J. Phys. Chem. A **2002,** *106,* 11945−11949

Hard Bends Soft: Bond Angle and Bending Force Constant Predictions for Dihalides, Dihydrides, and Dilithides of Groups 2 and 12

László von Szentpály*

Institut für Theoretische Chemie der Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received: July 31, 2002; In Final Form: September 25, 2002

A “hard-bends-soft” rule is proposed as a complement to the HSAB principle. The rule completely separates the unexpected bent structures of some heavy alkaline earth (Ca, Sr, Ba) dihalides and dihydrides from the linear geometries of all of the other group 2 and 12 triatomic molecules. A simple function of chemical softness reproduces the bond angle within ±4° for the group 2 and group 12 dihalides, dihydrides, and dilithides. The bending force constants of the heavy group 2 dihalides and dihydrides correlate linearly with the atomic softness difference. Predictions are made for the bond angles and bending force constants of RaX_2 (X = H and halogens) and MAt_2 (M = group 2 and 12 elements).

1. Introduction

The prediction, verification, and explanation of the unexpected bent structure of some alkaline earth dihalides[1−16] and dihydrides[17] pose extreme demands on experiment and theory and qualify among “the most intriguing problems of modern inorganic chemistry”.[14] It must have come as a real surprise when Klemperer et al. showed that CaF_2, SrF_2, $SrCl_2$, and all barium halides display permanent dipoles in the gas phase and are therefore bent.[1] According to the commonly invoked simple VB, MO, and ionic bonding models, these molecules should be linear; their valence-shell electron-pair repulsion (VSEPR) structures are also linear, whereas the Walsh rules indicate that nonhydride, 16 valence electron (double octet) AB_2 molecules form the dividing line between linear and bent structures.[18] Why and how the bending occurs has been controversially discussed over many years without finding unequivocal answers. Polarizable ions, A^{2+} (or M^{2+}) and B^-,[1,4,5,8,9] and d-orbital participation[3,7−10,13−17] on the central atom or ion may contribute to the bending and thus form the contrasting ingredients of the main mechanisms. Extended reviews have been published recently from both the experimental and theoretical points of view.[19,20]

Several all-electron ab initio calculations have indicated that large sets of d orbitals on the Ca, Sr, and Ba atoms are crucial for obtaining bent geometries.[3b,7−10,16,17] Therefore, it seems evident that the $(n - 1)$d orbitals cause the bending. For CaF_2, the d functions account for 153 kJ/mol or 1.59 eV of the total atomization energy of about 11.5 eV.[9] However, the $(n - 1)$d participation in the MOs is only marginal, and it is “not possible to single out one particular MO or interaction as responsible for bending”.[10] To gain more specific insight, the roles of core polarization and core-valence correlation have been critically evaluated by pseudopotential studies.[14,17] They have further emphasized the importance of extended sets of d functions and became, in addition, important checks for the polarizability input data of classical polarized-ion models. Whereas comparisons of several sets of ab initio calculations (e.g., with and without a core-polarization potential[21] and with large-core or small-core pseudopotentials[17]) are needed to gain case-by-case insight into the structures, the appeal of the classical polarized ion model rests on its sweeping treatment of whole groups of molecules in terms of a basic mechanism.

A common feature is that extensive d-orbital sets are also needed for a polarized-ion model.[9,10,16] Without using d orbitals, the Hartree−Fock dipole polarizability volume of Ca^{2+} amounts to $\alpha' = 0.064$ Å^3, which is less than 15% of its value of $\alpha' = 0.471$ Å^3 calculated after adding a large, optimized d-function set.[9] In addition, the exponents for d functions that maximize the polarizability of free Ca^{2+} are almost identical to those optimized variationally for the energy of CaF_2.[9,16] This result has been interpreted differently, however, (i) to suggest that “the seemingly alternative rationalizations of bent structures are the two sides of the same coin”[9] or (ii) to support the view that “core-polarization is the controlling structural factor in CaF_2”.[16] In this contribution, we seek (i) an overall rationale combining the different aspects of the problem, (ii) simple equations for predicting the bond angles and bending force constants of yet unreported molecules, and (iii) a rule or algorithm applicable to a wider variety of molecules, including clusters.

2. Theoretical Framework

2.1. Polarized-Ion Models. Ionic ligands induce an angle-dependent dipole moment on the polarizable central ion of a molecule AB_2, which stabilizes the bent structure relative to the linear structure. In highly ionic systems (e.g., crystobalite), the simplest polarized-anion model explains the bent Si−O−Si structure by balancing the gain in polarization energy and the loss in Coulombic energy upon bending the bonds. With R_e denoting the equilibrium bond length and $\alpha'(O^{2-})$, the static dipole polarizability volume of the dianion in a crystalline state,[22] the structure is bent if $8\alpha'(O^{2-}) - R_e^3 > 0$. If this inequality is fulfillled, the bond angle φ is calculated as[23]

$$\varphi = 2 \arcsin\{R_e{}^3/8\alpha'\}^{1/3} \qquad (1)$$

otherwise, it is $\varphi = 180°$. In eq 1, the polarizability of the cation Si^+ is entirely neglected. Patil has elegantly generalized eq 1 by including the polarizability volume of ligand X^-, α'_X, in addition to α'_M of the dication M^{2+} for metal halides, MX_2[5]:

$$\varphi = 2 \arcsin\{(R_e{}^3 + 2\alpha'_X)/8\alpha'_M(1 + 8\alpha'_X R_e{}^{-3})\}^{1/3} \qquad (2)$$

---

* E-mail: laszlo@tc10.theochem.uni-stuttgart.de.

10.1021/jp026658b CCC: $22.00

Again, $\varphi = 180°$ if the bracketed { } argument is ≥1. For eq 2, Patil's general equations for multihalides have been reformulated to highlight the similarity to eq 1. The case of a central cation M^{2+} polarized by anions is occasionally termed "inverse polarization", as opposed to the better-known polarization of central anions by ligand cations. The choice of polarizability volumes is, however, critical for reproducing the observed MX_2 geometries: (i) for calculating angles less than 180°, the M^{2+} polarizabilities have to be significantly augmented[1,4a,5,8] toward and even beyond their larger "crystal values"[22] instead of using the "free-ion" polarizabilities, and (ii) for the decidedly linear cadmium and mercury dihalides and dihydrides, however, much reduced ad hoc cation polarizabilities[24] are required to avoid bending! Whereas case i is a commonly accepted procedure,[1,4a,5,8,22] we cannot find any physical reason and theoretical justification for ii. Thus, the polarized-ion model is inconsistent in this respect and unable to reproduce all of the MX_2 structures without invoking additional effects.

2.2. d-Orbital Participation. For M = Be, Mg, Zn, Cd, and Hg, both the atomic and cationic *n*d terms are well above the respective *n*p terms, and there are no unoccupied $(n - 1)$d orbitals; therefore, d participation is disfavored, sd hybridization upon bending requires a promotion energy in addition to that of sp hybridization, and the bending force constant $k_f(MX_2)$ is increased beyond the value calculated from the polarized-ion model. For ions Ca^+, Sr^+, and Ba^+ and the Ba atom, however, the weighted-average energy of the excited $(n - 1)$d terms lies below that of the *n*p terms.[25] If the comparison is limited to the singlet terms only, then the corresponding sequence reversal has already occurred for atoms Ca and Sr.[3a] Qualitatively, the failure of the polarized-ion models is corrected by the opposite energy contributions from the d-orbital participation upon bending. The problem is to estimate the contribution of M^+ and the amount of d participation for a given polar structure. It has been argued that d participation and core polarization are not strictly separable and act simultaneously.[8−10,14,20] Is it thus not possible to find some simple rule or model allowing structure predictions without the need for explicit calculations?

2.3. Softness Criterion. In the quest for a simple description with the ability to merge the d participation and the polarized-ion pictures, chemical softness, σ, has been perceived as a measure of the combined effects of the two mechanisms.[9] A softness criterion has been published[9] that completely separates bent from linear structures for all (metallic and nonmetallic) 16 valence electron triatomic molecules AB_2, including the group 12 dihalides: the molecule is bent if the atomic softness difference

$$\Delta\sigma = \sigma_A - \sigma_B > 0.290\ \text{eV}^{-1} \qquad (3)$$

Here, $\sigma = 2(I_v - A_v)^{-1}$, with I_v and A_v being the valence-state ionization energy and electron affinity, respectively. Depending on the slightly different literature values[26,27] for I_v, and A_v, the calculated softness values vary within a small range. This, however, affects only the threshold value 0.290 eV^{-1}, not the success and validity of the criterion itself.[9] The robustness of the softness criterion may be characterized by the fact that even replacing σ_A by the cationic softness σ_{A+} does not change its validity: the threshold in eq 3 is simply shifted to $\sigma_{A+} - \sigma_B > 0.192\ \text{eV}^{-1}$. The qualitative criterion is now extended to a quantitative "hard-bends-soft" rule of considerable predictive power.

TABLE 1: Atomic Softness $\sigma = 2(I_v - A_v)^{-1}$ in eV^{-1}

M	σ_M	B	σ_B
Be	0.304	H	0.156
Mg	0.380	Li	0.419
Ca	0.446	F	0.114
Sr	0.480	Cl	0.175
Ba	0.509	Br	0.196
Ra	0.542	I	0.216
Zn	0.338	At	0.20
Cd	0.338		
Hg	0.344		

3. Results and Discussion

The softness data from ref 9 and the σ values for H and Li are given in Table 1. Shortly after introducing the softness criterion, calculated structural data became available for the group 2 dihydrides[17] and HgH_2,[28] followed by matrix IR studies on group 12 dihydrides[29,30] and more theoretical work on group 12 compounds.[30−32] Accordingly, only SrH_2 and BaH_2 are bent, whereas CaH_2 is quasi-linear, having a very small positive bending force constant.[17] All group 12 dihalides and dihydrides are linear.[28−32] The atomic softness of hydrogen is $\sigma_H = 2/12.84$ eV = 0.1558 eV^{-1}, which is between those for the F and Cl atoms (Table 1). Without any further adjustment, eq 3 correctly separates the bent from the linear hydrides. This is remarkable, as hydrides do not belong to the class of double-octet molecules for which the softness criterion has been originally formulated. It seems, therefore, worthwhile to investigate further the applicability of the softness concept to structural problems. In addition to hydrides, the dilithides of group 2 and 12 elements are considered and compared to the Hartree−Fock calculations in ref 15.

3.1. Bond Angles. No quantitative relation between $\Delta\sigma$ and the angle φ has been reported so far. Guided by the common threshold character of eqs 1 to 3, the analogy is extended further, and the inverse polarization model is invoked to give

$$\varphi(\Delta\sigma) = 2\ \arcsin\{0.290/\Delta\sigma\}^{m/3} \qquad (4)$$

where $\varphi = 180°$ if the { } bracketed term ≥ 1. For $m = 2$, there is an excellent correlation between the angles calculated from eq 4 and the recommended experimental[1,2,5,19,29,30,34,35] or calculated [7,14−17,28,30−33] angles as shown in Table 2.

Experimental data need significant corrections to yield equilibrium bond angles.[19,36] Note that many of the electron diffraction experiments are done above 1000 K,[19] where shrinkage effects must be corrected for;[36] otherwise, linear molecules may appear to be bent. Infrared spectroscopic data frequently depend on the rare-gas matrix used.[19] The theoretical angles show significant scatter according to the methods and approximations involved in the calculations. Thus, relatively large uncertainties[19] must be assigned to the reference data, and it seems fair to refer to their average value for comparison. Taken over a set of 18 AB_2 molecules of Table 2 (the first 15 and HgF_2, HgH_2, and $HgCl_2$), the regression line of the arithmetic mean of the experimental and theoretical bond angles from Table 2 on the expression from eq 4 is found as

$$\varphi_{\text{linreg}} = 0.946\varphi(\Delta\sigma) + 8.44° \qquad (5)$$

The regression coefficient is a highly significant $r = 0.9882$. The data are plotted in Figure 1. The standard error of the individual $\varphi(\Delta\sigma)$ values in eq 4 is ±4.1°, and the linear regression in eq 5 reduces it to $\pm 3.8_5°$. The correlation is considered to be excellent in view of the errors bars of the reference angles. Remarkably, the angles of all of the reported

TABLE 2: Comparison of the Equilibrium Bond Angle, *f*, According to Equation 4 with Recommended Reference Data

MB_2	$\Delta\sigma$	angle φ/deg eq 4	reference average φ/deg	φ(ab initio)/deg ref 14 or as indicated	φ(B3LYP)/deg ref 33	φ(obsd)/deg ref 19 or as indicated
BaF_2	0.395	109	109	123	117.8	95 [34,a] ; 100 [2,a]
BaH_2	0.352	123	119	119 ± 5 [17]		
$BaCl_2$	0.334	131	130	141	128.4	120 ± 10[a]
$BaBr_2$	0.313	144	143	143		137 ± 3[b]; 150 ± 30 [34,a]
BaI_2	0.293	167	157	152		148 ± 1 [35,b,c]; 170 [34,a]
$BaLi_2$	0.090	180	180	180[15]		
SrF_2	0.366	118	125	138.8	128.5	108 ± 3 [2,b]
SrH_2	0.324	136	140	140 ± 5 [17]		
$SrCl_2$	0.305	150	149	155.2 [19]	155.5 [19]	154.6 ± 1.0[b]; 130 ± 8[b]
$SrBr_2$	0.284	180	175	164		linear [1]; quasilinear[b]
SrI_2	0.264	180	180	180		linear [1]; linear[b]
$SrLi_2$	0.061	180	180	180 [15]		
CaF_2	0.332	132	141	152 [7,15]; 130 [8]	142	140 ± 5 [2,a]; 142 ± 2 [5,a]
CaH_2	0.290	180	180	180 [17]		
$CaCl_2$	0.271	180	180	180		linear
MgX_2	<0.29	180	180	180		linear
BeX_2	<0.29	180	180	180		linear
ZnX_2	<0.29	180	180	180 [32a]		linear
CdX_2	<0.29	180	180	180 [32a]		linear
HgF_2	0.230	180	180	180 [31]		
HgH_2	0.188	180	180	180 [28]		linear [29]
$HgCl_2$	0.169	180	180	180 [31]		
HgX_2	<0.29	180				

[a] Estimated by infrared spectroscopy. [b] Determined by electron diffraction. [c] Reference 19 mistakenly quotes the BaI_2 equilibrium angle determined in ref 35 as 138 ± 1°.

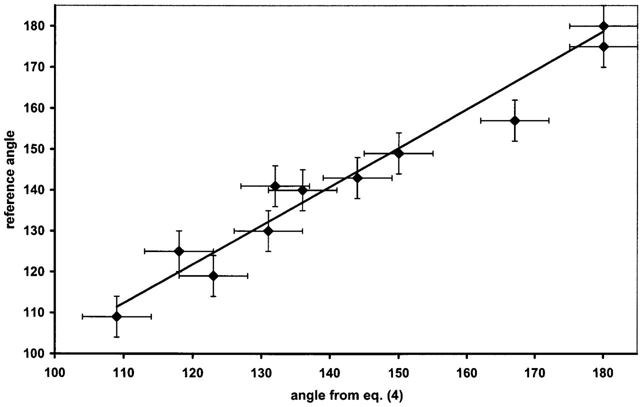

Figure 1. Averaged reference bond angles of MX_2, MH_2, and MLi_2 (M = groups 2 and 12; X = halogen) versus angles obtained from eq 4. The regression line is given by eq 5.

group 2 and 12 dihalides, dihydrides, and dilithides are calculated to ±4° from purely atomic input data, without the knowledge of the bond length R_e.

3.2. Bending Force Constants. Before turning to the prediction of angles for yet unreported bent or linear structures, the dependence of the bending force constants on $\Delta\sigma$ (as raised in ref 14) is revisited and discussed. To begin with, the softness criterion has not been devised for correlation with the bending force constants, k_φ and $k_\varphi R_e^{-2}$, and it seemed to be beyond expectation to obtain good results here. In addition, the calculated equilibrium bending frequencies do not regularly reproduce the observed ones and may be off by a factor of 2,[7,9,14,19] hence the values of $k_\varphi(180°)$ calculated for the linear ($\varphi = 180°$) transition structures of bent dihalides do not appear to be reliable. However, in an attempt to test the limits of our criterion, Kaupp et al.[14] have plotted $\Delta\sigma$ against their calculated $k_\varphi(180°)R_e^{-2}$, which is, by definition, negative for bent structures. The linear plots followed opposite trends: the sequences MF_2 to MI_2 showed negative slopes for M = Sr and Ba as opposed to positive slopes for the Be and Mg dihalides. More disturbingly, the Ca dihalides followed a V-shaped curve, and even the sequence became an irregular one (i.e., F, I, Br, Cl).[14] According to Kaupp, "the quantitative analysis indicates that the proposed criterion does not account for the structures of the entire series of alkaline earth dihalides".[20] We beg to disagree and find the conclusion premature. First, for nonlinear molecules, the bending force constant of the linear transition state is *not* even an observable, let alone a structural, property; even for linear molecules, stiffness does not belong to the structural features. Second, the bond angles of *all* of the group 2 and 12 halides, hydrides, and lithides are calculated to a high accuracy by eqs 4 and 5, and no exception to the validity of the hard-bends-soft rule has been found so far. Third, the type of plot chosen in ref 14 is but one of two options. For a correlation between $\Delta\sigma$ and the bending force constant, it is preferable to use k_φ so that both axes remain independent of the calculated bond length R_e. Table 3 lists the bending force constants for linear geometry, $k_\varphi(180°)$, calculated from refs 14, 17, and 35, and the corresponding $\Delta\sigma$ values for the dihalides of Ca, Sr, and Ba and the quasi-linear CaH_2. The linear regression of $k_\varphi(180°)$ in aJ rad^{-2} on $\Delta\sigma$ in eV^{-1} yields a

TABLE 3: Correlation between the Atomic Softness Difference $\Delta\sigma$ and the Bending Force Constant $k_f(180°)$ with Linear Geometry Imposed[a]

MB_2	$(0.290 - \Delta\sigma)$/eV^{-1}	$k_\varphi(180°)$/aJ rad^{-2} ref 14 or as indicated	$k_\varphi(180°)$/aJ rad^{-2} eq 6
BaF_2	−0.105	−0.54	−0.57
SrF_2	−0.076	−0.34	−0.40
$BaCl_2$	−0.044	−0.29	−0.22
CaF_2	−0.042	−0.10 (see text)	−0.20
$BaBr_2$	−0.023	−0.27	−0.09
$SrCl_2$	−0.015	−0.05	−0.05
BaI_2	−0.003	−0.07 ± 0.015 [35]	+0.02
CaH_2	+0.000	+0.015 [17]	+0.04
$SrBr_2$	+0.006	+0.05	+0.08
$CaCl_2$	+0.019	+0.33	+0.15
SrI_2	+0.026	+0.15	+0.19
$CaBr_2$	+0.040	+0.36	+0.28
CaI_2	+0.060	+0.38	+0.39

[a] Conversion factors: 1 aJ rad^{-2} = 1 mdyn Å rad^{-2} = 6.242 eV rad^{-2}.

TABLE 4: Predicted Bond Angles φ,[a] Bending Force Constants $k_\varphi(180°)$,[b] and k_φ(eq)[b] in aJ rad^{-2} from the Softness Difference $\Delta\sigma$

MB_2	$\Delta\sigma$/eV^{-1}	$\varphi(\Delta\sigma)$/deg eq 4	φ_{linreg}/deg eq 5	$k_\varphi(180°)$	k_φ(eq)
SrH_2	0.324	Table 2	137	−0.16	$+0.1_6$
BaH_2	0.352	Table 2	125	−0.32	$+0.3_2$
RaH_2	0.386	112	115	−0.52	$+0.5_2$
RaF_2	0.428	101	105	−0.76	+0.8
$RaCl_2$	0.367	118	121	−0.41	+0.4
$RaBr_2$	0.346	126	128	−0.29	+0.3
RaI_2	0.326	135	137	−0.17	+0.2
$RaAt_2$	0.34	128 ± 6	130 ± 6	−0.25 ± 0.11	$+0.2_5$
$BaAt_2$	0.31	150 ± 7	151 ± 7	−0.07 ± 0.11	+0.1
$SrAt_2$	0.28	180	180	+0.10 ± 0.11	+0.1
$CaAt_2$	0.25	180	180	+0.28 ± 0.11	+0.3
$MgAt_2$	0.18	180	180	(≥0.7)[c]	(≥0.7)[c]
$BeAt_2$	0.10	180	180	(≥1.2)[c]	(≥1.2)[c]
(Group12) At_2	0.14	180	180	(≥0.9)[c]	(≥0.9)[c]
(Group12) Li_2	<0.29	180	180	n/a	

[a] Predicted standard deviation of φ is ±4°, except for $RaAt_2$ and $BaAt_2$, where it is augmented because of the uncertainty of σ_{At}; cf. Table 1. [b] Individual standard error of predicted k_φ is ±0.09 aJ rad^{-2}, except if indicated otherwise. [c] Estimated lower limit of $k_\varphi(180°)$; see text.

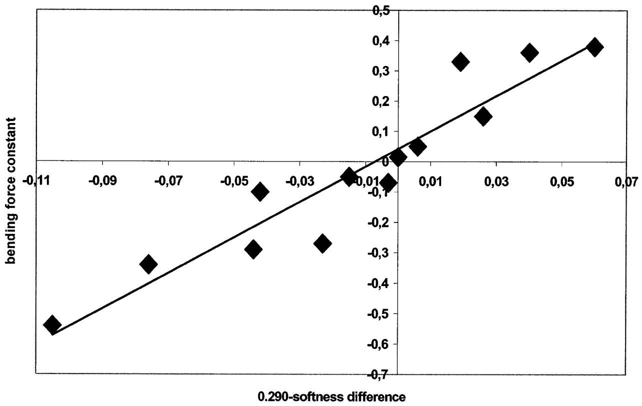

Figure 2. Bending force constants at imposed linear geometry, $k_\varphi(180°)$, (in aJ rad^{-2}) versus the softness difference $(0.290 - \Delta\sigma)$/eV^{-1} for the heavy group 2 dihalides and CaH_2. The regression line is given by eq 6.

correlation coefficient of $r = 0.9456$ for the 13 data pairs listed in Table 3:

$$k_\varphi(180°) = 0.042 + 5.843(0.290 - \Delta\sigma) \qquad (6)$$

The standard root-mean-square error of the individual $k_\varphi(180°)$ amounts to ±0.09 aJ rad^{-2}. It is gratifying that all five Ca compounds follow the general trend, repudiating the inferences of Kaupp et al.[14,20] For CaF_2, large differences were found between ab initio bending frequencies (90 cm^{-1} in ref 9, 65 cm^{-1} in ref 14) and experimental values (120 to 160 cm^{-1}).[19] Since both the equilibrium bending force constant, k_φ(eq), and the linearization energy barrier, $\Delta E_b \cong 0.33$ kcal mol^{-1}, calculated in refs 7 and 9 exceed those of ref 14 by factors of 1.9 and 1.7, respectively, it seems safe to conclude that $k_\varphi(180°) \cong -0.10$ aJ rad^{-2} represents an upper bound to the more-negative accurate force constant. This is reflected in Table 3 and Figure 2, where the regression line corresponding to eq 6 indicates a value of $k_\varphi(180°) \cong -0.20 \pm 0.09$ aJ rad^{-2} for CaF_2. For the Be and Mg halides, the hindrance of d participation must be additionally accounted for, thus they have been left out of the regression. Note that the molecules without reported k_φ values belong to the heavy alkaline earth compounds for which eq 6 is applicable.

3.3. Predictions. We are now able to make a series of predictions of yet unreported angles and bending force constants. Equations 4 and 5 are used for a number of yet unreported triatomic molecules AB_2. Table 4 contains, among others, the angles predicted for the dihydride and dihalides of radium and astatides of groups 2 and 12. As indicated in Table 4, the standard deviation of φ is predicted to be ±4°, except for $RaAt_2$ and $BaAt_2$. For different ligands B and C, such as in CaFCl, the arithmetic mean of the softness was used in ref 9. The validity of this approximation is yet to be tested; preliminary density functional calculations agree with the predictions of the softness criterion that CaFCl and SrFCl are bent whereas BeFCl and MgFCl are linear.[37] Softness has also been defined for chemical groups,[27,38] but the structure of larger polyatomic molecules is not the topic here. Patil has developed equations similar to eq 2 that are applicable to multihalides,[5] thus it would be of interest to extend the present approach to multihalides. It is, however, not yet possible to test the ability of a modified eq 4 to calculate the bond angles of multihalides and multihydrides because the experimental structural data and atomic softness values are not known to the required accuracy for a sufficiently large set of molecules.

We now turn to the predictions of bending force constants. The satisfactory correlation found for all of the reported heavy alkaline earth compounds allows us to predict the 180°-bending force constants of the radium halides and other yet unreported AB_2 molecules (Table 4). For SrH_2 and BaH_2, equilibrium $k_\varphi(\text{eq})R_e^{-2}$ values have been published, but no $k_\varphi(180°)$ data were reported.[17] A comparison with our predictions supports the simple rule that $k_\varphi(\text{eq}) \cong -k_\varphi(180°)$ for bent group 2 molecules. This rule of thumb, which is based on the force constants reported in refs 9, 14, and 17, allows k_φ(eq) to be estimated for several bent molecules (e.g., $k_\varphi(\text{eq}, RaH_2) \cong +0.5$ aJ rad^{-2} at $\varphi \cong 115°$). Only estimates of the lower limit of the bending force constant for the unreported $BeAt_2$, $MgAt_2$, and group 12 astatides is listed in Table 4 because the d participation upon bending is expected to increase the stiffness of the bonds.

3.4. Connections to Other Approaches. The earlier partly successful classifications of bent versus linear structures invoked the following criteria for bending: (i) large net charges in the proximity of a highly polarizable central ion,[1,4,5] (ii) low-lying sd valence states,[3,8] and (iii) large differences of pseudo-atomic-orbital nodal radii.[39] The latter is connected to large values of $\Delta\sigma$, considering the linear dependence between the softness and the covalent radius of atoms.[40] There are further simple relations between softness on one hand and polarizability,[41] frontier orbital $\langle r^{-1}\rangle$ expectation value,[42] small HOMO−LUMO gaps,[43] or low-lying sd and sp valence states on the other. The hard-

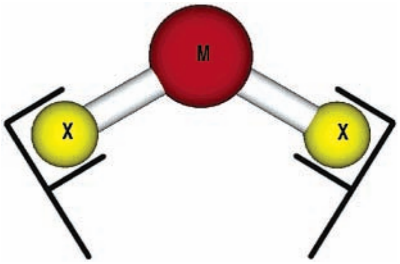

Figure 3. Hard ligands, X, exert a classical bending force on a soft central atom, M. The bending is further enhanced or hindered by d-orbital participation. The softness difference, $\Delta\sigma$, quantitatively describes the interplay between these forces.

bends-soft rule is thus connected to all of the previously attempted rationalizations for bent group 2 dihalides and, in fact, successfully unifies them. The important difference in the trends of atomic softness and dication polarizability is the fact that the softness of the group 12 metal atoms is smaller than that of Ca, whereas the dipole polarizabilities of Cd^{2+} and Hg^{2+} exceed that of Ca^{2+}. Ionic models in general must refer to some properties of ions in formal oxidation states;[23] however, other models or rationalizations may use purely atomic data even for highly polar systems.[9,39,44]

4. Concluding Remarks

The main statement of the study is summarized in Figure 3. In contrast to the previous descriptors and the polarized-ion model, the hard-bends-soft rule consistently discriminates between bent and linear structures and enables us to reproduce the angles of all the observed or calculated group 2 and 12 dihalides, dihydrides, and dilithides to ±4° and to predict their values for yet unreported AB_2 molecules. In addition, the 180°-bending force constants of the heavy alkaline earth dihalides correlate well with $\Delta\sigma$; thus predictions of $k_\varphi(180°)$, and even $k_\varphi(\mathrm{eq})$ are made for the radium dihalides and the similarly unreported group 2 and 12 astatides. Such predictions are feasible because of an invaluable advantage of the hard-bends-soft approach: the bond angle in eq 4 and the bending force constant in eq 6 are derived from simple spectral data of the atomic constituents and do *not* require any previous knowledge of bond properties such as R_e. This is reminiscent of the classifications of a large class of crystal compounds by atomic parameters[44] and contrasts with the various polarized-ion models, for which R_e is one of the necessary input data.[1,4,5,8]

In a mechanical context, the mnemonic hard-bends-soft rule is almost conventional wisdom. From the chemical point of view, it complements the “hard-likes-hard, soft-likes-soft” rule or HSAB principle.[41] The equations reported here widen the scope and open a new dimension of the hardness and softness concept, including new applications in the field of intriguing structural problems. The question of bending triatoms having soft central atoms and soft alkali metal ligands requires additional attention and will be dealt with in more detail in an upcoming communication.

Acknowledgment. Discussions with and encouragement from Drs. Ratna Ghosh and Guntram Rauhut and Professors Hermann Stoll, Peter Schwerdtfeger, and Hans-Joachim Werner are highly appreciated.

References and Notes

(1) (a) Wharton, L.; Berg, R. A.; Klemperer, W. *J. Chem. Phys*. **1963**, *39*, 2023. (b) Büchler, A. Stauffer, J. L.; Klemperer, W.; Wharton, L. *J. Chem. Phys*. **1963**, *39*, 2299. (c) Büchler, A.; Stauffer, J. L.; Klemperer, W.; Wharton, L. *J. Am. Chem. Soc*. **1964**, *86*, 4544.

(2) Calder, V.; Mann, D. E.; Seshardi, K. S.; Allavena, M.; White, D. *J. Chem. Phys*. **1969**, *51*, 2093.

(3) (a) Hayes, E. F. *J. Phys. Chem*. **1966**, *70*, 3740. (b) Gole, J. L.; Siu, A. K. Q.; Hayes, E. F. *J. Chem. Phys*. **1973**, *58*, 857.

(4) (a) Guido, F. M.; Gigli, G. *J. Chem. Phys*. **1976**, *65*, 1397. (b) Galli, G.; Tosi, M. *Nuovo Cimento Soc. Ital. Fis., D* **1984**, *4*, 431

(5) Patil, S. H. *J. Chem. Phys*. **1987**, *87*, 5949.

(6) Ramondo, F.; Rossi, V.; Bencivenni, L. *Mol. Phys*. **1988**, *64*, 513.

(7) Dyke, J. M.; Wright, T. *Chem Phys. Lett*. **1990**, *169*, 138.

(8) DeKock, R. L.; Peterson, M. A.; Timmer, L. K.; Baerends, E. J.; Vernoijs, P. *Polyhedron* **1990**, *9*, 1919. DeKock, R. L.; Peterson, M. A.; Timmer, L. K.; Baerends, E. J.; Vernoijs, P. *Polyhedron* **1991**, *10*, 1965 (erratum).

(9) von Szentpály, L.; Schwerdtfeger, P. *Chem. Phys. Lett*. **1990**, *170*, 555.

(10) Hassett, D. M.; Marsden, C. J. *J. Chem. Soc., Chem. Commun*. **1990**, 667.

(11) Salzner, U.; Schleyer, P. v. R. *Chem. Phys. Lett*. **1990**, *172*, 461.

(12) Beattie, I. R.; Jones, P. J.; Young, N. A. *Inorg. Chem*. **1991**, *30*, 2250.

(13) Seijo, L.; Barandiaran, Z.; Huzinaga, S. *J. Chem. Phys*. **1991**, *94*, 3762.

(14) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Am. Chem. Soc*. **1991**, *113*, 6012.

(15) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc*. **1992**, *114*, 491.

(16) Hassett, M.; Marsden, C. J. *J. Mol. Struct*. **1995**, *346*, 249.

(17) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys*. **1991**, *94*, 1360.

(18) Walsh, A. D. *J. Chem. Soc*. **1953**, 2260, 2266, 2288, 2296, 2301.

(19) Hargittai, M. *Chem. Rev*. **2000**, *100*, 2233.

(20) Kaupp, M. *Angew. Chem., Int. Ed*. **2001**, *40*, 3534.

(21) Fuentealba, P.; von Szentpály, L.; Preuss, H.; Stoll, H. *J. Phys. B: At. Mol. Opt. Phys*. **1985**, *18*, 1287.

(22) Schmidt, P. C.; Weiss, A.; Das, T. P. *Phys. Rev. B* **1979**, *19*, 5525.

(23) O’Keeffe, M. In *Structure and Bonding in Crystals*; O’Keeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; p 315.

(24) (a) Elizier, I. *Theor. Chim. Acta* **1970**, *18*, 77. (b) Elizier, I.; Reger, A. *Theor. Chim. Acta* **1972**, *26*, 283.

(25) Moore, Ch. E. *Atomic Energy Levels*; NBS Circular 467; U.S. Government Printing Office: Washington, DC, 1958.

(26) Bratsch, S. *J. Chem. Educ*. **1988**, *65*, 34, 223

(27) Bergmann, D.; Hinze, J. *Angew. Chem*. **1996**, *108*, 162. Bergmann, D.; Hinze, J. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 150.

(28) Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H.; Schwerdtfeger, P. *Mol. Phys*. **1991**, *74*, 1265.

(29) Legay-Sommaire, H.; Legay, F. *Chem. Phys. Lett*. **1993**, *207*, 123.

(30) Greene, T. M.; Brown, W.; Andrews, L.; Downs, A. J.; Chertihin, G. V.; Runeberg, N.; Pyykkö, P. *J. Phys. Chem*. **1995**, *99*, 7925.

(31) Schwerdtfeger, P.; Boyd, P. D. W.; Brienne, S.; McFeaters, J. S.; Dolg, M.; Liao, M. S.; Schwarz, W. H. E. *Inorg. Chim. Acta* **1993**, *213*, 233.

(32) (a) Kaupp, M.; Dolg, M.; Stoll, H.; von Schnering, H. *Inorg. Chem*. **1994**, *33*, 2122. (b) Kaupp, M.; von Schnering, H. *Inorg. Chem*. **1994**, *33*, 2555.

(33) Levy, J. B.; Hargittai, M. *J. Phys. Chem. A* **2000**, *104*, 1950.

(34) (a) Chase, M. W.; Davies, C. A.; Downey, J. R.; Furnip, D. J.; McDonald, R. A.; Syverd, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1. (b) *NIST-JANAF Thermochemical Tables*, 4th ed.; Chase, M. W., Ed.; J. Phys. Chem. Ref. Data. Monograph 9; American Chemical Society, Washington, DC, 1998.

(35) Spiridonov, V. P.; Gershnikov, A. G.; Altman, A. B.; Romanov, G. V.; Ivanov, A. A. *Chem. Phys. Lett*. **1981**, *77*, 41.

(36) (a) Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*; Oslo Universitets Forlaget: Amsterdam, 1968. (b) Nagarajan, G. *J. Mol. Spectrosc*. **1964**, *13*, 361.

(37) (a) Donald, K. Ph.D. Thesis, The University of the West Indies, Kingston, Jamaica, 2001; p 177. (b) Donald, K.; Liu, S.; von Szentpály. L. To be submitted for publication.

(38) von Szentpály, L. *Int. J. Quantum Chem*. **2000**, *76*, 222.

(39) Andreoni, W.; Galli, G.; Tosi, M. *Phys. Rev. Lett*. **1985**, *55*, 1734.

(40) Ray, N. K.; Samuels, L.; Parr, R. G. *J. Chem. Phys*. **1979**, *70*, 3680.

(41) (a) Pearson, R. G. *J. Am. Chem. Soc*. **1963**, *85*, 3533. (b) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc*. **1983**, *105*, 7512.

(42) Gázquez, J. L.; Ortíz, E. *J. Chem. Phys*. **1984**, *81*, 2741.

(43) Pearson, R. G. *Inorg. Chem*. **1988**, *27*, 734.

(44) (a) St. John, J.; Bloch, A. N. *Phys. Rev. Lett*. **1974**, *33*, 1095. (b) Chelikowsky, J. R. *Phys. Rev. B* **1982**, *26*, 3433. (c) Pettifor, D. *Bonding and Structure of Molecules and Solids*; Oxford University Press: Oxford, U.K., 1995, and references therein.