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An improved CNDO/2 standard parametrization for bromine containing molecules

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Bromine parameters are proposed, matching well the standard values of first and second row atoms, as introduced by Pople et al. This is shown by comparisons of geometries, configurations, conformations, and dipole moments, obtained with different approaches. The new parameter set was found in a very simple and efficient way that may also be useful for other tasks, e.g. in non-empirical calculations.

Key words: CNDO method—bromine compounds—parametrization method—geometries—conformations—dipole moments

1. Introduction

Nowadays the main applications of semi-empirical CNDO/INDO methods [1] usually concern molecules with a very large number of nuclei and thus not amenable to *ab initio* calculations by reasonable effort, and also molecules containing higher row elements. Recently, for example, the interdependencies of structural and conformational differences of 1,2-dihaloethanes $H_2XC-CXH_2$ (X: F, Cl, Br, I), as concealed in the experimental data, have been elucidated [2] by CNDO/2. This study was, in part, based on results communicated here.

Several CNDO/INDO parameters for the bromine atoms were published [3-5] in the past, but either they do not match [3, 5] the standard approach [1], or, if claimed to do [4], then calculated molecular properties proved to be less satisfactory (vide infra). Consequently, an attempt to find improved standard parameters

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turned out to be necessary. Encouraging in this respect was the experience with iodine [6].

2. Method

Four or five CNDO/2 parameters have to be determined for each non-hydrogen atom. In case of bromine these are the Slater exponent ζ_{Br}, to be used for 4*s*, 4*p* and 4*d* Slater orbitals, the bonding parameter β_{Br}, as well as the orbital electronegativities $\frac{1}{2}(I+A)_{s,p,d}$. Following the author's earlier proposal [6, 7], the $\frac{1}{2}(I+A)_d$ value is formally expressed in terms of the one-centre Coulomb integral γ_{Br} and the kinetic energy integral $\langle d|-\frac{1}{2}\nabla^2|d\rangle_{\mathrm{Br}}$ by

$$\tfrac{1}{2}(I+A)_d=-\tfrac{1}{2}\gamma_{\mathrm{Br}}+\langle d|-\tfrac{1}{2}\nabla^2|d\rangle_{\mathrm{Br}}. \qquad (1)$$

Meanwhile this has also been implemented in CNDO/*S* [8], whereas independently the inclusion of all types of kinetic energy integrals became an essential part of another semi-empirical method [9].

In a first attempt the $\frac{1}{2}(I+A)_{s,p}$ values were taken from a previous CNDO/2 parametrization [4]. Best results were obtained then with $\zeta_{\mathrm{Br}}=2.22$ and $\beta_{\mathrm{Br}}=-17$ eV. On the whole, however, the predicted molecular properties were less satisfactory, if compared with other calculations [1, 6, 7] on molecules not containing bromine. Then in a subsequent trial the electronegativity data [10], established for INDO, were transferred to CNDO/2. Such possibility is obvious from the common use of parameters in both methods [1]. Now the best ζ, β combination gave good results, as will be seen below, and the corresponding final selection of new bromine parameters is presented in Table 1.

Technically, any determination of parameters for semi-empirical methods has hitherto been considered a rather formidable task. It can be shown here, however, that this is not necessarily so. Namely, the search for optimum ζ, β pairs, as undertaken in this study, is based on the fact that, despite errors ε, both parameters satisfy approximately a linear relationship

$$\zeta=a\beta+b+\varepsilon \qquad (a, b=\text{const.}), \qquad (2)$$

such that the equilibrium molecular structure remains constant in at least one geometrical parameter. An appropriate choice for the latter is the bonding distance to the bromine atom, because β is a bonding parameter. A typical situation can be seen in Table 2. Although here *a* and *b* were determined only so roughly that

Table 1. CNDO/2 parameters for bromine

$\zeta=2.26$

$\beta^{a}=-16$ eV

$\frac{1}{2}(I+A)_s=21.367$ eV

$\frac{1}{2}(I+A)_p=7.108$ eV

$\frac{1}{2}(I+A)_d=$ equation (1)

[a] $\beta(a,b)=\frac{1}{2}K[\beta(a)+\beta(b)]$ with $K=0.75$ (c.f. [1]); where *a*, *b* denote atoms.

Table 2. A numberical example of the validity of Eq. (2). Optimized geometries were obtained by *sp*-CNDO/2 with electronegativity parameters $\frac{1}{2}(I+A)_{s,p,d}$ from Table 1. (Bond lengths in Å, angles in deg.)

ζ_{Br}		2.28	2.26	2.24	2.22	2.20
$-\beta_{Br}$ [eV]		15	16	17	18	19
HBr		1.5323	1.5288	1.5259	1.5233	1.5213
FBr		1.8010	1.8084	1.8161	1.8241	1.8323
ClBr		2.1273	2.1282	2.1294	2.1310	2.1329
Br_2		2.2824	2.2801	2.2787	2.2782	2.2786
IBr		2.3707	2.3683	2.3664	2.3648	2.3637
H_2CBr_2	C—Br	1.9242	1.9251	1.9263	1.9279	1.9298
	∢BrCBr	110.47	111.00	111.51	112.00	112.48
	∢HCH	113.16	112.57	111.98	111.40	110.82
H_3CBr	C—Br	1.9267	1.9267	1.9270	1.9277	1.9287
	∢HCBr	107.50	107.80	108.10	108.39	108.67

$100\times\zeta$ is integer for any integer β, the maximum variation in distances X-Br does not exceed 0.02 Å. This has its origin in the specific properties of constrained minimum energy paths, and minimum energy surfaces, respectively. The energy E of a molecule, as a function of the parameters X-Br, ζ_{Br}, and β_{Br}, can be expanded in a power series $\tilde{E}$. Truncated to first and second order terms, the function $\tilde{E}(\text{X-Br}, \zeta_{Br}, \beta_{Br})$ describes a surface of second degree. Then with X-Br satisfying condition

$$\underset{\text{X-Br}}{\text{minimum}}\ \tilde{E}(\text{X-Br}, \zeta_{Br}, \beta_{Br}), \tag{3}$$

Eq. (2) is correct [11, 12]. In other words, the error ε in (2) stems from third and higher order terms in the expansion of E.

This property served as a basis of the following procedure for finding the optimum ζ, β pair. i) Keep ζ fixed. Find a β value that gives X-Br bond lengths in overall good agreement with data of reference. Five diatomic molecules are sufficient for such purpose, as shown previously [6, 7]. Here X = H, F, Cl, Br, I were selected, each representing the main elements of one row of the periodic system. ii) Find the linear relationship (2), i.e. calculate the constants a, b. iii) Using a small number of molecules (here H_3CBr and H_2CBr_2), check whether all other parameters (not necessarily geometrical ones, but here bond angles were considered) are in satisfactory agreement with the reference data. Vary ζ, β, complying with Eq. (2), until the optimum is determined. So final parameters given in Table 1 were easily found, without application of statistical methods. These were superflous within such simple approach. (Note also that the procedure as such could, with appropriate modifications, be useful for other purposes as well, e.g. in non-empirical calculations.)

The molecular geometries were readily determined by means of first derivatives of the energy with respect to curvilinear internal coordinates [7].

Table 3. Calculated equilibrium geometries of bromine containing molecules, including the seven lead structures of the parametrization (separated by a dashed line). The reference of experimental values is [13], unless otherwise specified. (Bond lengths in Å, angles in deg., i.e. 360° = 2π)

molecule		experiment	*sp*[a]	*spd-mod*[b]
HBr		1.413	1.5288	1.5217
FBr		1.7590[c]	1.8084	1.7481
ClBr		2.1361[c]	2.1282	2.0666
Br_2		2.283	2.2801	2.2208
IBr		2.4691[c]	2.3683	2.3071
$BrCH_3$	C—Br	1.933	1.9267	1.8904
	C—H	1.086	1.1127	1.1124
	∡BrCH	107.71	107.80	107.61
$BrCH_2$	C—Br	1.927	1.9251	1.8856
	C—H	1.079	1.1127	1.1116
	∡BrCBr	112.7	111.00	106.76
	∡HCH	113.6	112.57	113.40
LiBr		2.35[d]	2.4377	2.4362
Br_3^- (linear)		2.54[e]	2.4178	2.3248
BBr_3 (planar)		1.8932	1.9615	1.9361
BrNO	Br—N	2.140	1.9032	1.8530
	N—O	1.146	1.1674	1.1695
	∡BrNO	114.5	113.06	111.14
$GeBr_2$	Ge—Br	2.337[f]	2.6323	2.5210
	∡BrGeBr	101.2	96.17	98.47
PBr_3	P—Br	2.2204	2.3097	2.2332
	∡BrPBr	101.0	99.21	98.57
$AsBr_3$	As—Br	2.329	2.5329	2.4349
	∡BrAsBr	99.7	96.51	97.61
BrF_5	$Br{-}F_{ax}$	1.689	1.8726	1.7671
	$Br{-}F_{eq}$	1.774	1.8601	1.7584
	$\measuredangle F_{ax}BrF_{eq}$	84.8[g]	79.62	84.11
$BrSiH_3$	Si—Br	2.210	2.4094	2.3092
	Si—H	1.481	1.6162	1.6071
	∡BrSiH	107.9	108.88	109.62
BrCN	C—Br	1.789	1.8782	1.8503
	C—N	1.158	1.1811	1.1814
$BrC{\equiv}CH$	C—Br	1.791	1.8836	1.8536
	C—C	1.204	1.1966	1.1968
	C—H	1.055	1.0928	1.0929
$ClC{\equiv}CBr$	C—Br	1.789	1.8843	1.8536
	C—C	1.212	1.1961	1.1962
	C—Cl	1.624	1.7345	1.7107
$BrC{\equiv}C{-}CN$	C—Br	1.7858	1.8805	1.8508
	C—C	1.2041	1.2080	1.2083
	$C{-}C_{CN}$	1.3699	1.3947	1.3947
	C—N	1.1593	1.1916	1.1917
$HCBr_3$	C—Br	1.930	1.9263	1.8819
	C—H	1.068	1.1136	1.1112
	∡BrCH	108.1	108.47	110.80
$BrCF_3$	C—Br	1.90	1.9416	1.9033
	C—F	1.33	1.3365	1.3365
	∡BrCF	109.4	110.20	109.87

Table 3 (*cont.*)

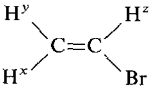
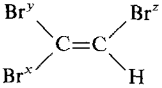
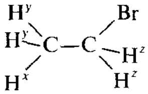
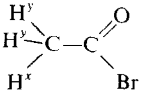
molecule		experiment	*sp*[a]	*spd-mod*[b]
$Br_2C{=}CBr_2$	C—Br	1.881	1.9303	1.8858
	C—C	1.362	1.2872	1.2845
	$\measuredangle$CCBr	122.4	125.29	125.87
cis-HBrC=CHBr	C—Br	1.87	1.9321	1.8938
	C—C	1.36	1.2962	1.2955
	C—H	—	1.1106	1.1095
	$\measuredangle$CCBr	124	124.00	119.37
	$\measuredangle$CCH	—	128.91	132.07
trans-HBrC=CHBr	C—Br	—	1.9385	1.8978
	C—C	—	1.2926	1.2923
	C—H	—	1.1083	1.1078
	$\measuredangle$CCBr	121	119.84	118.10
	$\measuredangle$CCH	—	132.53	133.30
	C—Br	1.882	1.9299	1.8909
	C—C	1.330	1.3034	1.3033
	C—H^x	1.084	1.1119	1.1122
	C—H^y	1.087	1.1139	1.1141
	C—H^z	1.079	1.1098	1.1091
	$\measuredangle$CCBr	122.7	122.25	120.34
	$\measuredangle$CCH^x	121.2	125.52	125.15
	$\measuredangle$CCH^y	119.2	122.69	123.28
	$\measuredangle$CCH^z	123.8	129.75	130.72
	C—Br^x	—	1.9331	1.8877
	C—Br^y	—	1.9246	1.8834
	C—Br^z	—	1.9376	1.8978
	C—C	—	1.2909	1.2893
	C—H	—	1.1092	1.1080
	$\measuredangle$CCBr^x	—	122.22	125.32
	$\measuredangle$CCBr^y	—	127.79	126.36
	$\measuredangle$CCBr^z	—	121.98	117.29
	$\measuredangle$CCH	—	130.96	133.92
$H_3C{-}CBr_3$	C—Br	1.927	1.9483	1.8963
	C—C	—	1.4351	1.4319
	C—H	—	1.1214	1.1218
	$\measuredangle$CCBr	107.7	112.20	113.73
	$\measuredangle$CCH	—	112.02	112.14
	C—Br	1.950	1.9496	1.9070
	C—C	1.518	1.4475	1.4473
	C—H^z	1.087	1.1188	1.1184
	C—H^x	1.093[h]	1.1221	1.1223
	C—H^y	1.093[h]	1.1197	1.1199
	$\measuredangle$CCBr	111.0	111.51	109.27
	$\measuredangle$CCH^x	112.3[h]	110.27	110.96
	$\measuredangle$CCH^y	112.3[h]	112.82[i]	112.63[i]
	$\measuredangle$CCH^z	112.3[h]	114.08[i]	114.63[i]
	C—Br	1.973	1.9513	1.9086
	C—C	1.516	1.4326	1.4317
	C—O	1.183	1.2506	1.2512
	$\measuredangle$CCBr	111.0	114.57	113.62
	$\measuredangle$CCO	127.1	131.99	133.18
	C—H^x	—	1.1170	1.1173

Table 3 (*cont.*)

molecule		experiment	*sp*^{a}	*spd-mod*^{b}
	C—H^y	—	1.1197	1.1198
	∡CCH^x	—	114.87	114.48
	∡CCH^y	—	109.06	109.35

[a] *sp*-CNDO/2.

[b] modified *spd*-CNDO/2, corresponding to Eq. (1).

[c] Ref. [14].

[d] Taken from the geometry of the dimer $(LiBr)_2$, Ref. [13].

[e] Ref. [15].

[f] Ref. [16].

[g] *ax*: axial, *eq*: equatorial.

[h] All ∡CCH assumed identical, as well as all distances C—H of the CH_3 moiety.

[i] Dihedral angles, too, were optimized.

3. Results and discussion

The seven reference molecules used so far are included in Table 3 of calculated bond lengths and angles of 30 compounds. Compared with previous results [6, 7] obtained upon parametrization [4], the accuracy of X-Br distances has much but that of bond angles has more modestly improved. Systematic errors of the modified *spd*-CNDO/2 (*spd-mod.*), as defined by Eq. (1), are avoided now. For example ∡BrCBr in H_2CBr_2 changed from former 91° [7], which is unacceptable, to 106°. Comparisons with the experimental data allow for the conclusion that *sp*-CNDO/2 is almost sufficient for the calculation of geometrical bonding parameters of molecules. Still the conventional *spd*-CNDO/2, with $\frac{1}{2}(I+A)_d = 0$ or $|\frac{1}{2}(I+A)_d| \ll |\frac{1}{2}(I+A)_p|$ instead of obeying Eq. (1), can be ruled out because of the reasons discussed elsewhere (complete breakdown of the chemical bond picture [7]).

The predictive power of CNDO/2 for conformations has also improved with the new parametrization. Some results are selected for Table 4. In the former parametrization [4] the rotational barrier of benzylbromide was too much overestimated relative to the chlorine compound, especially when experimental geometries were used together with the *sp*-CNDO/2. Moreover, with *spd-mod.*

Table 4. The CNDO/2 energy (in kJ/mol) of the coplanar conformation, relative to the perpendicular one, of benzyl compounds Ph-CH_2-X (coplanar: Ph-C-X in a plane; perpendicular: -CH_2X moiety rotated about the Ph-C bond by $\pi/2$)

		experimental geometry^a		optimized geometry	
X	*exp.*^{a}	*sp*	*spd-mod*	*sp*	*spd-mod*
Cl	6.3	7.96	1.00	3.45	1.48
Br	8.4	15.06	7.24	9.86	8.39

[a] Ref. [17]

the prediction of the minimum energy conformation was wrong (coplanar instead of perpendicular conformation). Using the energy partitioning technique [18], we identified an artificial bonding of bromine and ortho-hydrogen atom as the origin of that failure. Similarly, the *gauche* conformation of 1,2-dibromethane was predicted to be more stable than *trans*, in contrast to the experiment [19] and also to results obtained with the new parametrization. For details see [2]. Configurations may be considered a special case of conformations. Here penta-coordination compounds AX_5 were studied. CNDO/2 in its former [20] as well

Table 5. Dipole moments calculated for bromine containing molecules, using experimental or standard geometrical models. The reference of experimental data is [21, 22], unless otherwise specified. (All values in Debye units)

(*a*) Miscellaneous molecules

molecule	*exp.*	*sp*[a]	*spd-mod*[b]
HBr	0.834[c]	1.41	0.94
FBr	1.422	1.22	1.88
ClBr	0.519[d]	0.94	1.18
IBr	0.737[d]	0.39	0.54
LiBr	7.27	7.35	7.13
H_3CBr	1.82[e]	2.66	2.03
H_2CBr_2	1.43	1.99	1.44
$HCBr_3$	0.99	1.62	1.17
F_3CBr	0.65[f]	0.09	0.40
F_2CBr_2	0.66	1.50	1.23
$H_2C{=}CHBr$	1.42	1.98	1.49
cis-$HBrC{=}CHBr$	1.35	3.02	2.18
cis-$HClC{=}CHBr$	1.55	3.29	2.64
gauche-$H_2BrC{-}CH_2Br$	1.46[g]	3.21	2.43
gauche-$H_2ClC{-}CH_2Br$	1.19[g]	3.53	2.92
anti-$H_2ClC{-}CH_2Br$	—	0.53	0.74
gauche-$HBr_2C{-}CHBr_2$	1.31[g]	2.93	2.19
$H_3C{-}CHBr_2$	2.12	2.53	1.93
$H_3C{-}CH_2Br$	2.01	2.15	1.65
$H_3C{-}COBr$	2.43	3.02	2.75
$n^{-1}\sum\lvert\Delta\mu\rvert$[h]	—	0.64	0.35
$n^{-1}\sum\lvert\Delta\mu\rvert$[h] (former parametrization [4])	—	0.94	0.59 (0.61)[i]

[a] *sp*-CNDO/2.

[b] Modified *spd*-CNDO/2, corresponding to Eq. (1).

[c] Ref. [23].

[d] Ref. [24].

[e] Ref. [25].

[f] Ref. [26].

[g] Dipole moments based on a mixture of anti and gauche conformations, as present in the thermal equilibrium.

[h] Mean absolute deviation of experimental and theoretical values (*n*: number of molecules, excluding those with superscript *g*).

[i] spd-CNDO/2 [4] (not *spd-mod*).

Table 5 (*cont.*)

(*b*) Substituted benzenes

substituents	*exp.*	*sp*[a]	*spd-mod*[b]
CH_2Br[c]	1.85	2.06	1.56
Br	1.70	2.26	1.79
1-Br, 2-F	2.27	3.18	2.76
1-Br, 2-Cl	2.21	3.91	3.30
1-Br, 3-Cl	1.51	2.32	2.01
1-Br, 4-Cl	0.04	0.30	0.54
1-Br, 2-Br	1.87	3.68	2.88
1-Br, 3-Br	1.55	2.18	1.72
1-Br, 2-I	1.73	3.74	2.79
1-Br, 3-I	1.14	2.23	1.68
1-Br, 4-I	0.49	0.07	0.13
1-Br, 4-CN	2.64	1.03	1.50
1-Br, 2-NH_2[d]	1.77	3.66	3.20
1-Br, 3-NH_2[d]	2.65	3.72	3.26
1-Br, 4-NH_2[d]	2.99	2.81	2.44
1-Br, 2-OH[e]	1.36	3.89	3.43
1-Br, 4-OH[e]	2.12	2.33	2.02
1-Br, 4-F	0.00	0.59	0.12
1-Br, 2,4-NO_2[e]	3.1	4.30	4.39
1-Br, 3,5-NO_2[e]	2.4	3.02	3.52
1,3,5-Br, 6-NH_2[d]	1.80	1.53	1.53
1,2,3,5-Br	0.70	1.89	1.45
$n^{-1}\sum\lvert\Delta\mu\rvert$[h]	—	0.99	0.71
$n^{-1}\sum\lvert\Delta\mu\rvert$[h] (former parametrization [4])	—	1.24	0.88 (1.06)[i]

[a,b,h,i] See Table 5*a*.

[c] Perpendicular conformation.

[d] NH_2 pyramidal, the reflection plane perpendicular to the phenyl plane.

[e] Coplanar conformation.

as in its new parametrization predicts BrF_5 to be stable in quadratic pyramidal but not in trigonal bipyramidal form, and that is correct.

While *spd-mod.* is rarely superior but mostly equivalent to *sp*-CNDO/2 for geometries, conformations and configurations, it is absolutely necessary for good predictions of molecular dipole moments. This is clearly demonstrated by Tables 5*a* and 5*b*, containing a selection of calculated and experimental data. Mean absolute deviations, considered a general indicator for the quality of a method, are given in the row last but one. (Note that the actual results [27] underlying the last row of Tables 5*a* and 5*b* are left out.) Comparisons of both allow for the conclusion that also dipole moments have considerably improved with the new bromine parameters (Table 1).

Summing up, the new bromine parametrization is useful for calculating molecular structures, conformations and dipole moments. Only for the latter the modified *spd*-CNDO/2 must be used. It is the author's opinion, however, that such splitting could be avoided at the expense of dropping the standard parameters of second and higher row elements. Of course, such re-parametrization was not the aim of this study.

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