cause significant variation in σ^d particularly when they are of high atomic number, Z, and this approach has been successful in rationalizing the anomalous shifts engendered by fourth- and fifth-row atoms ("heavy-atom effect").[7–9,46] The correction to be applied to the free-atom Lamb term is given by the semiempirical relationship of Flygare and Goodisman:[47]

$$\sigma^d = \sigma^d(\text{free atom}) + (e_2/3mc_2)\sum Z_k/r_k$$

where the constants have their usual meaning and the Z/r term represents the atomic number of the directly attached atom divided by the length of its bond to the carbon. The values of this correction term for the halogens[48] are linearly related to the a_2 factors ($r = 0.964$).

It may be concluded that the a_2 parameters identified by factor analysis are linearly related to all significant substituent-dependent terms of theory! Unfortunately, experimental shielding tensors are not available for any of the ^{13}C nuclei in the halobenzenes (**2**) or vinyl halides (**1**) but, as noted in a previous article,[1] the a_2 factors are linearly related to the experimental ^{13}C tensors of the methyl halides.[49] The b_2 molecular cofactors, which reflect the sensitivity of each molecular position to the effect characterized by a_2, are consistent with virtually all of the possible interpretations of the a_2 factors since they alternate in sign and monotonically decrease in magnitude with increasing distance from the substituent. Any definitive conclusion as to the nature of the effect reflected in a_2 must, therefore, await the results of further factor analytical studies using nonhalogen substituents. These investigations are in progress.

In view of the difficulties associated with physical interpretation of the variable a_2 parameters, any discussion of the effectively constant a_1 factors beyond that given previously[1] would not be productive. We have suggested that these terms may reflect the essentially constant polar effect of halogens,[1] but this supposition must also await confirmation from the results of studies on substituent induced ^{13}C shifts in non-halogen-containing molecules.

The linear interrelationships among the a_2 factors, substituent constants, reciprocals of ionization potentials, charge densities, and contributions of σ^d might be accidental, but this seems highly unlikely. In any event, these linear correlations are not confined to quantities which affect ^{13}C shielding. Virtually all physical and spectroscopic properties of halogen-containing molecules are linearly related to each other and to the a_2 parameters! The consequences of such linear relationships are explored in a following paper.[25]

Experimental Section

Carbon-13 magnetic resonance spectra were recorded on a Bruker WH-90 spectrometer in the FT mode operating at 22.6 MHz by using 2.0 M solutions of compounds **2**–**5** (X = F, Cl, Br, I) in $CDCl_3$ at 30 °C and are referenced to internal Me_4Si. Assignments are based on the known chemical-shift substituent effects in these systems.[5–11]

The halides used in this study were either available from commercial sources and purified prior to use or were prepared from the appropriate aniline, via its diazonium salt, by classical methods.

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Registry No. **2** (X = F), 462-06-6; **2** (X = Cl), 108-90-7; **2** (X = Br), 108-86-1; **2** (X = I), 591-50-4; **3** (X = F), 95-52-3; **3** (X = Cl), 95-49-8; **3** (X = Br), 95-46-5; **3** (X = I), 615-37-2; **4** (X = F), 352-70-5; **4** (X = Cl), 108-41-8; **4** (X = Br), 591-17-3; **4** (X = I), 625-95-6; **5** (X = F), 352-32-9; **5** (X = Cl), 106-43-4; **5** (X = Br), 106-38-7; **5** (X = I), 624-31-7.

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(46) (a) Mason, J. *J. Chem. Soc. A* **1971**, 1038. (b) Mason, J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1671. (c) Mason, J. *Org. Magn. Reson.* **1977**, *10*, 188. (d) Mason, J. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 199.

(47) Flygare, W. H.; Goodisman, J., *J. Chem. Phys.* **1968**, *49*, 3122.

(48) The value of Z/r for the halogen substituents (X = F, Cl, Br, I) follows directly from the atomic numbers and bond lengths (ref 43): 6.77, 10.00, 18.92, and 25.85 amu·Å^{-1}, respectively.

(49) Appleman, B. R.; Dailey, B. P. *Adv. Magn. Reson.* **1974**, *7*, 310.

Intrinsic Linear Interrelationships among Physical and Spectroscopic Properties of Halogen-Containing Molecules[1]

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The effect of halogen substituents on the value of liquid and/or vapor phase properties, both physical and spectroscopic, of halogen-containing molecules has been studied by factor analysis. Two principal factors, a_1 and a_2, were found to account for 99.9% of the total variance in the data. The halogen parameters obtained in the analysis are essentially a constant for all halogens ($a_1 = 1.000 \pm 0.015$) and an arithmetic progression of integers ($a_2 \approx$ 1.0, 2.0, 3.0, and 4.0 for X = F, Cl, Br and I, respectively). These factors agree well with those previously obtained from factor analysis of ^{13}C chemical shifts of organic halides. The analysis reveals that there is an intrinsic linear interrelationship among virtually all measurable liquid and/or vapor phase properties of halogen-containing molecules. A qualitative rationale for this finding is offered in terms of the dominant role of polarizability in determining changes in the magnitude of property values as the halogen substituent is varied.

Factor analysis of ^{13}C chemical shifts for a variety of aliphatic, unsaturated, and aromatic halides[1,3] has revealed that the substituent induced shifts are controlled by two principal halogen factors. The most important parameter

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(a_1) was found to be essentially unity for all halogens and the second factor (a_2) for F, Cl, Br, and I as substituents approximated an arithmetic progression, i.e., 1, 2, 3, 4. Thus, the change in ^{13}C chemical shift resulting from variation in the halogen substituent from X = F to X = I is linearly related to the a_2 halogen factor, which, in turn, increases linearly for the series X = F through X = I.[1,3]

Examination of the a_2 substituent factor demonstrated that it is related in a linear way to a variety of fundamental properties of carbon–halogen bonds.[1,3] These observations suggested that many physical and spectroscopic properties of halogen-containing compounds might be linearly related to each other and to the a_2 factor. We have investigated this possibility using factor analysis and have found that virtually all measurable properties of molecules containing halogen are linearly interrelated.

A number of linear relationships between *pairs* of the properties discussed below have been noted, but the generality of such correlations for halogen-containing compounds does not appear to have been recognized. As a consequence of the linear relationship of the a_2 halogen substituent factor to both the physical properties and the ^{13}C chemical shifts of all types of compounds containing halogen, there exist a very large number of pairwise linear correlations which could be constructed to reflect the inherent regularities in physical and spectroscopic data for such molecules.

Results

The compounds and properties on which factor analysis was performed are given in Table I. In addition to the properties of halogen atoms, X_2 molecules, and C–X bonds (items 1–14), a variety of measurable properties of CH_3X, C_2H_5X, and C_6H_5X molecules were included (items 15–53) so as to provide a representation data base. The choice of methyl halides, ethyl halides, and halobenzenes as typical examples of halogen-containing organic molecules was dictated by the ready availability of physical data for complete sets of the halides (X = F, Cl, Br, I). It should be noted that other halides may be used in the analysis with equal success.

The objective of factor analysis is the discovery of intrinsic linear relationships that exist within a body of data. The technique, which has been described in detail in a recent monograph,[4] was applied to the analysis of the properties listed in Table I (items 1–53). Prior to factor analysis, the values must be adjusted so as to minimize the effects of different units in which the properties are typically measured. Ideally, the experimental error should be identical for each value in the data set and a normalization procedure has been described[4] which involves division of each property value by its associated error to give a new data set in which the errors are statistically scattered about unit standard deviation. We have, however, chosen to simply scale the property data by adjusting the magnitude of each value to lie between 1 and 10. This approach, which allows for presentation of experimental data in an easily recognizable fashion (Table I), does not materially affect the outcome of the analysis since a more rigorous normalization[4] would serve only to improve the correlations noted below.

Following the procedure outlined in the previous articles in this series,[1,3] the 212 property values were expressed as a 4 × 53 data matrix, **D**, which was factored into a 4 × n row matrix, **H**, and an n × 53 column matrix, **M**, such that **D** = **HM**. Analysis revealed that two major principal factors having eigenvalues[1,3,4] of 51 and 2.8, respectively, account for 99.9% of the total variance in the data set. From these results, summarized in Table II, it may be concluded that only two independent substituent factors are needed to adequately describe the properties of halogen-containing molecules. Indeed, many of the properties are reproduced to within the experimental error of measurement of these quantities.

Identification of the halogen parameters was accomplished by the technique of target-testing, using the target factor analysis program developed by Malinowski, Howery, and co-workers[4b] and described in detail in a recent monograph.[4]

The test vectors chosen for target analysis of the **H** matrix were those which had been found to be responsible for halogen substituent effects on ^{13}C chemical shifts in aliphatic,[3] unsaturated,[1] and aromatic[1] systems. Thus, a constant (1, 1, 1, 1) was used as a test vector for the most important halogen factor and an arithmetic progression (1, 2, 3, 4) was taken to approximate the second significant factor. Target transformation was successful[4] as adjudged by the values of the best-fit factors, a_1 and a_2, which closely match the test vectors. The a_1 and a_2 parameters are intrinsic to the substituents (F, Cl, Br, I) and charcterize the two independent ways in which halogen affects the properties of halogen-containing molecules.

	a_1	a_2
F	0.985	0.977
Cl	1.012	2.147
Br	1.015	2.831
I	0.986	4.045

A corresponding rotation of the reduced (2 × 53) **M** matrix gave a set of cofactors, b_1 and b_2, for each of the 53 properties analyzed. These property cofactors reflect the sensitivity of each of the 53 properties in Table I to the effect of the halogen factors. The b_1 and b_2 cofactors are listed in Table III (available as supplementary material).

The outcome of the analysis is the two-term correlation given by eq 1, which involves the two factors for each

$$\text{value of property } k = a_{x1}b_{1k} + a_{x2}b_{2k} \qquad (1)$$

halogen (a_{x1} and a_{x2}) and the two cofactors for each of the 53 properties (b_{1k} and b_{2k}). The values calculated via eq 1 for each property (items 1–53; X = F, Cl, Br, I) are included in Table I. In most instances the observed quantities are reproduced to within the experimental error of the property measurement. It should be noted that the a_1 and a_2 factors identified in this analysis are virtually identical with the halogen parameters obtained from analysis of substituent effects on ^{13}C chemical shifts of aliphatic, unsaturated, and aromatic halides.[1,3] Thus, the halogen factors serve to correlate not only physical properties (Table I, items 1–53) but also ^{13}C chemical shifts[1,3] of all types of molecules containing halogen.

The fact that the first substituent factor is essentially unity for all halogens ($a_1 = 1.000 \pm 0.015$ for X = F, Cl, Br, I) reduces the correlation to a linear relationship between the properties of halogen-containing compounds and the a_2 factor. Equation 2 demonstrates that, to a very good

$$\text{value of property } k = b_{2k}a_{x2} + \text{constant} \qquad (2)$$

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[1] For the previous paper in this series, see: Bailey, W. F.; Cioffi, E. A.; Wiberg, K. B. *J. Org. Chem.*, preceding paper in this issue.

[2] (a) University of Connecticut. (b) Yale University.

[3] Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Org. Chem.* **1980**, *45*, 4936.

[4] (a) Malinowski, E. R.; Howery, D. G. "Factor Analysis in Chemistry"; Wiley-Interscience: New York, 1980. (b) Malinowski, E. R.; Howery, D. G.; Weiner, P. H.; Soroka, T. H.; Funke, P. T.; Selzer, R. S.; Levinstone, A. "FACTANAL", Program 320, Quantum Chemistry Program Exchange; Indiana University, 1976.

approximation, linear correlations will be obtained from plots of the values for a given property (items 1–53; X = F, Cl, Br, I) vs. the values of any other property in Table I. Thus, 1378 linear, pairwise correlations exist between the 53 properties listed in Table I. Moreover, as noted above, the correlation expressed by eq 2 is general. *There is an intrinsic linear interrelationship among virtually all measurable liquid and/or vapor phase properties, both physical and spectroscopic, of molecules containing halogen.*

The nature of the general result of the factor analysis is best appreciated by a further simplification of the observed correlation between a_2 and property values for a series of halides (X = F–I). For many purposes an entirely satisfactory linear correlation may be written by replacing the a_2 parameters in eq 2 with the integers which were used above as a test vector for this factor. In fact, the a_2 values for F, Cl, Br, and I are linearly related with unit slope to the integers 1–4 ($r = 0.995$, slope = 1.002, intercept = −0.002). The overall result of using integers for the a_2 terms in eq 2 is the unexpected and apparently general conclusion that the value for a property of a halogen-containing molecule changes linearly with the numbers 1–4 as the halogen is varied from F through I. The following results are typical and serve to illustrate the remarkable linearity of the simple correlation between properties of halogen-containing molecules and the intergers 1, 2, 3, 4 (item number in Table I and correlation coefficient of the linear plot are given in parentheses): $\alpha_{\parallel}$ of C–X bond (item 1, $r = 0.994$); $\alpha_{\perp}$ of C–X bond (item 2, $r = 0.996$); boiling point of X_2 (item 15, $r = 0.996$); IP^{-1} of CH_3X (item 24, $r = 0.996$); boiling point of C_6H_5X (item 38, $r = 0.991$); η^{15} of C_6H_5X (item 47, $r = 0.987$); transverse $\chi_{\perp}$ of C_6H_5X (item 53, $r = 0.980$).

Discussion

The factor analysis results demonstrate that the a_1 and a_2 factors are excellent correlates for virtually every liquid and/or vapor phase property of halogen-containing compounds. These two factors (eq 1) serve to account for 99.9% of the variance in the data. The fact that the a_1 factor is essentially unity for all halogens further reduces the correlation to a linear relationship between the property values for a series of halides (X = F, Cl, Br, I) and the a_2 parameter (eq 2). Moreover, since the a_2 factor for F through I is well approximated by the integers 1–4, the property values for a series of halides are seen to be related in a remarkably linear way to the first four integers.

In addition to the properties listed in Table I, the a_2 factor (hence, the integers 1–4) is also linearly related to the ^{13}C chemical shifts of halogen-containing molecules[1,3] as well as the inductive (σ_I), resonance ($\sigma_R{}^0$), and steric (E_s) substituent constants for the halogens.[1] Thus, linear correlations between pairs of physical and spectroscopic properties should abound for organic halides.

The primary value of the linear interrelationships revealed by the factor analysis may well be empirical. For example, the boiling points of the *n*-propyl halides were not included in the analysis, but, as expected, they are linearly related to a_2 ($r = 0.990$), the integers 1–4 ($r = 0.989$), the boiling points of X_2 ($r = 0.997$), etc. The linearity among property values for molecules containing halogen could of course be used to advantage for the prediction of an unknown physical or spectroscopic property. Two examples, one using data listed in Table I and the other employing a property not used in the analysis, will serve to illustrate the typical accuracy of the procedure.

The critical temperature of C_6H_5F could be predicted from a plot of T_c for the remaining halobenzenes (item 40) vs. the integers 2, 3, and 4. The least-squares value of T_c at $x = 1.0$ is 313 °C, which is a reasonable agreement with the experimental critical temperature for fluorobenzene of 286.9 °C. A more accurate value (307 °C) is obtained when the a_2 parameters are used. Obviously, the procedure will give the best results when used to predict a value for a property of a chloride or bromide since both ends of the least-squares line are then anchored with experimental values. Thus, T_c for C_6H_5Cl (experimental value = 359.2 °C) is predicted as 341 °C by using an integer ordinate, and a more accurate value of 352 °C is obtained from a plot employing a_2 parameters. In a similar way, the value for a property not included in Table I may be approximated by using either integers or the a_2 factor. The surface tension, for example, of *n*-hexyl bromide ($\gamma^{42} = 25.66$ dyne·cm^{-1})[32] is given quite accurately as 25.6 dyne·cm^{-1} from a least-squares plot of γ^{42} for the fluoride, chloride, and iodide[32] vs. the numbers 1, 2, and 4.

In view of the generality of the linear interrelationships among properties of halogen-containing molecules it seems desirable to have at least a qualitative understanding of the basis for this unexpected linearity. As noted above, a number of linear correlations between *pairs* of the properties listed in Table I have been reported (much of the literature dates from the early part of this century)[33]

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(5) Le Fevre, R. *J. Adv. Phys. Org. Chem.* **1965**, *3*, 50.

(6) "CRC Handbook of Chemistry and Physics", 60th ed.; CRC Press: Cleveland, Ohio, 1979.

(7) Davies, M. "Some Electrical and Optical Aspects of Molecular Behavior"; Pergamon Press: New York, 1965; p 20.

(8) Vogel, A. I.; Cresswell, W. T.; Jeffery, G. H.; Leicester, J. *J. Chem. Soc.* **1952**, *514*.

(9) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972; p 107.

(10) Reference 9, p 114.

(11) Reference 6, E68.

(12) Pascal, P. "Chimie Generale"; Mason et Cie: Paris, 1949.

(13) Refernce 6, D190.

(14) Reference 6, B79, E382-387.

(15) Lange, N. L. "Handbook of Chemistry", 9th ed.; Handbook Publishers: Sandusky, OH, 1956; p 100.

(16) Calculated from critical data in ref 6 and ref 15.

(17) Grosse, A. V.; Wackher, R. C.; Linn, C. B. *J. Phys. Chem.* **1940**, *44*, 275.

(18) Computed from the molar volumes given in ref 17 and the refractive indicies given in ref 6, using the Lorentz expression: R_D = molar volume $[(n^2{}_D - 1)/(n^2{}_D + 2)]$.

(19) Lewis, D. T. *J. Chem. Soc.* **1931**, 1056.

(20) "Tables of Interatomic Distances and Configuration in Molecules and Ions"; Special Publication No. 18; The Chemical Society: London, 1965.

(21) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(22) Levitt, L. S.; Levitt, B. W. *Tetrahedron* **1979**, *29*, 941.

(23) Appleman, B. R.; Dailey, B. P. *Adv. Magn. Reson.* **1974**, *78* 231.

(24) Calculated from the molecular weights and the densities given in ref 6.

(25) Computed from the molar volumes (ref 24) and the refractive indices given in ref 6, using the Lorentz expression.

(26) Kudchadker, A. P.; Alani, G. H.; Zwdinski, B. J. *Chem. Rev.* **1968**, *68*, 659.

(27) Refernce 6, D194.

(28) Reference 6, F52-57; Ref 15, p. 1657.

(29) Reference 6, E123-136.

(30) Reference 6, E413-415.

(31) The boiling points (°C) of the *n*-propyl halides (X = F, Cl, Br, I) are 62, 105, 128.5, and 154.5, respectively. Cf. Vogel, A. I. *J. Chem. Soc.* **1943**, 636 and **1948**, 644.

(32) The surface tensions of the *n*-hexyl halides at 42 °C (X = F, Cl, Br, I) are 19.19, 24.2, 25.66 and 28.04 dyne·cm^{-1}, respectively. Cf. ref 31.

(33) For a summary of the more common linear correlations between pairs of molecular properties, see: Partington, J. R. "An Advanced Treatise on Physical Chemistry"; Longmans: New York, 1951–1953; Vol. 1–4.

Table I. Properties of Halogen-Containing Molecules on Which Factor Analysis Was Performed

		X = F		X = Cl		X = Br		X = I		
item	property	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	ref
				C-X Bond and X Group						
1	longitudinal bond polarizability ($\alpha_{\|\|}$), cm^3 × 10^{24}	1.20	1.19	3.80	3.79	5.30	5.33	8.10	8.06	5
2	transverse bond polarizability ($\alpha_\perp$), cm^3 × 10^{24}	0.40	0.40	1.80	1.83	2.70	2.67	4.20	4.21	5
3	atomic contribution to molar refraction ($R_D{}^{20}$), cm^3	0.81	0.86	5.84	5.78	8.74	8.70	13.95	14.00	6
4	bond contribution to $R_D{}^{20}$, cm^3	1.45	1.50	6.51	6.44	9.39	9.37	14.61	14.65	7
5	bond parachor (P)	28.2	30.4	57.4	55.0	70.9	69.3	92.4	94.2	8
6	av C-X bond length, Å	1.38	1.40	1.77	1.74	1.94	1.93	2.21	2.22	9
7	reciprocal of av C-X stretching force constant (k^{-1}), Å mdyne^{-1} × 10	1.68	1.81	2.75	2.63	3.20	3.09	3.77	3.88	10
8	reciprocal of first ionization potential of atom (IP^{-1}), eV^{-1} × 10^2	5.74	5.92	7.69	7.49	8.45	8.35	9.57	9.71	11
9	atomic contribution to molar diamagnetic susceptibility, (Pascal constants), esu mol^{-1} × 10^5	−0.64	−0.62	−1.99	−2.08	−3.04	−2.94	−4.46	−4.49	12
				X_2 Molecule						
10	bp, °C	−188.15	−179.95	−34.6	−38.1	58.78	45.10	184.35	193.75	13
11	$n_D{}^{20}$	1.0002	0.9855	1.0008	1.0129	1.0011	1.0163	1.0019	0.9882	14
12	$\Delta H°_{vap}$, kcal mol^{-1}	0.755	0.783	2.439	2.471	3.58	3.47	5.20	5.26	15
13	van der Waals a term, L^2 atm mol^{-2}	1.073	1.143	6.495	6.389	9.502	9.4999	15.095	15.135	16
14	van der Waals b term, L mol^{-1} × 10^2	2.688	3.247	5.622	4.845	5.874	5.755	6.942	7.301	16
				CH_3X Molecule						
15	bp, °C	−78.4	−76.3	−24.2	−26.0	3.56	1.32	42.40	44.37	6
16	$n_D{}^{20}$	1.1727	1.1717	1.3389	1.3391	1.4218	1.4235	1.5380	1.5367	6
17	$\Delta H°_{vap}$, kcal mol^{-1}	3.986	4.138	5.375	5.219	5.926	5.810	6.616	6.743	6
18	critical temp (T_c), °C	44.6	55.5	143.8	135.2	194.0	181.9	254.8	265.2	6
19	molar vol, cm^3 mol^{-1}	38.60	39.31	50.92	49.70	55.18	55.37	64.02	64.36	17
20	$R_D{}^{20}$, cm^3	4.291	4.465	10.642	10.432	14.016	13.928	20.024	20.153	18
21	parachor	81.8	82.8	110.4	109.1	124.1	123.8	146.9	147.6	19
22	bond length, Å	1.385	1.424	1.781	1.740	1.939	1.910	2.139	2.171	20
23	bond dissoc energy, kcal mol^{-1}	108.0	103.5	84.0	87.0	70.0	75.8	56.3	51.7	21
24	reciprocal of first ionization potential (IP^{-1}), eV^{-1} × 10^2	7.81	7.73	8.86	8.94	9.50	9.56	10.48	10.42	22
25	longitudinal magnetic susceptibility ($\chi_{\|\|}$), erg G^{-2} mol^{-1} × 10^5	−2.33	−2.26	−3.73	−3.87	−4.85	−4.81	−6.45	−6.42	23
26	transverse magnetic susceptibility ($\chi_\perp$), erg G^{-2} mol^{-1} × 10^5	−1.51	−1.52	−2.94	−3.01	−4.00	−3.87	−5.35	−5.40	23

Table I (*Continued*)

		X = F		X = Cl		X = Br		X = I		
item	property	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	ref
27	transverse ^{13}C shielding tensor ($\sigma_\perp$), ppm × 10^{-1}	9.9	10.0	16.1	15.7	18.5	18.8	24.4	24.4	23
28	anisotropy in ^{13}C tensor ($\Delta\sigma$), ppm × 10^{-1}	6.8	7.5	2.8	2.3	0.0	−0.8	−7.5	−6.8	23
				C_2H_5X Molecule						
29	bp, °C	−37.70	−36.14	12.27	11.21	38.40	36.32	72.03	73.89	6
30	n_D^{20}	1.2656	1.2524	1.3676	1.3785	1.4239	1.4374	1.5133	1.5010	6
31	$\Delta H°_{vap}$, kcal mol^{-1}	5.519	5.400	6.311	6.418	6.843	6.955	7.852	7.745	6
32	molar vol, cm^3 mol^{-1}	66.92	65.82	71.86	72.67	74.62	75.90	80.57	79.50	24
33	R_D^{20}, cm^3	11.18	11.07	16.16	16.23	19.04	19.16	24.23	24.12	25
34	parachor	121.8	122.6	150.9	150.0	165.4	164.7	186.6	187.3	8
35	bond length, Å	1.375	1.432	1.777	1.727	1.940	1.884	2.070	2.121	20
36	bond dissoc energy, kcal mol^{-1}	106.0	101.7	81.0	84.7	69.0	73.3	53.0	49.0	21
37	reciprocal of first ionization potential (IP^{-1}), eV × 10^2	8.33	8.17	9.11	9.28	9.72	9.83	10.67	10.54	22
				C_6H_5X Molecule						
38	bp, °C	85.1	84.5	132.0	132.5	156.0	156.5	188.3	187.8	6
39	n_D^{20}	1.4684	1.4468	1.5241	1.5427	1.5597	1.5809	1.6200	1.6003	6
40	T_c, °C	286.9	289.5	359.2	357.3	397.0	393.9	448.0	450.5	26
41	molar vol, cm^3	93.99	93.20	101.79	102.16	105.03	106.28	111.43	110.54	24
42	R_D^{20}, cm^3	26.15	25.84	31.15	31.37	33.95	34.33	39.14	38.83	25
43	parachor	214.4	213.6	243.2	243.4	257.1	258.4	279.2	278.3	8
44	bond length, Å	1.332	1.372	1.719	1.674	1.860	1.835	2.050	2.082	20
45	van der Waals *a* term, L^2 atm mol^{-2}	19.93	19.99	25.43	25.43	28.56	28.42	33.08	33.16	27
46	van der Waals *b* term, L mol^{-1} × 10	1.286	1.283	1.453	1.456	1.539	1.541	1.656	1.654	27
47	viscosity (η^{15}), cp × 10	5.98	5.31	9.00	9.77	11.96	12.35	17.40	16.88	28
48	surface tension (γ^{41}), dyne cm^{-1}	24.61	24.78	30.05	30.08	33.37	32.92	36.97	37.23	8
49	molar diamagnetic susceptibility (χ_m), cgs × 10^5	−5.84	−5.73	−7.00	−7.15	−7.89	−7.92	−9.20	−9.13	29
50	molecular rotatory value ($[\Lambda]_m^{D,15}$), rad G^{-1} cm^{-1} × 10^4	6.85	6.44	8.61	8.97	9.98	10.39	13.14	12.76	30
51	Verdet constant ($\Lambda^{D,15}$), min G^{-1} cm^{-1} × 10^5	2.51	2.38	2.92	3.03	3.26	3.38	4.06	3.95	30
52	in-plane magnetic susceptibility ($\chi_{\parallel}$), erg G^{-2} mol^{-1} × 10^5	−3.89	−3.87	−5.49	−5.48	−6.34	−6.39	−7.95	−7.92	23
53	transverse magnetic susceptibility ($\chi_{\perp}$), erg G^{-2} mol^{-1} × 10^5	−9.72	−9.48	−10.01	−10.45	−11.00	−10.90	−11.51	−11.40	

and additive-constitutive schemes have been devised for molar refraction,[7,8] polarizability,[34] parachor,[35] molar diamagnetic susceptibility,[12] molar volume,[36] and other properties.[37] Nevertheless, the general phenomenon of linearity among all liquid and/or vapor phase properties of molecules containing halogen does not seem to have been recognized.

A clüe as to the possible basis for the plethora of linear relationships is the failure of a_2 to correlate well with solid-state properties, such as melting point, and with

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(34) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206.

(35) (a) Sugden, S. "The Parachor and Valency"; Knopf: New York, 1930. (b) Exner, O. *Collect. Czech, Chem. Commun.*, **1967**, *32*, 34.

(36) Exner, O. *Collect. Czech. Chem. Commun.*, **1967**, *32*, 1.

(37) Glasstone, S. "Textbook of Physical Chemistry", 2nd ed; Van Nostrand: Princeton, NY, 1946.

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Table II. Statistical Analysis of Factorization

no. of factors	eigenvalue,[a] λ	cumulative % variance[b]
1	51.132	94.69
2	2.811	99.90
3	0.051	99.99
4	0.005	~100.00

[a] The remaining factors have vanishingly small eigenvalues. [b] Percentage of total variance in the data set accounted for by the reduction. The variance accounted for by each factor is given by: $\lambda_i/\Sigma_{i=1}^{n}\lambda_i$, where λ_i is the eigenvalue of factor i and the sum is over all factors needed to exactly reproduce the data. Cumulative percent variance is analogous to r^2 (× 100) for a regression curve.

properties of the hydrogen-bonded HX molecules. The a_1 and a_2 factors do not seem to account for properties which are dependent on specific (non-orientation-averaged) intermolecular interaction, but they do serve to correlate virtually all physical and spectroscopic properties of liquid and/or gas phase halides. These observations strongly suggest that the success of the correlation is due in large measure to the dominant role of polarizability in determining *changes* in the intermolecular attractive forces between halogen-containing molecules. The C–X bond dipoles are reasonably constant for the halide series (1.74 ± 0.12 D)[38] and, to a first approximation, properties dependent upon averaged intermolecular association (i.e., boiling point, $\Delta H°_{\mathrm{vap}}$, van der Waals terms, T_c, surface tension, etc.) should vary linearly with the polarizability, which, in turn, is related in an approximately linear way (items 1 and 2, Table I) to both a_2 and the integers 1–4.

The monotonic increase in halogen polarizability from F through I, when considered together with the fairly constant magnitude of the C–X bond dipole, provides a qualitatively reasonable (albeit incomplete) rationale for the success of the factor analysis. Most of the physical and spectroscopic (e.g., ^{13}C shifts, IR, and Raman vibrations via their relationship to the stretching force constants (item 7), photoelectron spectra, etc.) properties of halogen-containing molecules could be qualitatively attributed to the dominant role of the "freeness" or "deformability" of electrons associated with halogen. Unfortunately, as noted elsewhere,[3] we are unaware of any theory which can successfully relate all of the properties of such molecules much less account for the apparent linearity of the correlations. Despite the lack of a firm theoretical model, the unifying relationship presented above should prove useful for a variety of empirical investigations.

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Registry No. Methyl fluoride, 593-53-3; methyl chloride, 74-87-3; methyl bromide, 74-83-9; methyl iodide, 74-88-4; ethyl fluoride, 353-36-6; ethyl chloride, 75-00-3; ethyl bromide, 74-96-4; ethyl iodide, 75-03-6; phenyl fluoride, 462-06-6; phenyl chloride, 108-90-7; phenyl bromide, 108-86-1; phenyl iodide, 591-50-4.

Supplementary Material Available: Table III, the b_1 and b_2 property cofactors from the two-factor analysis (3 pages). Ordering information is given on any current masthead page.

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[38] The dipole moments of the methyl halides in the gas phase are as follows: CH$_3$F, 1.85 D; CH$_3$Cl, 1.87 D; CH$_3$Br, 1.81 D; CH$_3$I, 1.62 D. Cf. Cumper, C. W. N. *Tetrahedron* **1969**, *25*, 3131.

Thiosulfonium Ions by Gas-Phase Methylation and Thiomethylation of Sulfur Nucleophiles. 1. Methoxymethyl Cations

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Generation of gaseous thiosulfonium ions (CH$_3$SSCH$_3$)R$^+$, R = H, alkyl, and dithiosulfonium ions, R = alkylthio, has been achieved by ion cyclotron resonance techniques. Hitherto, dithiosulfonium ions have been inferred as transient intermediates in solution-phase reactions. It is here reported that these ions can be formed in the gas phase by displacement of methanethiol from protonated methyl disulfide with neutral disulfide. Related ions (CH$_3$S)$_2$CH$_3$$^+$ can also be formed in the gas phase by the methylation of methyl disulfide with CH$_3$OCH$_2$$^+$ derived from methyl ethers on electron impact. Gaseous thio- and dithiosulfonium ions have been shown to thiolate neutral sulfides and selected alkenes, as they do in condensed phase. The ion/molecule chemistry of methyl 1-phenylethyl sulfide has been studied and has been found to lead to thiosulfonium ions (CH$_3$S)$_2$R$^+$, R = 1-phenylethyl, by methylthiolation of the neutral sulfide by the molecular ion. A degenerative rearrangement of (CH$_3$S)$_2$R$^+$ which has been documented in solution was not evident in the behavior of the gaseous ion. The implication of this observation is discussed. Heats of formation of trimethylsulfonium and several thiosulfonium ions have been estimated.

Thiosulfonium ions having the general structure RSS$^+$R$_2$ are highly reactive ions and have been isolated as stable salts in relatively few instances.[1,2] The best characterized ion is dimethyl(methylthio)sulfonium, **1** (R = CH$_3$), which forms stable salts with nonnucleophilic counterions. However, in the presence of neutral or anionic nucleophiles, the ion readily dissociates by S–S$^+$ and C–S$^+$

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[1] (a) G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 933 (1965); (b) D. J. Pettitt and G. K. Helmkamp, *ibid.*, **28**, 2932 (1963); *ibid.*, **29**, 2702 (1964); (c) N. E. Hesler, G. K. Helmkamp, and G. L. Alford, *Int, J. Sulfur Chem., Part A*, 1, 65 (1971).

[2] (a) H. Meerwein, K. F. Zenner, and R. Gipp, *Justus Liebigs Ann. Chem.*, **688**, 67 (1965); (b) R. A. Goodrich and F. M. Treichel, *J. Am. Chem. Soc.*, **88**, 3509 (1966).

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