and *ab initio* values from Ritchie and Bacharach[1] as well as GAUSSIAN92 calculated values done for this study. Table 6 contains the TLSER correlation equations along with the statistical parameters. Table 5 contains eqns. (3–6) which refer to correlations of the experimental values against *ab initio* (6-31+G), MNDO, AM1 and PM3 calculated Δ_aH values, respectively. Correlations on the hydrocarbons alone and the nitro compounds alone were done but not recorded here. The equations accounted for considerably less than 80% of the variance. Table 3 contains TLSER parameters for the compounds; these are arranged in ascending (decreasing acidity) order of experimental Δ_aH values (where known). One more significant figure than is justified is retained since most empirical values are given to the nearest 0.1 kcal mol^{-1} and several compounds are very close in value. Table 4 contains the TLSER calculated Δ_aH values along with residuals where empirical values are known.

Discussion

Examination of Table 4 shows that empirical and directly calculated values do not agree as well as one would like; in fact, the 6-31+G *ab initio* values tend to be higher than empirical values. Consequently, correlation equations between the empirical and theoretical values were obtained in order to improve the fit. These appear as eqns. (3–6) in Table 5, and are repeated

$$\Delta_aH\,(\text{calc}) = 297.26\ \text{kJ mol}^{-1} + 0.783\,58\ \Delta_aH\,(\textit{ab initio}) \quad (3)$$

$$\Delta_aH\,(\text{calc}) = 518.13\ \text{kJ mol}^{-1} + 0.676\,91\ \Delta_aH\,(\text{MNDO}) \quad (4)$$

$$\Delta_aH\,(\text{calc}) = 557.19\ \text{kJ mol}^{-1} + 0.648\,92\ \Delta_aH\,(\text{AM1}) \quad (5)$$

$$\Delta_aH\,(\text{calc}) = 374.62\ \text{kJ mol}^{-1} + 0.771\,04\ \Delta_aH\,(\text{PM3}) \quad (6)$$

here without the statistical parameters. At this point it is helpful to recall that theoretically calculated results often are more useful for examining relative trends rather than getting absolute values. This is particularly appropriate here since the heats of formation of the molecule and ion are used to calculate Δ_aH. While semiempirical methods have been parameterized using empirical heats of formation, Δ_fH, calculated Δ_fH values do not always agree with experiment. That may contribute to the scatter in Table 4 and the variance in the equations of Table 6. [For that matter, the 6-31+G level *ab initio* values seem to have as much scatter as the semiempirical ones; most are higher than the empirical values. However, eqns (3–6) show that these 6-31+G values correlate better with the empirical value.]

A possible contribution to the lack of empirical and theoretical agreement could be in the $\Delta_fH(R^-)$ calculations; the exact location for the acidic hydrogen was not always evident from the experimental information. While there are consistent trends for these directly calculated values, Table 6 shows the MNDO regression fit, eqn. (4), of empirical Δ_aH values with the calculated values had a variance (R^2) of 0.56 and a standard deviation of 74 kJ mol^{-1} (when cyclopentadiene is retained). This should be compared with the early calculation of electron affinities by Dewar and Rzepa[20] which gave a standard deviation of 41 kJ mol^{-1} and exhibited systematic errors for different classes of molecules. The AM1 and PM3 eqns. (5) and (6), give better fits but still with variances less than 0.80 when the outliers are retained.

Hartree–Fock level *ab initio* techniques do not improve this situation. The methane values calculated with different basis sets by Ritchie and Bacharach[1] are all higher then empirical observation just as in other direct value cases. A calculation on another small molecule, ammonia, with the 6-31+G basis set corresponding to the Ritchie calculations also gives a much larger value of the acidity compared to experiment. Similarly, Koppel *et al.*[21] performed calculations on 14 very strong neutral CH acids using the 3-21G basis set. The calculated values of Δ_aG were systematically larger than the experimental values.

Table 3 Compounds with TLSER calculated Δ_aH values and residuals (kJ mol^{-1})[a]

Molecule	Calculated	Residual	Stud. resid.[b]	Empirical	Molecule	Calculated	Residual	Stud. resid.[b]	Empirical
Nitric acid	1391.7	−34.0	−0.96	1357.7	Benzene	1562.0	22.5	0.55	1584.5
Fluoradene	1461.7	−70.1	−1.77	1391.6	2-Phenylpropane	1565.3	20.5	0.50	1585.7
1,3-Diphenylindene	1424.1	−21.2	−0.54	1402.9	Bicyclo[3.2.1]octa-2,6-diene	1600.0	−11.8	−0.29	1588.2
1,2,3-Triphenylindene	1363.3	40.8	1.11	1404.2	Ethylbenzene	1577.4	11.7	0.29	1589.1
2-Phenyl-5-*p*-tolylcyclopentadiene	1462.9	−50.3	−1.27	1412.5	Pentyne	1591.5	−2.4	−0.06	1589.1
2,5-Diphenylcyclopentadiene	1479.4	−66.5	−1.67	1412.9	Propadiene	1676.3	−83.8	−2.1	1592.4
Nitrous acid	1457.0	−33.2	−0.89	1423.8	Toluene	1597.9	−4.6	−0.11	1593.3
9-Phenylfluorene	1447.4	−11.0	−0.27	1436.4	Propyne	1628.9	−34.4	−0.89	1594.5
9-Neopentylfluorene	1443.3	8.5	0.21	1451.8	3-Methyltoluene	1578.0	16.5	0.40	1594.5
9-Isobutylfluorene	1455.7	12.0	0.30	1467.7	4-Methyltoluene	1579.3	18.6	0.45	1597.9
9-Methylfluorene	1513.3	−45.1	−1.11	1468.2	2-Phenylpropane	1573.5	39.9	0.98	1613.4
9-*tert*-Butylfluorene	1453.4	15.2	0.38	1468.6	2-Methylbutadiene	1641.4	−27.6	−0.68	1613.8
9-Ethylfluorene	1491.1	−21.7	−0.53	1469.4	Cyclohexene	1626.5	−9.3	−0.23	1617.1
9-Isopropylfluorene	1476.1	−6.3	−0.16	1469.8	Cyclooctene	1593.7	23.4	0.57	1617.1
Fluorene	1525.9	−54.0	−1.34	1471.9	Methylenecyclobutane	1649.3	−29.2	−0.72	1620.0
Indene	1571.5	−98.8	−2.52	1472.8	2-Methylenenorbornene	1615.9	13.0	0.32	1628.8
4-Nitrotoluene	1466.5	8.4	0.21	1474.9	5-Methylenenorbornene	1598.1	34.1	0.83	1632.2
2-Methylfluorene	1501.8	−26.5	−0.65	1475.3	2-Methylpropene	1656.6	−23.6	−0.58	1633.0
6,6-Dimethylfulvene	1531.1	−49.6	−1.23	1481.6	Bicyclo[3.2.1]octa-2-ene	1601.7	33.0	0.81	1634.7
Nitrobenzene	1490.2	−8.2	−0.20	1482.0	Phenylethene	1586.8	49.2	1.21	1635.9
Nitro-2,2-dimethylpropane	1485.2	1.0	0.025	1486.2	Phenylcyclopropane	1573.9	65.4	1.62	1639.3
Nitroethane	1531.1	−41.5	−1.06	1489.5	Vinylcyclopropane	1650.8	−3.5	−0.09	1647.2
Nitroethyne	1416.1	73.4	1.97	1489.5	Naphthalene	1565.2	84.1	2.13	1649.3
2-Nitropropane	1516.8	−26.8	−0.68	1489.9	Cyclobutene	1641.6	20.3	0.50	1661.9
2-Nitrotoluene	1478.8	11.2	0.28	1489.9	Bicyclobutane	1670.5	−0.2	−0.01	1670.3
Nitromethane	1544.6	−53.4	−1.39	1491.2	Norbornadiene	1615.7	55.8	1.38	1671.5
Triphenylmethane	1456.6	44.2	1.12	1500.8	Benzene	1618.6	57.9	1.44	1676.5
Pentamethylcyclopentadiene	1560.8	−51.2	−1.27	1509.6	Norbornene	1612.5	69.9	1.74	1682.4
Nitroethene	1461.7	52.9	1.37	1514.6	Cyclohexane	1706.5	−16.2	−0.41	1690.3
9-Methylanthracene	1491.4	24.1	0.60	1515.4	Propene	1671.5	26.3	0.65	1697.9
3-Nitrotoluene	1479.4	39.0	0.97	1518.4	2,2-Dimethylpropane	1725.6	−14.7	−0.37	1710.8
Diphenylmethane	1520.2	1.1	0.028	1521.3	3,3-Dimethylbutene	1623.8	87.5	2.19	1711.3
Nitrocyclopropane	1499.2	35.1	0.88	1534.3	Methylcyclopropane	1703.8	8.3	0.20	1712.1
1-Phenylprop-2-ene	1570.6	−30.5	−0.74	1504.1	Ethene	1698.8	14.2	0.35	1712.9
1,4-Penta-1,4-diene	1641.8	−97.1	−2.46	1544.7	Bicyclopentane	1689.9	29.7	0.75	1719.6
Phenylethyne	1527.8	23.2	0.59	1551.0	But-1-ene	1655.3	68.5	1.71	1723.8
Cyclohexa-1,3-diene	1615.5	−53.6	−1.34	1561.9	2-Methylpropane	1722.3	5.3	0.13	1727.6
1-Methylnaphthalene	1549.1	16.1	0.40	1565.2	Propane	1740.8	−1.9	−0.05	1738.9
Cycloheptatriene	1585.3	−15.5	−0.38	1569.8	Butane	1721.1	18.2	0.46	1739.3
Cycloocta-1,3-diene	1588.0	−11.9	−0.29	1576.1	Cyclopentane	1708.1	32.9	0.83	1741.0
3,3-Dimethylbutyne	1581.8	−0.3	−0.01	1581.6	Methane	1787.3	−43.8	−1.17	1743.5
Ethyne	1651.4	−69.8	−1.84	1581.6	Cyclopropane	1724.6	20.1	0.50	1744.7
					Cyclobutane	1732.7	13.7	0.34	1746.4
					Ethane	1768.5	−10.8	−0.28	1757.7
The following compounds have no empirical values or are outliers.									
But-2-ene	1652.3				Nitrocubane	1462.1			
Cubane	1704.1				Nitramine	1458.3			
Cycloocta-1,4-diene	1596.6				Nitropropane	1515.8			
Cyclopentadiene	1626.5	−145.8	−3.54	1480.7	Nitropropene	1531.3			
Dinitramide	1260.5				Trinitromethane	1282.5			
2-Methyltoluene	1575.1				Triphenylcyclopropene	1414.7	198.2	4.81	1612.9
NH_3	1826.6	−137.9	−3.35	1688.7					

[a] See Table 2 for suggested acidic sites. [b] Student(ized) deleted residual error.

They got a straight line regression, $\Delta_aG(\text{calc}) = 208$ kJ mol^{-1} + 0.811 Δ_aG (3-21G). A simple regression of *ab initio* values in Table 3 calculated with 6-31+G basis set is written as eqn. (3) in Table 5. To produce *ab initio* results that are in close agreement with experiment it is necessary to use very high levels of theory. Smith and Radom[22] obtained gas phase acidity values for 23 small molecules using G2 theory with a mean error of 6 kJ mol^{-1} and consistently within 10 kJ mol^{-1}. In an earlier study of proton affinities, DeFrees and McLean[23] obtained results within 8 kJ mol^{-1} using MP4/6-311++G-(3df,3pd) for small neutral molecules and ions.

Examination of eqn. (7) for the TLSER descriptors shows that the correlation is physically reasonable and statistically acceptable. The physically reasonable nature is indicated by the way Δ_aH and Δ_aG decrease (indicating increase in acidity) with increasing acidity parameters, ε_A and q_+. Furthermore, they increase (indicating decrease in acidity) with increasing basicity parameter, ε_B. The decrease of Δ_aH and Δ_aG with V_{mc} is reasonable since a hydrogen atom can be more readily removed from a large molecule; less perturbation in structure is involved.

$$\Delta_aH = -101.9\ V_{mc} + 3471\ \varepsilon_B - 5568\ \varepsilon_A - 606.3\ q_+ + 2181 \quad (7)$$

The statistically reasonable nature of eqn. (7) is indicated as follows. The correlation coefficient values, *R*, show that they account for more than 80% of the variance. The coefficients are all significant above the 0.000 level. Furthermore, VIF values indicate that the descriptors are within the acceptable range for orthogonality. The SD values are about double the largest experimental uncertainty of *ca.* ±21 kJ mol^{-1}; this indicates

Table 4 Δ_aH (kJ mol^{-1}) values for selected compounds by various methods[a]

Molecule	Experiment	TLSER[b]	MNDO	AM1	PM3	6-31+G
Ethane	1757.7	1768.5	1727.0	1747.2	1738.4	1835.7
Cyclopropane	1744.7	1724.6	1721.4	1739.7	1714.0	1819.0
Methane	1743.5	1787.3	1817.8	1808.2	1800.0	1813.5
Bicyclopentane	1719.6	1689.9	1741.8	1729.5	1688.6	1805.4
Methylcyclopropane	1712.1	1703.8	1645.0	1702.5	1679.2	1813.3
Ethene	1712.9	1698.8	1763.1	1746.0	1718.6	1770.3
Benzene	1676.5	1618.6	1696.10	1679.5	1648.1	1743.8
Bicyclobutane	1670.3	1670.5	1714.2	1701.6	1659.0	1744.1
Toluene	1593.1	1597.9	1550.5	1556.6	1548.5	1680.1
Ethyne	1581.6	1651.4	1726.0	1674.8	1637.4	1610.3
3-Nitrotoluene	1518.4	1479.4	1565.2	1579.8	1540.9	1636.7
Nitromethane	1491.2	1544.6	1453.7	1449.4	1415.3	1471.8
2-Nitropropane	1489.9	1516.8	unstable[c]	unstable	unstable	1480.3
2-Nitrotoluene	1489.9	1478.8	1446.2	1441.8	1431.7	1520.8
4-Nitrotoluene	1489.9	1466.5	1422.8	1426.5	1415.3	1506.3
Nitroethane	1489.5	1531.1	1422.6	1380.7	1397.0	1474.2
Nitrobenzene	1482.0	1490.2	1605.9	1579.1	1572.5	1640.8
Cubane	una[d]		1739.9	1720.6	1687.0	1803.7
Nitrocubane	una		1666.0	1644.0	1619.3	1682.3

[a] See Table 2 for acidic sites. [b] TLSER values calculated with eqn. (7), Table 6. [c] Anion calculations resulted in fragmentation. [d] una, empirical value unavailable.

Table 5 Correlation equations for Δ_aH (empirical) *vs.* Δ_aH (theory)

Equation	N	R	SD	F	
Δ_aH (calc) = 297.26 kJ mol^{-1} + 0.783 58 Δ_aH (*ab initio*) Outlier: nitrobenzene retained	18[a]	0.936	40.5	112	(3)
Δ_aH (calc) = 318.45 kJ mol^{-1} + 0.774 44 Δ_aH (*ab initio*) Outlier: nitrobenzene removed	17	0.960	32.0	175	(3a)
Δ_aH (calc) = 518.13 kJ mol^{-1} + 0.676 91 Δ_aH (MNDO) Outlier: cyclopentadiene retained	37[b]	0.750	73.6	45.0	(4)
Δ_aH (calc) = 456.94 kJ mol^{-1} + 0.718 08 Δ_aH (MNDO) Outlier: cyclopentadiene removed	36	0.807	65.1	63.4	(4a)
Δ_aH (calc) = 557.19 kJ mol^{-1} + 0.648 92 Δ_aH (AM1) Outlier: nitrobenzene retained	37[b]	0.774	70.4	52.5	(5)
Δ_aH (calc) = 431.06 kJ mol^{-1} + 735 71 Δ_aH (AM1) Outlier: nitrobenzene, cyclopentadiene, 3-phenylpropene removed	34	0.913	44.5	161	(5a)
Δ_aH (calc) = 374.62 kJ mol^{-1} + 0.771 04 Δ_aH (PM3) Outlier: cyclopentadiene retained	37[b]	0.838	60.7	82.6	(6)
Δ_aH (calc) = 342.08 kJ mol$^{-1'}$ + 0.794 41 Δ_aH (PM3) Outlier: cyclopentadiene removed	36	0.881	52.1	118	(6a)

[a] See Table 4 for list of compounds. [b] See Table 2 for list of compounds, those with *.

Table 6 Correlation equation for Δ_aH and Δ_aG (kJ mol^{-1}) *vs.* TLSER descriptors

Δ_aH =	$-101.9\ V_{mc}$	$+3471\ \varepsilon_B$	$-5568\ \varepsilon_A$	$-606.3\ q_+$	+2181	(7)
±	10.6	573	525	126.9	76	
t-stat	9.58	6.05	10.6	4.78	28.9	
P(2-tail)	0.000	0.000	0.000	0.000	0.000	
VIF	2.00	2.64	2.39	1.49		
	N = 86	R = 0.920		SD = 41.2	F = 112	

Outliers: triphenylcyclopropene, cyclopentadiene, NH_3 dropped.

Δ_aG =	$-101.4\ V_{mc}$	$+3391\ \varepsilon_B$	$-5316\ \varepsilon_A$	$-616.0\ q_+$	+2117	(7*a*)
±	10.0	510	494	116.2	73	
t-stat	10.1	6.65	10.8	5.30	28.9	
P(2-tail)	0.000	0.000	0.000	0.000	0.000	
VIF	2.04	2.48	2.40	1.83		
	N = 85	R = 0.933		SD = 38.9	F = 133	

Outliers: triphenylcyclopropene, cyclopentadiene, NH_3 dropped.

that the equation is not an artifact. Also, the SD value represents about 10% of the range of Δ_aH and Δ_aG values.

Eqn. (7) is in essential agreement with correlations in an earlier paper on gas phase acidity.[12] With only eight small hydrocarbons, ε_A [with negative sign as in eqn. (7)] was the only significant parameter for Δ_aH, R was 0.823 with SD being 25. For 16 hydrocarbons, the activation energy for deuterium exchange, expected to be related to Δ_aH, ε_B (with positive sign) was the only significant parameter; R was 0.955 and SD was 9.6.

Comparison of calculated and empirical values in Table 3 gives an idea of the ability of TLSER to reproduce Δ_aH values. The SD value, ±41 kJ mol^{-1}, for eqn. (7), is from five to two times the empirical uncertainties, 8 to 21 kJ mol^{-1}; hence, the ordering of the TLSER gas phase acidities would not be expected to be highly consistent with the empirical order. This would be especially true for compounds with close empirical gas phase acidities. However, there are some groups that do follow the empirical trends fairly well. The TLSER predicted Δ_aH order for nitroalkanes is—nitro-2,2-dimethylpropane < 2-nitropropane < nitroethane < nitromethane. This essentially agrees with the empirical order—nitro-2,2-dimethylpropane < nitroethane < nitropropane < nitromethane—when noting that the empirical values for nitropropane and nitroethane are very close. Similarly, the relative Δ_aH order for a group of aromatics matches experiment—4-nitrotoluene < 2-nitrotoluene < 3-nitrotoluene < toluene < benzene. Another sequence—9-methylanthracene < 1-methylnaphthalene < the 3- and 4-methyltoluenes < benzene—matches experiment, also. However, the empirical sequence—toluene < 3-methyltoluene < 4-methyltoluene (2-methyltoluene value not available)—is not matched in the TLSER calculations. The TLSER sequence places toluene last—2-methyl- < 3-methyl- < 4-methyl- < toluene—the 3- and 4-methyltoluene sequence is correct.

The TLSER results suggest that the cubane structure is more like the alkanes than the aromatics. The average TLSER based difference, $\Delta_a H$ (alkane) − $\Delta_a H$ (nitroalkane), for the pairs—methane, nitromethane; ethane, nitroethane; propane, 2-nitropropane; cyclopropane, nitrocyclopropane; and 2,2-dimethylpropane, nitro-2,2-dimethylpropane—is 233 kJ mol^{-1} which agrees very well with their corresponding empirical average difference of 240 kJ mol^{-1}. The TLSER average difference for aromatic–nitroaromatic pairs—benzene, nitrobenzene and toluene with the 2-, 3- and 4-nitrotoluenes—is 124 kJ mol^{-1} which agrees very well with their corresponding empirical average difference of 123 kJ mol^{-1}. Thus, the cubane–nitrocubane TLSER calculated difference of 242 kJ mol^{-1} agrees very well with the alkane–nitroalkane difference. In fact, the TLSER predicted value for cubane is 1704.1 kJ mol^{-1} which is close to the 1700 kJ mol^{-1} estimated by Ritchie and Bacharach[1] from *ab initio* techniques. The TLSER predicted acidities for cubane–nitrocubane are different from acidities calculated directly. Table 4 shows differences in $\Delta_a H$ predicted from MNDO (*ca.* 74 kJ mol^{-1}), from PM3 (94 kJ mol^{-1}) and from AM1 (*ca.* 77 kJ mol^{-1}). The difference from 6-31+G direct calculations is *ca.* 121 kJ mol^{-1}. If these differences were obtained from the correlation equations in Table 5, these last differences would be scaled smaller by the factor of the corresponding slope.

We turn to other compounds (besides cubane) for which no empirical $\Delta_a H$ values were available. Nitramine and dinitramide had empirical $\Delta_a G$ values only; these are 1415.4 and 1242.6 kJ mol^{-1}, respectively. The $\Delta_a G$ TLSER regression, eqn. (7*a*) in Table 6, predicts 1429.2 and 1234.6 kJ mol^{-1}, respectively. The TLSER $\Delta_a H$ predicted values [eqn. (7), Table 6] are 1458.3 and 1260.5 kJ mol^{-1}, respectively. Consequently, the $T\Delta S$ terms are consistent with empirical values. This predicts the dinitramide to be the most acidic of the compounds in this set. For 2-methyltoluene, the TLSER predicted $\Delta_a H$ value is similar to those predicted for the 3- and 4-methyltoluenes. The predicted (empirical value not available) but-2-ene value (1652.3 kJ mol^{-1}) is close to the predicted value for but-1-ene (1655.2 kJ mol^{-1}). However, as one referee pointed out, this comparison raises questions regarding the but-2-ene isomer and the anion involved. The TLSER parameter calculations in eqn. (7) refer to the neutral molecule and say nothing about the anion. However, the (*E*)-but-2-ene isomer TLSER parameters were used since it is more stable than the (*Z*)-but-2-ene isomer as indicated by the MNDO heat of formation values. The referee pointed out that the *E*-form is more stable than the *Z*-form by *ca.* 7 kJ mol^{-1} and more stable than but-1-ene by *ca.* 11 kJ mol^{-1}; this is in keeping with Solomons.[24] For the most part, the acidities have been taken as referring to the most stable molecule going to the most stable anion; this appears to be the *E*-form of the but-2-ene ion. The predicted cycloocta-1,4-diene value is close to that of the predicted cycloocta-1,3-diene. Again, the TLSER predicts nitropropane to be similar in acidity to 2-nitropropane. Trinitromethane is predicted to be less acidic than dinitramide but much more acidic than nitromethane as would be expected.

Table 6 shows that triphenylcyclopropane, cyclopentadiene and NH_3 are outliers; these are only three out of the 89 selected compounds with empirical $\Delta_a H$ values. Removing these increased statistical significance but did not remove any descriptors. NH_3 is a small molecule and MNDO does not describe it well; removing it increased the statistical significance of the volume term. Considering the very good empirical precision and, hence, the likely good accuracy, it is difficult to suggest that the three outliers have poor empirical values. As they become available, more cyclic unstrained (but not aromatic) compounds should be included in correlation studies to help understand why the other two molecules are outliers.

Conclusion

At the computational levels used here, directly calculated $\Delta_a H$ values are not as close to the empirical values as one would like. However, a correlation equation between the empirical and calculated values provides improved fit and, hence, prediction. The 6-31+G equation [eqn. (3)] gives a better empirical to calculated fit, as evidenced by accounting for more of the variance, 0.992, than do those for the AM1, MNDO, PM3 and TLSER approaches. An advantage of the direct methods is that the calculations are straightforward for the parent molecule and the anion. A disadvantage is that the semiempirical results do not fit empirical values well, while the *ab initio* approach requires much more computer time for the higher order calculations necessary for a better fit. As was mentioned in the Introduction, the latter may present convergence problems. If empirical data are available, a correlation equation between directly calculated and empirical values can be used to improve the fit.

The TLSER correlation equations make good physical sense; $\Delta_a H$ and $\Delta_a G$ increase with basicity and decrease with acidity descriptors. The TLSER equation gives a respectable calculated to empirical value fit as evidenced by accounting for 0.846 of the $\Delta_a H$ variance. The SD value of 41 deviation makes it difficult to predict trends in acidity for compounds that have similar values. An advantage of the TLSER method is that once the correlation equation is found, calculations only have to be done on the molecule. A disadvantage is that a statistically valid set of empirical values must be known in order to get this correlation equation. A further drawback is that the equation only applies to types of compounds used in deriving it.

The reasonable gas phase acidity values for the nitro compounds suggest possible usefulness of the TLSER approach in studying other properties of these energetic materials.

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Two of the authors (G. R. F. and L. Y. W.) dedicate this paper to the memory of Alfred H. Lowery, initiator of and co-worker on this paper, whose untimely (1st September 1996) death leaves them with a great sense of loss.

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