bonding mainly because there are no metal tangential orbitals which are opportunely split in filled bonding e'_t and empty antibonding a'_2 combinations. On the other hand, there is some mixing of sp and x^2-y^2 character into the MO a'_1. But, at variance with many of the previous cases where mixing occurred with very little involvement of the ligand orbitals, here the level is largely M–S antibonding with the higher $2a'_1$ combination to avoid a greater destabilization. This is sufficient to prevent the M–M overlap population from vanishing. The calculated value has a small but not null value of 0.08.

Conclusions and Extensions

The correlations between stereochemistry, electron counts, nature of the ligands, M–M distances, etc., in skeletons of the type L_6M_3 are analyzed in some detail with the FMO method and perturbation theory arguments. In "unsupported-bridged" coordination the first-order interactions between the metal framework and the bridging ligands were found to be or primary importance in providing the necessary stability to the system. In addition, the origin of the M–M interactions occurring through second-order effects, such as a rehybridization of metal d–s–p orbitals, is clarified. Next the analysis of the "supported-unbridged" systems indicated that the most important cementing force within the M_3 triangle is the radial a'_1 bonding combination of the d–s–p metal hybrids. Tangential combinations of metal π orbitals help to strengthen the M–M linkages but do not seem

mandatory for the existence of the triangular shape. In fact, the tangential combinations in some cases are used for the formation of linkages between the metals and the supporting ligands (see the case of the bridging H_3 group). In other cases (44-e complexes) they are populated even in their antibonding levels.

Hopefully these concepts, based on the selection of the MOs by symmetry and by their relative M–M or M–L bonding–antibonding character, may be extended to clusters of higher nuclearity.

Appendix

The extended Huckel calculations[32] utilized a modified version of the Wolfsberg-Helmholz formula.[33] The parameters for C,O,H,S are standard ones,[32] those for Pt and Fe, Rh, Sn were taken from references 3b, 3i, 36 respectively. Unless otherwise specified the M–M distances are fixed at 2.70 Å in all calculations. The C–O distances used are 1.20 Å. In models **6** and **7** the cis (O)C-Pt-C(O) angles were 100°. In **16**, the model of compound (**7**), the Fe-Pt and Fe-H distances are 2.60 and 1.60 Å respectively.

(32) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179–2189, 3489–3493; **1962**, *37*, 2872. Hoffmann, R. *Ibid.* **1963**, *39*, 1397.
(33) Ammeter, J. H.; Burgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686–3692.
(34) Silvestre, J.; Albright, T. A.; Sosinsky, J. C. *Inorg. Chem.* **1981**, *20*, 3937–3940.

Theoretical Studies of the Polar Effect. 5.[1] The Use of the Isolated Molecule Approach

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Abstract: Substituent electronic effects on proton exchange reactions of various probes Y (Y = CO_2^-, NH_2, OH) according to the equation $XGYH^+ + HGY \rightleftharpoons XGY + HGYH^+$ have been shown to be closely approximated with isolated molecules instead of a molecular framework G. In particular, the equilibrium energies are well represented with use of calculations on the simple equilibrium $XH/HYH^+ + HH/HY \rightleftharpoons XH/HY + HH/HYH^+$. This latter equilibrium both allows a direct calculation of substituent field effects in systems of corresponding geometry and also provides a scale of σ_F values.

In recent years, the use of molecular orbital calculations has proved fruitful[2,3] in understanding the various modes of transmission of substituent electronic effects. Such calculations have also led to scales of inherent (that is, in the absence of solvent effects) substituent constants for field (σ_F),[4] electronegativity (σ_X),[5] and resonance effects (σ_R).[2,6] In both cases, considerable use has been made of, so called, isolated molecule calculations.

Calculations of isodesmic proton transfer reactions can be represented by the general reaction in eq 1, where X is a variable

$$XGYH^+ + HGY \rightleftharpoons XGY + HGYH^+ \qquad (1)$$

substituent, Y a probe group such as NH_2 or CO_2^-, and G a molecular framework. Experimental gas-phase energies for such processes where Y = NH_2 have been shown to be well reproduced by ab initio molecular orbital calculations (methylammonium,[7] quinuclidinium,[8] pyridinium, and anilinium ions[9]). Similar agreement has also been reported for substituted phenols[10] (Y = O^-).

Much recent interest[2,11,12] has concerned the relative importance of field and electronegativity effects. Experimental investigations here have mainly centered[13] on substituted quinuclidinium ions

(1) For Part 4 see ref 4.
(2) Topsom, R. D. *Acc. Chem. Res.* **1983**, *16*, 292.
(3) See, for example ref 4–10, 14–17, and the following: Wiberg, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 1229. Vorpagel, E. R.; Streitwieser, A.; Alexandros, S. D. *J. Am. Chem. Soc.* **1981**, *103*, 3777. Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1981**, *13*, 1. Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriott, S.; Von Nagy-Felsobuki, E.; Taft, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378. Marriott, S.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1984**, 113. Reynolds, W. F.; Mezey, P. G.; Hamer, G. K. *Can. J. Chem.* **1976**, *55*, 522.
(4) Marriott, S.; Topsom, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 7.
(5) Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 959.
(6) Marriott, S.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2*, in press. Marriott, S.; Topsom, R. D. *J. Mol. Struct.* **1984**, *106*, 277.

(7) Taagepera, M.; Hehre, W. J.; Topsom, R. D.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 7438.
(8) Taagepera, M.; Taft, R. W.; Hehre, W. J.; Grob, C. A., unpublished results.
(9) Taagepera, M.; Summerhays, W. J.; Hehre, W. J.; Topsom, R. D.; Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1981**, *46*, 891.
(10) Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 818.
(11) Reynolds, W. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 985 and references therein.
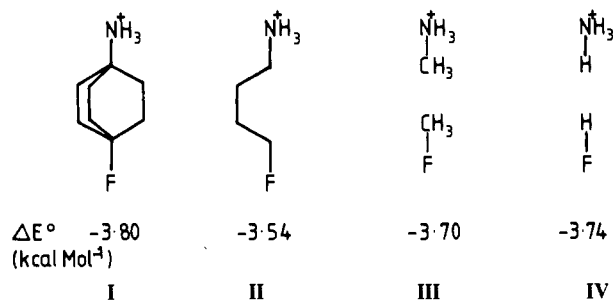(12) Exner, O. *Collect. Czech. Chem. Commun.* **1984**, *49*, 179 and references therein.
(13) See, for example: Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

Table I. Equilibrium Energies (STO-3G, ΔE in kcal mol^{-1}) for the Isodesmic Proton Transfer Process (See Text)

r	$-\Delta E(4)$	$-\Delta E(5)$	$-\Delta E(6)$	$-\Delta E(7)$
10.44	0.65	0.79	0.65	0.74
7.44	1.27	1.54	1.23	1.44
6.44	1.70	2.07	1.61	1.89
5.44	2.39	2.91	2.23	2.60
4.74	3.31	3.87	2.90	3.36
4.50	3.70	4.35	3.24	3.74
4.20	4.40	5.09	3.77	4.24
3.94	5.39	5.90	4.40	4.79
3.74	7.36	6.67	5.04	5.33
3.54		7.54	5.86	5.95
3.34				6.71
3.14				7.70

and bicyclo[2.2.2]octylcarboxylic acids, where the framework G is rigid and Y and X well separated to avoid the charge transfer that occurs[14] in substituted methylammonium ions (G = CH$_2$). The use of substituted amines such as XCH$_2$CH$_2$NH$_2$ is precluded by conformational mobility. Here, calculations have proved useful[15] since the geometry can be fixed and, for example, calculations on system 1, where G is –CH$_2$CH$_2$– and X and Y are restricted to a fully extended (all trans) molecular conformation, gave[7] ΔE values approximately linear vs. the corresponding σ_F values of the substituents. Similar calculations[16] have been made on substituted bicyclo[2.2.2]octyl systems but these take considerable computer time and are limited to the minimal STO-3G basis.

However, we have previously shown[15] that corresponding calculations can be made with isolated molecules. Thus, the isodesmic equilibrium energies for equilibrium 1 listed for the systems below indicate that the molecular framework has little effect in agreement with expectation from a simple field effect.

$$\begin{array}{cccc}
\overset{+}{N}H_3 & \overset{+}{N}H_3 & \overset{+}{N}H_3 & \overset{+}{N}H_3 \\
& & CH_3 & H \\
& & CH_3 & H \\
F & F & F & F \\
\end{array}$$

ΔE°	$-3 \cdot 80$	$-3 \cdot 54$	$-3 \cdot 70$	$-3 \cdot 74$
(kcal Mol^{-1})				
	I	**II**	**III**	**IV**

In these systems, the relative positions of the NH$_3^+$ and the F are held constant. More recently,[4] it has been found that system 4 provides an excellent measure of σ_F values.

We wished first to establish the utility of calculations on these and related isolated molecules. Second, we wished to extend the study to the use of isolated molecule calculations in equilibria 2 and 3. The only previous isolated molecule calculations here

$$XGCO_2H + HGCO_2^- \rightleftharpoons XGCO_2^- + HGCO_2H \quad (2)$$

$$XGOH_2^+ + HGOH \rightleftharpoons XGOH + HGOH_2^+ \quad (3)$$

appear to be the use of HCO$_2^-$/CH$_3$X pairs[17] to estimate field effects in substituted benzoic acids. Third, we wished to show that calculations on isolated carboxylic acid pairs would, like the corresponding amines above, provide a scale of σ_F values.

Calculations

All calculations were made at the ab initio molecular orbital STO-3G or 3-21G levels with either the GAUSSIAN-80[18] or GAUSSIAN-82[19] programs

Figure 1. Plot of ΔE values for the proton exchange equilibria of isolated amines plotted against $1/r^2$ (see text). Equilibria: no. 4, solid line; no. 5, •; no. 6, ■; no. 7, O.

and with standard molecular geometries[20] unless otherwise indicated.

Results and Discussion

In Table I we list the equilibrium energies for the isodesmic proton transfer process (A) for various distances apart (r) of the molecular pairs. The distance r is taken between the mid point

$$\begin{array}{cccc}
\overset{+}{N}H_3 & \overset{+}{N}H_2 & \overset{+}{N}H_3 & \overset{+}{N}H_2 \\
CH_3 & CH_3 & CH_3 & CH_3 \\
\rightleftharpoons & & & \\
CH_3 & CH_3 & CH_3 & CH_3 \\
F & H & H & F \\
\end{array} \quad (4)$$

of the CF bond and the center of charge in the methylammonium ion (on the NC axis, 0.2 Å from the N toward the C atom[15]). Also listed are energies for the corresponding equilibrium with the following molecular pairs:

$$^+NH_3-CH_3/HF \quad (5)$$

$$^+NH_3-H/CH_3F \quad (6)$$

$$^+NH_3-H/HF \quad (7)$$

It has earlier[15] been pointed out that the equilibrium energies for process 4 correlate well when plotted against $1/r^2$, for values of r greater than 5 Å, as expected for a dipole–point charge interaction according to (8). However, for $r < 5$ Å, the ΔE values

$$E \propto q\mu \cos \theta / r^2 \quad (8)$$

are greater than expected and this has been explained in terms of charge transfer between the molecules.

Figure 1 shows a plot of ΔE vs. $1/r^2$ for process 4 (solid line, no points shown) and processes 5, 6, and 7. It is seen that each is linear at high values of r. The ΔE values deviate from linearity for process 4 below $r = 4.5$ Å, for processes 5 and 6 below $r = 4.2$ Å, but for process 7 are still linear down to some 3 Å. Furthermore, ΔE values for process 7 are very close to those for process 4 for the linear position of that curve.

The values for process 5 are generally above that for process 7 and those for process 6 below. This is probably a result of the

(14) Hehre, W. J.; Taagepera, M.; Taft, R. W.; Topsom, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 1344.

(15) Topsom, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 39.

(16) Adcock, W.; Butt, G.; Kok, G. B.; Marriott, S.; Topsom, R. D., submitted for publication. Marriott, S.; Topsom, R. D., unreported results.

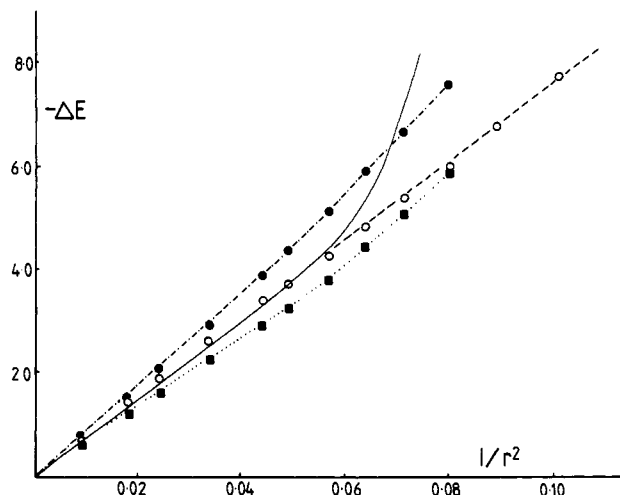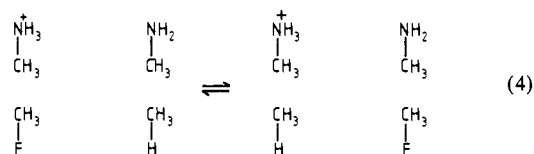(17) Mezey, P. G.; Reynolds, W. F. *Can. J. Chem.* **1977**, *55*, 1567.

(18) Binkley, J. S.; Whiteside, R. A.; Khrishnan, R.; Seeger, R.; DeFrees, D. J.; Schleger, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. "Gaussian 80—An Ab-Initio Molecular Orbital Program", Department of Chemistry, Carnegie-Mellon University, Pittsburg, 1980.

(19) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, F.; Seeger, R.; Pople, J. A. "Gaussian 82, Release A", Department of Chemistry, Carnegie-Mellon University, Pittsburg, 1982.

(20) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

closer center of charge to the HF dipole in process 5 compared to that in process 7 and the smaller dipole in process 6 compared to that in process 7. (Dipole moments are as follows: CH_3F, 1.08 D; HF, 1.28 D as calculated at the STO-3G level[21]).

The ΔE values for process 7 have already been shown[22] to give an excellent correlation against experimental σ_F values where these are well established and thus provides additional σ_F values for other substituents. The correlation is better than with ΔE values obtained from process 4, probably because of polarization of CH bonds leading to secondary effects.

Overall then, process 7 provides an excellent and exceedingly simple method of determining the field component of substituent electronic effects and is to be preferred to processes 4, 5, or 6. Furthermore, the closer approach possible of the NH_4^+ and HX molecules allows the estimate of field effects in such molecules as ortho- and meta-substituted anilines.

We have also made corresponding calculations for systems 2 and 3. The results are illustrated below where in each system the probe Y and mid point of the CF or HF dipole are kept at constant geometry. The values are for $-\Delta E$ in kcal mol^{-1}.

Y					
NH_3^+	3.80	3.54	3.70	4.35	3.24	3.74
CO_2H	3.17	3.31	3.37	3.93	2.79	3.13
OH_2^+	3.88	3.96	4.25			3.92

The results for the carboxylic acids and alcohols parallel those for the amines. In particular, we again note that the simplest systems well reproduce the results in the bicyclo[2.2.2]octyl and 4-substituted butyl carboxylic acids and alcohols. The ΔE values are rather similar for the amines and alcohols and somewhat smaller for the carboxylic acids reflecting the mean distance from the center of charge to the CF dipole.

The field effect in para-substituted benzoic acids (V) was earlier[17] estimated by use of the isolated molecule system (VI).

V   VI

The results above indicate that this is not the most satisfactory model, as it underestimates the appropriate ΔE value. The authors

(21) Marriott, S.; Topsom, R. D. *J. Mol. Struct.* **1982**, *89*, 83.
(22) Marriott, S.; Topsom, R. D. *Tetrahedron Lett.* **1982**, 1485.

Table II. Equilibrium Energies (3-21G, ΔE in kcal mol^{-1}) for the Isodesmic Proton Exchange of $HCO_2^-//HX$ Pairs (See Text)

X	$-E(HCO_2H/HX)$	$-E(HCO_2^-/HX)$	ΔE
H	188.760 27	188.228 29	0.0
NH_2	243.508 76	242.979 15	1.49
NMe_2	321.122 23	320.592 79	1.59
OMe	302.032 80	301.506 15	3.34
F	287.095 42	286.572 22	5.51
Me	227.614 12	227.082 11	-0.02
CN	279.988 35	279.466 43	6.31
CF_3	522.585 99	522.061 99	5.00
COMe	339.688 32	339.160 53	2.63
CO_2Me	414.133 14	413.605 29	2.59
NO_2	391.057 86	390.539 11	8.30
CHO	300.857 17	300.329 99	3.01

of the earlier work estimated that the overall field effect in the benzene (V), including any π-polarization and any differences arising from the sp^2 hybridization of the carbon atoms to which the X and CO_2^- were attached, was 1.71 greater than in IV. Use of the preferable HCO_2^-/HX pair as a model reduces this to a factor of 1.5.

In Table II, we list the values of ΔE for equilibrium 9 determined at the same geometry as for corresponding 4-substituted bicyclo[2.2.2]octylcarboxylic acids. The results were correlated

$$\rightleftharpoons \qquad (9)$$
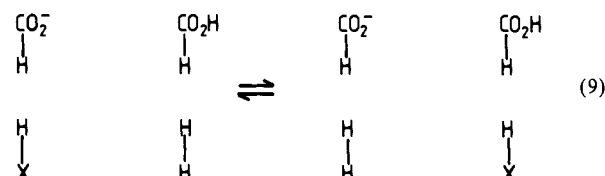
against the σ_F values derived[4] from the corresponding process 7 for amines to give eq 10, with correlation coefficient 0.990.

$$\Delta E = 12.69\sigma_F - 0.10 \qquad (10)$$

Equation 11 shows the excellent correlation (goodness of fit, as the standard deviation of the estimates divided by the best mean square of the data, being 0.10) obtained against σ_F and σ_R° with use of the dual substituent parameter equation.[23] Here the dependence on σ_R° is clearly insignificant. Thus, the use of

$$\Delta E = 11.60\sigma_F - 0.64\sigma_R^\circ \qquad (11)$$

isolated molecule calculations is clearly applicable and useful for carboxylic acids as well as for amines.

(23) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.