A fast empirical method for the calculation of molecular polarizability

Robert C. Glen

Department of Physical Sciences, Wellcome Research Laboratories, Langley Court, Beckenham, Kent BR3 3BS, U.K.

SUMMARY

A simple empirical method for the calculation of static molecular polarizability is described. The method is based on Slater's rules for the calculation of effective atomic nuclear shielding constants. The calculated molecular polarizabilities of a series of organic molecules correlated well (r = 0.98) with experimental measurements. Accurate calculated polarizabilities can be obtained rapidly by this method and may prove useful in deriving relationships between chemical structure and properties.

INTRODUCTION

The polarizability of an atom or molecule describes the response of the electron density to the application of an external electric field. As such, polarizability is a contributor to dispersion forces and is therefore closely associated with intermolecular interactions. When a molecule is placed in an external electric field, a displacement of charges results such that a dipole is induced. The magnitude of this induced dipole is given by

$$\upsilon = A.E$$

where υ is the induced dipole, E is the electric field operator and A is the polarizability tensor of the molecule. The average polarizability α is the most often described. $\alpha = 1/3 \, (\alpha_1 + \alpha_2 + \alpha_3)$, where α_1, α_2 and α_3 are the principal components of the polarizability tensor. Polarizability may be derived from a large range of experimentally measured parameters. For example, derivations have been made from the index of refraction and density [1], dipole moment and magnetic bire-fringence [2], dielectric constant [3] (via the Lorenz–Lorentz relationship [4]), quadrupole spectra [5], or more recently, nuclear magnetic resonance measurements in an applied electric field [6].

Polarizability may be calculated quantum-mechanically from the wave function [7,8] via the variational principal, by means of summing bond polarizabilities [9], by summing atomic hybrid

TABLE 1
n* VALUES OBTAINED FROM PRINCIPAL QUANTUM NUMBERS OF ELECTRONS

n	1	2	3	4	5	6
n*	1	2	3	3.7	4.0	4.2

components [10], by the additivity of static atomic polarizabilities [11] or, for atoms, by the use of atomic nuclear screening constants. Here, the treatment used for the calculation of atomic nuclear screening constants for atoms is modified to reproduce static molecular polarizabilities of molecules.

METHODS

In 1939, Slater [12] described a method for the calculation of atomic screening constants based on the calculation of the effective nuclear charge. From the effective screening constants, such diverse properties as atomic radius and ionization potential may be calculated [12]. The basis for this treatment is the fact that each electron in an atom does not 'see' the nucleus in an equal fashion; the view of the nucleus for electrons in outer shells is modified by the presence of inner-shell electrons. So, although the nuclear charge may be Ze, an electron in an atom behaves as though it is moving in a field of nuclear charge $(Z-s)e$. The quantity s is called the screening constant. From the knowledge of one property of an atom, for example the radius, it is possible to derive atomic screening constants and then include these derived screening constants in similar calculations to deduce new properties. In other words, the atomic screening constants are important contributors to a wide range of observed properties of an atom.

An approximation for atoms with more than one shell is that the nodes in the wave function are unimportant. Hence, we need only the radial part of the wave function and use the asymptotic form at large distances, which for one electron is:

$$Rn^*(r) = r^{n^*-1} e^{-(Z-s)r/n^*}$$

where n^* is the effective quantum number and the effective nuclear charge is $(Z-s)$. Z is the nuclear charge and s is a screening constant. r is expressed in units of the Bohr radius, $a_0 = 0.5292$ Å.

The effective quantum number n^* and the effective nuclear charge $(Z-s)$ are determined by the following empirical rules [8]:

(1) If the principal quantum number of an electron is n, the value of n^* is obtained from Table 1.
(2) For determining $(Z-s)$, the electrons are divided into the groups given in Table 2, each having a different shielding constant. The s and the p are grouped together, but the d and f are considered separately. The groups are arranged from the inside out in the order shown in Table 2, with $1s$ innermost.

TABLE 2
GROUPS OF ELECTRONS USED TO DETERMINE EFFECTIVE NUCLEAR CHARGES

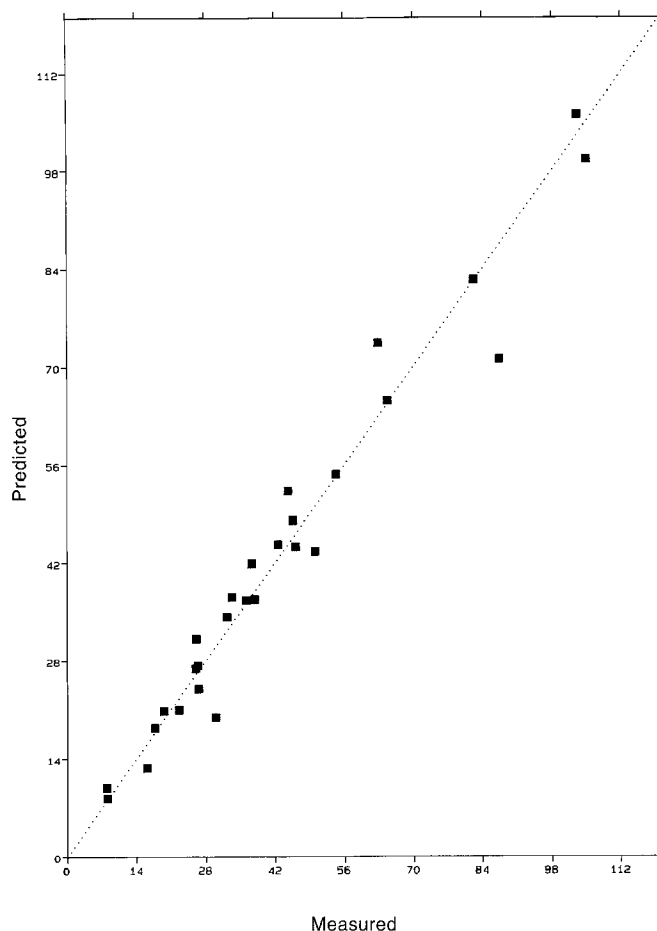| 1s	2s	3s	3d	4s	4d	4f	5s	5d	...
	2p	3p		4p			5p		...

Fig. 1. Calculated versus training set polarizability data.

(3) The screening constant s is formed for any group of electrons from the following contributions: (i) nothing from any shell outside the one considered; (ii) an amount of 0.35 from each other electron in the group considered (except in the 1s group where 0.30 is used instead); (iii) if the shell considered is an s or p shell, an amount of 0.85 is contributed from each electron with total quantum number less by one, and an amount of 1.00 from each electron still further in; (iv) if the shell is a d or f shell, each electron in the groups closer in contributes 1.00 to the screening constant.

An example is the chlorine atom: $Cl = 1s^2 2s^2 2p^6 3s^2 3p^5$, for which the effective nuclear charge components are calculated as follows:

$$Z - s_{1s} = 17 - 0.3 = 16.7$$

$$Z - s_{2s,2p} = 17 - (7 \times 0.35) - 2(0.85) = 12.85$$

$$Z - s_{3s,3p} = 17 - (6 \times 0.35) - (8 \times 0.85) - 2(1.0) = 6.1$$

TABLE 3
TRAINING SET OF MOLECULES OF KNOWN POLARIZABILITY

Molecule	Polarizability (10^{-25} cm^3)	Molecule	Polarizability (10^{-25} cm^3)
H_2	7.9	NH_3	22.6
N_2	17.6	$(CN)_2$	50.1
O_2	16.0	HCN	25.9
Cl_2	46.1	CH_4	26.0
HF	8.2	C_2H_6	44.7
HCl	26.4	$CH_2{=}CH_2$	42.6
HBr	36.1	Acetylene	33.3
HI	54.4	C_3H_8	62.9
N_2O	30.0	C_6H_6	103.2
CO	19.5	CH_3Cl	45.6
CO_2	26.5	CH_2Cl_2	64.8
SO_2	37.2	$CHCl_3$	82.3
H_2S	37.8	CCl_4	105.0
CS_2	87.4	CH_3OH	32.3

Polarizability may be expressed in terms of the atomic radius [3], i.e., for i electrons:

$$\alpha = \frac{4}{9a_0} \sum_i (\bar{r}_i^2)^2$$

For the calculation of polarizabilities of atoms, we need to know r_i (the radius of maximum electron density) [8]. The maximum of the radial charge density for one of these shells (found by taking the radial part of the shell squared, multiplying by $4\pi r^2$ and then differentiating the radial function with respect to the radius, r) can be expressed as [12]:

$$\left(\frac{n^{*2}}{Z-s} \right)$$

For the simple wave function adopted, the average value of the kth power of the radius for the ith electron is:

$$\bar{r}_i^k = \frac{\int_0^\infty r^{k+2} |R_i|^2 \, dr}{\int_0^\infty r^2 |R_i|^2 \, dr} = \left[\frac{n_i^*}{2(Z-s_i)} \right]^k \left[\prod_{j=1}^k (2n_i^* + j) \right] a_0^k$$

Hence, using the example of the chlorine atom,

$$r_{1s}^2 = (1/(2 \times 16.7))^2 \times 3 \times 4 = 0.0107$$

$$r_{2s2p}^2 = (2/(2 \times 12.85))^2 \times 5 \times 6 = 0.1816$$

$$r_{3s3p}^2 = (3/(2 \times 6.1))^2 \times 7 \times 8 = 3.386$$

The polarizability of the chlorine atom is therefore $4/9 [2(0.0107)^2 + 8(0.1816)^2 + 7(3.386)^2] a_0^3 = 5.29$ (units are in $\alpha \times 10^{-25}$ cm^3).

For atoms, these calculations reproduce atomic radii, diamagnetic susceptibilities, X-ray levels and ionisation potentials fairly well. However, in molecules, the electron density distribution
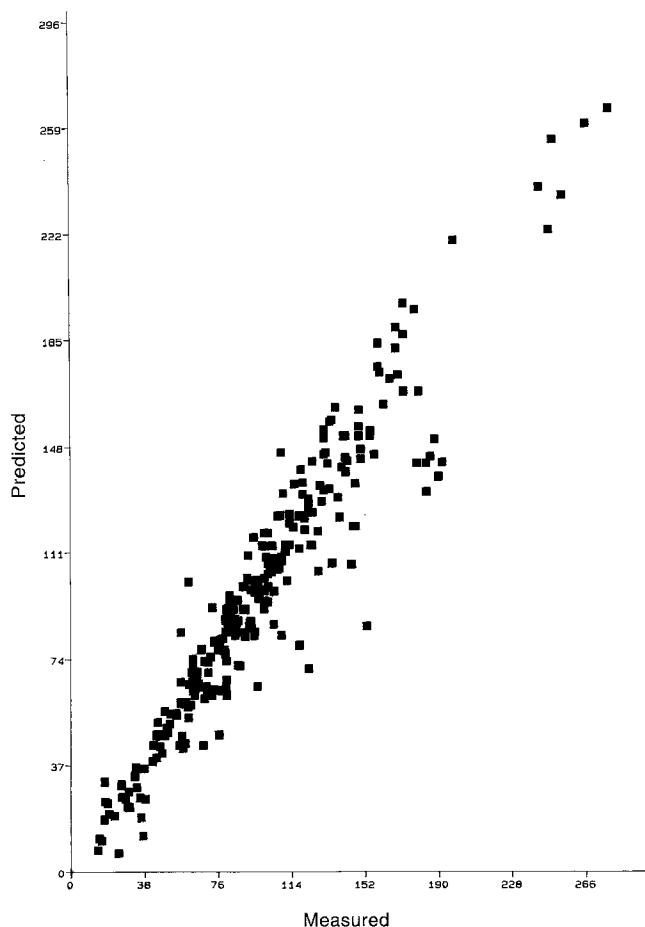
Fig. 2. Calculated versus experimental polarizability data for the compounds in Table 5.

around atoms is modified to such a degree that this calculation no longer gives accurate results.

The atomic orbitals have combined to form molecular orbitals with adjustment of their size and occupancy. Thus, bonding orbitals or orbitals on electronegative atoms have a relative increase in electron density. To take this into account, the effective quantum numbers n^* were adjusted to better reproduce the situation found in bonded atoms. Also, the occupancy of the valency orbitals was modified by addition of the atom-centered electron density calculated by the Gasteiger and Marsili method [13–16] (Partial Equalisation of Orbital Electronegativity, PEOE). This simple empirical method was used for speed of computation.

To determine the best values for n^* where polarizability is required, a training set (Table 3) of small organic molecules whose polarizabilities had been measured was utilized [8].

TABLE 4
n^* VALUES OBTAINED BY USING A TRAINING SET OF MOLECULES WITH KNOWN POLARIZABILITY

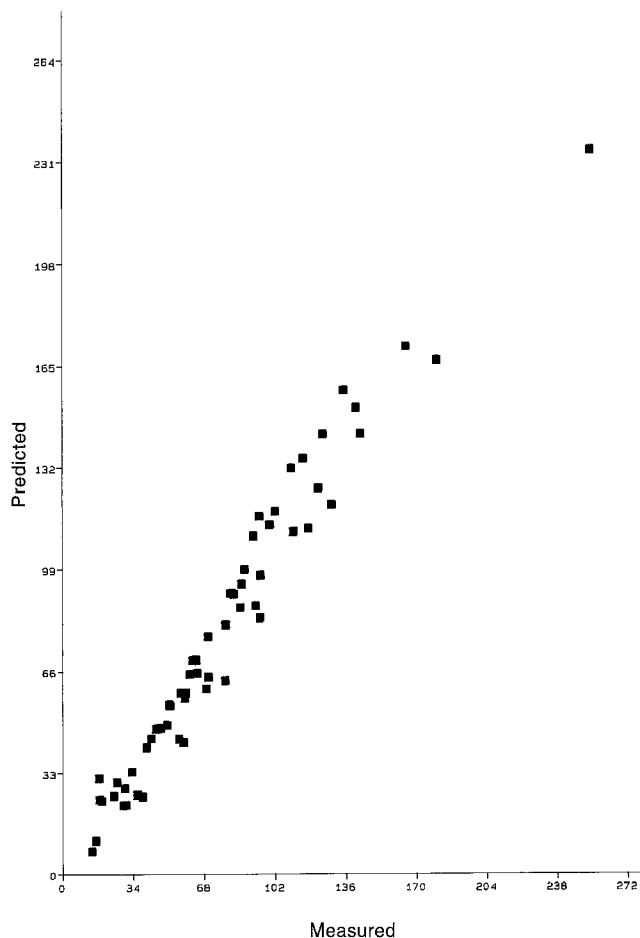| n	1	2	3	4	5
n^*	0.94	1.88	2.65	3.15	3.35

462

Fig. 3. Calculated versus experimental polarizability data (accurate subset).

Starting with molecules having only two shells, the values of n* for principal quantum numbers n = 1 and n = 2 were adjusted until the experimental polarizabilities were reproduced. This was continued for molecules in the training set having more filled shells (for n = 3,4,5). By following this sequence, it was expected that the cumulative effects of extra shells could be introduced. This led to the values for n* listed in Table 4.

A plot of the experimental versus calculated results for the training set is shown in Fig. 1. From this, the following values are obtained:

Polarizability = 0.96 (0.04) CalcP + 2.2 (1.9)

CalcP = calculated value, r = 0.98, F = 635.07

Percent explained variation = 96.07%, Standard error of estimate = 5.28

The correlation coefficient is high at r = 0.98 and the slope and intercept are small, implying that the chosen values for n* are reasonable.

TABLE 5
PREDICTION OF MOLECULAR POLARIZABILITIES

Molecule	Measured	Calculated	Molecule	Measured	Calculated
Br_2	70.2	62.5	3-Methyl-1,3-pentadiene	118	124
CO	19.3	20.2	2-Methyl-1,3-pentadiene	121	124
Cl_2	46.1	43.6	2,3-Dimethyl-1,3-butadiene	118	124
F_2	13.8	7.4	Cyclohexene	107	124
HBr	36.1	35.7	Cyclohexane	110	132
HCl	26.3	26	n-Hexane	119	140
HF	24.6	6.4	Toluene	123	130
HI	54.4	54.4	Methylcyclohexane	131	154
ICl	123	70.5	n-Heptane	137	162
N_2	17.4	31.3	Styrene	150	144
NO	17	18.2	Ethylbenzene	142	152
O_2	15.8	10.8	o-Xylene	149	152
CO_2	29.1	22.6	p-Xylene	141	152
CS_2	87.4	71.5	m-Xylene	149	152
H_2O	14.5	11.6	Ethylcyclohexane	159	176
H_2S	37.8	35.8	n-Octane	159	184
CN	25.9	30.6	Isopropylbenzene	160	174
N_2O	30.3	22.6	Isopropylcyclohexane	172	198
NO_2	30.2	22.4	Naphthalene	165	171
CS_2	57.1	47.1	t-Butylbenzene	178	195
SO_2	37.2	12.5	t-Butylcyclohexane	198	219
CF_3I	63.2	71.2	Anthracene	254	235
NF_3	36.2	19	CBr_2F_2	90	81.8
NH_2	22.6	19.4	$CClF_3$	55.9	44.1
PCl_3	128	104	CCl_2F_2	78.1	63
PH_3	48.4	55.9	Phosgene	72.9	61.5
SO_3	48.4	47.4	Thiophosgene	102	93.7
SO_2Cl_2	105	86	CCl_3F	94.7	82
Methane	25.9	30	CCl_3NO_2	108	96.4
Acetylene	33.3	36.2	CCl_4	112	101
Ethylene	42.5	44.1	CF_4	38.3	25.4
Ethane	44.7	52	CF_2O	18.8	23.9
Propyne	61.8	58	$CHBr_3$	118	112
Propene	62.6	66	CH_2BrF	57	83.1
Cyclopropane	56.6	65.8	$CHClF_2$	59.1	44.9
Propane	62.9	73.9	$CHCl_2F$	68.2	64
1-Butyne	74.1	80	$CHCl_3$	95	83.3
1-Butene	79.7	87.9	CHF_3	35.7	25.9
2-Butene	84.9	87.9	CHFO	17.6	24.5
trans-2,3-Epoxybutane	82.2	90.9	CHI_3	180	167
2-Methylpropene	82.9	87.9	CH_2Br_2	93.2	84.8
Butane	82	95.8	Chloronitromethane	69	60.4
1,3-Cyclopentadiene	86.4	71.8	CH_2Cl_2	64.8	65.4
1-Pentyne	91.2	102	CH_3Br	60.3	57.4
trans-1,3-Pentadiene	100	102	CH_3Cl	47.2	47.7
Isoprene	99.9	102	CH_3F	29.7	28
Cyclopentane	91.5	110	CH_3I	79.7	76
Pentane	99.9	118	C_2ClF_5	63	63.1
Neopentane	102	118	$C_2Cl_2F_4$	85	82
Benzene	103	108	Trichloroacetonitrile	61	101
1-Hexyne	109	146	C_2F_6	68.2	44.1
2-Ethyl-1,3-butadiene	118	124	Bromoacetylene	73.9	63.3

TABLE 5 (continued)

Molecule	Measured	Calculated	Molecule	Measured	Calculated
Chloroacetylene	60.7	53.7	Bromobenzene	147	135
C_2HCl_5	140	141	Chlorobenzene	123	125
1,1-Dichloro-2,2-difluoroethane	84	84.2	Chlorophenol	130	129
Chloroacetylchloride	89.2	83.1	Fluorobenzene	103	106
1,2,2-Trichloro-1-fluoroethane	102	103	Iodobenzene	155	153
1,1,2,2-Tetrachloroethane	121	123	Fluorotoluene	123	128
Chloroacetonitrile	61	65.1	1-Bromoheptane	168	189
1,1-Difluoroethylene	50.1	48.6	4,4'-Dibromodiphenylether	278	265
Bromoethylene	75.9	79.3	4-Bromodiphenylether	242	238
1-Chloro-1,1-difluoroethane	80.5	66.7	p-Bromophenyl-p-tolyl ether	266	260
Acetylchloride	66.2	65.3	Tetranitromethane	153	85.4
Ethylchloroformate	71.0	69.4	Formaldehyde	28	25.6
1,1,1-Trichloroethane	107	105	Formic acid	34	29.6
1,1,1-Trifluoroethane	44	47.7	Formamide	42	38.5
C_2H_3I	93	97.9	Methanol	32.9	33.3
1-Bromo-2-chloroethane	95	97	Ethylamine	47	41.3
1,2-Dibromoethane	107	107	Ketene	44	39.8
1-Chloro-2-fluoroethane	65	67.7	Acetonitrile	44	47.4
1-Chloro-1-nitroethane	109	82.2	Acetaldehyde	45.9	47.5
1,1-Dichloroethane	86.4	87.3	Acetic acid	51	51.4
1,2-Dichloroethane	80	87.3	Acetamide	56.7	59
C_2H_5Cl	64	69.6	Methylformamide	59.1	59
2-Chloroethanol	71	73	Nitroethane	96.3	64.2
C_2H_5F	49.6	50	Ethylnitrite	70	64.2
C_2H_5I	100	97.9	Ethanol	54.1	55.3
Dichloropropene	101	109	Methylether	51.6	55
Chloropropene	83	91.6	Ethyleneglycol	57	58.6
Chloroacetone	84	87.1	Dimethylsulphone	73	91.9
Ethylchloroformate	90	91.3	Ethanethiol	74.1	79.8
1-Chloro-1-nitropropane	104	104	Ethylamine	71	63.3
Dichloropropane	109	109	Dimethylamine	63.7	63.2
1-Bromopropane	94	101	Ethylenediamine	72	74.7
2-Bromopropane	96	101	Alononitrile	57.9	43
Chloropropane	100	91.6	Acrylonitrile	80.5	61.4
C_3H_7I	115	120	Propenal	63.8	61.5
4-Chloro-1,2-butadiene	100	97.6	Propionitrile	62.4	69.3
1-Chloro-2-methylpropene	108	106	Acetone	63.3	69.3
1,4-Dichlorobutane	120	131	Allyl alcohol	76.5	47.5
Bromobutane	139	123	Propionaldehyde	65	69.4
Chlorobutane	113	114	Propionic acid	69	73.4
1-Chloro-2-methylpropane	111	114	Ethylformate	80.1	73.2
2-Chloro-2-methylpropane	125	113	Methylacetate	69.4	73.1
2-Chlorobutane	124	113	Dimethylcarbonate	77	77.2
1-Iodobutane	133	142	Methylacetamide	78.2	82.4
1-Bromopentane	131	145	N-dimethylformamide	78.1	80.8
1-Chloropentane	120	135	Nitropropane	85	86.2
2,5-Dichloro-1,4-benzoquinone	184	142	2-Propanol	76.1	77.2
p-Bromofluorobenzene	134	133	1-Propanol	67.4	77.2
p-Chloronitrobenzene	146	120	Methoxyethane	79.3	77
Dichlorobenzene	143	143	Dimethoxyethane	77	80.4
p-Fluoroiodobenzene	155	152	n-Propylamine	92	85.2
p-Fluoronitrobenzene	128	118	Trimethylamine	81.5	85.1
m-Difluorobenzene	103	104	Fumaronitrile	118	78.7

TABLE 5 (continued)

Molecule	Measured	Calculated	Molecule	Measured	Calculated
Succinonitrile	81	86.7	Diethoxyethane	113	124
Pyrimidine	85.3	86.5	Tetramethylorthocarbonate	184	132
Pyridazine	92.7	87.2	p-Benzoquinone	145	107
Diketene	80	63.5	Nitrobenzene	147	120
Thiophene	96.7	100	Phenol	111	111
Methacrylonitrile	80	83.3	Aniline	121	119
trans-Crotonitrile	82	83.3	Phenylenediamine	138	130
Crotonaldehyde	85	83.4	Ethylacetoacetate	129	134
Methacrylaldehyde	83	83.4	Cyclohexanol	116	135
Biacetyl	82	94.7	Amylformate	142	139
Acetic anhydride	89	91.2	Paraldehyde	179	142
Divinylsulfide	109	108	Propylether	125	143
Butyronitrile	84	91.3	1,1-Diethoxyethane	132	146
Isobutyronitrile	80.5	91.2	Triethylamine	131	151
Butyraldehyde	82	91.4	p-Cyanobenzene	190	137
Methylethylketone	81.3	91.3	Benzonitrile	125	125
Ethylacetate	97	95	Nitroanisole	157	145
1,4-Dioxane	100	94	Anisole	131	133
p-Dioxane	86	94.3	o-Anisidine	142	144
2-Methyl-1,3-dioxolane	94.4	116	Cyclohexylmethylether	134	157
1-Nitrobutane	104	108	Diisopropylketone	135	157
2-Methyl-2-nitropropane	103	108	Amylacetate	149	161
Ethylether	102	98.9	p-Dicyanobenzene	192	142
1-Butanol	88.8	99.2	Acetophenone	150	147
2-Methylpropanol	89.2	99.2	2,5-Dimethyl-1,4-benzoquinone	188	151
Ethylsulfide	108	124	Phenetole	149	155
n-Butylamine	135	107	N-Dimethylaniline	162	163
Diethylamine	102	107	Ethylsorbate	172	167
Pyridine	95	97	Tetramethylcyclobutane-1,3-dione	186	145
4-Cyano-1,2-butadiene	105	97.3	Diethylsuccinate	168	182
Acetylacetone	105	109	n-Butylether	172	187
Valeronitrile	104	113	Ethylbenzoate	169	173
Diethylketone	99.3	113	4-Nitrodiphenylether	247	223
Methylpropylketone	99.3	113	Di-p-tolylether	249	255
Diethylcarbonite	113	121			

RESULTS

Using this empirical calculation (not the regression model), polarizabilities were calculated for a larger set of molecules whose experimentally derived molecular polarizabilities [17] were available. These are tabulated in Table 5 (and include some of the molecules in the training set). In this exercise, atom-centered atomic charges were calculated using the PEOE method and the charges subtracted (the charges for excess electron density are negative) from the occupancy of the valence orbitals to better simulate the changes in electron density in going from atomic to molecular orbitals. A plot of experimental vs. calculated polarizabilities is shown in Fig. 2.

The data in Ref. 17 contain many derived polarizabilities. By removing those polarizabilities based on dipole moment, dielectric constant and molar refraction in experiments performed before the year 1952 and replotting the remaining calculated versus experimental data, Fig. 3 is

obtained. The average error in this test set is 12.5%. For comparison, many recent measured values quoted in Ref. 17 for organic molecules may be in error by up to 14%. A regression calculation for this dataset gave (note that the constant is not significant):

Polarizability = 0.942 (0.025) CalcP + 2.3 (2.3)

CalcP = Calculated value, R = 0.978, F = 1341

Percent explained variation = 95.6%, Standard error of estimate = 9.37

CONCLUSIONS

A simple method for the calculation of static molecular polarizabilities based on Slater's rules is presented. The calculation is fast and applicable to a wide range of molecules. The average error is of the order of 12.5% for a 64-molecule test set.

The model may be improved by better consideration of conjugation (for example, anthracene and phenanthrene give almost the same values), a more accurate charge scheme and by introduction of anisotropy in the atom-centred parameters which may make the polarizability tensor accessible.

Calculated polarizabilities are useful parameters in the derivation of quantitative structure–property relationships. For example, calculated polarizability was recently found to be useful in the prediction of thin-layer chromatography retention times [18].

REFERENCES

1 Takahashi, M., Mita, S. and Kondo, S., Mol. Cryst. Liq. Cryst., 132 (1986) 53.
2 Cheng, C.L., Murthy, D.S.N. and Ritchie, G.D.L., Aust. J. Chem., 25 (1972) 1301.
3 Bonnet, P. and Barriol, J., J. Chim. Phys., 83 (1986) 519.
4 Miller, T.M. and Bederson, B., Adv. At. Mol. Phys., 13 (1977) 1.
5 Machmer, P., Z. Naturforsch., 23B (1968) 295.
6 Ruessnik, B.H. and MacLean, C., Mol. Phys., 60 (1987) 1059.
7 Amos, R.D. and Rice, J.E., CADPAC: The Cambridge Analytic Derivatives Package, Version 4.0, Cambridge, 1987.
8 Hirschfelder, J.O., Curtiss, C.F. and Byrd, R.B., Molecular Theory of Gases and Liquids, 2nd ed., Wiley, New York, NY, 1964.
9 Subramhanyam, H.S., Prabha, C.S. and Krishnamurti, D., Mol. Cryst. Liq. Cryst., 28 (1974) 201.
10 Miller, K.J. and Savchik, J.A., J. Am. Chem. Soc., 101 (1979) 7206.
11 Kang, Y.K. and Ihon, M.S., Theor. Chim. Acta, 61 (1982) 41.
12 Slater, J.C., Phys. Rev., 36 (1930) 57.
13 Gasteiger, J. and Marsili, M., Tetrahedron, 36 (1980) 3219.
14 Hinze, J. and Jaffe, H.H., J. Am. Chem. Soc., 84 (1962) 540.
15 Hinze, J., Whitehead, M.A. and Jaffe, H.H., J. Am. Chem. Soc., 85 (1963) 148.
16 Hinze, J. and Jaffe, H.H., J. Am. Chem. Soc., 67 (1963) 1501.
17 Lide, D.R. (Ed.) Handbook of Chemistry and Physics, 71st ed., CRC Press, Boca Raton, FL, 1991.
18 Glen, R.C., Rose, V.S., Lindon, J.C., Ruane, R.J., Wilson, I.D. and Nicholson, J.K., J. Planar Chromatogr., 4 (1991) 432.