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Semi-empirical Parameters in π-Electron Systems

IX. Bromine Substituents

PAUL G. SEYBOLD* and INGA FISCHER-HJALMARS

Quantum Chemistry Group, University of Uppsala, S-751 20 Uppsala 1, Sweden, and Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden

A modification of the Pariser-Parr-Pople method has been extended to include bromine substituents, and applied to bromoethylenes, bromobenzenes, and bromonaphthalenes. Calculations of ionization potentials, electronic transitions, and π-electron charge densities and bond orders are presented.

The semi-empirical molecular orbital scheme developed by Pariser, Parr and Pople (PPP) [1,2] has become the most widespread method for the calculation of spectra, and often other properties, of π-electron systems. The success of the method rests heavily on the evaluation of the semi-empirical parameters involved, and a number of different schemes for this have been proposed. A central feature of the PPP method is the zero differential overlap (ZDO) approximation. One of us [3] has examined this approximation in detail and shown that it can be described as a second-order theory in the overlap integral. An important conclusion was that the "one-center" parameter W_μ should properly include terms due to neighbouring atoms. Based on this analysis, Roos and Skancke [4,5] have developed a scheme in which most of the necessary parameters are determined from experimental data for a few standard molecules. This was first applied to pure hydrocarbons,[4] and has subsequently been expanded to include methyl substituents,[5] and molecules with nitrogen,[6] chlorine,[7] oxygen,[8,9] and sulfur [10] atoms. In the present paper the method is extended to bromine substituents.

METHOD

The detailed features of the method have been described in earlier papers,[4,5] so only a brief summary will be given here. The scheme is based on the Pariser-Parr-Pople approximation to the more general LCAO-MO-SCF method. The

* U.S. Public Health Service Postdoctoral Fellow 1967–1969. Present address: Department of Chemistry, Wright State University, Dayton, Ohio, U.S.A.

following integrals between atomic basis orbitals are to be evaluated within the ZDO framework:

Overlap: $(\mu|\nu) = S_{\mu\nu} = \delta_{\mu\nu}$

One-center core: $(\mu|H^{\text{core}}|\mu) = \alpha_\mu \neq 0$

Two-center core: $(\mu|H^{\text{core}}|\nu) = \beta_{\mu\nu}$ $\begin{cases} \neq 0 \text{ when } \mu \text{ and } \nu \text{ are neighbours} \\ = 0 \text{ when } \mu \text{ and } \nu \text{ are non-neighbours} \end{cases}$

Electron interaction: $(\alpha\beta|\ 1/r_{12}|\mu\nu) = \delta_{\alpha\mu}\ \delta_{\beta\nu}\ \gamma_{\mu\nu}$

It has been shown [3] that the resonance integral, $\beta_{\mu\nu}$, and the Coulomb integral, $\gamma_{\mu\nu}$, are local, *i.e.* only dependent on atoms μ and ν and their separation, up to terms of second order in the overlap integral. Consequently, these integrals can be considered transferable from one molecule to another. The diagonal core integral, α_μ, can be written, according to Goeppert-Mayer and Sklar,[11] as

$$\alpha_\mu = W_\mu - (n_\mu - 1)\gamma_{\mu\mu} - \sum_{\mu \neq \nu} n_\nu \gamma_{\mu\nu}$$

where n_μ is the number of π-electrons contributed by AO μ. The parameter W_μ incorporates the so-called "penetration integrals" from the immediate neighbours.[3] W_μ is local only to first order, containing second-order contributions from the nearest neighbours.[3] Accordingly, Roos and Skancke [4] have introduced terms $\Delta W_\mu(\nu)$ which depend on the kind of neighbours ν and their bond distances to center μ:

$$W_\mu = W_\mu^\circ + \sum_\nu \Delta W_\mu(\nu)$$

The various parameters are then evaluated in the following manner. Because bond distances for specific bond types vary only within rather narrow ranges, the parameters $\beta_{\mu\nu}$, $\gamma_{\mu\nu}$, and $\Delta W_\mu(\nu)$ for bonded atoms are assumed to depend linearly on the bond distance $R_{\mu\nu}$. The resulting six parameters and the parameter W_μ° are chosen to give the best fit of experimental data for a small set of standard molecules. The values of $\gamma_{\mu\nu}$ for non-neighbour atoms are calculated using the ball approximation,[1,12] and the single-center $\gamma_{\mu\mu}$'s are obtained using Slater-Condon parameters from atomic spectral data,[13]

$$\gamma_{\mu\mu} = F_0 + 4\ F_2$$

In the case of carbon, the parameter W_C° was set equal to the first ionization potential of the methyl radical.[4]

The ground state properties and molecular orbitals are calculated by the usual SCF procedure. The excited stated are calculated with configuration interaction including all singly excited configurations.

BROMINE PARAMETERS

The procedure for determining the semi-empirical parameters for bromine follows closely the one used by Grabe [7] for chlorine. The bromine substituent is treated as a heteroatom contributing two electrons to the molecular π-system. Because bromine occurs in all cases as a single substituent bound to an sp^2 hybridized carbon, it is reasonable to regard the carbon-bromine bond distance as a constant, thus reducing by three the number of parameters. The value $R_{CBr}^{\circ} = 1.880$ Å has been taken from recent structural determinations.[14,15] The formula given by Parr [12] for the sphere diameter in the ball approximation was derived for $2p$ electrons (see especially footnote 17 of Ref. 1) and cannot be used for bromine $4p$ electrons. An analogous calculation using $4p$ orbitals yields a diameter of 1.82 Å for bromine. It might be mentioned that the calculated results are very insensitive to the values assumed for R_{CBr} and the sphere diameter.

The standard molecules chosen for this study were vinyl bromide, *cis*-dibromoethylene, and bromobenzene. The geometry for *cis*-dibromoethylene was taken from the gas phase electron diffraction study of Davis, Kappler and Cowan.[16] For bromobenzene the carbon skeleton was assumed to have the same geometry as in benzene. A carbon-carbon bond distance of 1.34 Å was used for vinyl bromide. As in the case of vinyl chloride,[7] the calculated ionization potential of vinyl bromide is somewhat sensitive to this value; a distance of 1.344 Å is obtained from the bond order-bond length relationship.

Unfortunately, very little work has been reported on the absorption spectra of the bromoethylenes, and no such data was satisfactory for use in the parameter determination. Accordingly, the parameters β_{CBr}°, γ_{CBr}°, $\Delta W_C(Br)$, and $W_{Br} = W_{Br}^0 + \Delta W_{Br}^0(C)$ were determined from a least squares fit for six experimental values: the ionization potentials of the three standard molecules, and the lowest three singlet-singlet absorption transitions of bromobenzene. It was desired that the bromine parameters should apply strictly to effects resulting from substitution and not also be used to counteract any small discrepancies in the pure hydrocarbon results, so that the spectral values used were experimental and calculated *shifts* of the transitions relative

Table 1. Results of the least squares fit of experimental data used for the determination of the semi-empirical parameters. All values are in eV.

	Calculated		Observed		References
Vinyl bromide IP	9.79		9.80		17,18
cis-Br_2 ethylene IP	9.41		9.45		17,19
Bromobenzene IP	9.04		8.98		17,20
Bromobenzene 1st abs.[a]	4.79	(0.10)	4.76	(0.13)	21
» 2nd abs.[a]	5.85	(0.32)	5.84	(0.33)	21
» 3rd abs.[a]	6.79	(0.19)	6.65	(0.33)	21

[a] The calculated values are corrected to represent spectral shifts from benzene. Values in parenthesis are the spectral shifts.

to benzene, rather than absolute values. The parameter γ_{BrBr} (or $\gamma_{\pi\pi}$) was calculated from atomic spectral data.[13] The results of the parameter fit are shown in Table 1. The calculation underestimates the splitting of the 3rd and 4th transitions in bromobenzene, thereby giving a low value for the spectral shift of the third transition. However, the average shift for the two bands is well reproduced (0.18 eV calculated, 0.17 eV observed). The resulting parameters along with those used for carbon, which have been taken from Ref. 5, are listed in Table 2.

Table 2. Semi-empirical parameters.

Carbon parameters from Ref. 5.		Bromine and bromine-carbon parameters.	
R_{CC}°	= 1.397 Å	R_{CBr}°	= 1.880 Å
$\gamma_{\pi\pi}$	= 11.97 eV	$\gamma_{\pi\pi}$	= 9.35 eV
γ_{CC}°	= 6.91 eV	γ_{CBr}°	= 6.42 eV
δ_{CC}^{γ}	= − 3.99 ev/Å		
β_{CC}°	= − 2.42 eV	β_{CBr}°	= − 1.84 eV
δ_{CC}^{β}	= 3.05 eV/Å		
W_C°	= − 9.84 eV	W_{Br}°	= −11.25 eV
ΔW_C°	= 0.07 eV	ΔW_C(Br)	= − 2.01 eV
δ_{CC}^{W}	= 9.22 eV/Å		

APPLICATIONS

The parameters thus derived have been applied in a series of calculations on other bromine-substituted compounds. The information obtained relates to ionization potentials, absorption spectra, and π-electron densities and bond orders.

Table 3. Information on the input geometries used for the calculations. R_{CBr} = 1.880 Å.

Molecule	R_{CC} (Å)	∠CCBr	Ref.
Ethylene	1.336	—	—
Vinyl bromide	1.340	121°	—
cis-Dibromoethylene	1.360	124.1°	16
trans-Dibromoethylene	1.340	121°	—
Tribromoethylene	1.362	122.4°	—
Tetrabromoethylene	1.362	122.4°	15
o-Dibromobenzene	1.402	121.8°	14
2,3,5,6-Tetrabromobenzene			
Hexabromobenzene	1.401	120°	14
Benzene and remaining substituted benzenes	1.397	120°	—
Naphthalene and bromonaphthalenes	Distances and angles from Ref. 22.		

1. *Input geometries.* Numbering of positions and the orientation of coordinate axes are as shown in Fig. 1. Information on input bond distances and angles is given in Table 3. Because of the large size of the bromine atom steric crowding occurs in several of the molecules studied here. Hexabromobenzene, *e.g.*, is known to be distorted to S_6 symmetry with alternate bromine atoms sticking above and below the plane of the benzene ring.[14] Two calculations were done for comparison, the first employing the normal benzene geometry and the second using the geometry obtained by Strand [15] with electron diffraction, but flattened into a plane. The results for the spectra were virtually identical for the two cases, while the ionization potentials were 8.65 eV and 8.60 eV, respectively. This is a general result, that the ionization potentials are more sensitive than the spectra both to the input geometry and the choice of parameters. *o*-Dibromobenzene remains planar in C_{2v} symmetry, with an angle 63.6° between the two carbon-bromine bonds.[14] This geometry was also assumed for 2,3,5,6-tetrabromobenzene.

2. *Ionization potentials.* Ionization potentials were calculated from Koopmans' theorem, *i.e.* from the absolute energies of the occupied molecular

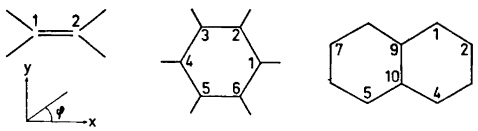

Fig. 1. Numbering of positions and orientation of molecular axes.

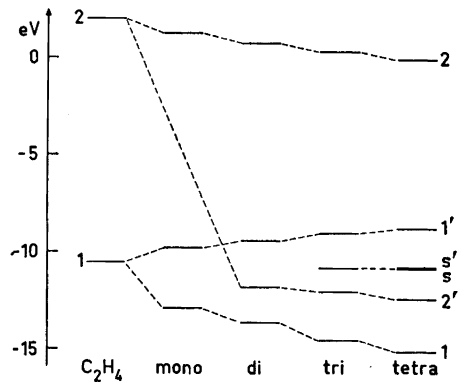

Fig. 2. Orbital levels of the ground state of brominated ethylenes; from left to right: C_2H_4, C_2H_3Br, $C_2H_2Br_2$(1,2) (*cis*- and *trans*-indistinguishable), C_2HBr_3 and C_2Br_4. Filled orbitals: 1, 1′, 2′, *s*, *s*′; empty orbital: 2.

orbitals. Since the calculation holds the nuclei in fixed positions, these should, strictly speaking, refer to vertical ionization potentials. However, most of the ionization potentials reported in the literature are adiabatic values, and adiabatic values have been used for parameter calibration in the present and earlier papers. More recently, Turner and his coworkers have measured both adiabatic and vertical ionization potentials by means of photoelectron spectroscopy.[23,24] The vertical values of the lowest IPs for these compounds tend to lie 0.1 to 0.3 eV above the adiabatic potentials. Calculated and experimental lowest ionization potentials are given in Table 4. The agreement is, in general, very good.

Table 4. Comparison of calculated and experimental lowest ionization potentials (eV).

Molecule	Calculated	Observed
Ethylene	10.53	10.52 [20,23]
Vinyl bromide	9.79	9.80 [17,18]
cis-Dibromoethylene	9.41	9.45,[17-19] 9.69 [19]
trans-Dibromoethylene	9.46	9.47,[17] 9.46,[19] 9.54 [19]
Tribromoethylene	9.09	9.27 [17,18]
Tetrabromoethylene	8.82	—
Benzene	9.25	9.25,[23] 9.245 [16,20] 9.40,[24] 9.38 [27]
Bromobenzene	9.04	8.98,[17,20] 8.96 [23] 9.25 [24]
o-Dibromobenzene	8.84	—
m-Dibromobenzene	8.98	—
p-Dibromobenzene	8.94	8.97 [24]
sym-Tribromobenzene	8.96	—
2,3,5,6-Tetrabromobenzene	8.73	—
Hexabromobenzene	8.60	—
1-Br,4-Cl-Benzene	8.96	9.04 [24]
1-Br,4-CH_3-Benzene	8.73	8.67,[17,20] 8.71 [24]
1-Br,4-OH-Benzene	8.43	8.52 [24]
1-Br,4-NH_2-Benzene	7.72	—
Naphthalene	8.28	8.26,[27] 8.12 [20]
1-Br-Naphthalene	8.27	—
2-Br-Naphthalene	8.28	—

The influence of substituents on ionization potentials in delocalized systems is exerted through alteration of the occupied molecular orbitals. The change is most easily envisaged in the case of substituted ethylenes. The orbital energies calculated for the various bromoethylenes are displayed in Fig. 2. In the mono-substituted compound the occupied ethylene orbital, 1, is split into two orbitals, 1 and 1′. In the lower one the contributions from ethylene and from bromine are in phase and in the higher one out of phase. The empty orbital, 2, is almost unchanged. In the dibromoethylenes the third occupied orbital, 2′, is mainly a bromine orbital with a small, in phase, contribution from the excited ethylene orbital. In the tri- and tetrabromoethylenes the added levels originate from pure bromine orbitals, denoted *s* and *s*′ in Fig. 2.

The benzene compounds show a similar picture. When symmetry allows, the occupied orbitals have an appreciable bromine admixture, in phase for the lowest orbitals and out of phase for the higher ones. The empty orbitals are only slightly changed. Since the number of bromine atoms never exceeds the number of carbons, there are no pure bromine orbitals, not even in C_6Br_6. The results for chlorine compounds [7] are very similar to those described here. This mixing of the substituent orbitals with those of benzene will raise the π_3 (e_{1g}) level (out of phase mixing), thereby lowering the first IP, but lower the π_1 (a_{2u}) level (in phase mixing), thus raising the corresponding IP. A second substituent should increase these tendencies. This is illustrated in Table 5, which also gives experimental values.

Table 5. Effect of a halogen substituent on the calculated π-ionization potentials of benzene. Values in parentheses are experimental results.[23,24] Energies are in eV.

Molecular orbital	Benzene	Br-Benzene	*para*-Br_2-Benzene	Cl-Benzene [7]
π_3 (e_{1g})	9.25 (9.25)[a] (9.40)[b]	9.04 (8.96)[a] (9.25)[b]	8.94 (8.97)[b]	9.12 (8.99)[a] (9.31)[b]
π_2 (e_{1g})	9.25 (9.25)[a] (9.40)[b]	9.19 (9.59)[a] (9.78)[b]	9.11 (9.95)[b]	9.22 (9.60)[a] (9.71)[b]
π_1 (a_{2u})	12.35 (11.49)[a,c] (11.86 or 12.24)[b,c]	13.28 (11.8)[a,c]	13.61(11.9)[a,c]	12.75 (12.2)[a,c]

[a] Adiabatic value.
[b] Vertical value.
[c] The assignments of the higher IP's are still debated; cf. Refs. 24–26.

3. *Absorption spectra.* Electronic transitions have been calculated with configuration mixing including all singly excited configurations. The results should be compared with vertical transitions (absorption peaks) in the vapor phase, when such information is available. Calculated transitions for the

Table 6. Calculated electronic transitions for the bromoethylenes. Energies in $cm^{-1} \times 10^{-3}$ (kK).

Molecule	Energy	Oscillator strength	Pol.[a] ϕ^0	Main transition component
Ethylene	61.5	0.60	0	1 – 2
Vinyl bromide	51.0	0.50	18	1′ – 2
	71.2	0.20	–28	1 – 2
cis-Dibromoethylene	45.0	0.57	0	1′ – 2
	59.5	0.21	90	2′ – 2
	72.6	0.11	0	1 – 2
trans-Dibromoethylene	44.7	0.66	27	1′ – 2
	58.4	forb.	—	2′ – 2
	72.9	0.22	–42	1 – 2
Tribromoethylene	40.2	0.64	–12	1′ – 2
	48.7	0.19	91	s – 2
	57.9	0.10	84	2′ – 2
	76.1	0.09	22	1 – 2
Tetrabromoethylene	35.9	0.68	0	1′ – 2
	45.8	forb.	—	s′ – 2
	46.6	0.47	90	s – 2
	58.5	forb.	—	2′ – 2
	77.7	0.04	0	1 – 2

[a] See Fig. 1 for orientation of axes.

bromoethylenes are given in Table 6, and show the expected red shift with bromination. The polarizations of the lowest and highest transitions (1 – 2 and 1′ – 2) are all close to the x-axis. The middle transition, (2′ – 2) is polarized along the y-axis, when allowed. From symmetry restrictions it is forbidden in *trans*-dibromoethylene and in tetrabromoethylene.

The lowest absorption band of benzene (^1L_b, $^1B_{2u}$) is symmetry forbidden, being made slightly allowed through a 520 cm^{-1} e_{2g} vibration in the excited state.[28] Because of its low intensity it provides a suitable object for the study of substituent effects on intensity, which themselves are often quite small in absolute magnitude. The second transition (^1L_a, $^1B_{1u}$), although also symmetry-forbidden, has a vibrationally induced intensity 60 times as large[33] as that of the ^1L_b (it is, for one thing, closer to the third transition, from which both states "borrow" intensity). The third transition (^1B, $^1E_{1u}$) is symmetry-allowed and intense. Petruska[33] has made an extensive analysis of substituent effects on benzene spectra and derived formulas from perturbation theory for frequency shifts and intensity changes. These formulas generally hold rather well for substituents which shift the ^1L_b band by less than 1500 cm^{-1}. An extension of this analysis to substituents with stronger effects has been given by Stevenson,[37] who introduces a slope factor and charge-transfer states. By his method reasonable predictions can be made for frequency shifts up to 25 kK. Kimura and Nagakura[21] have taken vapor absorption spectra of a number of mono-substituted benzenes. From theoretical studies these authors have concluded that intra-molecular charge-transfer configurations play a strong role in determining the absorption spectra.[21]

The results of the present calculations for the bromobenzenes are shown in Tables 7 and 8 with experimental observations. For consistency, the frequency shifts listed refer to work by the same authors in the same solvents. Many of the experimental values are from solution spectra, and thereby contain effects due to the solvent which are difficult to estimate quantitatively. For the lowest absorbtion band of *benzene* (^1L_b), Petruska[33] has taken the red shifts of the 0 – 0 level (38089 cm^{-1} in the vapor) to be 240 cm^{-1} in aliphatic hydrocarbon solvents, 230 cm^{-1} in alcohol, and 110 cm^{-1} in water. He estimated a general solvent shift of 200 cm^{-1} for the absorption peak. The second (^1L_a) and third (^1B) transitions are more strongly shifted, Petruska's estimates[33] being 1100 cm^{-1} and 1850 cm^{-1}, respectively, in going from the vapor to heptane solution. Forbes has reported a shift for the ^1L_a bond of bromobenzene in going from vapor to cyclohexane solution, but finds the location of the band to be rather similar in cyclohexane, ether, ethanol, and aqueous solutions.[31] In addition to solvent effects, poorly resolved vibrational structure and the overlap of different bands, as well as ordinary experimental uncertainties, can somewhat cloud the analysis of the experimental data.[31,33,37] An error of 1 mμ at 200 mμ equals a shift of 250 cm^{-1}; furthermore, the absorption bands for these compounds typically extend over several thousand cm^{-1}.

Considering the experimental uncertainties mentioned above, the present calculations give generally good agreement with the experimental results. When a single substituent is introduced onto benzene the molecular symmetry is reduced from D_{6h} to C_{2v}. As a result the formerly symmetry-forbidden ^1L_b

Table 7. Electronic transitions for the bromobenzenes.[a] Energies in $cm^{-1} \times 10^{-3}$ (kK).

Present calculation				Observations			
Energy	$-\Delta\nu$	f	Pol.	Reference, Solvent	Energy	$-\Delta\nu$	Intensity
				Benzene			
39.1		Forb.		vapor [21]	39.4		
50.6		Forb.			49.8		
56.1		1.19			56.3		
				hexane [30]	39.4		$f=0.0014$
					49.5		0.10
					54.4		0.69
				vapor [28]	39.5[b]		$f=0.0016$
				vapor [29]	50.6[b]		
					55.9[b]		
				Bromobenzene			
38.3	0.8	0.018	y	vapor [21]	38.4	1.0	$f=0.007$
48.0	2.6	0.16	x		47.1	2.7	0.254
54.5	1.6	1.08	x		53.6	2.7	0.625
54.7	1.4	1.05	y		56.3	0.0	0.745
				vapor [33]	37.0[c]	1.1[c]	
				hexane [30]	46.5	3.0	$\varepsilon=8000$
					52.4	2.0	$\varepsilon=36000$
				cyclo-hexane [31]	37.7	1.5	$\varepsilon=200$
					46.9	1.9	$\varepsilon=9000$
				water [32]	38.3	0.6[d]	$\varepsilon=192$
					47.6	1.5	$\varepsilon=7900$
				isooctane [33]	36.8[c]	1.1[c]	$f=0.0028$
				p-Dibromobenzene			
37.2	1.9	0.066	y	cyclo-	36.4	2.8	$\varepsilon=390$
45.5	5.1	0.36	x	hexane [31]	43.7	5.1	$\varepsilon=15\,000$
54.1	2.0	0.96	y				
54.2	1.9	1.05	x				
				hexane [33]	35.4[c]	2.5[c]	$f=0.0052$
				o-Dibromobenzene (2,3)			
37.2	1.9	0.030	y	cyclo-	36.8	2.4	$\varepsilon=295$
45.6	5.0	0.14	x	hexane [31]	45.6	3.2	$\varepsilon=12500$
52.2	3.9	1.26	y				
53.1	3.0	0.89	x	hexane [33]	36.0[c]	1.9[c]	$f=0.0034$
				m-Dibromobenzene (2,6)			
37.6	1.5	0.018	y	hexane [33]	35.9[c]	2.0[c]	$f=0.0044$
46.9	3.7	0.095	x				
52.2	3.9	1.21	y				
53.4	2.7	0.95	x				
				sym-Tribromobenzene			
37.0	2.1	Forb.		hexane [33]	35.1[c]	2.8[c]	$f=0.0021$
46.3	4.3	Forb.					
51.2	4.9	1.18		ethanol [38]	36.2		

Table 7. Continued.

		Tetrabromobenzene (2,3,5,6)		
35.3	3.8	0.11	*y*	
42.5	8.1	0.26	*x*	
50.4	5.7	1.38	*y*	
51.8	4.3	0.81	*x*	
		Hexabromobenzene		
34.2	4.9	Forb.		
40.9	9.7	Forb.		
47.3	8.8	1.36		

[a] Explanation of symbols: $\Delta\nu$=Energy shift relative to benzene; f=Oscillator strength; Pol.=Polarization (see Fig. 1).
[b] Used for parameter calibration in Ref. 4.
[c] 0–0 band.
[d] *Cf.* Ref. 37.

Table 8. Electronic transitions for some mixed parasubstituted benzenes. [a] Energies in $cm^{-1} \times 10^{-3}$.

Present calculation				Observation in cyclohexane [b,31]		
Energy	$-\Delta\nu$	f	Pol.	Energy	$-\Delta\nu$	ε_{max}
		1-Br,4-CH_3-Benzene				
38.3	0.8	0.0012	*y*	36.9(36.0)[c]	2.3(1.9)[c]	425(f=0.0058)[c]
47.4	3.2	0.20	*x*	45.2	3.6	10 500
54.2	1.9	1.05	*y*			
54.7	1.4	1.11	*x*			
		1-Br,4-Cl-Benzene				
37.9	1.2	0.029	*y*	36.5	2.7	415
46.9	3.7	0.25	*x*	44.6	4.2	13 500
54.3	1.8	1.02	*y*			
54.4	1.7	1.08	*x*			
		1-Br,4-OH-Benzene				
37.6	1.5	0.0005	*y*	35.5	3.7	1 750
44.9	5.7	0.31	*x*	44.6	4.2	10 000
52.5	3.6	0.88	*y*			
54.6	1.5	1.06	*x*			
		1-Br,4-NH_2-Benzene				
36.4	2.7	0.014	*y*	33.7(34.5)[d]	5.5(4.4)[d]	1 750(1 340)[d]
42.3	8.3	0.41	*x*	41.5(41.8)[d]	7.3(7.3)[d]	14 000(12 800)[d]
50.2	5.9	0.54	*y*			
54.5	1.6	0.92	*x*			

[a] Parameters for substituents other than bromine were obtained as follows: Cl, Ref. 7; CH_3, Ref. 5; OH, Ref. 9; NH_2, Ref. 6.
[b] Benzene absorption maxima at 39.2 kK (255 mμ) and 48.8 kK (205 mμ).
[c] Ref. 33, 0–0 band in hexane solution.
[d] Ref. 32, in aqueous solution; *cf.* also Ref. 37.

and ^1L_a transitions become allowed and the degenerate ^1B band is split into ^1B_a and ^1B_b bands. As mentioned earlier, the present calculations tend to underestimate the ^1B band splitting for bromobenzene but give a correct value for the average frequency shift. The observed intensities of the ^1L_b band for substituted benzenes can be regarded [33] as the sum of two components, one vibrationally-induced as for benzene and the other due directly to the substituent. Molecular orbital calculations, such as the present, treat only the second component and tend to overestimate it. Nevertheless, the calculations correctly represent many experimentally observed trends, *e.g.* the red shift and intensification of the ^1L_a band of bromobenzene relative to that of chlorobenzene, as noted by Forbes [31] (*cf.* Ref. 7). With the exception of *o*-dibromobenzene, where steric effects are involved, this is also true for the energy shifts of the ^1L_b band for the compounds in Table 7. *Ortho*-substituents are well known to cause smaller red shifts than expected theoretically.[33,36] Table 8 compares calculated and experimental (solution) results for some mixed *para*-disubstituted benzenes. The parameter values for CH_3, Cl, OH, and NH_2 have been taken from earlier papers in this series.[5,7,9,6] The calculations give the correct order for the shifts of both the ^1L_b and ^1L_a bands (NH_2>OH>Cl>CH_3), but underestimate the magnitudes of the ^1L_b shifts.

Table 9. Electronic transitions in bromonaphthalenes.[a] Energies in $cm^{-1} \times 10^{-3}$.

Present calculation				Observations in vapor phase [35]			
Energy	$-\Delta\nu$	f	Pol.	Energy	$-\Delta\nu_{00}$	f	Pol.
			Naphthalene				
33.8		0.030	x	(32.4)[b] 32.0[c]		(0.002)[b]	x[e]
40.0		0.19	y	(36.3)[b] 35.9[c] 37.2[d]		(0.18)[b]	y[e]
47.1		Forb.		—		—	
48.5		Forb.		—		—	
49.6		2.09	x	(45.5)[b]		(1.70)[b]	x?[e]
			1-Br-Naphthalene				
33.1	0.67	0.081		32—33	31.5[c]	0.48	
38.6	1.37	0.26		35.9	34.6[c]	1.26	
45.9		0.02					
46.3		0.10					
49.5	0.15	1.80					
			2-Br-Naphthalene				
33.3	0.48	0.034		32.8	31.2[c]	0.81	
39.3	0.69	0.17		38.3	35.4[c]	0.50	
46.2		0.09					
47.5		0.88					
48.6	1.00	1.11					

[a] Explanation of symbols: $\Delta\nu$=Energy shift relative to naphthalene, $\Delta\nu_{00}$=shift of 0—0 band relative to naphthalene, f=oscillator strength, Pol.=polarization (see Fig. 1). [b] Solution results from Refs. 30 and 34. [c] 0—0 band energy. [d] Ref. 40. [e] Ref. 39.

Table 10. Calculated π-electron densities and bond orders. The bromine subscript refers to the carbon atom to which it is bonded; see Fig. 1.

Molecule	Atom	π-Electron density	Bond	Bond order
Vinyl bromide	1	0.876	1–2	0.959
	2	1.182	2–Br	0.219
	Br_2	1.942		
cis-Dibromo-	1	1.074	1–2	0.926
ethylene	Br	1.926	1–Br	0.262
trans-Dibromo-	1	1.077	1–2	0.923
ethylene	Br	1.923	1–Br	0.266
Tribromoethylene	1	0.984	1–2	0.870
	2	1.255	$1–Br_1$	0.306
	Br_1	1.908	$2–Br_2$	0.233
	Br_2	1.927	$2–Br_2'$	0.235
	Br_2'	1.926		
Tetrabromo-				
ethylene	1	1.183	1–2	0.817
	Br	1.908	1–Br	0.274
Bromobenzene	1	1.184	1–2	0.643
	2	0.937	2–3	0.670
	3	1.004	3–4	0.665
	4	0.978	1–Br	0.189
	Br_1	1.956		
o-Dibromobenzene				
(2,3)	1	0.940	1–2	0.655
	2	1.128	2–3	0.618
	5	0.982	4–5	0.661
	Br	1.950	5–6	0.669
			2–Br	0.208
m-Dibromobenzene				
(1,3)	1	1.188	1–2	0.647
	2	0.873	3–4	0.640
	4	0.915	4–5	0.668
	5	1.007	1–Br	0.186
	Br	1.957		
1-Br, 4-OH-				
benzene	1	1.199	1–2	0.639
	2	0.932	2–3	0.676
	3	1.038	3–4	0.641
	4	0.968	1–Br	0.182
	Br	1.958	4–O	0.261
	O	1.933		
1-Br,4-NH_2-				
benzene	1	1.220	1–2	0.634
	2	0.927	2–3	0.684
	3	1.084	3–4	0.616
	4	0.927	1–Br	0.174
	Br	1.961	4–N	0.368
	N	1.871		

Table 9 lists calculated and experimental results for naphthalene, 1-Br-naphthalene and 2-Br-naphthalene. The small changes in the present calculated results for naphthalene from those given in Ref. 4 are due to the use of the slightly different later parameters [5] and the ball approximation for non-neighbor $\gamma_{\mu\nu}$ integrals. The energy shifts calculated for the lowest two transitions in these bromonaphthalenes are seen to agree with experiment to within $200-300$ cm^{-1}.

4. *Charge densities and bond orders.* The results of the calculations for the π-electron charge densities and bond orders are found in Tables 10 and 11.

Table 11. Calculated π-electron densities and bond orders for naphthalene and the bromonaphthalenes. For numbering of atoms see Fig. 1.

Atom	π-Electron densities			Bond	Bond orders		
	Naph-thalene	1-Br-Naph.	2-Br-Naph.		Naph-thalene	1-Br-Naph.	2-Br-Naph.
1	1.014	1.202	0.933	1— 2	0.767	0.734	0.737
2	1.012	0.932	1.196	2— 3	0.554	0.564	0.533
3	1.012	1.017	0.967	3— 4	0.767	0.761	0.773
4	1.014	0.987	1.019	4—10	0.517	0.520	0.513
5	1.014	1.018	1.015	5—10	0.517	0.516	0.517
6	1.012	1.015	1.007	5— 6	0.767	0.768	0.767
7	1.012	1.013	1.014	6— 7	0.554	0.554	0.554
8	1.014	1.005	1.013	7— 8	0.767	0.767	0.767
9	0.948	0.909	0.949	8— 9	0.517	0.518	0.516
10	0.948	0.948	0.932	9—10	0.575	0.572	0.572
Br	—	1.954	1.955	1— 9	0.517	0.500	0.522
				C—Br	—	0.189	0.189

Bond lengths for several of the bond types found here can be estimated from the bond orders ($p_{\mu\nu}$) using the following relationships:[41,42]

$$R_{CC} = 1.517 - 0.18\ p_{CC}$$
$$R_{CN} = 1.458 - 0.18\ p_{CN}$$
$$R_{CO} = 1.430 - 0.214\ p_{CO}$$

Hence a change in C—C bond order of 0.010 corresponds to a bond length change of $\sim$0.002 Å. The values in Table 10 indicate a steady increase in the ethylene C—C bond length with increasing bromination, going from 1.344 Å (assumed 1.340 Å) in vinyl bromide to 1.370 Å (assumed 1.360 Å) in tetrabromoethylene. The benzene C—C bonds are not strongly affected, the calculated values being generally very close to the experimental input values. The most extreme deviation occurs for the case of the C—C bond adjacent to the position of NH_2-substitution in 1-Br, 4-NH_2 benzene, where R_{calc} = 1.407 Å. In the bromonaphthalenes only the 1—2 bond length is noticeably affected ($\Delta R \sim +0.006$ Å) by bromination.

Within the present computational scheme, the change of the π-electron densities originating from bromination must necessarily result in a net increase

on the carbon skeleton. Since bromine is, as expected from chemical evidence, electron-releasing, and contributes two electrons to the overall π-system, the number of electrons donated to the parent molecules is $\Delta q = 2.0 - q_{Br}$, where q_{Br} is the π-electron density on Br. Looking at the result for bromobenzene in Table 10, one sees that bromine contributes 0.044 of an electron to the ring π-system. But another fact also stands out, which is that the π-electron densities indicate that bromine should have a *meta*-directing effect, which is contrary to the experimental evidence. The reason for this is quite clear when one looks at the π-electron density, q_{C1}, on carbon *C*1, to which the bromine is attached. The value of q_{C1} is 1.184, which means that although the bromine shoves 0.044 of an electron onto the ring, this is more than cancelled by the charge buildup on C1. This buildup originates from the large negative value of $\Delta W_C(\mathrm{Br}) = -2.01$ eV, which may be compared to $\Delta W_C(\mathrm{Cl}) = -0.76$ eV, found by Grabe.[7] This comparison indicates that the value obtained for $\Delta W_C(\mathrm{Br})$ is an artefact, due to the limited number of observations available for the parameter fitting, *cf.* Table 1. In particular, it should be remembered that the adiabatic IP-values of Table 1 ought to be replaced by vertical IP-values. As soon as such values are available for the standard molecules of the present series a revised parameter scheme can be worked out, which is expected to show a more reasonable result for $\Delta W_C(\mathrm{Br})$.

Table 12. Calculated π-electron dipole moments and experimentally observed total dipole moments [43] (Debyes).

Molecule	Calculated μ_π	Observed π_{total}
Vinyl bromide	0.69	1.28, 1.42
cis-Dibromoethylene	1.10	1.35
Tribromoethylene	0.82	—
Bromobenzene	0.24	1.70—1.79[a], 1.49—1.57[b]
o-Dibromobenzene	0.36	1.53—2.14
m-Dibromobenzene	0.25	1.10—1.56
1-Br,4-Cl-Benzene	0.23	0.1
1-Br,4-CH_3-Benzene	0.84	1.95—2.17
1-Br,4-OH-Benzene	1.06	2.14—2.28
1-Br,4-NH_2-Benzene	2.02	2.88—3.34
1-Bromonaphthalene	0.29	1.49—1.59
2-Bromonaphthalene	0.33	1.70—1.73

[a] Vapor.
[b] Benzene solution.

The calculated π-part of the dipole moments are reproduced in Table 12, which also shows the observed values of the total dipole moment. The latter is composed of a σ-part, a lone-pair part, and a π-part. A division of the total moment into the various contributions is not an easy matter and will not be attempted here.

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