A Set of *Atom-in-Molecule* Polarizability Increments Derived by Means of the MINDO/3-FP Method

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In continuation of earlier work, a set of 90 non-cyclic organic compounds was used to determine *atom-in-molecule* polarizability increments employing Metzger's combination of the semiempirical MINDO/3-FP method and a partitioning of the molecular dipole moment. The group contained alcohols, ethers, amines, amides, and carboxylic acids. More than one hundred arbitrarily chosen molecules were then used to evaluate the new set of increments. This set of compounds does not overlap with the one used to derive the increments. The molecular polarizabilities calculated employing the increments were found to correlate nicely with the corresponding "experimental" values determined by means of the *Lorenz-Lorentz* equation. Thus, the atomic increments together with the correlation equation provide access to polarizabilities which might for example be used to calculate the dispersion- and induction contributions to the lattice energies of organic molecular crystals.

1. Introduction

Previously we reported the results of a semiempirical investigation [1 a] in which we calculated the molecular and *atom-in-molecule* polarizabilities of fourteen aliphatic amines using the MINDO/3-FP method together with a partitioning of the molecular dipole moment [2]. In spite of numerical differences the molecular MINDO/3-FP values were found to correlate nicely not only with the corresponding experimental polarizabilities, which can be calculated from densities, molecular weights, and refraction indices by means of the *Lorenz-Lorentz* equation, but also with those obtained by the method of Miller and Savchik [3]. Averaging the calculated polarizabilities of corresponding atoms in different molecules resulted in a set of *atom-in-molecule* polarizability increments for hydrogen, carbon, and nitrogen which could be used quite successfully to predict molecular polarizabilities [1]. While our earlier investigation was carried out as part of our work on the protonation energies of aliphatic amines [4–8], polarizabilities are also of high interest in many other fields like organic solid state chemistry. So, for example, they can be used together with molecular ionization potentials and atomic charges to calculate the dispersion [9] and induction contributions [2] to the lattice energy of organic molecular crystals. Otherwise these componentes are difficult to obtain [10–12] since large basis sets of high flexibility are required to calculate them directly.

In this paper we report the results of further work which led to additional polarizability increments for atoms in olefins with conjugated and isolated double bonds, carbonyl compounds such as aldehydes, ketones, amides, and carboxylic acids, as well as for those in mono- and polyfunctional alcohols and ethers. Ninety molecules were used to determine the increments. A complete geometry optimization was performed for each molecule with the MINDO/3 method [13], employing the standard program package [14]. The optimized structural parameters were then used to calculate molecular and atomic polarizabilities according to the method which has been outlined in more detail elsewhere [1, 2].

Choice of the electric field strength in the elements of the modified $\mathbf{H}^{\text{core}}$ matrix is by no means a trivial problem [1, 2]. On the one hand it has to cause a significant change in the molecular dipole moment, while on the other hand it should be still so low that hyperpolarizabilities do not play a significant role. In this paper we use a value of 1000 esu/cm$^2 = 5.83 \cdot 10^{-5}$ a.u., which turned out to yield quite satisfying results in our previous study [1].

2. Results and Discussion

The molecules used to determine the polarizability increments and their calculated molecular polarizabil-

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Table 1. MINDO/3-FP polarizabilities (α_{MFP}) of the molecules used to derive atomic polarizability increments in comparison w those obtained by the method of Miller and Savchik (α_{MS}) [3] and the experimental data (α_{ex}) which have been calculated from t listed densities (ϱ), molecular masses (M_r), and indices of refraction (n) by means of the *Lorenz-Lorentz* equation. All values in If not mentioned otherwise, the experimental data are from [15] ($\alpha_{ex} = 1.194 \cdot \alpha_{MFP} + 1.706$; $|r| = 0.981$).

Molecule	α_{MFP}	α_{MS}	α_{ex}	M_r	ϱ	n
1. H$_2$O	0.455	1.471	1.472	18.02	0.9982[1a]	1.332988[1b]
2. MeOH	1.757	3.277	3.263	32.04	0.7914	1.3288
3. EtOH	3.002	5.108	5.120	46.07	0.7893	1.3611
4. *n*-PrOH	4.225	6.946	6.949	60.11	0.8035	1.3850
5. *i*-PrOH	4.125	6.946	6.986	60.11	0.7855	1.3776
6. *n*-BuOH-1	5.471	8.788	8.782	74.12	0.8098	1.39931
7. *s*-BuOH	5.375	8.788	8.790	74.12	0.8063	1.3978[2]
8. *i*-BuOH	5.362	8.788	8.827	74.12	0.8027	1.39768[3,4]
9. *t*-BuOH	5.242	8.788	8.786	74.12	0.7887	1.3878
10. HOCH$_2$CH$_2$OH	3.519	5.851	5.753	62.07	1.1088	1.4318
11. HOCH$_2$CH(OH)Me	4.701	7.670	7.558	76.11	1.0361	1.4324
12. HOCH$_2$CH$_2$CH$_2$OH	4.752	7.670	7.500	76.11	1.0597	1.4398
13. HOCH$_2$CH(OH)Et	5.957	9.498	9.351	90.12	1.0024	1.4378[2]
14. HOCH$_2$CH$_2$CH(OH)Me	5.920	9.498	9.383	90.12	1.0053	1.4410[2]
15. HOCH$_2$CH$_2$CH$_2$CH$_2$OH	6.017	9.498	9.365	90.12	1.0171	1.4460
16. MeCH(OH)CH(OH)Me	5.952	9.498	9.350	90.12	1.0003	1.4367[8,9]
17. HOCH$_2$CMe$_2$(OH)	5.859	9.498	9.299	90.12	1.0024	1.4350
18. HOCH$_2$CHMeCH$_2$OH	5.909	9.498[10]				
19. MeOMe	3.224	5.108	5.160[5]			
20. MeOEt	4.561	6.946	6.919	60.10	0.7252	1.3420[6]
21. MeO*n*-Pr	5.831	8.788	8.740	74.12	0.738	1.3579
22. MeO*i*-Pr	5.743	8.788	8.913	74.12	0.7237	1.3576[7]
23. EtOEt	5.908	8.788	8.916	74.12	0.7138	1.3526
24. MeOCH$_2$CH$_2$OMe	6.776	9.498	9.580	90.12	0.8629	1.3796
25. EtOCH$_2$CH$_2$OEt	9.578	13.168	12.969	118.18	0.8484	1.3860[11]
26. MeOCH$_2$CH$_2$OH	5.094	7.670	7.621	76.11	0.9647	1.4024
27. EtOCH$_2$CH$_2$OH	6.449	9.498	9.479	90.12	0.9297	1.4080
28. MeOCH$_2$CH(OH)Me	6.362	9.498[10]				
29. MeOCH$_2$CH(Me)OH	6.279	9.498[10]				
30. MeOCH$_2$CH$_2$CH$_2$OH	6.381	9.498[10]				
31. HOCH$_2$NHMe	4.233	6.637[10]				
32. HOCH$_2$NMe$_2$	5.565	8.474[10]				
33. HOCH$_2$CH$_2$NH$_2$	4.062	6.637	6.443	61.09	1.0180	1.4541
34. HOCH$_2$CH$_2$CH$_2$NH$_2$	5.302	8.474	8.327	75.11	0.9824	1.4617[12]
35. HOCH$_2$CHMeNH$_2$	5.275	8.474[10]				
36. HCOOH	2.046	3.469	3.394	46.03	1.220	1.3714
37. MeCOOH	3.154	5.255	5.151	60.05	1.0492	1.3716
38. H$_2$CO	1.569	2.676[10]				
39. MeHCO	2.792	4.496	4.567	44.05	0.7834	1.3316[13]
40. H$_2$C=CHCH$_2$CHO	5.419	7.927[10]				
41. Z-*cis*-MeHC=CHCHO	5.791	7.927[10]				
42. E-*cis*-MeHC=CHCHO	5.928	7.927[10]				
43. Z-*trans*-MeHC=CHCHO	5.966	7.927[10]				
44. E-*trans*-MeHC=CHCHO	6.077	7.927[10]				
45. E-MeHC=CHCH$_2$CHO	7.267	9.770[10]				
46. *trans*-H$_2$C=CHCHO	4.256	6.086	6.430	56.07	0.8410	1.4017
47. *trans*-H$_2$C=CMeCHO	5.525	7.927	8.301	70.09	0.8370	1.4144
48. Me$_2$CO	3.888	6.330	6.413	58.08	0.7899	1.3588
49. EtMeCO	5.189	8.169	8.198	72.12	0.8054	1.3788
50. Et$_2$CO	6.482	10.01	10.000	86.14	0.8138	1.3924
51. H$_2$C=CHCH$_2$COMe	6.850	9.770[10]				
52. Z-*cis*-MeHC=CHCOMe	7.043	9.770[10]				
53. E-*cis*-MeHC=CHCOMe	7.168	9.770[10]				
54. Z-*trans*-MeHC=CHCOMe	7.125	9.770	10.089	84.13	0.8624	1.4350
55. E-*trans*-MeHC=CHCOMe	7.216	9.770[10]				
56. HCONH$_2$	2.585	3.850	4.210	45.04	1.1334	1.4472
57. HCONHMe	4.100	5.658	6.006	59.07	1.011	1.4319[1
58. HCONMe$_2$	5.463	7.482	7.897	73.09	0.9487	1.4305
59. MeCONH$_2$	3.707	5.658	6.030	59.07	0.9986	1.4278[1
60. MeCONHMe	5.251	7.482	7.822	73.10	0.9571	1.4301[1
61. MeCONMe$_2$	6.672	9.314	9.678	87.12	0.9366	1.4380[1
62. EtCONH$_2$	4.995	7.482	7.850	73.10	0.9262	1.4160[1
63. H$_2$C=CHCH$_2$NH$_2$	4.862	7.572[10]				
64. H$_2$C=CHCH$_2$NHMe	6.391	9.419[10]				
65. H$_2$C=CHCH$_2$NMe$_2$	7.784	11.266[10]				
66. H$_2$C=CHCMeHNMe$_2$	8.893	13.113[10]				
67. H$_2$C=CMeCH$_2$NMe$_2$	8.979	13.113[10]				
68. H$_2$C=CH$_2$	2.350	4.227	4.26[5]			
69. MeHC=CH$_2$	3.874	6.068	5.643	42.08	0.647	1.3567[1
70. E-MeHC=CHMe	5.620	7.912	8.624	56.12	0.6042	1.3848[1
71. Z-MeHC=CHMe	5.384	7.912	8.547	56.12	0.6213	1.3931[1
72. Me$_2$C=CH$_2$	5.128	7.912	8.925	56.11	0.5942	1.3926[1
73. Me$_2$C=CHMe	6.800	9.575	9.892	70.14	0.6623	1.3874
74. Me$_2$C=CMe$_2$	8.174	11.603	11.729	84.16	0.7080	1.4122
75. *trans*-H$_2$C=CHCH=CH$_2$	5.681	7.693	8.903	54.09	0.6211	1.4292[1
76. E-*trans*-H$_2$C=CHHC =CHMe	7.731	9.536	10.322			
77. Z-*trans*-H$_2$C=CHHC =CHMe	7.592	9.536	10.322	68.13	0.6760	1.4301
78. *trans*-H$_2$C=CMeHC =CH$_2$	6.851	9.536	10.075	68.13	0.6810	1.4219
79. Z-*trans*-MeHC=CHHC =CHMe	9.680	11.38	12.160	82.15	0.7196	1.4500
80. Z-*trans*-H$_2$C=CMeHC =CHMe	8.756	11.380[10]				
81. *trans*-H$_2$C=CHHC =CMe$_2$	9.230	11.380[10]				
82. *trans*-Me$_2$C=CMeHC =CMe$_2$	14.338	16.541[10]				
83. *trans*-Me$_2$C=CMeMeC =CMe$_2$	14.337	16.917[10]				
84. *trans*-H$_2$C=CMeHC =CMe$_2$	10.334	13.225[10]				
85. *trans*-Me$_2$C=CHHC =CMe$_2$	13.308	15.071	16.230	110.20	0.7625	1.4785
86. *trans*-Me$_2$C=CHMeC =CHMe	15.071	12.566[10]				
87. *trans*-H$_2$C=CHMeC =CMe$_2$	10.402	13.225[10]				
88. *trans*-Me$_2$C=CHHC =CHMe	11.286	13.225[10]				
89. *trans*-Me$_2$C=CMeHC =CHMe	12.584	15.071[10]				
90. *cis*-H$_2$C=CHCHO	4.130	6.086[10]				

[1] from [16]; [2] racemat; [3] from [17]; [4] n_D^{15}; [5] experimental polarizability from [3]; [6] d_0^{10}, n_D^{4}; [7] d_4^{15}; [8] n_D^{25}; [9] meso; [10] no experimental d available in [15] and [17]; [11] d^{20}; [12] d_4^{26}; [13] d_4^{18}; [14] d^{19}; [15] d_4^{85}; n_D^{78}; [16] d_4^{25}; [17] d^{110}, n_D^{110}; [18] n_D^{-70} [15], d^{-79} [17a], [19] n_D^{-25}; [20] n_D

ities are listed in Table 1 together with the available "experimental" values calculated by means of the *Lorenz-Lorentz* equation. In addition the corresponding values obtained by the method of Miller and Savchik [3] are listed. The influence of alkyl substitution on *atom-in-molecule* polarizabilities has been studied only for the methyl group. However, the effect of alkyl substituents different from methyl on the atomic polarizabilities of the heavy atom skeleton is not likely to differ significantly from that of the methyl group. Thus we believe that the influence discussed for methyl is a good approximation to the influence of other alkyl substituents, too.

Taking into account the modest size of the basis set employed within the framework of the MINDO/3 method and especially the lack of diffuse and polarization functions it is not surprising that the MINDO/3-FP polarizabilities are clearly smaller than the empirical data (cf. Table 1). On the average the molecular MINDO/3 polarizabilities amount to 65% of the experimental values.

With a correlation coefficient of about 0.980 the relationship between calculated and empirical data is close to linearity as shown in Fig. 1, where the MINDO/3-FP polarizabilities of 57 molecules are plotted against the corresponding experimental values.

2.1. Hydrogen

As before [1] we calculated a mean polarizability for the hydrogen atoms of each molecule and subsequently averaged those mean values over all molecules. The finally obtained average value for hydrogen is 0.187 Å^3 and, therefore, essentially identical with the one obtained previously.

2.2. Oxygen

2.2.1. Alcohols

Among the alcohols considered in this study were mono- (**2–9**[a], cf. Table 1.) and polyfunctional species (**10–18**), amino alcohols (**31–35**), but also mixed compounds containing ether oxygen besides alcoholic hydroxyl groups (**26–30**).

The polarizabilities of the hydroxylic oxygen atoms are quite similar in all compounds of this class and thus calculation of a global average value does not cause any problem. If a molecule contains more than one hydroxylic oxygen atom, first the average value for each molecule was determined. The final atomic increment was then derived subsequently by averaging over the mean values of all members of the class. The increment to be used for the hydroxylic oxygen atom in alcohols obtained in this way is 0.372 Å^3.

2.2.2. Ethers

Substitution of the hydrogen atom in alcohols by an alkyl group, resulting in an ether (**19–30**), almost doubles the polarizability of the oxygen atom. The scattering range of the polarizabilities of the ether oxygen atoms is somewhat wider than among the alcohols and the calculated general mean value is 0.631 Å^3 for the ethers.

2.2.3. Aldehydes

The aldehydes have to be divided into two main categories: (i) those containing a C=C double bond which is in conjugation with the carbonyl group like **41–44**, **46**, **47**, and **90**, and (ii) such molecules which either do not contain an additional C=C double bond like **38** and **39** or where the C=C segment is separated from the carbonyl groups by a methylene group (**40**, **45**).

For the carbonyl oxygen atom of the aldehydes which are either entirely aliphatic (including H_2CO) or contain only isolated C=C bonds we calculated an average polarizability of 0.374 Å^3.

It is interesting to compare the polarizability of the carbonyl oxygen in *cis*[b] compounds **41**, **42**, and **90** with those in *trans* species **43**, **44**, and **46**. On the average, the polarizability is 0.077 Å^3 higher in the *trans* isomers. The corresponding increments are 0.365 Å^3 for the *cis* and 0.442 Å^3 for the *trans* isomer, respectively. The general mean value amounts to 0.403 Å^3.

2.2.4. Ketones

For the carbonyl oxygen of those ketones which do not contain C=C double bonds in conjugation with the C=O group (**48–51**) we obtained an average polarizability of 0.380 Å^3. Like in the case of the aldehydes, if the carbonyl group of the ketone is conjugated with an olefinic double bond, the polarizability of the carbonyl oxygen is higher in the *trans* than in the *cis* species. The mean value obtained from **54** and **55** is 0.449 Å^3. From **52** and **53** we obtain a value of 0.367 Å^3 for the *cis* species. These polarizabilities are almost identical with those calculated for the aldehydes, indicating that the influence of the second alkyl substituent on the relatively remote carbonyl oxygen is only weak.

2.2.5. Carboxylic Acids

For the carbonyl oxygen and the oxygen atom of the hydroxyl group we obtained average polarizabilities of 0.361 and 0.406 Å^3, respectively.

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[a] The numbers refer to Table 1.

[b] The *cis/trans*- and Z/E nomenclatures are used side by side in this paper. While Z/E defines the arrangement of substituents at a double bond, *cis/trans* describes the relative orientation of two conjugated double bonds.

2.2.6. Amides

The polarizability of the carbonyl oxygen in amides is almost independent of the number of alkyl groups at the nitrogen atom. The values cover the range between 0.378 Å^3 in **60** and 0.401 Å^3 in **57**, and the average value calculated from compounds **56–62** is 0.398 Å^3.

2.3. Nitrogen

2.3.1. Amines

The group of amines considered here comprises the primary amines **33–35** and **63**, secondary amines **31** and **64**, and the tertiary nitrogen bases **32** and **65–67**.

Use of the molecules **33–35** and **63** together with those examined in [1] leads to an average polarizability of 0.612 Å^3 for the primary nitrogen atom, a value almost identical with the one obtained previously. Re-evaluation of the values for the secondary and tertiary nitrogen atoms under inclusion of the bases used in [1], resulted in slightly higher values of 0.778 Å^3 (vs. 0.77 Å^3 in [1]) and 0.951 Å^3 (vs. 0.94 Å^{3}in [1]).

2.3.2. Amides

An adjacent carbonyl group increases the polarizability of a nitrogen atom. This surprising result shows that the proton affinity of nitrogen bases is obviously not predominantly determined by the polarizability of the basic center. Compared with the corresponding amines the proton affinities (protonation of the nitrogen atom) of the amides are significantly reduced. Thus, for example, the proton affinity of methylamine (298 K)[c] calculated at the ZPE + MP2/6-31 + +G**// HF/6-31 + +G**[d] level is $PA_{\mathrm{cal}} = 216.5$ kcal/mol (experimental value: 218.4 kcal/mol [18]), while the corresponding value for protonation of the nitrogen atom of formamide is 190.9 kcal/mol.

Three primary amides were considered (**56**, **59**, and **62**), from which we calculated an average value of 0.662 Å^3 for the polarizability of the nitrogen atom. From the molecules **57** and **60** we got an increment of 0.880 Å^3 for the nitrogen in secondary amides, while using **58** and **61** a value of 1.104 Å^3 is obtained in the case of the tertiary compounds.

2.4. Carbon

In the preceding paper [1] we did not differentiate between carbon atoms in methyl- and methylene groups. In order to make our increment system more sensitive toward structural differences, we decided to determine not only separate increments for carbon atoms in formally different hybridization states (sp, sp^2, sp^3) but also for those with a different chemical environment within one of these groups.

2.4.1. Singly Bonded Carbon

2.4.1.1. Methyl Groups

In the case of the methyl group we calculated separate carbon increments for those attached to carbon, oxygen, and nitrogen. So, e.g., using compounds **31**, **32**, **57**, **58**, **60**, **61**, **64–67** we obtained an average polarizability of 0.781 Å^3 for methyl carbons attached to a nitrogen atom. From **2**, **19–22**, **26**, and **28–30** we calculated a value of 0.764 Å^3 for a methyl carbon atom attached to oxygen. Finally the polarizability increment of a methyl carbon attached to another carbon atom turned out to be 0.729 Å^3.

2.4.1.2. Methylene Groups

The polarizability of the carbon atom of a methylene group is in general higher than that of a methyl carbon. Thus the value for those methylene groups which are bonded to a hydroxylic oxygen and another carbon atom is 0.853 Å^3 (**3**, **4**, **6**, **8**, **10–15**, **17**, **18**). A significantly higher polarizability of 0.937 Å^3 is obtained for the carbon atom of a methylene group attached to an alkoxy group and another carbon atom (**20**, **21**, **24–30**), while the average value for the atomic polarizability of methylene carbons linked to two other carbon atoms is 0.874 Å^3 (**4**, **6**, **7**, **12–15**, **21**). In those cases where the methylene group is bonded to both, a hydroxyl group and a nitrogen atom (**31**, **32**), the increment is 0.944 Å^3. For the C atom of a CH$_2$ groups attached to one nitrogen and another carbon atom only (**33**, **34**, **63–65**, **67**) we calculated a value of 0.971 Å^3.

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[c] $\mathrm{PA}_{\mathrm{cal}} = -\Delta E_{\mathrm{tot}} + 5/2 \cdot R \cdot T$, where R is the gas constant (8.31441(26) J · mol^{-1} · K^{-1} [15]), T the temperature in K, and ΔE_{tot} the energy difference between the protonated base ($E_{\mathrm{tot}}(\mathrm{B}^+ - \mathrm{H})$) and the neutral molecule ($E_{\mathrm{tot}}(\mathrm{B})$) including zero point energy and correlation effects.

[d] ZPE + MP2/6-31 + +G**//HF/6-31 + +G** means that an *ab initio* calculation was performed with the 6-31 + +G** basis set including correlation energy calculated with the MP2 method. The zero point energy and the geometry wave obtained with the same basis set at the one determinant level (Hartree Fock, HF).

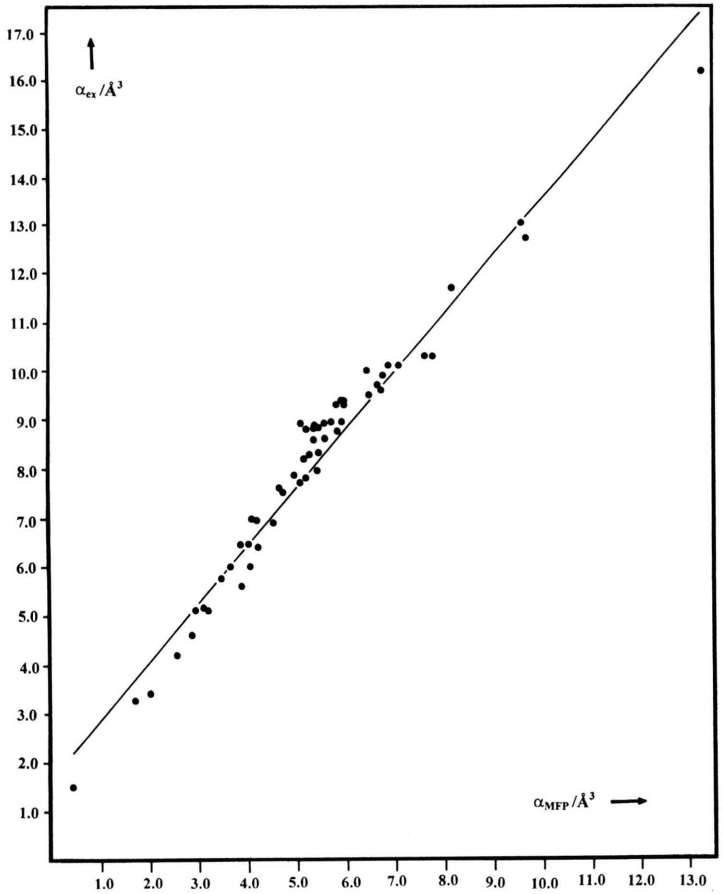

Fig. 1. Molecular MINDO/3-FP polarizabilities (α_{MFP}) and the corresponding experimental values calculated by the equation of *Lorenz* and *Lorentz* (α_{ex}). All values in $Å^3$.

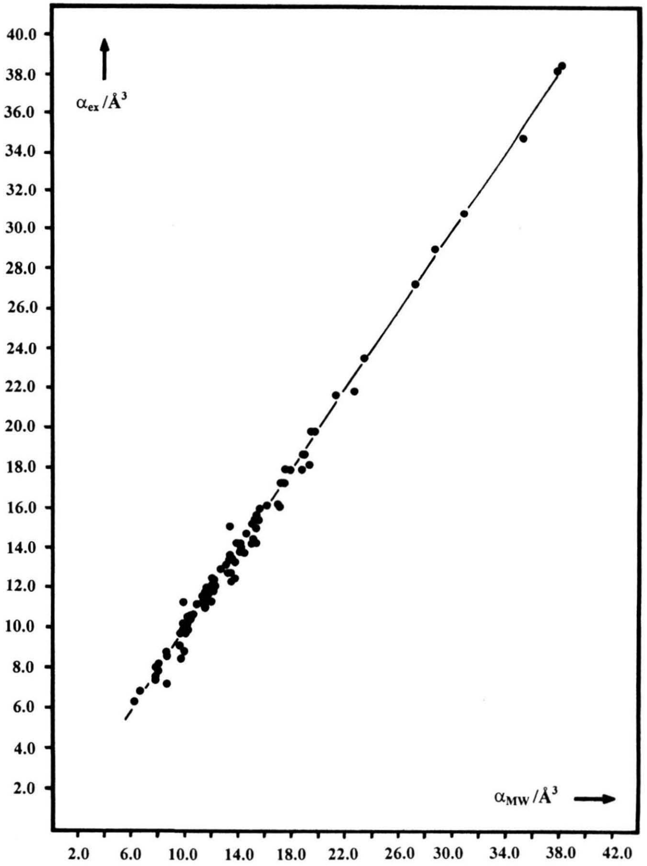

Fig. 2. Comparison of molecular polarizabilities calculated from the *atom-in-molecule* increments in Table 2 and the correlation equation in Table 3 (α_{MW}) with the corresponding experimental values calculated by means of the equation of *Lorenz* and *Lorentz* (α_{ex}). All values in $Å^3$.

2.4.1.3. Methine Groups

The average polarizability of the methine carbons connected only to C atoms, is 1.026 Å^3, while we obtained a slightly lower value of 0.977 Å^3 if one of the substituents is oxygen. A higher value of 1.134 Å^3 is obtained from **66** where one carbon atom is replaced by nitrogen. Finally, for carbon atoms which are of the formal sp^3 type but do not carry any hydrogen atoms (**17**) we calculated a polarizability of 1.086 Å^3.

2.4.2. Doubly Bonded Carbon Atoms

2.4.2.1. Olefins

The polarizabilities of olefinic doubly bonded carbon atoms scatter widely. The lowest value among the molecules under consideration (0.841 Å^3) is obtained for ethene (**68**), while the highest polarizability for an olefinic carbon atom (2.027 Å^3) was calculated for pentamethyl butadiene (**82**). If one hydrogen atom in ethene is replaced by a methyl group the polarizability of both doubly bonded carbon atoms is increased. The value for the carbon atom carrying the substituent is somewhat higher (1.075 Å^3) than that of the carbon atom of the $=CH_2$ residue (0.960 Å^3). Very similar values were calculated if one of the hydrogens in ethene is substituted by $R^1 = -CH_2-CHO$ (**40**), $-CH_2-CO-CH_3$ (**51**), $-CH_2-NH_2$ (**63**), $-CH_2-NH-CH_3$ (**64**), $-CH_2-N(CH_3)_2$ (**65**), $-CH(CH_3)-N(CH_3)_2$ (**66**), or even a $-CHO$ group (**46**). Thus, an average polarizability of 1.106 Å^3 was calculated for the $R^1HC=$ carbon atom, while we obtained a value of 0.961 Å^3 for the carbon atom in the adjacent $=CH_2$ group. The polarizabilities of both olefinic carbon atoms are further increases if the remaining hydrogen atom of the $H-CR^1$ group is replaced by $R^2 = -CH_3$. The values are 1.225 Å^3 for the olefinic carbon of the $=C(CH_3)_2$ group and 1.035 Å^3 for that of the $=CH_2$ residue (**72**). Again, quite similar values are obtained when R^2 is $-CHO$ (**47**) or $-CH_2N(CH_3)_2$ (**67**). The average polarizability of a doubly bonded carbon atom carrying two alkyl groups or one alkyl substituent besides a $-CHO$ group is 1.266 Å^3, while the polarizability increment for the carbon of the corresponding $=CH_2$ group is 1.034 Å^3. Somewhat higher values are obtained when both carbon atoms of the double bond are singly substituted. In this case we have to differ between molecules where the relative orientation of the methyl groups is Z or E. Slightly higher values are obtained if the relative orientation of the substituent is E (1.249 Å^3 in **70** vs. 1.212 Å^3 in **71**). If the second substituent R^2 (E) is not a simple alkyl group but $-CH_2CHO$ (**45**), the polarizabilities of both C atoms of the $C=C$ unit are higher. From **45**, **70**, and **71** we obtained an average value of 1.243 Å^3 for the atoms of the olefinic double bond. Somewhat higher values for the doubly bonded carbon atom of the $R^2HC=$segment are obtained if R^2 is a $-CHO$ group (**41–44**). In this case we not only have to distinguish between E and Z isomeres but also to make a distinction between *cis* and *trans* orientation of the two double bonds. Regardless whether the double bonds are *cis* or *trans*, the polarizabilities of the olefinic carbon atoms are slightly higher in the E than in the Z isomer. Moreover, they are higher for the *trans* than for the *cis* form. However, since these differences are not too large we calculated average values which are 1.319 Å^3 for the olefinic carbon atom carrying the $-CHO$ substituent and 1.249 Å^3 for the one being bonded to the alkyl group. If the hydrogen atom of the $-CHO$ residue is replaced by a methyl group (**52–55**) especially the polarizability of the α-carbon atom is somewhat increased. As to be expected, the influence on the remote second C atom of the double bond is only weak. The calculated average polarizabilities of the ethylene carbons are 1.350 Å^3 for the one carrying the acetyl group and 1.264 Å^3 for the one bonded to the alkyl substituent. Averaging over the values for aldehydes and ketones results in an *atom-in-molecule* polarizability of 1.257 Å^3 for the carbon atom carrying the alkyl substituent in a 1,2-disubstituted ethylene while the second substituent is $-CHO$ or an acetyl group.

A third (**73**) and a fourth (**74**) methyl group further increases the polarizabilities of the doubly bonded carbons and the corresponding values are 1.372 Å^3 (average) and 1.531 Å^3, respectively.

Things are much more complicated in the case of conjugated olefinic double bonds. If one hydrogen in ethene is substituted by a vinyl group, resulting in *trans*-butadiene (**75**), the polarizabilities of both doubly bonded carbon atoms increase significantly (C^2: 1.266 and C^1: 1.073, vs. 0.841 Å^3 in ethene). If one of the hydrogen atoms at C^1

$$C^1=C^2-C^3=C^4$$

is replaced by a methyl group, the polarizabilities of all four carbon atoms are further increased. Again, the stronger increase is obtained for the E isomer (**76**). In both, the Z- as well as the E-isomer, the stronger raise

Table 2. Polarizability increments derived using the MINDO3/FP *atom-in-molecule* polarizabilities of the molecules listed in Table 1 (in Å^3). The relevant atoms are flagged with a (*).

Hydrogen	
H	: 0.187
Oxygen	
(i) alcohols, ethers	
R^1-O^*-H	: 0.372 R^1 = alkyl
$R^1-O^*-R^2$	: 0.631 R^1, R^2 = alkyl
(ii) aldehydes, ketones, amides, acids	
$R^1-HC=O^*$	: 0.374 R^1 = H, alkyl
	0.403 $R^1 = -C=C-$ average
	0.365 $R^1 = -C=C-$ *s-cis* fixed
	0.442 $R^1 = -C=C-$ *s-trans* fixed
$R^1R^2C=O^*$	: 0.380 R^1 = alkyl
	0.408 $R^1 = -C=C-$ average
	0.367 $R^1 = -C=C-$ *s-cis* fixed
	0.449 $R^1 = -C=C-$ *s-trans* fixed
$R^1C(=O)O^*H$	: 0.406 R^1 = H, alkyl
$R^1C(=O^*)OH$	: 0.361 R^1 = H, alkyl
$R^1-C(=O^*)NR^2R^3$	: 0.389 R^1 = H, alkyl; R^2, R^3 = H, alkyl
Nitrogen	
(i) amines	
$R^1N^*H_2$	: 0.612 R^1 = alkyl
$R^1R^2N^*H$	: 0.778 R^1, R^2 = alkyl
$R^1R^2R^3N^*$	: 0.951 R^1, R^2, R^3 = alkyl
(ii) amides	
$R^1-C(=O)N^*H_2$	: 0.662 R^1 = H, alkyl
$R^1-C(=O)N^*HR^2$	: 0.880 R^1 = H, alkyl, R^2 = alkyl
$R^1-C(=O)N^*R^2R^3$	: 1.104 R^1 = H, alkyl; R^2, R^3 = alkyl
Carbon	
(i) saturated	
$N-C^*H_3$	: 0.781
$O-C^*H_3$	: 0.764
$C-C^*H_3$	: 0.729
$HO-C^*H_2R^1$	: 0.853 R^1 = alkyl
$R^1O-C^*H_2R^2$	: 0.937 R^1, R^2 = alkyl
$C-C^*H_2-C$	: 0.874
$N-C^*H_2-OH$	: 0.944
$N-C^*H_2R^1$	: 0.971 R^1 = alkyl
C_3C^*-H	: 1.026
C_2OC^*-H	: 0.977
C_2NC^*-H	: 1.134
C_3C^*-C	: 1.086
(ii) olefinic	
$H_2C^*=C^*H_2$	: 0.841
$R^1HC^*=CH_2$	: 1.106 $R^1 = -CHO$, $-CH(CH_3)-N(CH_3)_2$, $-CH_2R^2$ (R^2 = H, $-CHO$, $-COCH_3$, $-NH_2$, $-NHCH_3$, $-N(CH_3)_2$)
$R^1HC=C^*H_2$	: 0.961 $R^1 = -CHO$, $CH(CH_3)-N(CH_3)_2$, $-CH_2R^2$ (R^2 = H, $-CHO$, $-COCH_3$, $-NH_2$, $-NHCH_3$, $-N(CH_3)_2$)
$R^1R^2C^*=CH_2$	: 1.266 R^1 = alkyl, $R^2 = -CH_2N(CH_3)_2$, $-CHO$
$R^1R^2C=C^*H_2$	: 1.034 R^1 = alkyl, $R^2 = -CH_2N(CH_3)_2$, $-CHO$
$R^1HC^*=C^*HR^2$	: 1.243 R^1 = alkyl, $R^2 = -CH_2-CHO$
$R^1HC=C^*H-CHO$	: 1.319 R^1 = alkyl
$R^1HC^*=CH-CHO$	: 1.249 R^1 = alkyl
$R^1HC=C^*H-CO-R^2$	: 1.350 R^1, R^2 = alkyl
$R^1HC^*=CH-CO-R^2$	: 1.264 R^1, R^2 = alkyl
$R^1HC^*=C^*R^2R^3$	: 1.372 R^1, R^2, R^3 = alkyl
$R^1R^4C^*=C^*R^2R^3$	: 1.531 R^1, R^2, R^3, R^4 = alkyl
$H_2C=C^*HCH=CH_2$	: 1.266
$H_2C^*=CHCH=CH_2$	: 1.073
$R^1HC^*=C^*HCH=CH_2$	: 1.447 R^1 = alkyl
$H_2C^*=C^*R^1HCH=CH_2$	: 1.252 R^1 = alkyl
$R^1R^2C=CR^3C^*H=CH_2$	: 1.382 R^1, R^2, R^3 = alkyl
$R^1R^2C=CR^3CH=C^*H_2$	: 1.146 R^1, R^2, R^3 = alkyl
$R^1R^2C^*=C^*R^3CH=CH_2$	: 1.758 R^1, R^2, R^3 = alkyl
$R^1R^2C^*=C^*HCH=CH_2$	: 1.641 R^1, R^2 = alkyl
(iii) carbonylic	
$R^1R^2C^*=O$	: 1.062 R^1, R^2 = alkyl; R^1 = alkyl, R^2 = vinyl
$R^1HC^*=O$	: 0.980 R^1 = alkyl, vinyl
R^1C^*OOH	: 0.980 R^1 = H, alkyl
$R^1(C^*=O)NR^2R^3$	: 1.140 R^1 = H, alkyl, R^2, R^3 = alkyl

occurs at carbon atom C^2. The increase of the polarizability is less pronounced when the methyl group is bonded to C^2 (**78**). In contrast to 1-methyl butadiene now the polarizability of the substituted carbon atom is the highest. If the methyl group is linked to carbon atom C^1, one obtains an average polarizability of 1.447 Å^3 for C^1 and C^2 (**76**, **77**), while a clearly lower value of 1.252 Å^3 emerges when C^2 carries the methyl group (**78**).

If an additional hydrogen atom at C^4 is replaced by a methyl group, so that both double bonds are substituted (**79**), a further significant increase of the polarizability of the doubly bonded carbon atoms occurs (average value 1.542 Å^3). And again, the polarizabilities of the two central carbons (1.584 Å^3) are higher than those of the *termini* (1.499 Å^3). If the second methyl group is bonded to C^3 (**80**), the polarizabilities of the multiply bonded carbon atoms are lower than in the former case (average value: 1.368 Å^3) with the highest value at carbon atom C^3. In 1,1-dimethyl butadiene the highest polarizability is not obtained for C^1 but rather for C^2 (**81**).

In molecules where only one of the vinyl groups (C^1 = C^2) of butadiene is substituted, the polarizabilities of the carbon atoms of the unsubstituted moiety (C^3 = C^4) only slightly depends on the number of methyl substituents in the former one. Thus, we used **76–78**, **81**, and **87** to calculate average values of 1.382 and 1.146 Å^3 for C^3 and C^4, respectively.

In the case of the higher substituted butadienes the relationship between the substitution pattern and the polarizabilities of the backbone carbons is so complex that it is the best not to determine any average values but rather to use the individually calculated *atom-in-molecule* polarizabilities.

Table 3. Polarizabilities of several molecules chosen arbitrarily to test the derived increments. α'_{MW} denotes the values calculated directly from the increments listed in Table 2. α_{MW} was obtained form the correlation between the experimental values and α'_{MW}. For reasons of comparison the corresponding values calculated by the method of Miller and Savchik [3] (α_{MS}) are also listed. The experimental data were calculated by means of the *Lorenz-Lorentz* equation using the molecular masses, indices of refraction, and densities listed in Table 4. All values in Å^3. $\alpha_{MW} = 1.472 \cdot \alpha'_{MW} + 0.151$; $|r| = 0.997$.

Molecule	α'_{MW}	α_{MW}	α_{MS}	α_{ex}
1. *n*-$C_5H_{11}OH$	6.820	10.19	10.63	10.63
2. *n*-$C_6H_{13}OH$	8.068	12.03	12.48	12.54
3. *n*-$C_7H_{15}OH$	9.316	13.86	14.32	14.33
4. *n*-$C_8H_{17}OH$	10.564	15.70	16.17	16.11
5. *n*-$C_9H_{19}OH$	11.812	17.54	18.01	17.97
6. *n*-$C_{10}H_{21}OH$	13.060	19.37	19.86	19.82
7. *n*-$C_{11}H_{23}OH$	14.308	21.21	21.70	21.66
8. $C_{13}H_{27}CH(OH)CH_3$	19.279	28.54	29.09	29.01
9. *n*-$C_{20}H_{41}OH$	25.540	37.73	38.32	38.20
10. $HOC_5H_{10}OH$	7.316	10.92	11.33	11.15
11. $HOC_6H_{12}OH$	8.564	12.76	13.17	13.04
12. $HOC_7H_{14}OH$	9.812	14.59	15.01	14.77
13. $HOCH_2CH(OH)CH_2OH$	5.295	7.94	8.43	8.14
14. $HOCH_2CH(OH)C_2H_4OH$	6.543	9.78	10.24	11.50
15. $HOC_2H_4CH(OH)C_2H_4OH$	7.791	11.62	12.06	11.95
16. $HOCH_2CH(OH)CH(OH)C_3H_7$	9.018	13.42	13.89	13.67
17. $HOC_3H_6CH(OH)C_3H_7OH$	10.287	15.29	15.72	15.32
18. *n*-PrOEt	7.081	10.57	10.63	10.69
19. *n*-PrO*n*-Pr	8.329	12.41	12.48	12.77
20. *n*-BuO*i*-Pr	9.472	14.09	14.32	14.28
21. *n*-BuO*n*-Bu	10.825	16.08	16.17	16.25
22. *n*$C_7H_{15}OEt$	12.073	17.92	18.01	17.98
23. *n*-C_5H_{11}O*n*-C_5H_{11}	13.321	19.76	19.86	19.93
24. *n*-C_6H_{13}O*n*-C_6H_{13}	15.817	23.43	23.55	23.59
25. *n*-C_7H_{15}O*n*-C_7H_{15}	18.313	27.11	27.24	27.27
26. *n*-C_8H_{17}O*n*-C_8H_{17}	20.809	30.78	30.94	30.96
27. *n*-$C_{10}H_{21}$O*n*-$C_{10}H_{21}$	25.801	38.13	38.32	38.35
28. $MeOC_2H_4OEt$	7.810	11.65	11.33	11.39
29. *n*-$PrOC_2H_4OH$	7.557	11.27	11.33	11.30
30. *n*-$BuOC_2H_4OH$	8.825	13.14	13.17	13.14
31. $HOC_2H_4OC_2H_4OC_2H_4OH$	10.078	14.98	14.63	14.27
32. $MeOC_2H_4OC_2H_4OC_2H_4OMe$	13.040	19.34	18.28	18.18
33. *n*-$BuOC_2H_4OC_2H_4OC_2H_4OH$	15.331	22.72	21.94	21.93
34. $HOCH_2CH(OMe)CH_2OH$	6.692	10.00	10.24	10.07
35. $HOCH_2CH(OH)CH_2OMe$	6.776	10.12	10.24	10.00
36. $HOCH_2CH(OMe)CH_2OMe$	8.173	12.18	12.06	11.93
37. $MeOCH_2CH(OMe)CH_2OMe$	9.654	14.36	13.89	13.79
38. $HOC_2H_4CH(OMe)CH_2CH(OMe)Me$	11.812	17.54	17.55	17.35
39. *cyclo*-$C_6H_{11}OH$	7.963	11.87	11.74	11.38
40. C_4H_4O [1]	5.749	8.61	8.06	7.20
41. $C_4H_8O_2$ [2]	6.506	9.73	8.79	8.59
42. $H_2C(OMe)_2$	5.223	7.84	7.67	7.58
43. $H_2C(OEt)_2$	7.775	11.60	11.33	11.35
44. $H_2C(\text{O-}n\text{-Pr})_2$	10.271	15.27	15.01	15.02
45. $H_2C(\text{O-}n\text{-Bu})_2$	12.767	18.94	18.69	18.76
46. $MeCH(OEt)_2$	8.918	13.28	15.01	15.12
47. $C_4H_9CH(OEt)_2$	12.662	18.79	18.69	18.69
48. $C_{15}H_{31}CH(OMe)_2$	23.838	35.24	35.29	34.91
49. $H_2C=CHC_3H_7$	6.414	9.59	9.76	9.85
50. Z-MeHC=CHEt	6.688	10.00	9.76	9.89
51. E-MeHC=CHEt	6.688	10.00	9.76	9.92
52. H_2C=CH*n*-Bu	7.662	11.43	11.60	11.58
53. $(H_2C=CHCH_2\text{-})_2$	7.752	11.56	11.38	11.58
54. H_2C=C(Me)*n*-Pr	7.750	11.56	11.60	11.69
55. Z-MeHC=CH*n*-Pr	7.936	11.83	11.60	11.71
56. E-MeHC=CH*n*-Pr	7.936	11.83	11.60	11.75
57. $H_2C=CHC_2H_4HC=CHMe$	9.274	13.80	13.23	13.43
58. H_2C=CH*n*-C_5H_{11}	8.910	13.27	13.45	13.53
59. H_2C=C(Me)*n*-Bu	8.998	13.40	13.45	13.60
60. $[H_2C=C(Me)CH_2\text{-}]_2$	10.424	15.49	15.07	15.32
61. H_2C=CH*n*-C_6H_{13}	10.158	15.10	15.30	15.37
62. E-*n*-PrHCCH*n*-Pr	10.432	15.51	15.30	15.48
63. H_2C=C(Me)*n*-C_5H_{11}	10.246	15.23	15.49	15.38
64. H_2C=C(Me)*n*-C_6H_{13}	11.494	17.07	16.05	17.19
65. E-*n*-PrHC=CH*n*-Bu	11.680	17.34	17.14	17.32
66. Z-*cyclo*-$(C_3H_6HC=CH)$	6.604	9.87	9.01	8.90
67. Z-*cyclo*-$(C_4H_{10}HC=CH)$	7.852	11.71	10.60	11.73
68. Z-*cyclo*-$(C_5H_{10}HC=CH)$	9.100	13.55	12.70	12.57
69. Z-*cyclo*-$(C_6H_{12}HC=CH)$	10.348	15.38	14.55	14.38
70. Z-*cyclo*-$(C_7H_{14}HC=CH)$	11.596	17.22	16.39	16.15
71. $H_2C=C(Me)HC=CH_2$	6.592	9.85	9.54	10.07
72. $H_2C=CHHC=CHMe$	6.778	10.13	9.54	10.32
73. $H_2C=CHHC=CHEt$	8.026	11.96	11.38	12.12
74. MeHC=CHHC=CHMe	8.300	12.37	12.16	12.16
75. MeHC=CHHC=CHEt	9.548	14.20	13.23	14.08
76. EtCHO	4.079	6.15	6.33	6.36
77. *n*-PrCHO	5.327	7.99	8.17	8.19
78. MeCO*n*-Pr	6.518	9.74	10.01	9.99
79. EtMeCHCHO	6.582	9.84	10.01	10.01
80. *n*-BuCHO	6.575	9.83	10.01	10.10
81. Me_2CHCH_2CHO	6.582	9.84	10.01	10.15
82. EtCO*n*-Pr	7.766	11.58	10.40	11.87
83. MeCO*n*-Bu	7.766	11.58	11.85	11.88
84. *n*-$C_5H_{11}CHO$	7.823	11.67	11.85	11.93
85. Et_2CHCHO	7.830	11.68	11.85	11.93
86. *n*-$C_6H_{13}CHO$	9.071	13.50	13.70	13.24
87. EtCO*n*-Bu	9.014	13.42	13.70	13.58
88. *n*-PrCO*n*-Pr	9.014	13.42	13.70	13.63
89. MeCO*n*-C_5H_{11}	9.014	13.42	13.70	13.79
90. EtCO*n*-C_5H_{11}	10.262	15.26	15.54	15.49
91. MeCO*n*-C_6H_{13}	10.262	15.26	15.54	15.52
92. *n*-$C_7H_{15}CHO$	10.319	15.34	15.54	15.72
93. *cyclo*-(C_3H_6CO)	5.186	7.78	7.49	7.39
94. *cyclo*-(C_4H_8CO)	6.434	9.62	9.28	9.20
95. *cyclo*-$(C_5H_{10}CO)$	7.682	11.46	11.12	11.05
96. *cyclo*-$(C_6H_{12}CO)$	8.930	13.30	12.81	12.83
97. *cyclo*-$(C_7H_{14}CO)$	10.178	15.13	14.81	14.55
98. *cyclo*-$(C_8H_{16}CO)$	11.426	16.97	16.65	16.31
99. *cyclo*-$(C_9H_{18}CO)$	12.674	18.81	18.50	18.01
100. $H_2C=CHCOMe$	5.360	8.04	7.93	7.94
101. $H_2C=C(Me)COMe$	6.696	10.01	9.77	9.94
102. $H_2C=CHCOEt$	6.608	9.88	9.77	9.95
103. E-*n*-PrHC=CHCOMe	9.506	14.14	10.74	13.89
104. EtCOOH	4.472	6.73	7.07	6.86
105. $Me_2CHCOOH$	5.727	8.58	8.89	8.61
106. *n*-PrCOOH	5.720	8.57	8.89	8.80
107. EtCH(Me)COOH	6.975	10.42	10.72	10.55
108. *n*-BuCOOH	6.968	10.41	10.72	10.65
109. *n*-$C_5H_{11}COOH$	8.216	12.24	12.55	12.47
110. *n*-$C_6H_{13}COOH$	9.464	14.09	14.39	14.11

[1] Furan, [2] 1,4-Dioxane

2.4.2.2. Aldehydes, Ketones, and Carboxylic Acids

For the *atom-in-molecule* polarizability of the carbonyl carbon atom in aldehydes we obtained an average value (**39–47**, **90**) of 0.980 Å^3 and the same value calculated for the carbonyl C atom in carboxylic acids. A somewhat higher value of 1.062 Å^3 was obtained for ketones (**48–55**).

Table 4. Molecular masses (M_r), pycnometric densities (ϱ) and refractive indices (n) used to calculate the experimental polarizabilities in Table 3 with the equation of *Lorenz* and *Lorentz*. If not mentioned otherwise d is d_4^{20} in g/ml, n is n_d^{20} and M_r in g/mol.

Molecule	M_r	ϱ	n	Molecule	M_r	ϱ	n
1. *n*-$C_5H_{11}OH$	88.15	0.8144	1.4101	56. E-MeHC=CH*n*-Pr	84.16	0.6784	1.3935
2. *n*-$C_6H_{13}OH$	102.18	0.8136	1.4178	57. H_2C=CHC_2H_4HC=CHMe	96.17	0.7186	1.4200
3. *n*-$C_7H_{15}OH$	116.21	0.8219	1.4249	58. H_2C=CH*n*-C_5H_{11}	98.19	0.6970	1.3998
4. *n*-$C_8H_{17}OH$	130.23	0.8270	1.4295	59. H_2C=C(Me)*n*-Bu	98.19	0.7000	1.4040
5. *n*-$C_9H_{19}OH$	144.26	0.8273	1.4333	60. (H_2C=C(Me)CH_2-)$_2$	110.20	0.7512	1.43995[21]
6. *n*-$C_{10}H_{21}OH$	158.29	0.8297	1.43719	61. H_2C=CHC_6H_{13}	112.22	0.7149	1.4087
7. *n*-$C_{11}H_{23}OH$	172.31	0.8298	1.43918	62. E-*n*-PrHC=CH*n*-Pr	112.22	0.7141	1.4114
8. $C_{13}H_{27}CH(OH)CH_3$	228.42	0.8328	1.4463	63. H_2C=C(Me)*n*-C_5H_{11}	112.21	0.72025	1.4123[22]
9. *n*-$C_{20}H_{41}OH$	298.56	0.8405	1.4550	64. H_2C=C(Me)*n*-C_6H_{13}	126.24	0.7343	1.4184
10. $HOC_5H_{10}OH$	104.15	0.9939	1.4494[1]	65. E-*n*-PrHC=CH*n*-Bu	126.24	0.7318	1.4205
11. Me(HO)C_4H_6(OH)Me	118.18	0.9610	1.4475	66. Z-*cyclo*-(C_3H_6HC=CH)	68.13	0.7720	1.4225
12. $HOC_7H_{14}OH$	132.21	0.9569	1.4520[2]	67. Z-*cyclo*-(*n*-C_4H_{10}HC=CH)	82.15	0.8102	1.4465
13. $HOCH_2CH(OH)CH_2OH$	92.11	1.2613	1.4746	68. Z-*cyclo*-(*n*-C_5H_{10}HC=CH)	96.17	0.8228	1.4552
14. $HOCH_2CH(OH)C_2H_4OH$	106.12	1.018	1.4688[3]	69. Z-*cyclo*-(*n*-C_6H_{12}HC=CH)	110.20	0.8472	1.4698
15. $HOC_2H_4CH(OH)C_2H_4OH$	120.15	1.1291	1.4785	70. Z-*cyclo*-(*n*-C_7H_{14}HC=CH)	124.23	0.8671	1.4805
16. $HOCH_2CH(OH)CH(OH)C_3H_7$	134.18	1.089	1.472[4]	71. H_2C=C(Me)HC=CH_2	68.13	0.6810	1.4219
17. $HOC_3H_6CH(OH)C_3H_7OH$	148.20	1.075	1.4725	72. H_2C=CHHC=CHMe	68.13	0.6760	1.4301
18. *n*-PrOEt	88.15	0.7386	1.3695	73. H_2C=CHHC=CHEt	82.15	0.7050	1.4380
19. *n*-PrO*n*-Pr	102.18	0.7360	1.3809	74. MeHC=CHHC=CHMe	82.15	0.7196	1.4500
20. *n*-BuO*i*-Pr	116.21	0.7594	1.3870[5]	75. MeHC=CHHC=CHEt	96.17	0.7384	1.4578
21. *n*-BuO*n*-Bu	130.23	0.7689	1.3992	76. EtCHO	58.08	0.8058	1.3636
22. *n*$C_7H_{15}OEt$	144.26	0.790	1.4111[6]	77. *n*-PrCHO	72.12	0.8170	1.3843
23. *n*-C_5H_{11}O*n*-C_5H_{11}	158.29	0.7833	1.4119	78. MeCO*n*-Pr	86.14	0.8089	1.3895
24. *n*-C_6H_{13}O*n*-C_6H_{13}	186.34	0.7936	1.4204	79. Et(Me)CHCHO	86.14	0.8029	1.3869[23]
25. *n*-C_7H_{15}O*n*-C_7H_{15}	214.40	0.8008	1.4275	80. *n*-BuCHO	86.14	0.8095	1.3944
26. *n*-C_8H_{17}O*n*-C_8H_{17}	242.45	0.8063	1.4327	81. Me_2CHCH_2CHO	86.14	0.7977	1.3902
27. *n*-$C_{10}H_{21}$O*n*-$C_{10}H_{21}$	298.56	0.8150	1.4410[7]	82. EtCO*n*-Pr	100.16	0.8118	1.4004
28. $MeOC_2H_4OEt$	104.15	0.8529	1.3868	83. MeCO*n*-Bu	100.16	0.81127	1.4007
29. *n*-$PrOC_2H_4OH$	104.15	0.9112	1.4133	84. *n*-$C_5H_{11}CHO$	100.16	0.81392	1.4039
30. *n*-$BuOC_2H_4OH$	118.18	0.9015	1.4198	85. Et_2CHCHO	100.16	0.8110	1.4025
31. $HOC_2H_4OC_2H_4OC_2H_4OH$	150.18	1.1274	1.4531[8]	86. *n*-$C_6H_{13}CHO$	114.19	0.8495	1.4113
32. $MeOC_2H_4OC_2H_4OC_2H_4OMe$	178.23	0.990	1.4233[9]	87. EtCO*n*-Bu	114.19	0.8183	1.4057
33. *n*-$BuOC_2H_4OC_2H_4OC_2H_4OH$	206.29	0.9890	1.4389	88. *n*-PrCO*n*-Pr	114.19	0.8174	1.4069
34. $HOCH_2CH(OMe)CH_2OH$	106.12	1.124	1.4505[10]	89. MeCO*n*-C_5H_{11}	114.19	0.8111	1.4088
35. $HOCH_2CH(OH)CH_2OMe$	106.12	1.1189	1.4445[11]	90. EtCO*n*-C_5H_{11}	128.22	0.8221	1.4153
36. $MeOCH_2CH(OH)CH_2OMe$	120.15	1.0085	1.4192	91. MeCO*n*-C_6H_{13}	128.22	0.8202	1.4151
37. $MeOCH_2CH(OMe)CH_2OMe$	134.18	0.946	1.4055[5]	92. *n*-$C_7H_{15}CHO$	128.22	0.8211	1.4217
38. $HOC_2H_4CH(OMe)CH_2CH(OMe)Me$	162.23	0.9631	1.4329[12]	93. *cyclo*-(C_3H_6CO)	70.09	0.9548	1.4215[24]
39. *cyclo*-$C_6H_{11}OH$	100.16	0.9624	1.4641	94. *cyclo*-(C_4H_8CO)	84.13	0.94869	1.4366
40. C_4H_4O	68.08	0.9514	1.4214[13]	95. *cyclo*-($C_5H_{10}CO$)	98.15	0.9478	1.4507
41. $C_4H_8O_2$	88.12	1.0337	1.4224[14]	96. *cyclo*-($C_6H_{12}CO$)	112.17	0.9508	1.46.08
42. $H_2C(OMe)_2$	76.11	0.8593	1.3513	97. *cyclo*-($C_7H_{14}CO$)	126.20	0.9581	1.4694
43. $H_2C(OEt)_2$	104.15	0.8319	1.3748[15]	98. *cyclo*-($C_8H_{16}CO$)	140.23	0.9560	1.4729
44. H_2C(O*n*-Pr)$_2$	132.21	0.8345	1.3939[16]	99. *cyclo*-($C_9H_{10}CO$)	154.26	0.9654	1.4806
45. H_2C(O*n*-Bu)$_2$	160.26	0.834	1.4072[17]	100. H_2C=CHCOMe	70.09	0.8636	1.4081
46. $Me_2CH(OEt)_2$	132.21	0.8200	1.3891[18]	101. H_2C=C(Me)COMe	84.13	0.8527	1.4220
47. *n*-$C_4H_9CH(OEt)_2$	160.26	0.829	1.4029[19]	102. H_2C=CHCOEt	84.12	0.8468	1.4192
48. *n*-$C_{15}H_{31}CH(OMe)_2$	286.50	0.8542	1.4382[20]	103. E-*n*-PrHC=CHCOMe	112.17	0.8496	1.4436
49. H_2C=CHC_3H_7	70.14	0.6405	1.3715	104. EtCOOH	74.08	0.9930	1.3809
50. Z-MeHC=CHEt	70.14	0.6556	1.3830	105. $Me_2CHCOOH$	88.11	0.96815	1.3930
51. E-MeHC=CHEt	70.14	0.6482	1.3793	106. *n*-PrCOOH	88.12	0.9577	1.3980
52. H_2C=CH*n*-Bu	84.16	0.6731	1.3837	107. EtCH(Me)COOH	102.13	0.9410	1.4051[25]
53. (H_2C=$CHCH_2$-)$_2$	82.15	0.6880	1.4042	108. *n*-BuCOOH	102.13	0.9391	1.4085
54. H_2C=C(Me)*n*-Pr	84.16	0.6799	1.3920	109. *n*-$C_5H_{11}COOH$	116.16	0.9274	1.4163
55. Z-MeHC=CH*n*-Pr	84.16	0.6869	1.3977	110. *n*-$C_6H_{13}COOH$	130.19	0.9200	1.4170

[1] d_{20}^{20}; [2] d_4^{25}; n_D^{25}; [3] d^{20}, density in [15] is probably in error and yields a polarizability of 9.92 Å^3; [4] d^{26}, n_D^{26}; [5] d_4^{15}, n_D^{15}; [6] d_4^{16}; [7] from [19]; [8] d_4^{15}; [9] from [21]; [10] d_4^{25}, n_D^{17}; [11] from [17c], d^{17}, n_D^{17}; [12] d_4^{25}, n_D^{25}; [13] Furan; [14] 1,4-Dioxane; [15] n_D^{18}; [16] n_D^{19}; [17] $n_D^{17.2}$; [18] d_4^{21}; [19] n_D^{22}, d^{22}; [20] n_D^{25}; [21] n_D^{21}; [22] from [20]; [23] d^{18}; [24] d_0^0; [25] dl form.

2.4.2.3. Amides

Only formamides and acetamides were considered, and the common average value (calculated from **56–62**) for the carbonyl C atom is 1.140 Å^3.

2.5. Test of the Derived Increments

While the numerical values of the polarizability increments are of importance for actual calculations, a general scheme might be of interest for qualitative considerations. Thus the conclusions drawn from our computational results are summarized in Scheme 1.

Oxygen

$$\alpha_O(\text{alcohol}) \approx \alpha_O(\text{aldehyde}) \approx \alpha_O(\text{ketone}) \approx \alpha_O(\text{carboxylic acid})$$

$$\approx \alpha_O(\text{amide}) < \alpha_O(\text{ethers})$$

$$\alpha_O(=C-C=O, \textit{trans}) > \alpha_O(=C-C=O, \textit{cis})$$

Nitrogen

$$\begin{array}{ccccc} \alpha_N(\text{amine}, p) & < & \alpha_N(\text{amine}, s) & < & \alpha_N(\text{amine}, t) \\ \wedge & & \wedge & & \wedge \\ \alpha_N(\text{amide}, p) & < & \alpha_N(\text{amide}, s) & < & \alpha_N(\text{amide}, t) \end{array}$$

Carbon

$$\alpha_C(\text{methyl}) < \alpha_C(\text{methylene}) < \alpha_C(\text{methine})$$

$$\alpha_C(R^1HC^*=C^*H_2) < \alpha_C(R^1R^2C^*=C^*H_2) < \alpha_C(R^1HC^*=C^*HR^2)$$

$$\alpha_C(R^1HC=CHR^2, Z) < \alpha_C(R^1HC=CHR^2, E)$$

$$\alpha_C(C^*=C^*-C=O, \textit{trans}) > \alpha_C(C^*=C^*-C=O, \textit{cis})$$

$$\alpha_C(R^1HC=CH-CH=C, Z) < \alpha_C(R^1HC=CH-CH=C, E)$$

$$\alpha_C(C=O, \text{aldehyde}) \approx \alpha_C(C=O, \text{acide})$$

$$< \alpha_C(C=O, \text{ketone}) < \alpha_C(C=O, \text{amide})$$

Scheme 1.

110 arbitrarily chosen molecules were now used to test the derived increments. The molecular weights, densities and refraction indices used to calculate the corresponding experimental values are listed in Table 4. There is no overlap between this group and the set used to calculate the increments. Table 3 contains the molecular polarizabilities (α'_{MW}) calculated directly from the increments in Table 2. At a correlation coefficient of $|r| = 0.997$ they correlate nicely with the corresponding experimental values. The correlation equation was then employed to calculate the polarizabilities denoted as α_{MW} (cf. Table 3). The average difference between α_{MW} and the experimental data is 0.34 Å^3, corresponding to a mean deviation of 2.7%. α_{MW} and α_{ex} of the 110 compounds are compared in Figure 2.

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